CHEMISTRY
MODULE-V

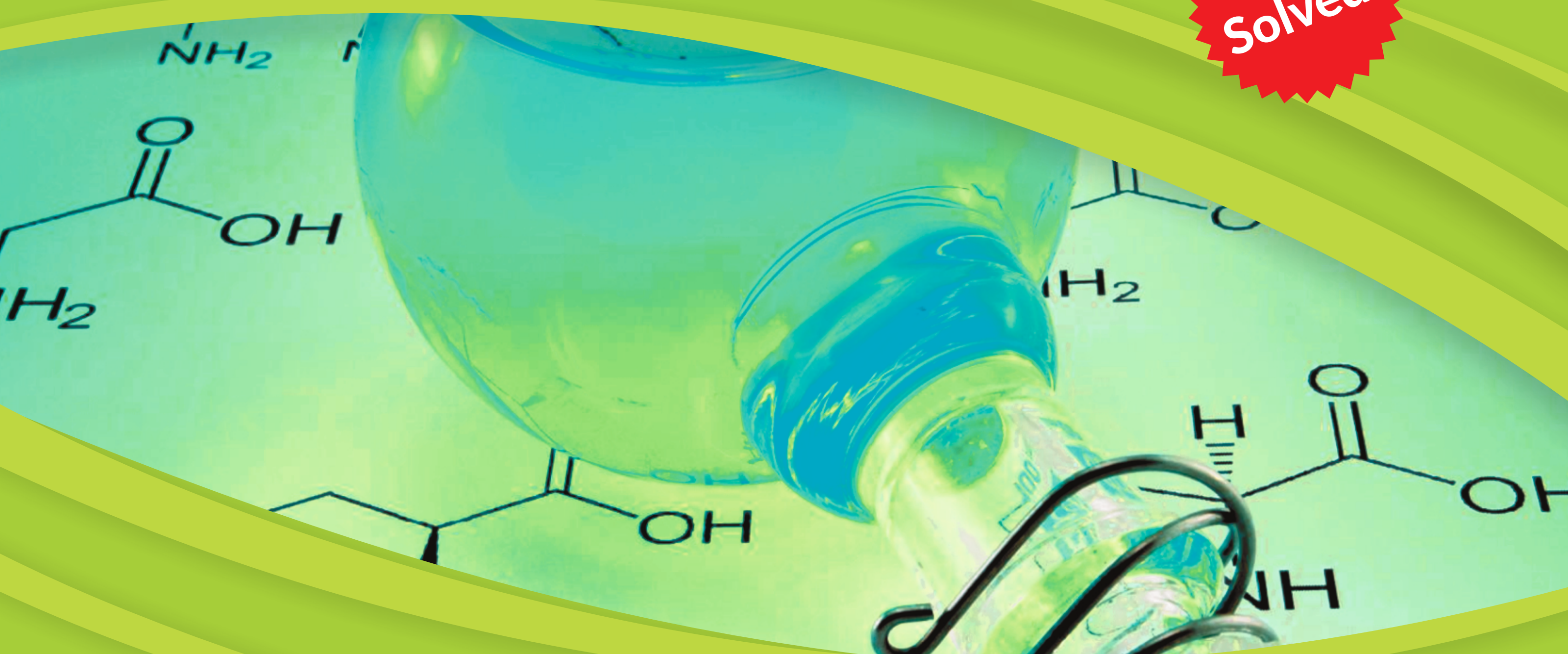
ORGANIC CHEMISTRY-II

for

JEE

(MAIN & ADVANCED)

Fully Solved



Rajesh Agarwal

Mc Graw Hill Education

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About the Author

The author is a key member of the founding team of CollegeDoors.com (an online Test Prep and Test Analytics Platform). A lot of thought behind the composition of this book has taken shape because of the challenging experience of leading the academics vertical of CollegeDoors.com.

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Rajesh Agarwal

McGraw Hill Education (India) Private Limited

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Dedicated to a great Chemistry teacher,
my father,
Late Shri J. P. Agarwal

Preface

Organic Chemistry-II has been written for students who want to undertake well-rounded preparations for JEE (Main as well as Advanced). It is imbued with the essence of 20+ years' experience of coaching and mentoring IIT aspirants. It has been written in a manner that students may learn the concepts from a basic level. It will also sharpen the concepts of learners who have already prepared well.

This book has eight chapters with all the important concepts and multiple choice questions with solutions for clear understanding of concepts. The chapters have been classified into sections such as key points, solved examples, exercises and solutions.

Exercises given at the end of every chapter are further categorised into three difficulty levels of questions and their patterns as asked in the JEE along with the previous years' questions with solutions.

- Level-1 has the questions mainly suitable for JEE-Main exam
- Level-2 contains slightly difficult questions suitable for JEE-Advanced
- Level-3 has the toughest questions of various patterns asked in JEE-Advanced (such as more than one correct answer, comprehension, match the column and single-digit integer)

The content of this book has been laid in a manner that will engage students meaningfully and in turn help them to acquire deep knowledge of concepts. This book stands out in terms of satisfying the need of students for a focussed study material for specific competitive exams like JEE-Main and Advanced.

I have put my best effort towards making the book error free. Nevertheless, constructive suggestions and feedback from readers are welcome as it is important for the continuous improvement of the same.

Acknowledgements

This work would not have been possible without the support of my colleagues, friends and family.

I express my gratitude to the publisher for providing this opportunity and the editorial team for the immensely painstaking task of copyediting and typesetting. My thanks also go to the scores of students who have helped me in learning for more than 20 years. I also thank my wife, Sunita, for allowing me to spend time on this work despite an already hectic coaching schedule.

Contents

CHAPTER 1

Haloalkanes and Haloarenes

INTRODUCTION

- Haloalkanes and haloarenes are organic compounds in which halogen atom is directly linked with carbon atom.
- Haloalkanes are also called as alkyl halides.
- General formula of haloalkanes is $C_nH_{2n+1}X$, (X = F, Br, Cl, I).
- The carbon that bears functional group (halogen atom) is sp^3 hybridised in alkyl halides.
- In these compounds, geometry of carbon is tetrahedral.
- Central carbon atom has a bond angle of 109°28′.
- On the basis of number of halogen atom(s), haloalkanes are of following types:
  - (i) Monohalides – They possess only one halogen atom; e.g., CH_3Cl, CH_3CH_2Br, etc.
  - (ii) Dihalides – They possess two halogen atoms. These are of following three types:
    geminal dihalide, vicinal dihalide, and α, ω or terminal dihalide.
  - (iii) Trihalides – They possess three halogen atoms; e.g., $CHCl_3$, CHI_3, etc.
  - (iv) Tetrahalides – They possess four halogen atoms; e.g., CCl_4, etc.
- Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present, then it shows optical isomerism also.
- Alkyl halides do not show functional isomerism, metamerism, tautomerism, and geometrical isomerism.

PHYSICAL PROPERTIES HALOAIKANES

- Alkyl halides are colourless with sweet smell or pleasant smelling oily liquid. However, CH_3F, CH_3Cl, CH_3Br, CH_3CH_2F, CH_3CH_2Cl are gaseous in nature.
- Although carbon–halogen bond is polar in nature, alkyl halides are partially soluble in H_2O.
- Alkyl halides are completely soluble in organic solvents.
- Boiling point ∝ molecular weight

$$\propto \frac{1}{\text{branching (for isomers)}}$$

- Chloroform is colourless and pleasant smelling liquid while iodoform is yellow crystalline solid.
- Chloroform is used as an anaesthetic agent.
- Iodoform is more reactive than chloroform due to large size of iodine atom.

$$CHI_3 + AgNO_3 \rightarrow AgI \text{ (yellow ppt)}$$

$$CHCl_3 + AgNO_3 \rightarrow \text{No white ppt of AgCl}$$

- Carbon tetrachloride is colourless liquid and used as **FIRE EXTINGUISHER** under the trade name **PYRENE**.
- Chloroform is kept in dark coloured bottles to avoid the following oxidation reaction.

$$CHCl_3 \xrightarrow[\text{air and light}]{[O]} \underset{\text{(Poisonous)}}{COCl_2} \quad \text{(Phosgene)} + HCl$$

- **Test of Chloroform (Before Anaesthetic use):**

Serial Number	Test	Pure $CHCl_3$	$[COCl_2 + HCl]$
(i)	Litmus paper	Blue $\rightarrow$ Blue	Blue $\rightarrow$ Red
(ii)	$AgNO_3$	No ppt	While ppt (AgCl)
(iii)	H_2SO_4	No colouration	Yellow colour

- Polarity order is RF > RCl > RBr > RI
- Reactivity order is RI > RBr > RCl > RF
- For same halide group, the reactivity order is 3° halide > 2° halide > 1° halide
- Fluorides and chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to more density of bromine than oxygen. CH_2I_2 is heavier liquid after Hg.
- All haloalkanes burn on copper wire with green flame (**BELESTEIN TEST** for halogens)

ALIPHATIC NUCLEOPHILIC SUBSTITUTION

If a substitution reaction is brought about by a nucleophile then it is known as nucleophilic substitution reaction. A general nucleophilic substitution reaction may be represented as:

$$R–L + \overset{\ominus}{Nu} \longrightarrow R–Nu + \overset{\ominus}{L}$$

where L is a leaving group and $\overset{\ominus}{Nu}$ is an incoming nucleophile.

In nucleophilic substitution two changes occur:

(i) breaking of the bond with leaving group

(ii) formation of bond with nucleophile

The principal mechanistic variations are associated with changes in the timing of the two processes.

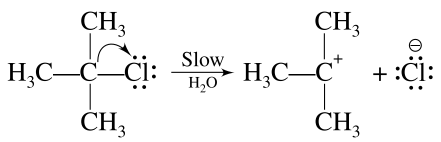
Depending on nucleophiles, substrates, leaving groups and reaction conditions, several mechanisms are possible but the most common are S_N1 and S_N2 mechanisms.

S_N1 Mechanism or S_N1 Reaction

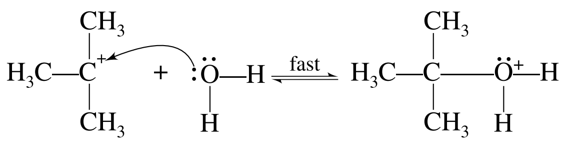
The mechanisms for the reaction of tert-butyl chloride with water are given below:

$$(CH_3)_3\,CCl + 2\,H_2O \rightarrow (CH_3)_3\,COH + H_3O^+ + Cl^-$$

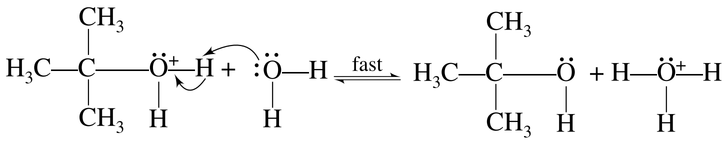
Step 1



Step 2



Step 3



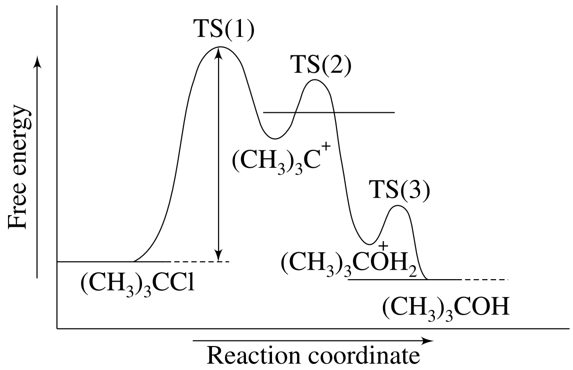
Main characteristics:

(1) The S_N1 mechanism is mostly two-step process.

(2) The first step is a slow ionisation to form carbocation and thus rearrangement into stable carbocation accompanied frequently.

(3) The second step is a fast attack on the carbocation by the nucleophile. The carbocation being a very strong electrophile reacts very fast with both strong and weak nucleophiles.

(4) **Energy profile diagram**



(5) **Kinetics**

The S_N1 reaction is first order reaction which follows the rate law given below:

Rate = K [Substrate]

So that nucleophile plays no role in the mechanism.

(6) **Effect of substrate structure:**

The more stable the carbocation intermediate, the faster the S_N1 mechanism.

The following is the decreasing order of reactivity of some substrates in S_N1 reaction:

$Ar_3CX > Ar_2CHX > R_3CX > ArCH_2X > CH_2 = CH–CH_2–X > R_2CHX > RCH_2X$

(a) S_N1 reactions are highly favoured if there is a heteroatom at the α-carbon because it highly stabilises the carbocation formed.

(b) Substrate containing carbonyl group on β-carbon does not gives S_N1 reaction because carbonyl group has very strong–I effect which destabilises the carbocation reaction intermediate.

(c) The greater the crowding around the carbon having leaving group, the greater is the possibility of S_N1 reaction.

For some tertiary substrates the rate of S_N1 reactions is greatly increased if the β-carbon is highly substituted.

(7) **Effects of solvent:** Polar solvents accelerate the S_N1 reaction because it favours the formation of polar transition state.

(8) **Effect of leaving group:** Weaker bases are good leaving groups and thus favour S_N1 mechanism. Thus the reactivity order among the halide ions is:

$I^- > Br^- > Cl^- > F^-$

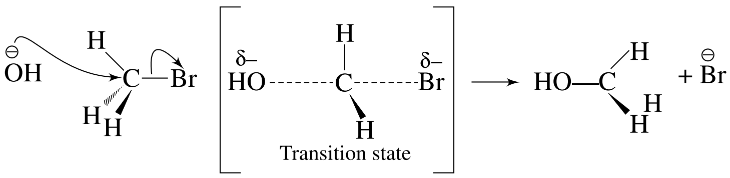
(9) **Effect of attacking nucleophile:** Since the rate determining step of S_N1 reaction does not involve the incoming nucleophile, and neither its nucleophilicity nor its concentration has any effect on the rate of the reaction, so an S_N1 reaction can proceed with weak nucleophiles of low concentration.

(10) **Stereochemistry:** The S_N1 reaction on a chiral starting material ends up with the racemisation of the product (enantiomers) because the carbocation formed in the first step of an S_N1 reaction has a trigonal planar structure, when it react with nucleophile, it may do so form either front side or back side.

S_N2 Mechanism or S_N2 Reaction:

A typical example of this process is the hydrolysis of methyl bromide in the presence of NaOH.

$$CH_3\text{–}Br + NaOH \longrightarrow CH_3\text{–}OH + NaBr$$



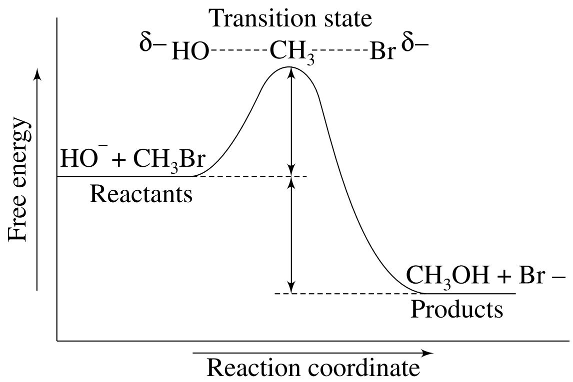
Main characteristics:

(1) S_N2 mechanism is a one-step (concerted) process.

(2) There is no intermediate, only transition state is formed.

(3) The conversion of reactants to transition state is the rate determining step.

(4) **Energy profile diagram**



(5) **Kinetics:** The S_N2 reaction is a second order reaction that follows the rate law given below:

Rate = K [Substrate] [Nucleophile]

(6) **Effect of substrate structure:** The rate of reaction depends on the steric bulk of the alkyl group. Kinetic studies have shown that the methyl halides are the most reactive in S_N2 reactions. The increase in the length of chain of alkyl group decreases the rate of reaction. Alkyl branching next to the leaving group decreases the rate drastically. The reactivity order for S_N2 reactions follows the following order.

$CH_3 > 1° > 2° >> \text{neopentyl} > 3°$

(7) **Effects of solvent:** Aprotic solvents increase the rate of S_N2 reactions.

(8) **Effect of leaving group:** Weaker bases are good leaving groups and thus favour S_N2 mechanism. Thus the reactivity order among the halide ions is:

$I^- > Br^- > Cl^- > F^-$

(9) **Effect of attacking nucleophile:** Since the single step S_N2 reaction involves the substrate and the nucleophile, the rate of the reaction depends on largely on the concentration of nucleophile and its nucleophilicity. Strong nucleophiles increases the rate of the S_N2 reaction while weak nucleophiles decrease it.

(10) **Stereochemistry:** S_N2 reaction involves the inversion of stereochemistry around carbon atom of the substrate. This inversion is known as Walden inversion because in this reaction the nucleophile attaches the substrate from the just opposite (back) side (at 180°) to the leaving group.

Summary of structural variations and nucleophilic substitution:

We are now in position to summarise structural variation for S_N1 and S_N2 reaction in ordinary condition:

Substrate		S_N1 reaction	S_N2 reaction
1.	CH_3–X	no	very good
2.	R–CH_2–X	no	good
3.	R_2CH–X	yes	yes
4.	R_3C–X	very good	no
5.	CH_2=CH–CH_2–X	yes	good
6.	Ar–CH_2–X	yes	good
7.	R–CO–CH_2–X	no	excellent
8.	R–O–CH_2–X	excellent	good
9.	R_2N–CH_2–X	excellent	good
10	CH_2=CH-X/Ar–X	no	no

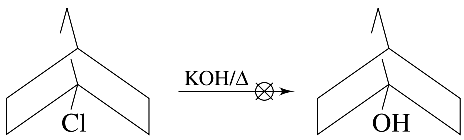
No substitutions at bridgehead carbons:

S_N1 reactions proceed through carbocation which must be planar. Because of rigid like structures of the substrate, bridgehead carbon atoms cannot assume planarity. Hence, heterolysis leading to the formation of carbocation is also prevented.

S_N2 reaction proceed through backside attack by the nucleophile, inversion of configuration and coplanarity of the nonreacting groups in the TS all of which are prevented at the bridgehead carbons due to rigid cage like structures of the compounds containing the bridgehead carbons.

Thus bridgehead carbons are resistant towards substitution by the SN1 and SN2 mechanism.

For example:



(No reaction)

Elimination Reaction:

In the presence of alcoholic KOH and heating, elimination reaction occurs resulting into a double bond. If more than one product is possible, the major product is of more substituted alkene (Saytzeff rule).

$$CH_3–CH_2–\underset{\substack{|\\ Br}}{CH}–CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}} \underset{80\%}{CH_3CH=CHCH_3} + \underset{20\%}{CH_3CH_2CH=CH_2}$$

Competition between Substitution and Elimination Reactions:

The relative proportion of products depends on mainly three factors, namely, basicity of the nucleophile, hindrance in the haloalkane, and steric bulk around the nucleophilic atom.

Factor 1: Weak bases (H_2O, ROH, halides, RS^-, N_3^-, NC^-, $RCOO^-$) lead to more substitution.

Strong bases (HO^-, RO^-, H_2N^-, R_2N^-) lead to more elimination.

Factor 2: Steric hindrance around the reacting carbon.

Sterically unhindered (primary) haloalkanes lead to more substitution.

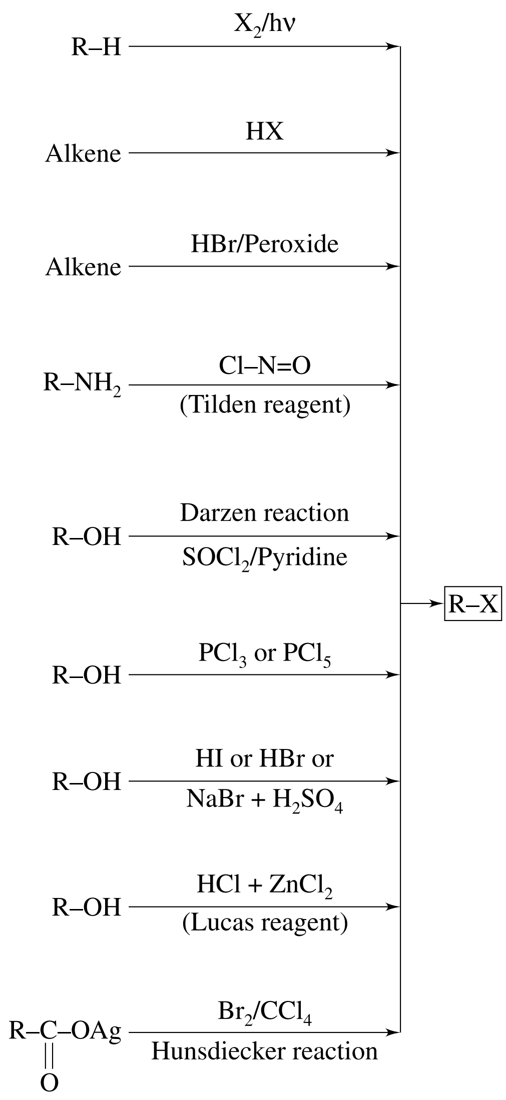
Sterically hindered (branched primary, secondary, tertiary) haloalkanes lead to more elimination.

Factor 3: Steric hindrance in the nucleophile.

Sterically unhindered (HO^-, CH_3O^-, $CH_3CH_2O^-$, H_2N^-) nucleophile lead to more substitution.

Sterically hindered $(CH_3)_3CO^-$, $[(CH_3)_2CH_2NH^-]$ nucleophiles lead to more elimination.

Methods of Preparation of Haloalkanes:



Chemical Properties of Haloalkane:

$\boxed{R\text{–}X}$

- (Wurtz reaction) Na/dry ether → R–R
- (Frankland reaction) Zn/dry ether → R–R
- Corey-House reaction (i) Li (ii) CuX (iii) R′–X → R–R′
- Reduction $LiAlH_4$ or $NaBH_4$ or Ph_3SnH → R–H
- R–MgX or RLi or RNa or R_2Zn or R_2CuLi (Organo metallic reagents) → R–R
- R–CH=CH–MgX → R–CH=CH–R
- R–C≡C–Na or R–C≡C–MgX → R–C≡C–R
- (Finkelstein reaction) NaI/acetone → R–I
- (Swart reaction) AgF/DMSO → R–F
- (Williamson reaction) RONa → R–O–R
- (Streker reaction) Na_2SO_3 → $R\text{–}SO_3Na$
- $R\ddot{\underset{..}{O}}H$ or dry Ag_2O → $R\text{–}\ddot{\underset{..}{O}}\text{–}R$
- $H_2\ddot{\underset{..}{O}}$ or aq. NaOH or moist Ag_2O → $R\text{–}\ddot{\underset{..}{O}}H$
- RCOONa or RCOOAg → R–COOR
- $\ddot{N}H_3$ → $R\text{–}\ddot{N}H_2$
- $R\text{–}\ddot{N}H_2$ → $R\text{–}\ddot{N}H\text{–}R$
- $R\text{–}\ddot{N}H\text{–}R$ → $R_3\ddot{N} \xrightarrow{R\text{–}X} R_4\overset{\oplus}{N}\overset{\ominus}{X}$
- KCN/(Ionic) → R–C≡N
- AgCN (covalent) → $R\text{–}N\overset{\rightarrow}{\equiv}C$
- KO–N=O (Ionic) → R–O–N=O
- Ag–O–N=O (covalent) → $R\text{–}N(\rightarrow O)(=O)$

Formation and reaction of Grignard Reagent

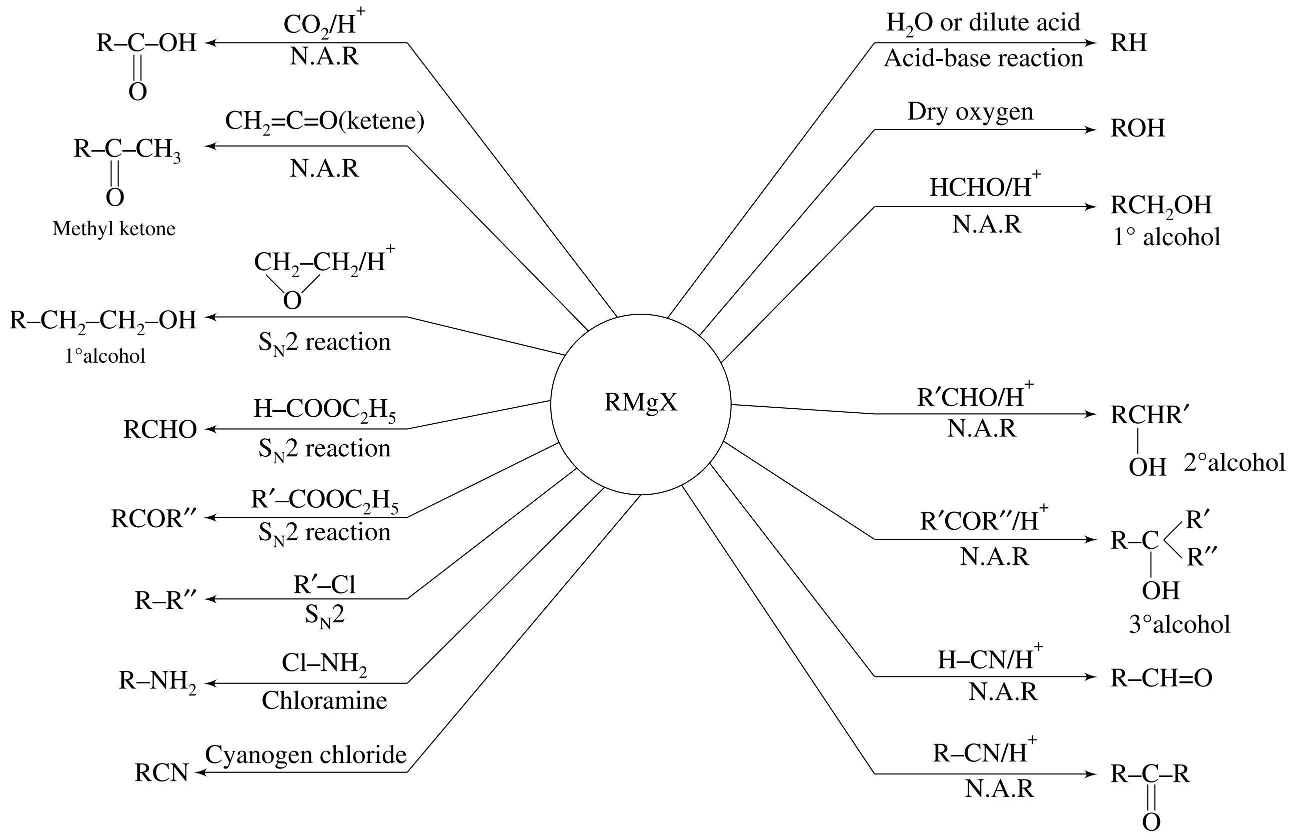
Haloalkanes react with magnesium metal (turnings) in dry ether to form alkyl magnesium halide, known as Grignard reagent.

$$\left.\begin{array}{l} RX + Mg \xrightarrow{\text{Dry ether}} RMgX \\ ArX + Mg \xrightarrow{\text{Dry ether}} ArMgX \end{array}\right\} \text{Grignard reagents}$$

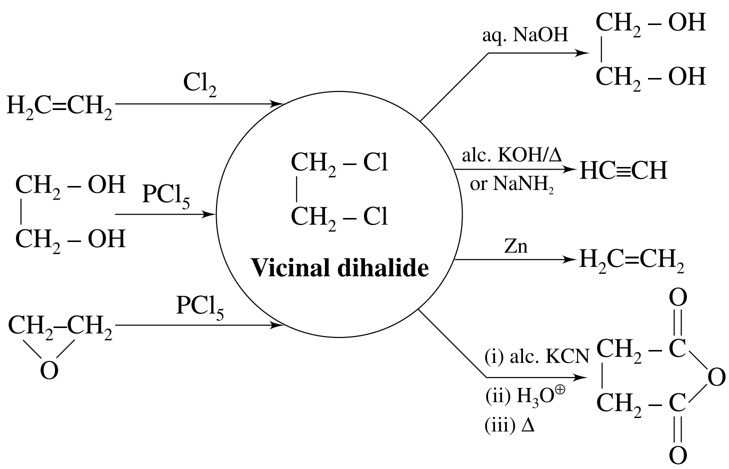
The order of reactivity of halides with magnesium is RI > RBr > RCl.

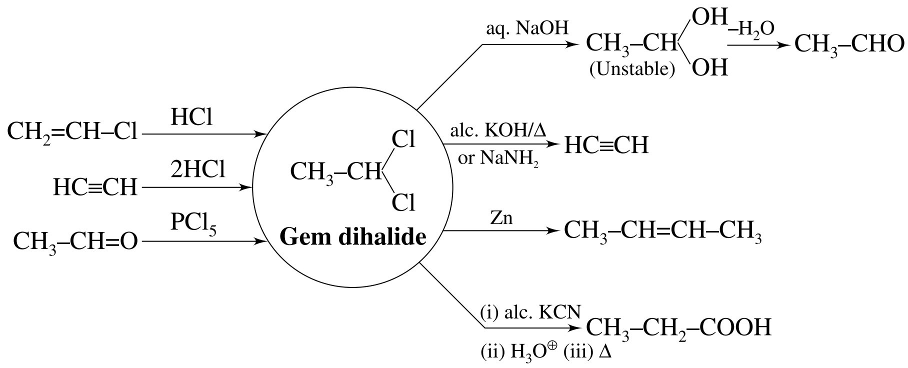
Reaction of Grignard reagent:

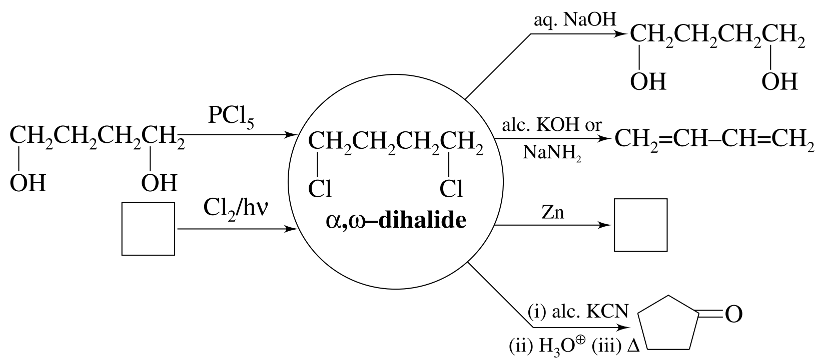
Grignard reagent is most versatile compound as it can be used in the preparation of many different types of compounds.



Chemical Properties and Methods of Preparation of Dihalides:





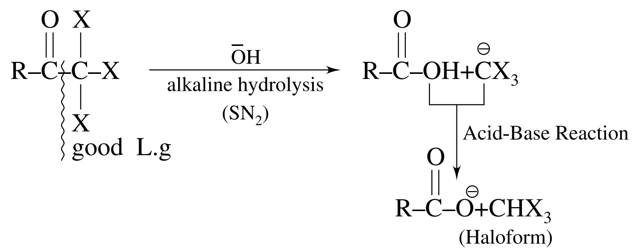


Trihalides

Haloform Reaction

When methyl ketones react with halogens in the presence of base multiple halogenations always occur at the carbon of the methyl group. Multiple halogenations occur because introduction of the first halogen (owing to its electronegativity) makes the remaining α hydrogens on the methyl carbon more acidic.

$$R-\underset{\|}{\overset{O}{C}}-CH_3 + 3X_2 + 3OH^- \xrightarrow{\text{base}} R-\underset{\|}{\overset{O}{C}}-CX_3 + 3X^- + 3H_2O$$



The Iodoform Test

The haloform reaction using iodine and aqueous sodium hydroxide is called the iodoform test. The iodoform test was once frequently used in structure determinations because it allows identification of the following two groups:

$$-\underset{\underset{O}{\|}}{C}-CH_3 \text{ and } -\underset{\underset{OH}{|}}{CH}-CH_3$$

Compounds containing either of these groups react with iodine in sodium hydroxide to give a bright yellow precipitate of iodoform (CHI_3, mp 119°).

Compounds containing the $-CHOHCH_3$ group give a positive iodoform test because they are first oxidized to methyl ketones:

$$-\underset{\underset{OH}{|}}{C}HCH_3 + I_2 + 2OH^- \longrightarrow \underset{\underset{O}{\|}}{C}CH_3 + 2I^- + 2H_2O$$

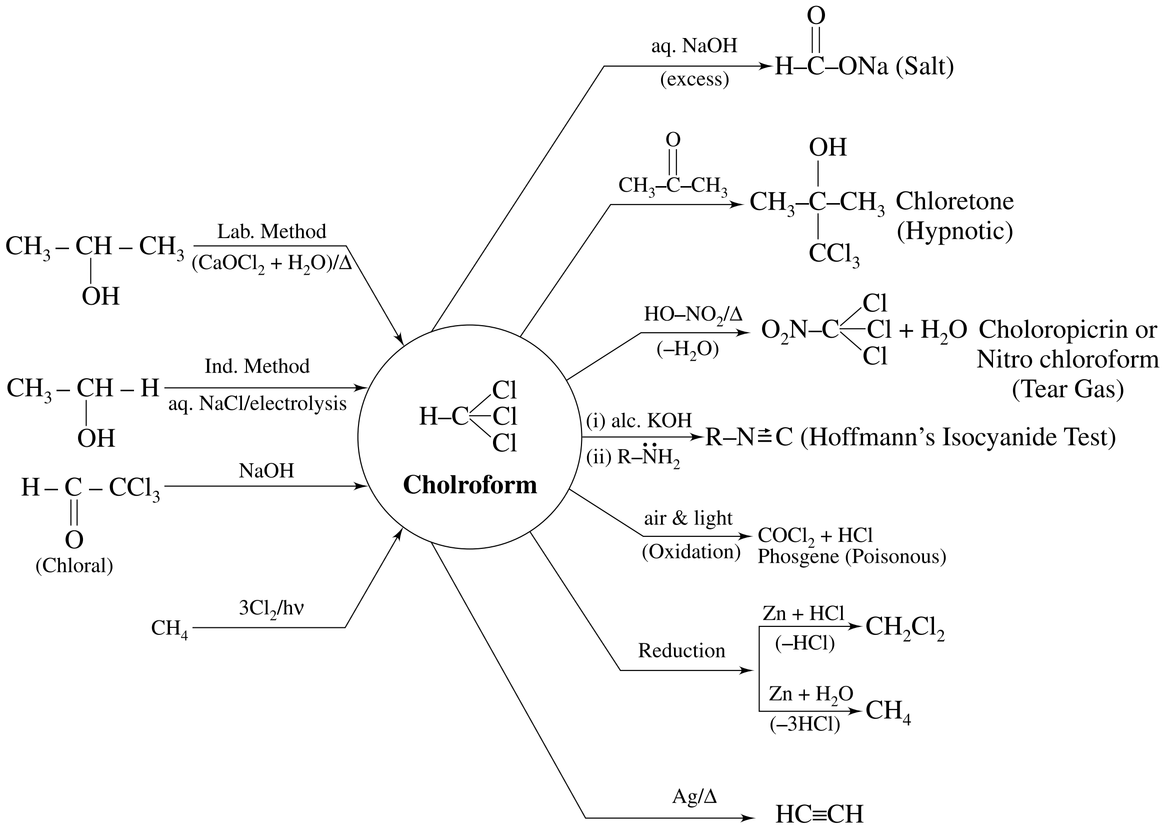
Methyl ketones then react with iodine and hydroxide ion produce iodoform:

$$-\underset{\underset{O}{\|}}{C}-CH_3 + 3I_2 + 3OH^- \longrightarrow -\underset{\underset{O}{\|}}{C}-CI_3 + 3I^- + 3H_2O$$

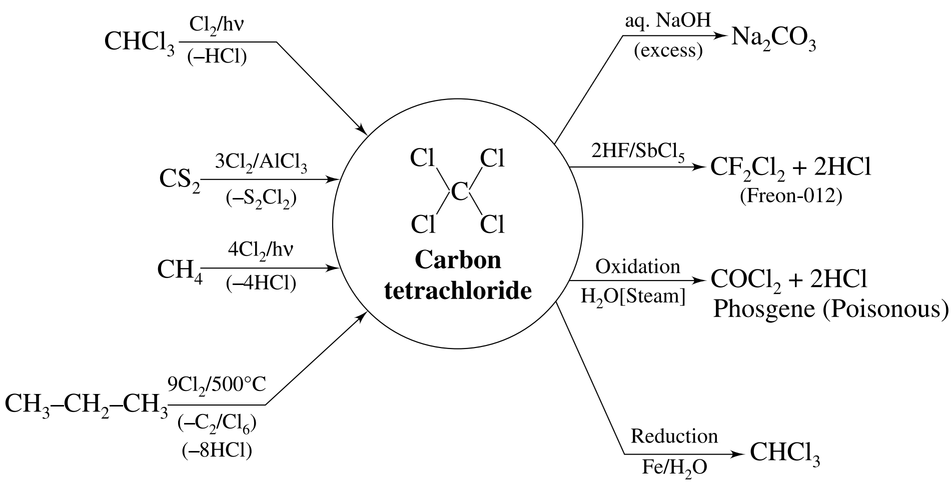
$$-\underset{\underset{O}{\|}}{C}-CI_3 + OH^- \longrightarrow -\underset{\underset{O}{\|}}{C}-O^- + \underset{\text{Yellow precipitate}}{CHI_3\downarrow}$$

The group to which the $-COCH_3$ or $-CHOHCH_3$ function is attached can be aryl, alkyl, or hydrogen. Thus, even ethanol and acetaldehyde give positive iodoform test.

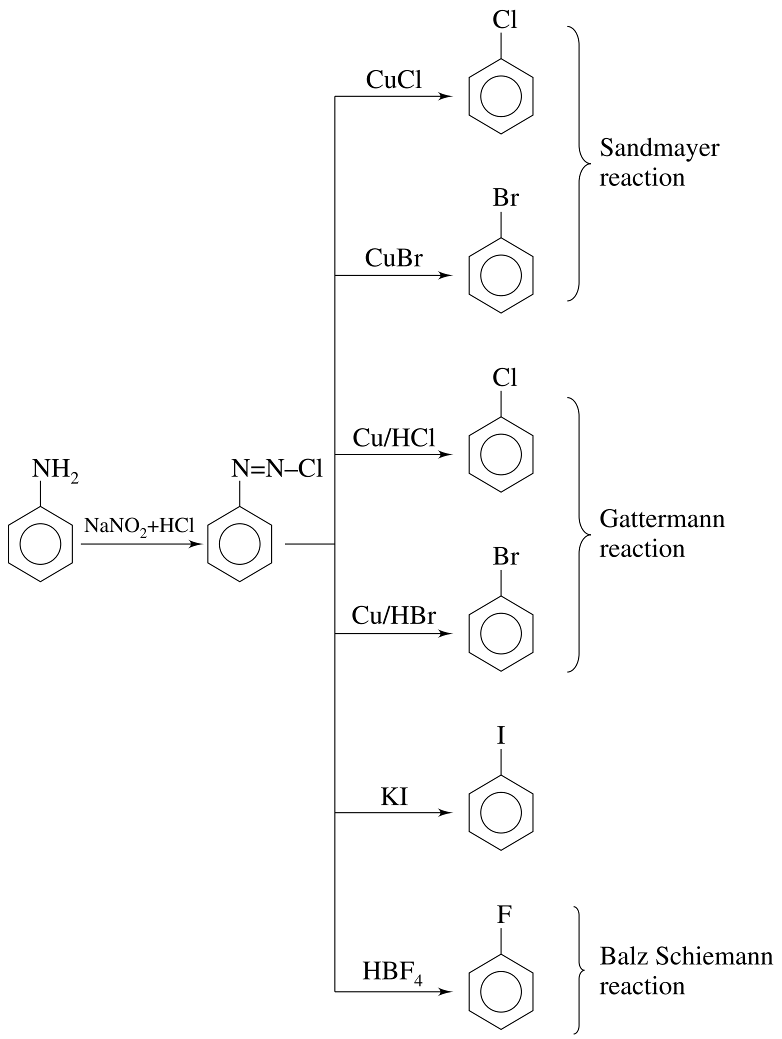
Chemical Properties and Methods of Preparation of Chloroform:

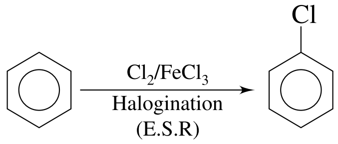


Chemical Properties and Methods of Preparation of Carbon Tetrachloride:



Methods of Preparation of Aryl Halides:

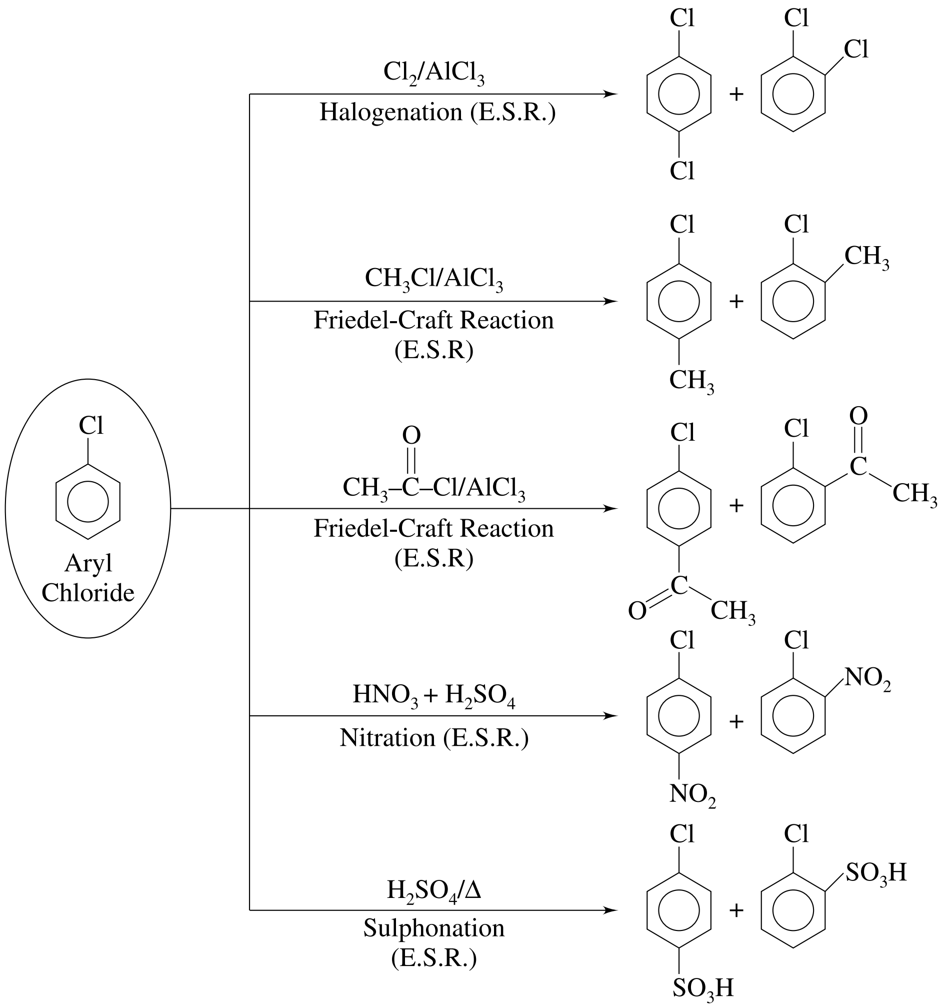




Chemical Properties of Aryl Halides:

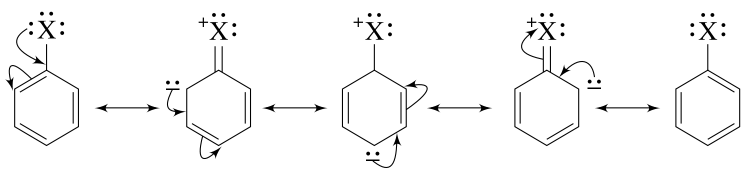
(1) Electophilic Aromatic Substitution Reaction (Ar-S_E)

The halo groups are the only ortho-para directors even that are deactivating group. It is due to the fact that electron withdrawing inductive effect influences reactivity and their electron donating resonace effect governs orientation.



(2) Nucleophilic Aromatic Substitution Reaction (Ar-SN)

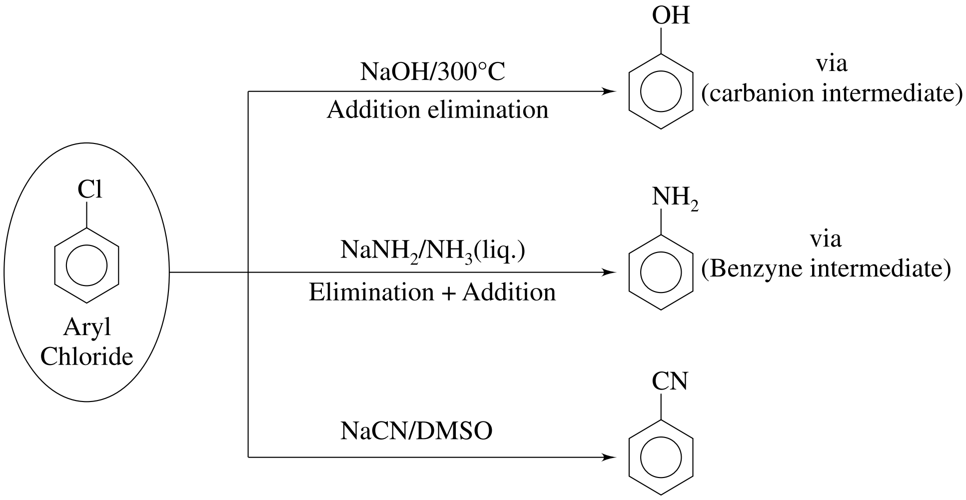
In general, aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions. This is due to the resonance effect in which lone pair of electron on halogen atom is delocalised to benzene ring imparting a partial double bond character to C–X bond.



In alkyl halide, the C–X bond involves sp^3(C) whereas in aryl halide, sp^2(C) is involved. Since the sp^2(C) is more electronegative than the sp^3(C), the C–X bond in aryl halide is shorter than in alkyl halides. This makes C–X bond more strong in aryl halides.

Under normal conditions, halobenzenes are inert to nucleophiles. However, Chlorobenzene can be made to react if the experimental conditions are:

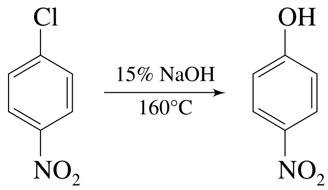
1. At high temperature and high pressure.
2. In presence of strong electron-withdrawing substituent at ortho and/or para positions.

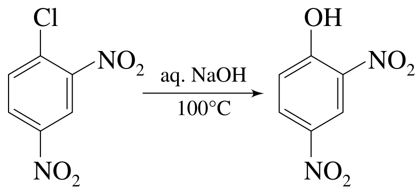


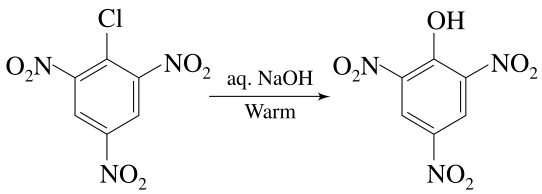
(A) Addition Elimination reaction

The presence of electron-withdrawing substituent at ortho and/or para positions is a favourable factor for the nucleophilic substitution reaction.

More such substituents, the faster the reaction.





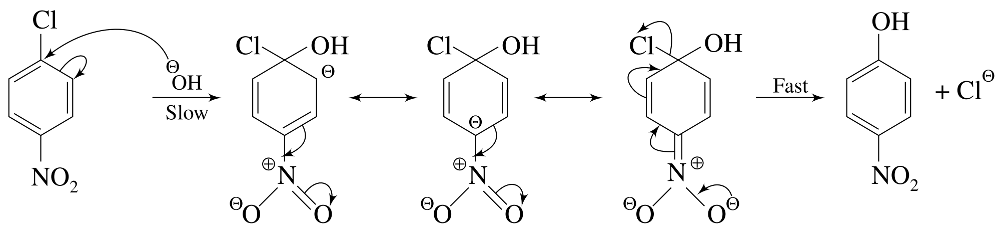


Mechanism

S_N Ar reaction takes place by a two steps reaction,

In the first step nucleophile attacks on the carbon bearing the leaving group.

In the second step leaving group departs, re-estabilishing the aromaticity of the ring.

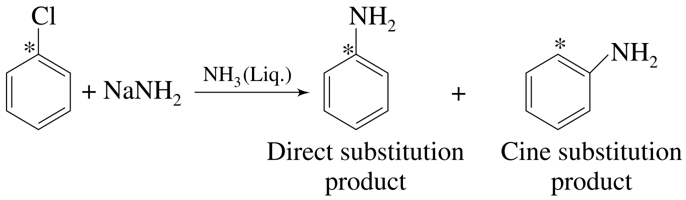


Meisenheimer complex

The carbanion is stabilised by electron-withdrawing groups in the positions ortho and para to the halogen atom.

(B) Elimination Addition Reaction (Benzyne)

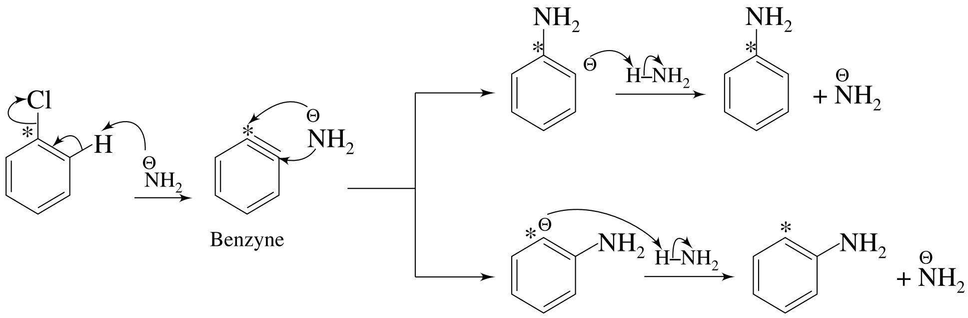
An aromatic halide such as chlorobenzene can undergo nucleophilic substitution in presence of very strong base such as $NaNH_2$ or KNH_2



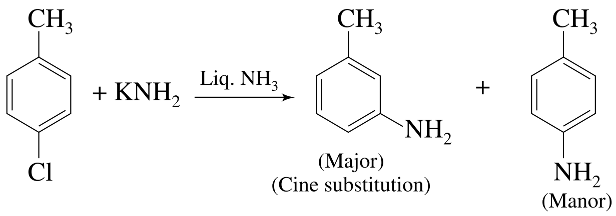
Substitution at the carbon that was attached to the leaving group is called direct substitution. Substitution at the adjacent carbon is called cine substitution.

Mechanism

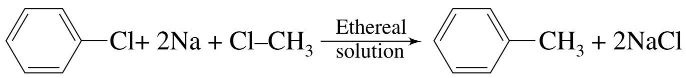
The mechanism of reaction proceed through benzyne intermediate.



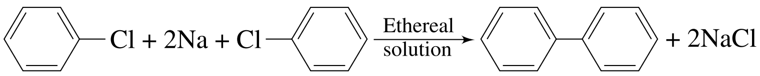
The substituted halobenzene give different products through benzyne formation. The major product formation can be predicted on the basis of inductive electronic effect of the stability of the intermediate carbanion.



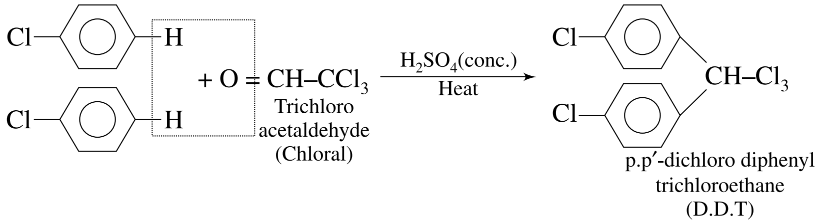
(3) Wurtz-Fittig Reaction



(4) Fittig Reaction



(5) Chlorobenzene to D.D.T



SOLVED EXAMPLE

1. $CH_3–CH_2–\overset{\overset{\displaystyle O}{||}}{C}–O\,Ag \xrightarrow[CCl_4]{Br_2} X \xrightarrow[(2)\ CuI]{(1)\ Li} Y \xrightarrow[\text{dry ether}]{CH_3–CH_2–Br} Z;$

Z is:

(1) $CH_3–CH_3$ (2) $CH_3–CH_2–CH_3$

(3) $CH_3–CH_2–CH_2–CH_3$ (4) $CH_3–\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}–CH_3$

Sol. **[3]**

$$H_3C–CH_2–\overset{\overset{\displaystyle O}{||}}{C}–O\,Ag \xrightarrow[CCl_4]{Br_2} \underset{(X)}{CH_3–CH_2–Br} \xrightarrow[(ii)\ CuI]{(i)\ Li} \underset{(Y)}{Li[Cu(CH_2–CH_3)_2]} \xrightarrow{CH_3–CH_2–Br} \underset{(Z)}{CH_3–CH_2–CH_2–CH_3}$$

2. An S_N1 reaction at the asymmetric carbon of an enantiomerically pure chiral alkyl halide gives a product:

(1) with retention of configuration

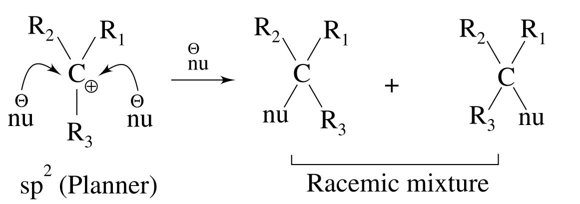
(2) with inversion of configuration

(3) with racemisation

(4) with partial racemisation

Sol. **[3]**

Since intermediate is carbocation thus nucleophile attack from both front as well back side.



3. 1, 1-Dichloropropane on hydrolysis gives:

(1) propanone (2) propanal

(3) ethanal (4) 1, 1-Propanediol

Sol. **[2]**

$$CH_3–CH_2–CH{<}^{Cl}_{Cl} \xrightarrow{\text{Aq. KOH}} CH_3–CH_2–CH{<}^{OH}_{OH} \xrightarrow[\text{unstable}]{–H_2O} \underset{\text{Propanal}}{CH_3–CH_2–CH{=}O}$$

4. Which of the following reagents may not be used to convert alkyl chlorides and alkyl bromides into alkyl fluorides?

(1) Hg_2F_2 (2) SbF_5

(3) AgF (4) CaF_2

Sol. **[4]**

$$R–Br \xrightarrow[\substack{\text{or} \\ SbF_5 \\ \text{or} \\ AgF}]{HgF_2} R–F$$

Swart reaction

5. Which of the following statements is incorrect for ethylene dichloride and ethylidene chloride?

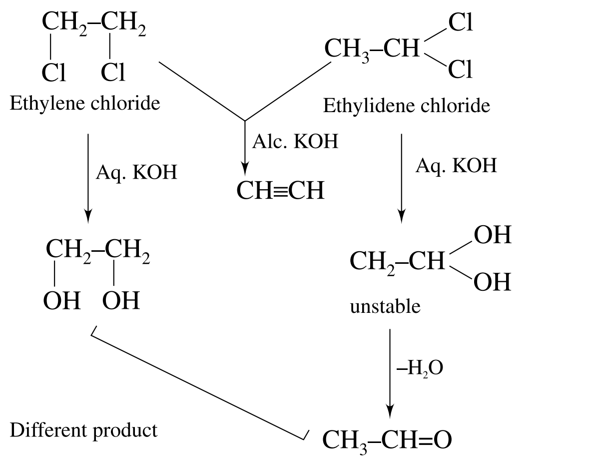
(1) These are structural isomers

(2) Both of these yield same product on reaction with alcoholic KOH solution

(3) Both of these yield same product on treatment with aqueous KOH solution

(4) Both of these yield same product on reduction

Sol. **[3]**



6. $CH{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4} (X) \xrightarrow{LiAlH_4} (Y) \xrightarrow{P_4/Br_2} (Z)$

In this sequence of reaction, (Z) is:

(1) Ethylene bromide (2) Ethanol
(3) Ethyl bromide (4) Ethylidene bromide

Sol. **[3]**

$$CH \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3-CH=O \xrightarrow[\text{reduction}]{LiAlH_4} CH_3-CH_2-OH \xrightarrow{Br_2/P_4} \underset{\text{Ethyl bromide}}{CH_3-CH_2-Br}$$

7. When HCl gas is passed through propene in the presence of benzoyl peroxide it gives

(1) n-propyl chloride (2) 2-chloropropane
(3) allyl chloride (4) no reaction

Sol. **[2]**

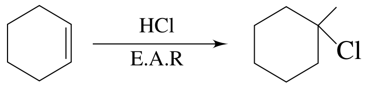
HCl is not affected by peroxide so major product formed by E.A.R.

$$CH_3-CH=CH_2 \xrightarrow[\substack{\text{(Peroxide)} \\ \text{E.A.R}}]{HCl} CH_3-\overset{+}{C}H-CH_3 \xrightarrow{Cl^{\ominus}} CH_3-\underset{\displaystyle Cl}{\underset{|}{C}H}-CH_3$$

8. 1-Methylcyclohexene on addition of HCl produces

(1) 1-chloro-1methylcyclohexane
(2) (±)-trans-2-chloro-1-methylcyclohexane
(3) (±) cis-2-chloro-1-methylcyclohexane
(4) 1-chloro-2-methylcyclohexane

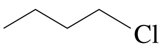
Sol. **[1]**

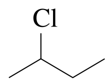


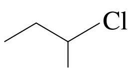
Markowrikaff addition No chiral C

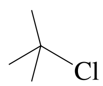
l-chloro-lmethylcyclohexane

9. Which of the following compounds has the highest boiling point?

(1) 

(2) 

(3) 

(4) 

Sol. **[1]**

Boiling point ∝ Molecular weight

$$\propto \frac{1}{\text{Branching (for isomer)}}$$

10. Ethyl alcohol is heated with bleaching powder and water. The final product formed is:

(1) Cl_3CCHO (2) CH_3CH_2Cl
(3) Cl_3CCO_2H (4) $CHCl_3$

Sol. **[4]**

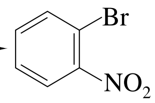
$$Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$CH_3-CH_2-OH \xrightarrow[\text{Oxidataion}]{Cl_2} CH_3-CH=O$$

$$CH_3-CH=O \xrightarrow[\text{Chlorination}]{Cl_2/Ca\,(OH)_2} CCl_3-\underset{\underset{\displaystyle O}{||}}{C}-H \quad \text{Chloral}$$

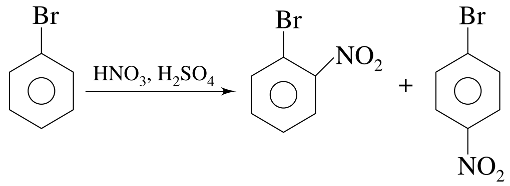
$$CCl_3-\underset{\underset{\displaystyle O}{||}}{C}-H \xrightarrow[\text{Alkaline hydrolysis}]{Ca(OH)_2} CHCl_3 + (HCOO)_2Ca$$

11. For the given reaction, A is:

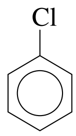
A ⟶ 

(1) $C_6H_5Br + HNO_3, H_2SO_4$
(2) $C_6H_5NO_2 + Br_2, FeBr_3$
(3) $C_6H_5Br + H_2SO_4$, heat
(4) $C_6H_5NO_2 + HBr$

Sol. **[1]**

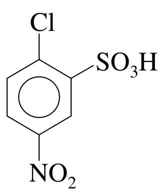


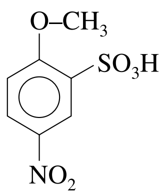
Br → o/p directive

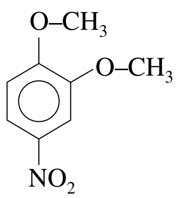
12. 

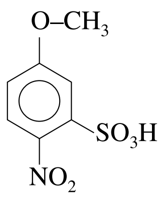
$\xrightarrow{\text{(i) } HNO_3/H_2SO_4}$ Product
(ii) NaOH, 150°C
(iii) CH_3-I
(iv) Conc. H_2SO_4

Product is:

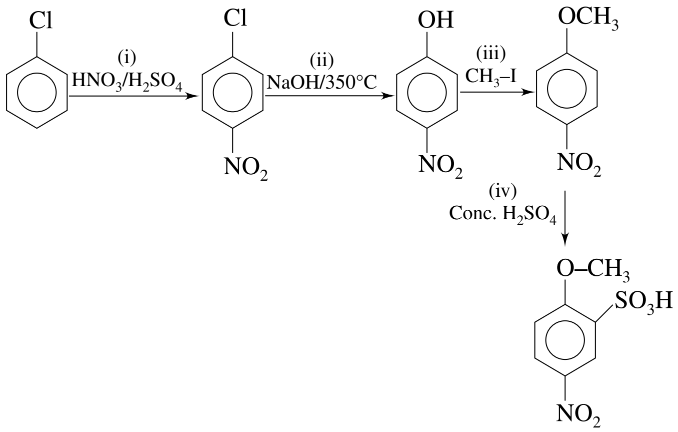
(1) 

(2) 

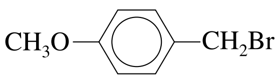
(3) 

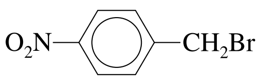
(4) 

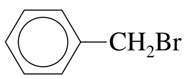
Sol. **[2]**

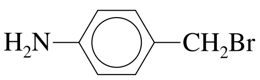


13. Which one of the following compounds undergoes predominantly S_N2 reaction with aqueous NaOH in a polar aprotic solvent?

(1) 

(2) 

(3) 

(4) 

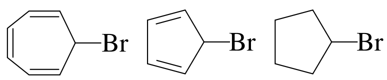
Sol. **[2]**

In primary halide

Rate of $S_N2 \propto \text{EWG} \propto \dfrac{1}{\text{ERG}}$

–O–CH_3(ERG), –NO_2(EWG), –NH_2(ERG)

14. Among the compounds



I II III

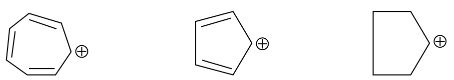
The order of decreasing S_N1 reactivity is

(1) I > II > III (2) I > III > II

(3) II > III > I (4) III > I > II

Sol. **[2]**

Rate of SN_1 reaction ∝ stability of carbocation



Aromatic (I) Anti Aromatic (II) Non Aromatic (III)

(I) > (III) > (II)

15. Which of the following alcohols will give the positive iodoform test?

(1) $CH_3-\underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2CH_3$

(2) $CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$

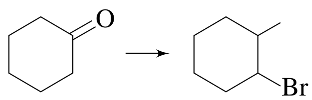
(3) $C_6H_5-CH_2-CH_2OH$

(4) $CH_3-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$

Sol. **[1]**

Substance like $R-\underset{OH}{\underset{|}{CH}}-CH_3$ will give positive iodoform test.

16. Which combination of reagents will bring about the following conversion?



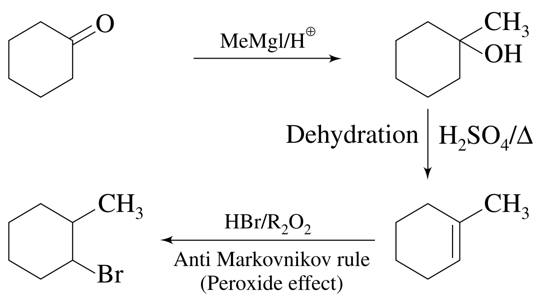
(1) (i) MeMgl/H^+, (ii) H_2SO_4/Δ, (iii) HBr/R_2O_2

(2) (i) MeMgl/H^+, (ii) H_2SO_4/Δ, (iii) HBr

(3) (i) MeMgl/H^+, (ii) HBr

(4) (i) MeMgl/H^+ (ii) H_2SO_4/Δ, (iii) $Br_2/h\nu$

Sol. **[1]**



17. In the reaction

$$\underset{\displaystyle |\atop Br}{CH_3CHCH_3} \xrightarrow{\text{alc. KOH}} A \xrightarrow[\text{Peroxide}]{\text{HBr}} B \xrightarrow[\text{acetone}]{\text{NaI}} C$$

C is–

(1) $CH_3CH_2CH_2–I$ (2) $\underset{\displaystyle |\atop I}{CH_3CH–CH_3}$

(3) $CH_3–\underset{\displaystyle |\atop I}{CH}–CH_2–I$ (4) $CH_3CH{=}CHI$

Sol. **[1]**

$$CH_3–\underset{\displaystyle |\atop Br}{CH}–CH_3 \xrightarrow{\text{alc. KOH}} CH_3–CH{=}CH_2$$

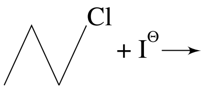
$$\downarrow \text{HBr/Perorcide}$$

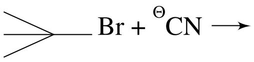
$$CH_3–CH_2–CH_2–Br$$

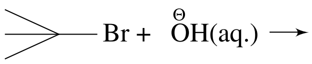
$$\downarrow \text{NaI/Acetone}$$

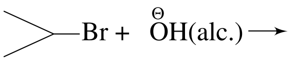
$$CH_3–CH_2–CH_2–I$$

18. Which of the following is an S_N2 reaction?

(1) 

(2) 

(3) 

(4) 

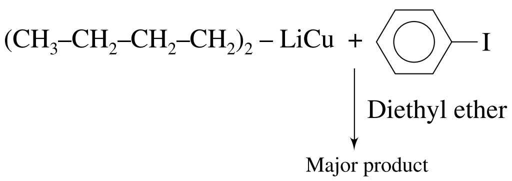
Sol. **[1]**

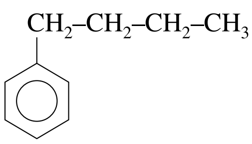
→ 3° halide gives β-elimination

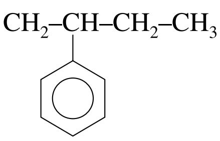
→ 2° halide also gives β-elimination with alcohalic $\overset{\ominus}{O}H$

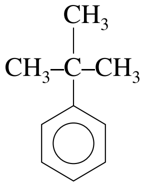
→ 1° halide give SN_2 reaction predominantly.

19. Major product of given chemical reaction is



(1) 

(2) 

(3) 

(4) No reaction takes place

Sol. **[1]**

S_N2 reaction takes place in presence of diethyl ether (Polar aprotic solvent) and $CH_3–CH_2–CH_2–\overline{C}H_2(Nu^-)$

20. These given number of factor influences relative rate of SN_1 reaction except

(1) The structure of substrate

(2) The concentration and reactivity of nucleophile

(3) The effect of solvent

(4) The nature of leaving group

Sol. **[2]**

Rate = k[substrate]^1

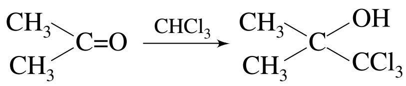
Independent of concentration of nucleophile

21. The reaction of chloroform with acetone gives

(1) Mesitylene (2) Ethylidene chloride

(3) Chloretone (4) Chloral

Sol. **[3]**



Chloretone

22. $CH_3CH_2–OH$ can be converted to CH_3CH_2CN by the following reactions:

(1) $CH_3CH_2OH + KCN \xrightarrow{\Delta}$

(2) $CH_3CH_2OH + HCN \xrightarrow{\Delta}$

(3) $CH_3CH_2OH \xrightarrow{\text{Na}/\Delta} \xrightarrow{\text{KCN}}$

(4) $CH_3CH_2OH \xrightarrow{SOCl_2} \xrightarrow{\text{KCN}}$

Sol. **[4]**

$$CH_3–CH_2–OH \xrightarrow{SOCl_2} CH_3–CH_2–Cl$$

$$\downarrow \text{KCN}$$

$$CH_3–CH_2–CN$$

23. Which of the following reactions will proceed the fastest?

(1) $CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$

(2) $CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$

(3) $(CH_3)_2CHOH + HBr \longrightarrow (CH_3)_2CHBr + H_2O$

(4) $(CH_3)_2CHOH + HI \longrightarrow (CH_3)_2CHI + H_2O$

Sol. **[4]**

→ Reactivity of alcohol (towards HX) ∝ stability of carbocation

→ If $-\overset{|}{\underset{|}{C}}{}^{\oplus}$ is same, then HI > HBr > HCl > HF

24. Major product of which of the following reactions shows zero dipole moment?

(1) CH_3OH, $SOCl_2$

(2) C_2H_5OH, OH^-, Cl_2

(3) $CHCl_3$, Cl_2, hν

(4) CHI_3, Zn, HCl

Sol. **[3]**

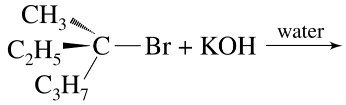
$$CH_3\text{–}OH \xrightarrow{SOCl_2} CH_3\text{–}Cl \qquad \mu \neq 0$$

$$\underset{\large OH}{CH_3\text{–}\overset{}{CH}\text{–}H} \xrightarrow[\text{Chloroform reaction}]{OH^-/Cl_2} CHCl_3 + H\text{–}COO^- \quad \mu \neq 0$$

$$CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4 \qquad \mu = 0$$

$$CHI_3 \xrightarrow[\text{reduction}]{Zn/HCl} CH_2Cl_2 \qquad \mu \neq 0$$

25. In the reaction



If the concentration of both the reactants is doubled, the rate of the reaction will

(1) double

(2) quadruple

(3) be reduced to one-fourth

(4) remain unchanged

Sol. **[1]**

Substrate is tertiary halide so reaction is SN_1

Thus $\frac{dx}{dt}$ = K [substrate]

Rate of SN_1 reaction is independent of concentration of alkali.

EXERCISE 1

1. Consider the reaction:

(i) $(CH_3)_2CH\text{–}CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH\text{–}CH_2\,OC_2H_5 + HBr$

(ii) $(CH_3)_2CH\text{–}CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH\text{–}CH_2\,OC_2H_5 + Br$

The mechanisms of reaction (i) and (ii) are, respectively:

(1) S_N2 and S_N1 (2) S_N1 and S_N2

(3) S_N1 and S_N1 (4) S_N2 and S_N2

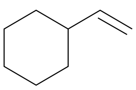
2. 2, 2-Dichloropentane can best be synthesised by:

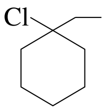
(1) $CH_2CH_2CH_2C{\equiv}CH \xrightarrow{Cl_2}$

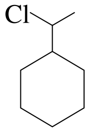
(2) $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{H_2} [A] \xrightarrow{Cl_2}$

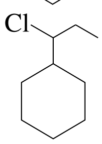
(3) $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{2HCl}$

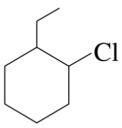
(4) $CH_3CH_2CH{=}CHCH_3 \xrightarrow{HCl}$

3.  $\xrightarrow{HCl}$ Major product:

(1) 

(2) 

(3) 

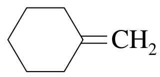
(4) 

4. $CH_2\begin{matrix}\diagup COOH \\ \diagdown COOH\end{matrix} \xrightarrow{\Delta} (A) \xrightarrow[\text{Reagent}]{\text{Tollen's}} (B) \xrightarrow[CS_2]{Br_2} (C)$

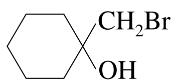
The end product (C) of given sequence of reaction is:

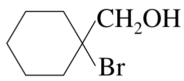
(1) $CH_2BrCOOAg$ (2) CH_3COOBr

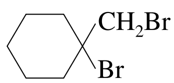
(3) CH_3CH_2Br (4) CH_3Br

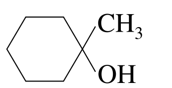
5. 

$\xrightarrow[H_2O]{Br_2}$ A; A is:

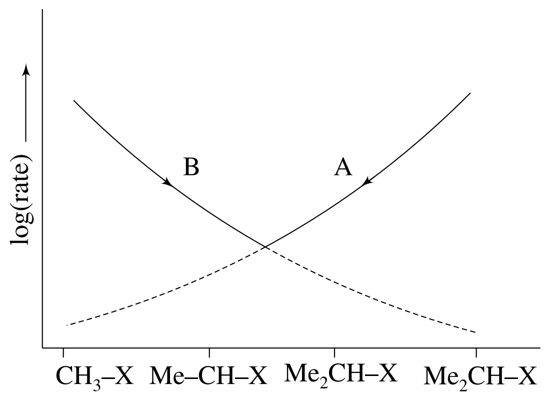
(1) 

(2) 

(3) 

(4) 

6.



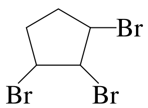
Which of the following is true about given graph A and B?

(1) A $\rightarrow S_N1$ B $\rightarrow S_N2$ (2) A $\rightarrow S_N2$, B $\rightarrow S_N1$
(3) A and B $\rightarrow E_1$ (4) A and B $\rightarrow E_2$

7. Ethyl alcohol reacts at faster rate with HI than with HCl in forming the corresponding ethyl halides under identical conditions mainly because:

(1) HI, being a stronger acid, protonates ethyl alcohol at oxygen much better and helps substitution
(2) the bond length in HI is much shorter than that in HCl
(3) I^- derived from HI is a much better leaving group
(4) I^- derived from HI is a much better nucleophile than Cl^-

8. Identify the correct reaction to synthesise the following compound from cyclopentane.



(1) $\xrightarrow[h\nu]{Cl_2} \xrightarrow{\text{Alc. KOH}} \xrightarrow[CCl_4]{Br_2}$

(2) $\xrightarrow[h\nu]{Br_2} \xrightarrow{C_2H_5O^{\ominus}} \xrightarrow{Br_2,\ CCl_4}$

(3) $\xrightarrow[h\nu]{Br_2} \xrightarrow{\text{Alc. KOH}} \xrightarrow{\text{NBS}} \xrightarrow[CCl_4]{Br_2}$

(4) None of these

9. Which of the following reactions will result in the formation of a chiral centre in the product?

(1) $CH_3CH{=}CH_2 + HBr \longrightarrow$
(2) $CH_2{=}CH_2 + HOBr \longrightarrow$
(3) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{H_2O_2}$
(4) $CH_3CH_2CH{=}CH_2{+}HBr \longrightarrow$

10. In the presence of dibenzoyl peroxide, addition of HBr to 1-butene produces

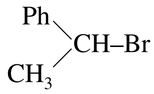
(1) 2-bromobutane (2) 1-bromobutane
(3) (±)-2-bromobutane (4) 1-bromobutene

11. The reaction of (S) – 2-bromobutane with OH^- to produce (R)-butan-2-ol will be

(1) first order in 2-bromobutane only
(2) first order in OH^- only
(3) first order in 2-bromobutane and first order in OH^-
(4) second order in OH^-

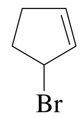
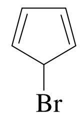
12. The correct order of increasing reactivity of the substrates (I), (II), (III), and (IV) below, towards S_N1 reaction with a given nucleophile is:

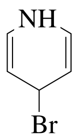
(I) CH_3CH_2—Br (II) $(CH_3)_2CH$—Br

(III) $CH_2{=}CHCH_2$—Br (IV) 

(1) I < II < III < IV (2) II < I < III < IV
(3) IV < II < I < III (4) III < IV < II < I

13. Among the bromides I–III given below, the order of reactivity of S_N 1 reaction is:

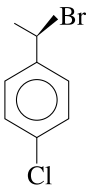
(I)  (II) 

(III) 

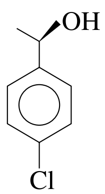
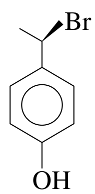
(1) III > I > II (2) III > II > I
(3) II > III > I (4) II > I > III

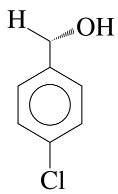
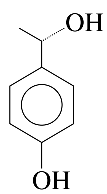
14. The S_N^2 reaction of 1-chloro-3-methylbutane with sodium methoxide is relative slow, but can be accelerated by the addition of a small amount of NaI. How this catalysis is best explained?

(1) The sodium cation helps pull off the chloride anion
(2) The iodide anion activates the methoxide nucleophile
(3) S_N^2 reaction of iodide ion converts the alkyl chloride to the more reactive alkyl iodide
(4) The NaI changes the mechanism to S_N^1

15.  $\xrightarrow[\text{DMF}]{\text{aq. KOH}}$ Major product is:

The major product in this reaction is:

(1)  (2) 

(3)  (4) 

16. Isopropylidene chloride is hydrolysed with aqueous NaOH. The product formed is:

(1) 1-propanal (2) propanal
(3) 2-propanal (4) propanone

17. $CH_3-C(CH_3)_2-Cl \xrightarrow[\substack{20\%\ H_2O \\ (25°C)}]{80\%\ C_2H_5OH}$

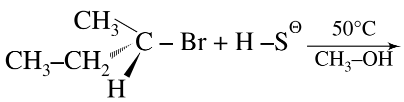
The given reaction undergoes

(1) unimolecular substitution predominantly.
(2) unimolecular elimination predominantly.
(3) bimolecular substitution predominantly.
(4) bimolecular elimination predominantly.

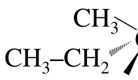
18. $CH_3-C(CH_3)_2-O^{\ominus} + CH_3-CH_2-CH_2-Br \xrightarrow{(CH_3)_3-C-OH,\ 40°C}$

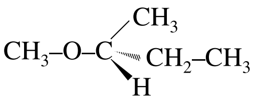
Major product

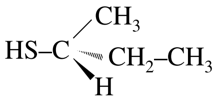
(1) $CH_3-CH = CH_2$ by E_2 pathway
(2) $CH_3-CH_2-CH_2-O-C(CH_3)_2-CH_3$ by SN_2 pathway
(3) $CH_3-CH = CH_2$ by E1 pathway
(4) $CH_3-CH_2-CH_2-O-C(CH_3)_2-CH_3$ by SN^1 pathway

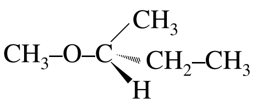
19.  Major product

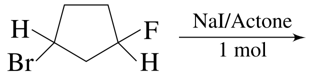
Select the major product and path of mechanism of given reaction

(1)  by S_N2 reaction

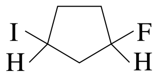
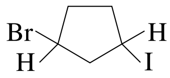
(2)  by S_N2 reaction

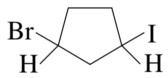
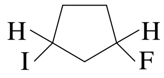
(3)  by S_N2 reaction

(4)  by S_N2 reaction

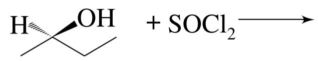
20. 

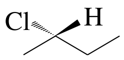
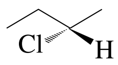
What would be major product of given reaction?

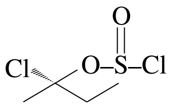
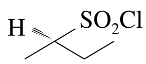
(1)  (2) 

(3)  (4) 

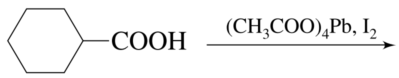
21. The product formed in the reaction is:

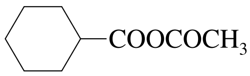


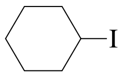
(1)  (2) 

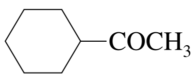
(3)  (4) 

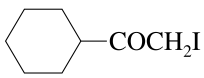
22. The product formed in the reaction is:



(1) 

(2) 

(3) 

(4) 

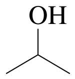
23. $CHCl_3 \xrightarrow{OH^-/H_2O}$ A, A is

(1) CO_3^{2-} (2) $H-C(=O)-H$
(3) $H-C(=O)-O^-$ (4) $C_2O_4^{2-}$

24. Identify (X):

$$CHCl_3 \xrightarrow[HF]{SbF_5} CHF_2Cl \xrightarrow{1070K} (X) + 2HCl$$

(1) $F_2C = CF_2$ (2) $ClFC = CFCl$
(3) $F_2C = CFCl$ (4) $F_2C = CCl_2$

25.  + aI_2 + bNaOH ⟶ CHI_3, ratio of moles (a) and (b) is:

(1) 3:4 (2) 2:3

(3) 3:2 (4) 4:3

26. Chloropicrin is a strong lachrymatory compound and is used in war. It is prepared by:

(1) heating acetone with chloroform in the presence of dilute NaOH.

(2) heating chloroform with HNO_3.

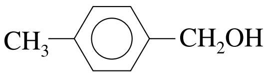
(3) heating nitormethane with carbon tetrachloride.

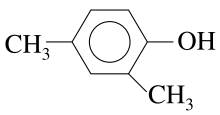
(4) the reaction of acetylene and arsenic chloride.

27. An aromatic compound A of the molecular formula $C_8H_{10}O$ on reaction with iodine and dilute NaOH gives a yellow precipitate. The structure of the compound is expected to be:

(1) $C_6H_5CH_2CH_2OH$

(2) $C_6H_5CHOHCH_3$

(3) 

(4) 

28. Which of the following has zero dipole moment?

(1) *o*-Dichlorobenzene

(2) *m*-Dichlorobenzene

(3) *p*-Dichlorobenzene

(4) *p*-chlorotoluene

29. The boiling points of methyl bromide (I), ethyl bromide (II), n-propyl bromide (III) and n-butyl bromide (IV) decrease in the order:

(1) I > II > III > IV (2) IV > III > II > I

(3) I > III > II > IV (4) III > IV > I > II

30. The stabilities of alkyl fluorides (I), alkyl chlorides (II), alkyl bromides (III) and alkyl iodides (IV) decrease in the order

(1) I > II > III > IV (2) IV > III > II > I

(3) I > IV > II > III (4) II > I > IV > III

31. The strengths of carbon–halogen bonds follow the order:

(1) R–F > R–Cl > R–Br > R–I

(2) R–I > R–Br > R–Cl > R–F

(3) R–F > R–I > R–Br > R–Cl

(4) R–Cl > R–Br > R–I > R–F

32. Arrange the following compounds in the increasing order of their boiling points:

(a) $(CH_3)_2CH–CH_2Cl$

(b) $CH_3CH_2CH_2CH_2Cl$

(c) $H_3C–C(CH_3)(Cl)–CH_3$

(1) (b) < (a) < (c) (2) (a) < (b) < (c)

(3) (c) < (a) < (b) (4) (c) < (b) < (a)

33. Positive Beilstein's test for halogens shows that:

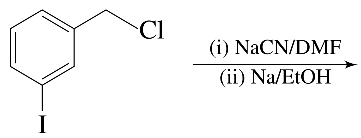
(1) a halogen is definitely present.

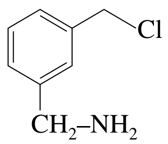
(2) a halogen may be present.

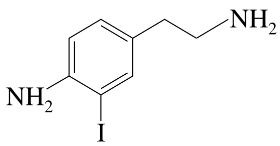
(3) a halogen is absent.

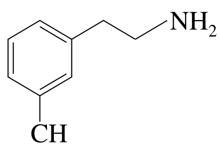
(4) None of the above

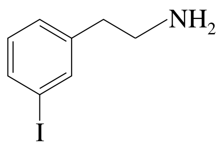
34. The structure of the major product formed in the following reaction is:



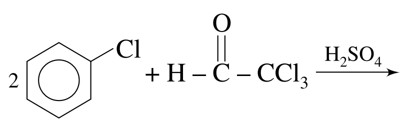
(1) 

(2) 

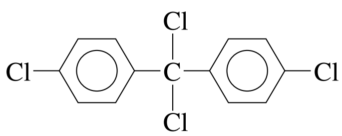
(3) 

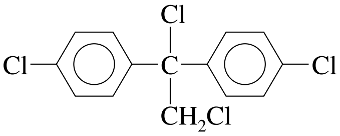
(4) 

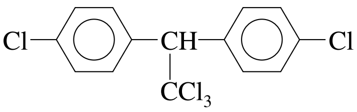
35. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4

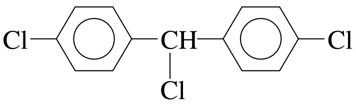


The major product formed is:

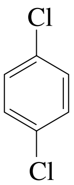
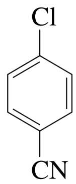
(1) 

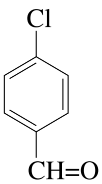
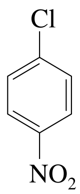
(2) 

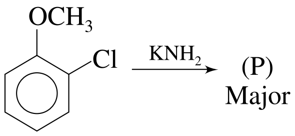
(3) 

(4) 

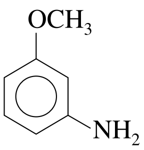
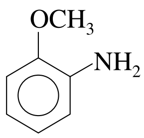
36. Which of the given aryl halide is most readily hydrolysed?

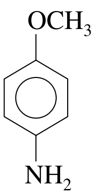
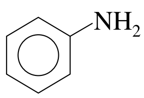
(1) 
(2) 

(3) 
(4) 

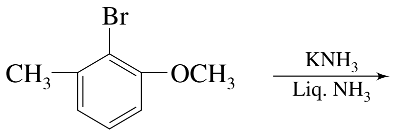
37. 

What is P?

(1) 
(2) 

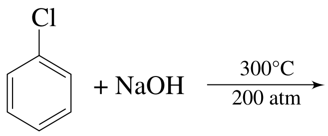
(3) 
(4) 

38. Which of the following reaction does not takes place?

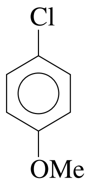
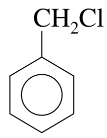
(1) 

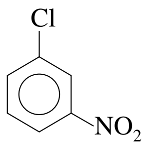
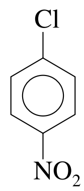
(2) Cl + aq. KOH ⟶

(3) Cl + alc. KOH ⟶

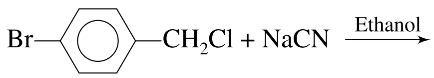
(4) 

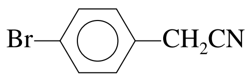
39. Among the following compounds, which one undergoes nucleophilic substitution of chlorine atom by OH^- most readily?

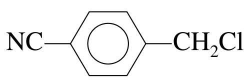
(1) 
(2) 

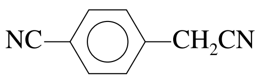
(3) 
(4) 

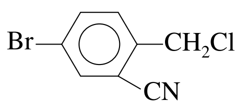
40. The product obtained from the reaction

 is:

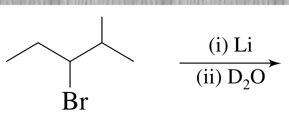
(1) 

(2) 

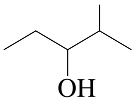
(3) 

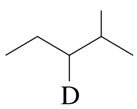
(4) 

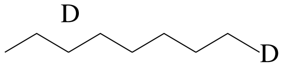
EXERCISE 2

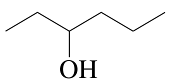
1. 

What is the product in the above reaction?

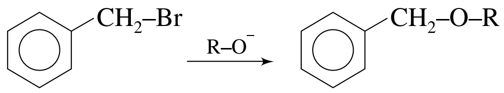
(1) 

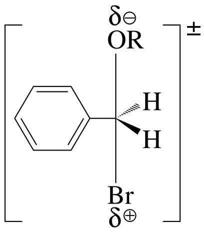
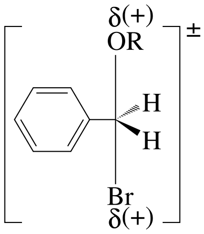
(2) 

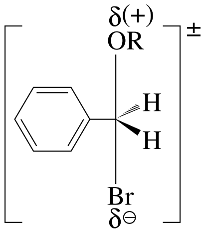
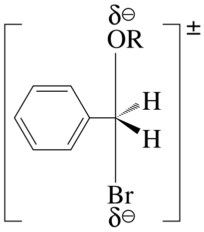
(3) 

(4) 

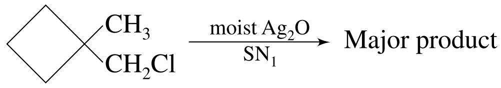
2. Transition state of given S_{N_2} is:

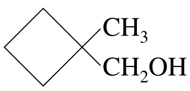
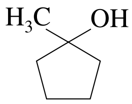


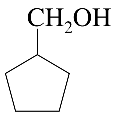
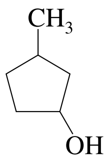
(1)  (2) 

(3)  (4) 

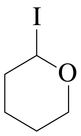
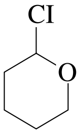
3. Which are possible products in following?

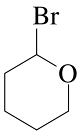
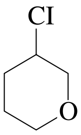


(1)  (2) 

(3)  (4) 

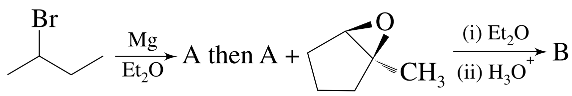
4. Arrange the following compound for S_N^1 reactivity order:

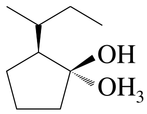
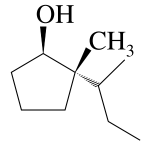
(I)  (II) 

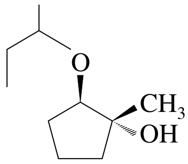
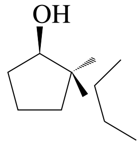
(III)  (IV) 

(1) I > II > III > IV (2) I > III > II > IV
(3) IV > III > II > I (4) II > IV > III > I

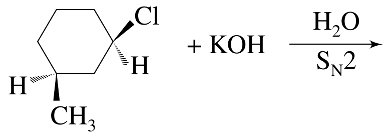
5. What is the product of the given reaction?



(1)  (2) 

(3)  (4) 

6. Consider the following reaction:



(1R, 3S)-Cis-1-chloro-3-methylcyclohexane

The product formed in the reactions is:

(1) (1R, 3S)-cis-3-methylcyclohexanol
(2) (1S, 3R)-cis-3-methylcyclohexanol
(3) (1S, 3S)-Trans-3-methylcyclohexanol
(4) (1R, 3R)-Trans-3-methylcyclohexanol

7. The reaction $RCH{=}CH{-}CH_2{-}X \xrightarrow{y^-} R{-}\underset{\substack{|\\y}}{CH}{-}CH{=}CH_2$ is:

(1) an S_N1 reaction (2) an S_N2 reaction
(3) an S_Ni reaction (4) None of these

8. In the reaction

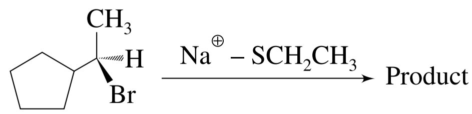
$R{-}COOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$

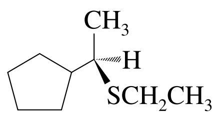
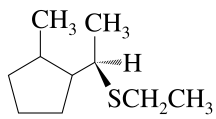
The reaction proceeds through the intermediate formation of:

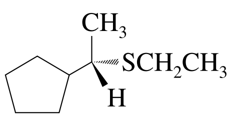
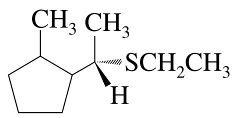
(1) $R{-}\overset{\overset{O}{\|}}{C}{-}O{-}Br$ (2) $R{-}\overset{\overset{O}{\|}}{C}{-}O^{\bullet}$

(3) $R^{\bullet}$ (4) All of these

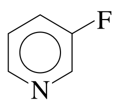
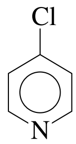
9. Consider the following reaction and select best choice that represents the reaction.

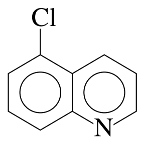
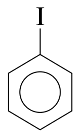


(1)  (2) 

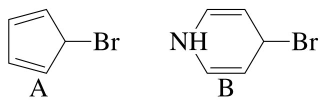
(3)  (4) 

10. Which is most reactive towards nucleophilic aromatic substitution?

(1)  (2) 

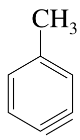
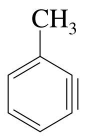
(3)  (4) 

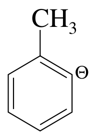
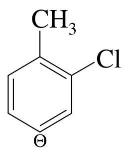
11. Which of the following statements is correct regarding the rate of hydrolysis of the compounds (A) and (B) by S_N1 reaction?



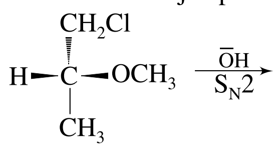
(1) A reacts faster than B
(2) B reacts faster than A
(3) Both A and B reacts at the same rate
(4) Neither A nor B reacts

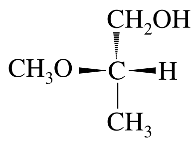
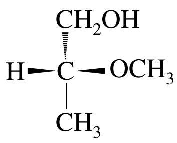
12. o-Chlorotoluene reacts with $NaNH_2$ in liquid ammonia to give o-toluidine and m-toluidine. This reaction proceeds through the intermediate

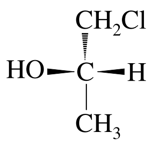
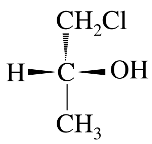
(1)  (2) 

(3)  (4) 

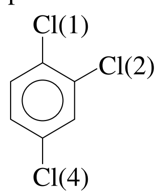
13. What is the major product of the given reaction?



(1)  (2) 

(3)  (4) 

14. Which chlorine is most easily replaced under nucleophilic attack?



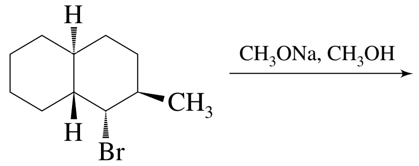
(1) Cl(1) (2) Cl(2)
(3) Cl(4) (4) Cl(1) and Cl(4)

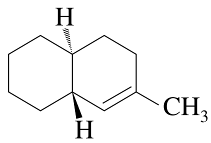
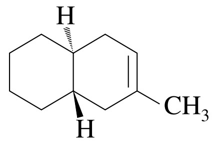
15. Arrange the following compounds in order of increasing dipole moment:

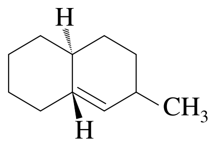
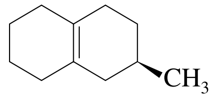
Toluene (I) m-dichlorobenzene (II)
o-dichlorobenzene (III) p-dichlorobenzene (IV)

(1) I < IV < II < III (2) IV < I < II < III
(3) IV < I < III < II (4) IV < II < I < III

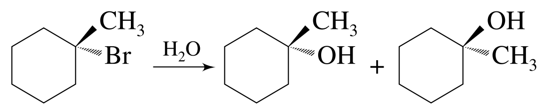
16. Provide the structure of the major organic product which results in the following reaction:

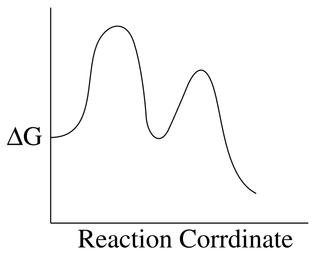


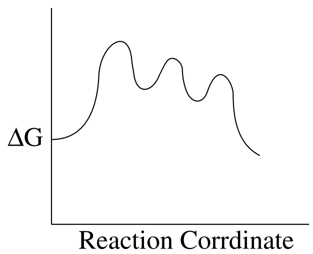
(1)  (2) 

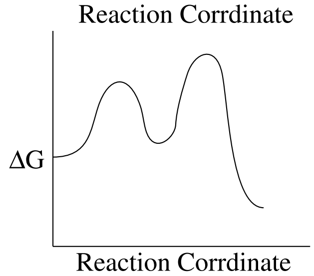
(3)  (4) 

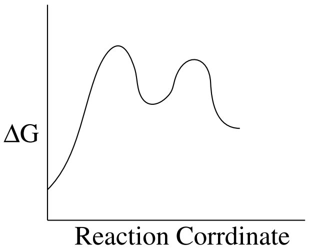
17. Which is the correct reaction coordinate diagram for the following solvolysis reaction?



(1) 

(2) 

(3) 

(4) 

18. Which of the following reagents can be used to distinguish chlorobenzene from chlorocyclohexane?

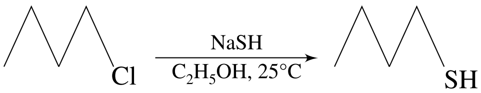
(1) $AgNO_3/C_2H_5OH$

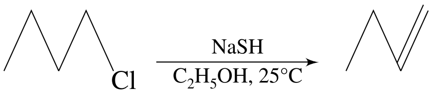
(2) $Ag(NH_3)_2OH$

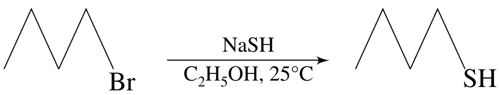
(3) Na fusion; HNO_3, $AgNO_3$

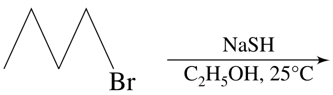
(4) Br_2/CCl_4

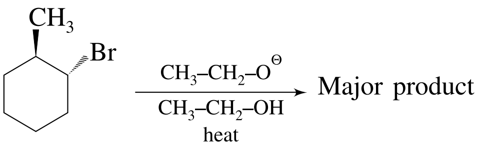
19. Which reaction takes place at the fastest rate?

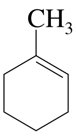
(1) 

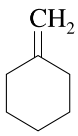
(2) 

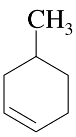
(3) 

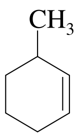
(4) 

20. 

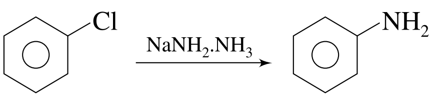
(1) 

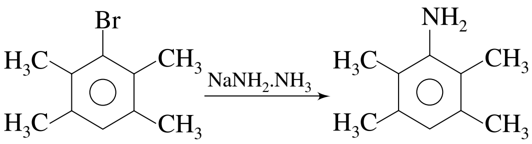
(2) 

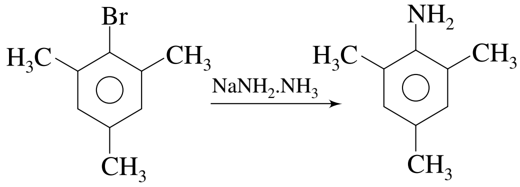
(3) 

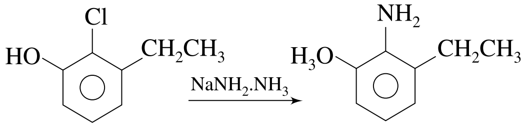
(4) 

21. Which of the following reaction is feasible?

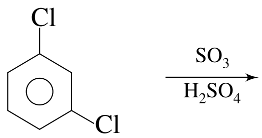
(1) 

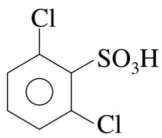
(2) 

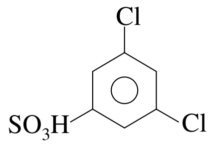
(3) 

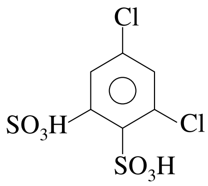
(4) 

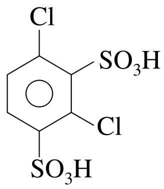
22. The major product obtained in the reaction



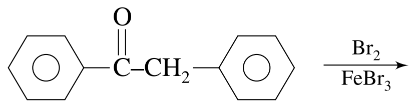
(1) 

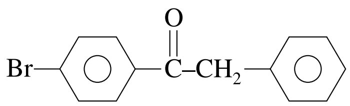
(2) 

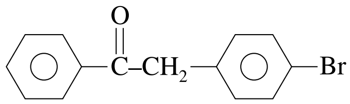
(3) 

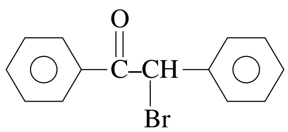
(4) 

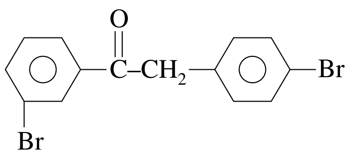
23. The major product obtained in the reaction



(1) 

(2) 

(3) 

(4) 

24. 2-Bromo-1-phenylpropane can be synthesised by

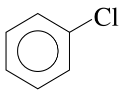
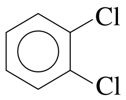
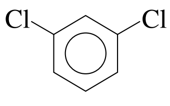
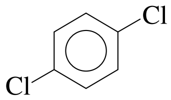
(1) $C_6H_5CH_2CH(OH)CH_3 + HBr \xrightarrow{\Delta}$

(2) $C_6H_5CH{=}CHCH_3$ + HBr + benzoyl peroxide $\rightarrow$

(3) $C_6H_5CH_2CH_2CH_3 + Br_2 + \text{light} \longrightarrow$

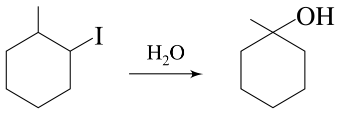
(4) none of these

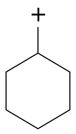
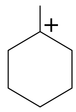
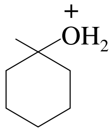
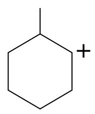
25. Which of the following substituted benzene derivatives would produce three isomeric products when one more constituent is introduced?

(I) 
(II) 
(III) 
(IV) 

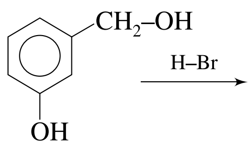
(1) I, II and III
(2) I
(3) II and IV
(4) I and III

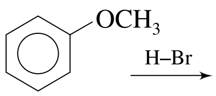
26. Which of the following is not expected to be an intermediate of the following reaction?



(1) 
(2) 
(3) 
(4) 

27. In which reaction Halide is not obtained?

(1) 

(2) 

(3) $CH_3–CH_2–OH + SOCl_2 \longrightarrow$

(4) $CH_3–CH_2–OH + KBr \longrightarrow$

28. What is the correct increasing order of reactivity of the followings in S_N2 reaction?

(I) $CH_2=CH–CH_2–Br$

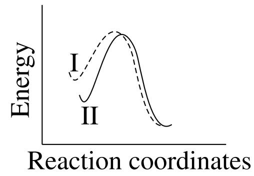
(II) $CH_2=CH–I$

(III) $CH_3CH_2CH_2–I$

(IV) $CH_3OCH_2CH_2–I$

(1) I < II < III < IV
(2) III < II < I < IV
(3) II < III < IV < I
(4) III < I < II < IV

29. Consider the two lines shown in the diagram given below



Which of the following apply appropriately to a S_N2 reaction?

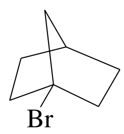
(1) Graph I could represent Cl^- and Graph II represents I^- leaving group

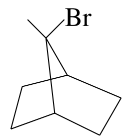
(2) Graph I could represent HO^- and Graph II represents CH_3COO^- nucleophile

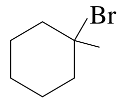
(3) Graph I could represent H_2O and Graph II H_2S as nucleophile

(4) Graph I could represent $(CH_3)_2NH$ and Graph II to $(CH_3)_2N–$ nucleophiles

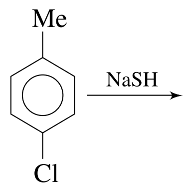
30. Which of the following alkyl halides is respectively most and least electrophilic in S_N1 reaction?

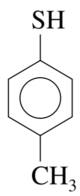
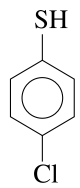
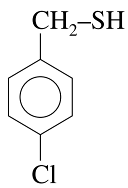

(I)


(II)

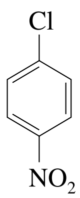
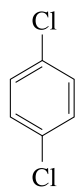

(III)

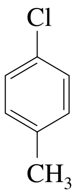
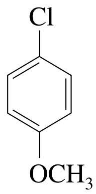
(1) Both I and III
(2) Both II and III
(3) Both III and I
(4) Both I and II

31.  A; Product (A) of the reaction is:

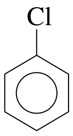
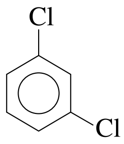
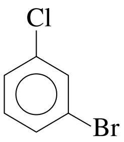
(1) 
(2) 
(3) 
(4) no reaction

32. Which one of the following undergoes nucleophilic aromatic substitution at the fastest rate?

(1) 
(2) 

(3) 
(4) 

33. Arrange the following compounds in the increasing order of their densities:

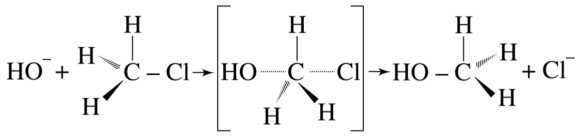
(a) 
(b) 
(c) 

(1) (a) < (b) < (c)
(2) (a) < (c) < (b)
(3) (c) < (b) < (a)
(4) (b) < (c) < (a)

34. Among the following halides, the one which reacts most readily with ethanol is

(1) *p*-nitrobenzyl bromide
(2) *p*-chlorobenzyl bromide
(3) *p*-methoxybenzyl bromide
(4) *p*-methylbenzyl bromide

35. Which of the statements is incorrect about below reaction?



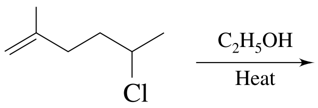
(a) (b) (c) (d) (e)

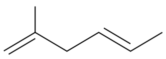
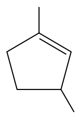
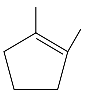
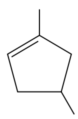
(1) The given reaction follows S_N2 mechanism.
(2) In (c) carbon atom is sp^3 hybridised.
(3) In (c) carbon atom is sp^2 hybridised.
(4) (b) and (d) have opposite configuration.

EXERCISE 3

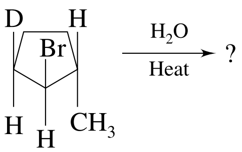
One and More than One Option Correct Type Question

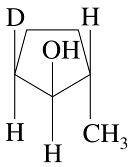
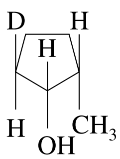
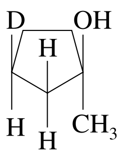
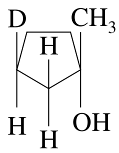
1. Consider the following elimination reaction:



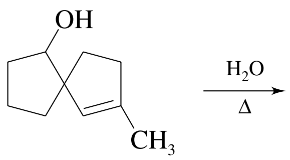
(1) 
(2) 
(3) 
(4) 

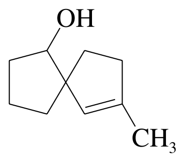
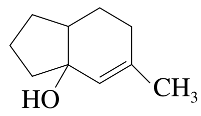
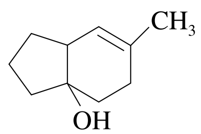
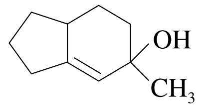
2. When the reactants shown below undergo substitution, which of the products will form?



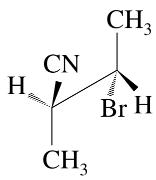
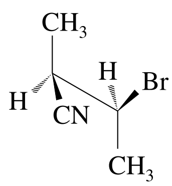
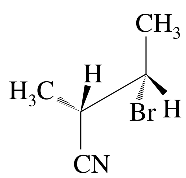
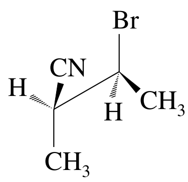
(1) 
(2) 
(3) 
(4) 

3. What is/are the expected solvolysis product(s) in the following reaction?

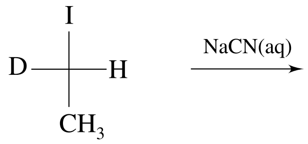


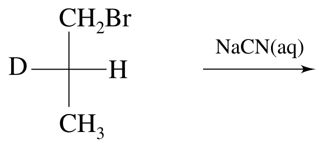
(1) 
(2) 
(3) 
(4) 

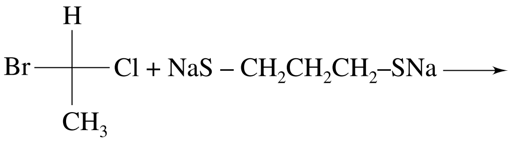
4. Which of the following on treatment with NaCN(aq) results in a chiral product?

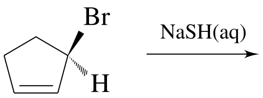
(1) 
(2) 
(3) 
(4) 

5. In which of the following reaction, inversion of configuration at chiral carbon takes place?

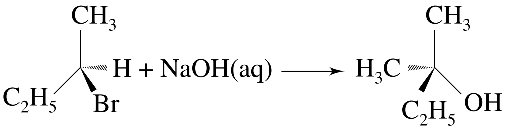
(1) 

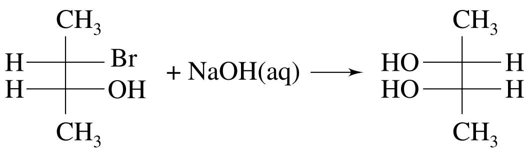
(2) 

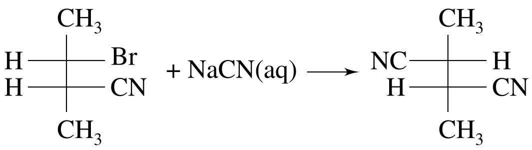
(3) 

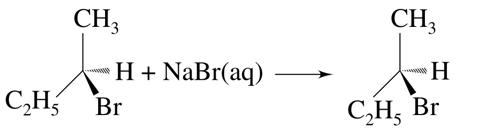
(4) 

6. In which of the following reaction(s), reactant and product are correctly matched?

(1) 

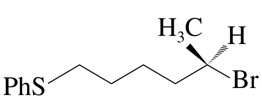
(2) 

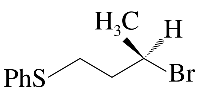
(3) 

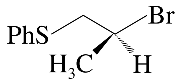
(4) 

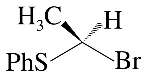
(+)-dextro (±)-racemic

7. Pick out the alkyl bromides which proceed with retention of configuration in an S_N2 reaction with $CH_3ONa(aq)$:

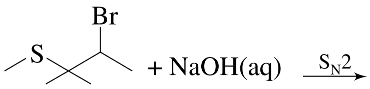
(1) 

(2) 

(3) 

(4) 

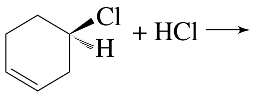
8. Consider the following substitution reaction



The correct statement(s) is/are:

(1) reaction occur at much faster rate than when substrate is 2-bromo-3, 3-dimethyl pentane
(2) reaction occur with inversion of configuration
(3) reaction occur with retention of configuration
(4) E2 product is preferred over S_N2

9. Consider the following reaction

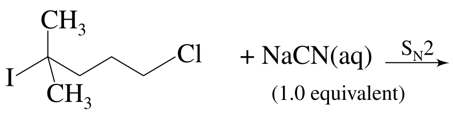


X

When a pure enantiomer of X is taken in the above reaction, correct completion regarding is/are

(1) Four different dichlorocyclohexane are formed as significant products
(2) a pair of enantiomers is formed
(3) two pairs of diastereomers are formed
(4) product mixture has zero specific rotation

10. Consider the reaction given below:



The correct statement(s) applicable to the above reaction is/are:

(1) Cl^- is substituted predominantly
(2) Cl^- is a better leaving group
(3) substitution of I^- in the above reaction required greater activation energy than for Cl^-
(4) addition of some NaI catalyse the substitution reaction

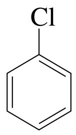
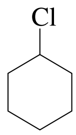
11. Which one of the following statements is true?

(1) Major part of energy needed for the heterolysis of C–X bond in S_N1 reaction mechanism is obtained by the solvation of X^- by the polar protic solvent.
(2) Greater solvation of attacking nucleophile & poor solvation of transition state promotes the reaction by S_N2 mechanism.

(3) Increase in the number of phenyl ring at C of C–X causes a shift in mechanism from S_N2 to S_N1.

(4) Allyl and benzyl halides undergo S_N1 reactions as they give resonance stabilized carbocation.

12. Which of the statements is correct?

(1)  is more reactive than  towards S_N1 mechanism due to aromaticity.

(2) Inversion of configuration takes place during S_N2 mechanism at α-chiral carbon.

(3) Formation of R–CI from R–OH by reaction with $SOCI_2$ is best method because byproducts are gases.

(4) CH_4 can be prepared by decarboxylation of carboxylic acid.

13. Which of the following reactions yield an alkyl halide?

(1) $CH_3CH_2OCH_2CH_3 \xrightarrow[h\nu]{Cl_2}$

(2) $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{\text{Conc. HI}}$

(3) $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{PCl_5}$

(4) $CH_3CH_2OH \xrightarrow{SOCl_2}$

14. $(CH_3–CH_2)_3–C–Br \xrightarrow[25°C]{CH_3OH} (CH_3–CH_2)_3–C–O–CH_3 + CH_3–CH = C(CH_2–CH_3)_2$

Pick out correct statement for given reaction.

(1) Major product is $(CH_3–CH_2)_3–C–O–CH_3$

(2) At low temperature reaction preceding through SN_1

(3) On increasing temperature major product is $CH_3–CH = C(CH_2–CH_3)_2$

(4) At high temp reaction preceding through E_2

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

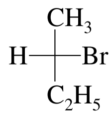
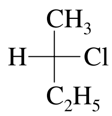
(4) If Statement-I is incorrect and Statement-II is correct

15. Statement 1: Bromobenzene upon reaction with Br_2/Fe gives 1, 4-dibromobenze as the major product.

Statement 2: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect for directing the incoming electrophile.

16. Statement I: Aryl halides undergo nucleophilic substitution with ease.

Statement II: The carbon halogen bond in aryl halides has partial double bond character.

17. Statement I: If the mixture of  and  reacts with the excess of NaSH in DMF, the molecularity of the SN^2 reaction will be two but not three.

Statement II: In the SN^2 reaction two molecules e.g. R–X and Nu take part in the formation of transition state.

18. Statement I: Aryl halides are extremely less reactive towards nucleophilic substitution reactions.

Statement II: In haloarenes the electron pairs of halogen atom are in conjugation with π electrons of the ring. More over due to more 'S' character of sp^2 carbon of ring, the C–X bond strength increases and cleavage becomes difficult.

19. Statement I: n-Butyl chloride has higher boiling point than n-butyl bromide.

Statement II: C–Cl bond is more polar than C–Br Bond.

20. Statement I: The London force of attraction and the dipole–dipole attraction (of C – X bond) are two types of forces which influence boiling point of alkyl halides.

Statement II: The London force is a surface attraction.

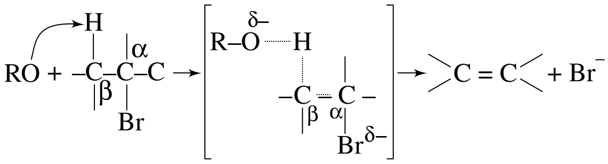
21. Statement I: Aryl halide cannot be prepared by Gabriel phthalamide method.

Statement II: Aryl halide does not give substitution reaction in ordinary condition.

Comprehension Type Question

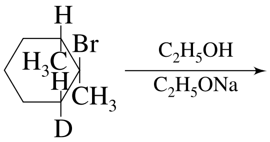
Comprehension (Q. 22–24)

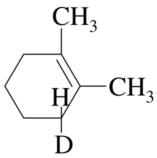
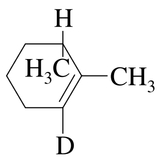
In an E2 reaction, following one step mechanism is involved.

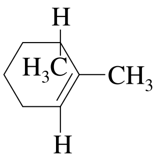
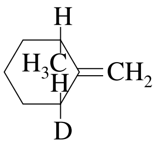


As shown in the above mechanism, a β-proton anti to leaving group is abstracted by the alkoxide base. If a less bulky base is used, β-proton is eliminated giving most substituted, most stable product as the major product. On the other hand if a bulky base is used, β-proton is abstracted from β-carbon where there is least steric hindrance and this gives least substituted, although least stable, alkene as the major product.

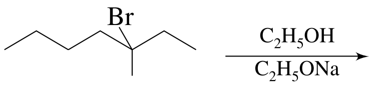
22. What is the major product in the following elimination reaction?



(1)  (2) 

(3)  (4) 

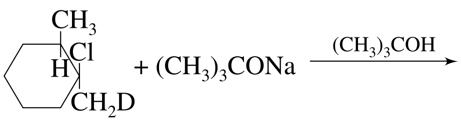
23. In the following reaction, how many elimination products would be formed in principle by E2 mechanism?

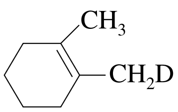
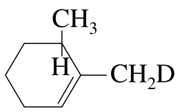


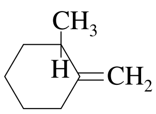
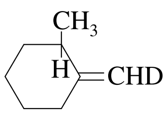
(1) 2 (2) 3

(3) 4 (4) 5

24. What is the major elimination product in the following reaction?

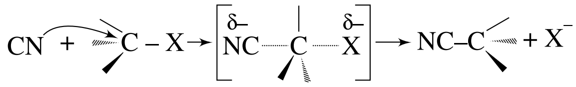


(1)  (2) 

(3)  (4) 

Comprehension (Q. 25–27)

The general mechanism of a SN_2 reaction is as follows



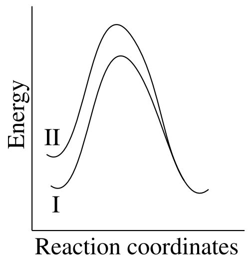
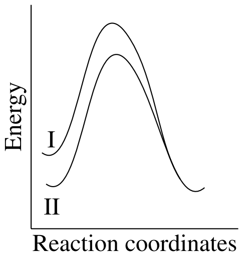
Factors that limit the rate of reaction are steric hindrance at α-carbon of substrate and strength of C–X bond. Any factor which stabilises transition state increases the rate of reaction.

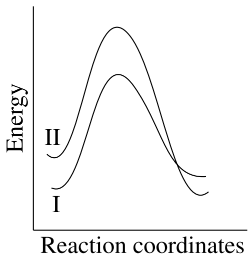
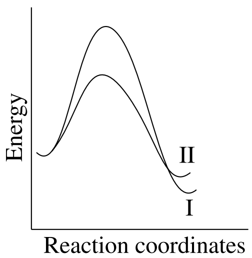
25. Consider the following S_N2 reaction

$$CH_3-I+HO^- \xrightarrow{K_1} CH_3-OH+I^- \quad \text{(I)}$$

$$CH_3-Cl+HO^- \xrightarrow{K_2} CH_3-OH+Cl^- \quad \text{(II)}$$

Which of the following energy diagram is correctly labeled?

(1)  (2) 

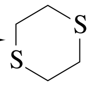
(3)  (4) 

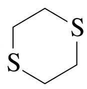
26. In the previous question, under identical reaction condition, i.e., temperature, concentration of substrate and nucleophile, the correct relationship between rate constant is

(1) $k_I < k_{II}$ (2) $k_I = k_{II}$

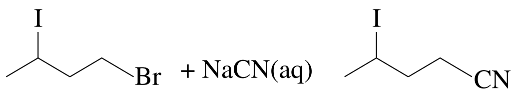
(3) $k_I > k_{II}$ (4) $k_I = k_{II}$

27. Which of the following is not a correct representation of S_N2 reaction?

(1) $Br-CH_2CH_2-Br + NaS-CH_2CH_2-SNa \rightarrow$ 

(2) $Br-CH_2CH_2CH_2CH_2-Br + NaS \rightarrow$ 

(3) $CH_3CH_2OH + NaNH_2 \rightarrow CH_3CH_2NH_2$

(4) 

(1.0 equivalent)

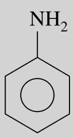
Column Matching Type Question

28. Match the following

Column-I	**Column-II**
(A) $CH_3CH(CH_3)—CH(OH)CH_3 + HCl \longrightarrow$	(p) $CH_3CH(CH_3)—CH(Cl)CH_3$
(B) $CH_3CH(CH_3)CH_2CH_2OH + PCl_5 \longrightarrow$	(q) $CH_3CH(CH_3)CH_2CH_2Cl$
(C) $CH_3CH(CH_3)—CH(OH)CH_3 + PCl_3 \longrightarrow$	(r) $CH_3C(Cl)(CH_3)CH_2CH_3$
(D) $CH_3CH(CH_2OH)CH_2CH_3 + SOCl_2 \longrightarrow$	(s) $CH_3CH(CH_2Cl)CH_2CH_3$

(1) A → r; B → q; C → p; D → s
(2) A → q; B → p; C → s; D → r
(3) A → s; B → r; C → q; D → p
(4) A → p; B → s; C → r; D → q

29. Make the correct match of the following from List-I and List-II.

List-I		List-II	
(A)	$RCCOAg + Br_2 \xrightarrow{CCl_4} RBr + CO_2 + AgBr$	(P)	Carbylamine
(B)	 $+CHCl_3 \xrightarrow{\text{Potash}}$ isocyanide	(Q)	Hundiecker Reaction
(C)	$2R–COOAg + I_2 \longrightarrow RCOOR + CO_2 + AgI$	(R)	Baurn Simonini Reaction
(D)	$2CH_3Cl + HgF_2 \longrightarrow 2CH_3 - F + HgCl_2$	(S)	Swarts Reaction

(1) A → R, B → S, C → Q, D → P
(2) A → P, B → R, C → S, D → R
(3) A → Q, B → P, C → R, D → S
(4) A → Q, B → R, C → S, D → P

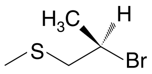
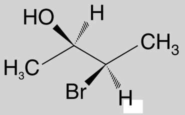
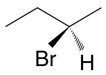
30. Make the correct match of the following from List-I and List-II.

List-I		List-II	
(A)	Gammexane	(P)	Pesticide
(B)	D.D.T.	(Q)	Insecticide
(C)	Chloroform	(R)	Anesthetic Agent
(D)	Westron	(S)	Solvent

(1) A → Q, B → R, C → S, D → P
(2) A → P, B → Q, C → S, D → R

(3) A → R, B → S, C → Q, D → P
(4) A → P, B → Q, C → R, D → S

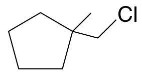
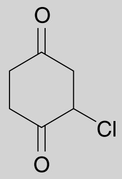
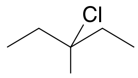
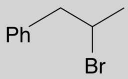
31. Match the column-I with Column-II and mark the correct option from the codes given below

	Column-I		Column-II
i.	 $\xrightarrow{\text{NaOH(aq)}}$	p.	Net inversion of configuration in S_N2 reaction
ii.	 $\xrightarrow{\text{NaOH(aq)}}$	q.	Net retention of configuration in S_N2 reaction
iii.	 $\xrightarrow{\text{NaCN(aq)}}$	r.	Formation of achiral product
iv.	$MeO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2Br \xrightarrow{\text{NaCN(aq)}}$	s.	Neighbouring group participation

Codes

	i	ii	iii	iv
(1)	q, s	p, r	p	r, s
(2)	q, s	s	p, s	q, s
(3)	p	q, r	s	p
(4)	p, r	q, s	p, r	q

32. Match the reaction from Column-I with the type of mechanism from Column-II and mark the correct option from the codes given below.

	Column-I		Column-II
i.	 $\xrightarrow{\text{NaOH(aq)}}$	p.	S_N1
ii.	 $\xrightarrow{\text{NaOH(aq)}}$	q.	S_N2
iii.	 $\xrightarrow{H_2O/\text{Heat}}$	r.	E2
iv.	 $\xrightarrow[\text{Heat}]{C_2H_5ONa}$	s.	E1cb

Codes

	i	ii	iii	iv
(1)	p	p, q	p, q, r	r, s
(2)	q	q, r, s	p	p, q, r, s
(3)	s	p	r, s	p, q
(4)	p, q	r, s	q, s	p, r, s

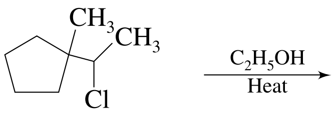
33. Match the reactions in Column-I with the appropriate name in the Column-II.

Column-I	Column-II
(A) $C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$	(p) Elimination reaction
(B) $C_6H_5N_2^+Cl^- + HBr \xrightarrow{Cu} C_6H_5Br + N_2 + HCl$	(q) Finkelstein reaction
(C) $CH_3\underset{\underset{\displaystyle Br}{\|}}{C}HCH_2CH_3 \xrightarrow{\text{alc.KOH}} CH_3\text{–}CH = CHCH_3$	(r) Groove's process
(D) $CH_3CH_2CH_2Cl + NaI \xrightarrow{\text{Acetone}} CH_3CH_2CH_2I + NaCl$	(s) Gattermann reaction

(1) A → r; B → s; C → p; D → q
(2) A → r ; B → p; C → q; D → s
(3) A → p; B → q; C → s; D → r
(4) A → q; B → s; C → r; D → p

Single Digit Integer Type Question

34. Consider the following reaction,



In principle, how many different alkenes are possible by the above elimination reaction?

35. How many of the following are denser than water?

(i) CCl_4

(ii) $CH_3CH_2CH_2CH_2Cl$

(iii) Bromocyclohexane

(iv) Chlorocyclopentane

(v) 1,3-difluorocyclopentane

(vi) CH_3I

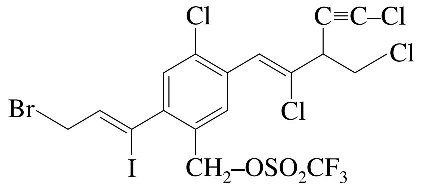
(vii) 1-fluorodecane

(viii) CH_2Br_2

(ix) CH_3Cl

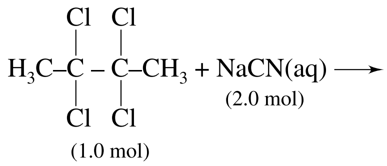
(x) $CHCl_3$

36. Consider the following compound



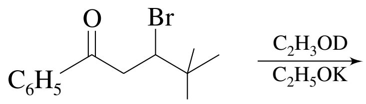
If the above compound is treated with excess of NaCN (aq), how many CN^- group would be incorporated by S_N2 reaction?

37. In the following reaction



How many different dicyano products are expected?

38. In the reaction given below how many elimination products are formed in principle if reaction proceeds by E1cb mechanism?



EXERCISE 4

1. The reaction is a **[AIEEE-2002]**

$(CH_3)_3\ CBr + H_2O \longrightarrow (CH_3)_3\ COH + HBr$

(1) Substitution reaction

(2) Debromination reaction

(3) Rearrangement reaction

(4) Elimination reaction

2. The correct order of the thermal stability of hydrogen halides (H–X) is **[AIEEE-2005]**

(1) HF > HCl > HBr > HI

(2) HI > HBr > HCl > HF

(3) HI > HCl < HF > HBr

(4) HCl < HBr > HBr < HI

3. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of **[AIEEE-2005]**

(1) Instability (2) Insolubility

(3) Steric hindrance (4) Inductive effect

4. Alkyl halides react with dialkyl copper reagents to give **[AIEEE-2005]**

(1) Alkyl copper halides

(2) Alkenes

(3) Alkenyl halides

(4) Alkanes

5. Elimination of HBr from 2-bromobutane results in the formation of **[AIEEE-2005]**

(1) Predominantly 2-butene

(2) Equimolar mixture of 1 and 2-butene

(3) Predominantly 2-butyne

(4) Predominantly 1-butene

6. Among the following the one that gives positive iodoform upon reaction with I_2 and NaOH is **[AIEEE-2006]**

(1) $C_6H_5CH_2CH_2OH$

(2) $CH_3\text{–}\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2OH$

(3) $PhCHOHCH_3$

(4) $CH_3CH_2CH(OH)CH_2CH_3$

7. Which of the following is the correct order of decreasing SN^2 reactivity? **[AIEEE-2007]**

(1) $RCH_2X > R_3CX > R_2CHX$

(2) $RCH_2X > R_2CHX > R_3CX$

(3) $R_3CX > R_2CHX > RCH_2X$

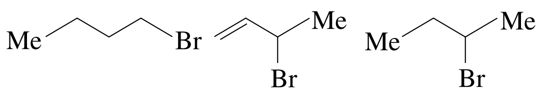
(4) $R_2CHX > R_3CX > RCH_2X$

8. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction is: **[AIEEE-2008]**

(1) $(CH_3)_3CCl$ (2) $(CH_3)_2CHCl$
(3) CH_3Cl (4) $(C_2H_5)_2CHCl$

9. Which of the following on heating with aqueous KOH, produces acetaldehyde? **[AIEEE-2009]**
(1) CH_3COCl (2) CH_3CH_2Cl
(3) CH_2ClCH_2Cl (4) CH_3CHCl_2

10. Consider the following bromides **[AIEEE-2010]**

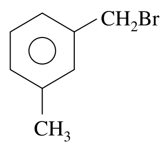
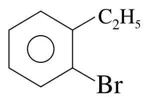


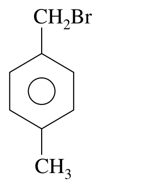
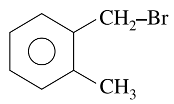
(A) (B) (C)

The correct order of S_N1 reactivity is
(1) A > B > C (2) B > C > A
(3) B > A > C (4) C > B > A

11. By heating which mixture, propane nitrile will be obtained? **[AIEEE-2011]**
(1) Ethyl alcohol + KCN
(2) Propyl alcohol + KCN
(3) Ethyl chloride + KCN
(4) Propyl chloride + KCN

12. Compound A, (C_8H_9Br) gives a white precipitate when warmed with alcoholic $AgNO_3$ oxidation of A gives an acid B, ($C_8H_6O_4$) B easily forms anyhydride on heating. Identify the compound A.
[JEE Main-2011]

(1)  (2) 

(3)  (4) 

13. Iodoform can be prepared from all except
[AIEEE-2012]
(1) Isopropyl alcohol (2) 3-Methyl-2-butanone
(3) Isobutyl alcohol (4) Ethyl methyl ketone

14. $C_2H_5Br \xrightarrow{AgCN} X \xrightarrow[\text{Zn–Hg/HCl}]{\text{Reduction}} Y$; Here, Y is:
[JEE Main Online-2012]
(1) n-propylamine (2) Isopropylamine
(3) Ethyl methyl amine (4) Ethylamine

15. Copper wire test for halogens is known as:
[JEE Main Online-2012]
(1) Duma's Test (2) Beilstein's Test
(3) Lassigne's Test (4) Liebig's Test

16. Among the following the molecule with the lowest dipole moment is: **[JEE Main Online-2012]**
(1) $CHCl_3$ (2) CH_2Cl_2
(3) CCl_4 (4) CH_3Cl

17. Beilstein test is used for estimation of which one of following elements? **[JEE Main Online-2012]**
(1) S (2) Cl
(3) C and H (4) N

18. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by
[JEE Main Online-2012]
(1) Azo coupling reaction
(2) Friedel–Crafts reaction
(3) Reimer–Tiemann reaction
(4) Gattermann reaction

19. Aryl fluoride may be prepared from arene diazonium chloride using **[JEE Main Online-2013]**
(1) HBF_4/Δ (2) $HBF_4/NaNO_2$, Cu, Δ
(3) CuF/HF (4) Cu/HF

20. In Williamson synthesis of mixed ether having a primary and tertiary alkyl group if tertiary halide is used, then **[JEE Main Online-2013]**
(1) Rate of reaction will be slow due to slow cleavage of carbon-halogen bond
(2) Alkene will be the main product
(3) Simple ether will form instead of mixed ether
(4) Expected mixed ether will be formed

21. The Wurtz–Fittig reaction involves combination of
[JEE Main Online-2013]
(1) Two molecules of aryl halides
(2) One molecule of each of aryl halide and alkyl-halide
(3) One molecule of each aryl-halide and phenol
(4) Two molecules of alkyl-halides

22. Carbylamine forms from aliphatic or aromatic primary amine via which of the following
[JEE Main Online-2013]
(1) Carbanion (2) Carbene
(3) Carbocation (4) Carbon radical

23. A solution of (–)-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of
[JEE-Main-2013]

(1) Carbanion (2) carbene
(3) carbocation (4) free radical

24. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: **[JEE Main-2014]**

(1) An alkane diol (2) an alkyl cyanide
(3) an alkyl isocyanide (4) an alkanol

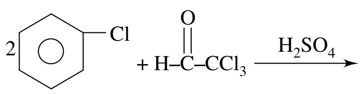
25. In S_N2 reaction, the correct order of reactivity for the following compounds:
CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is **[JEE Main-2014]**

(1) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(2) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(3) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$
(4) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

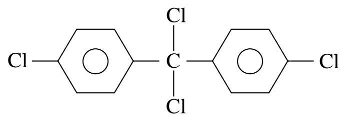
26. In a nucleophilic substitution reaction:
$R–Br + Cl^- \xrightarrow{DMF} R–Cl + Br^-$, which one of the following undergoes complete inversion of configuration? **[JEE Main Online-2014]**

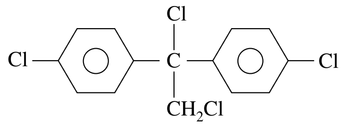
(1) $C_6H_5CHC_6H_5Br$ (2) $C_6H_5CH_2Br$
(3) $C_6H_5CHCH_3Br$ (4) $C_6H_5CCH_3C_6H_5Br$

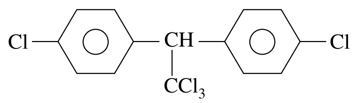
27. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4

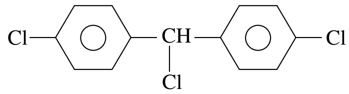


The major product formed is: **[MEE Main Online-2014]**

(1) 

(2) 

(3) 

(4) 

28. Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reaction? **[JEE Main Online-2014]**

(1) Claisen (2) Friedel–Craft
(3) Sandmeyer (4) Wurtz

29. The major product formed when 1, 1, 1-trichloropropane is treated with aqueous potassium hydroxide is **[JEE main Online-2014]**

(1) Propyne (2) 1-Propanol
(3) 2-Propanol (4) Propionic acid

30. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is **[JEE Main-2014]**

(1) acetylene (2) ethane
(3) 2-butyne (4) 2-butene

31. The synthesis of alkyl fluorides is best accomplished by **[JEE main-2015]**

(1) Free radical fluorination
(2) Sandmeyer's reaction
(3) Finkelstein reaction
(4) Swarts reaction

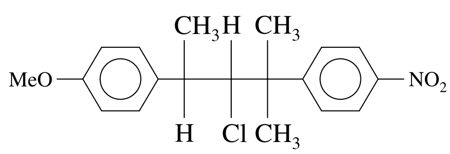
32. The order of reactivity of the following alkyl halides for a S_N2 reaction is **[IIT-2000]**

(1) RF > RCl > R–Br > R-I
(2) R-F > R-Br > R-Cl > R-I
(3) R–Cl > R–Br > RF > RI
(4) R–I > R–Br > R–Cl > R–F

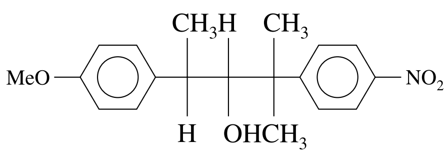
33. Identify the set of reagents/reaction of the following alkyl halides for a S_N2 reaction is **[IIT-2002]**

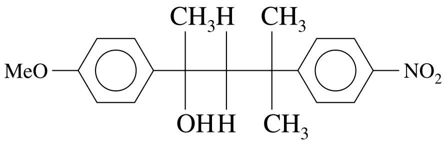
$$CH_3CH_2–CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3–\underset{\displaystyle Br}{\underset{|}{CH}}–CH_3$$

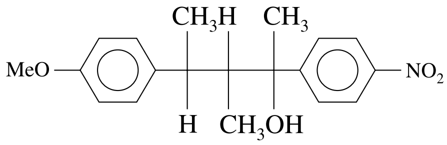
(1) X = dilute aqueous NaOH, 20°C
Y = HBr/acetic acid, 20°C
(2) X = concentrated alcoholic NaOH, 80°C
Y = HBr/acetic acid, 20°C
(3) X = dilute aqueous NaOH, 20°C
Y = $Br_2/CHCl_3$, 0°C
(4) X = concentrated alcoholic NaOH, 80°C
Y = $Br_2/CHCl_3$, 0°C

34.  **[IIT-2005]**

on hydrolysis in presence of acetone?

(A) 

(B) 

(C) 

(1) A & B (2) Only B

(3) Only C (4) A & C

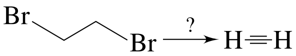
35. Match the Column-I with Column-II and mark the correct option from the codes given below.
[JEE Adv.-2006]

Column-I	Column-II
(A) CH_3–CHBr–CD_3 on treatment with alc. KOH Gives CH_2=CH–CD_3 as the major product.	(p) E1 reaction
(B) Ph–CHBr–CH_3–reacts Faster than Ph–CHBr–CD_3	(q) E2 reaction
(C) Ph–CH_2–CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph–CD=CH_2 as the major product.	(r) E1cb reaction
(D) $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	(s) First order reaction

Codes

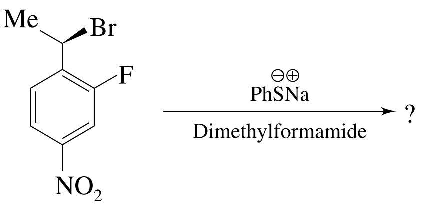
	A	B	C	D
(1)	q	q	r	p, s
(2)	p, s	p	q	r, s
(3)	q	q, r	p, q, r	q
(4)	q	s	q, r	p, r, s

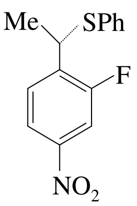
36. The reagent in form the following conversion is/are
[IIT-2007]

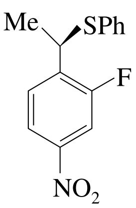


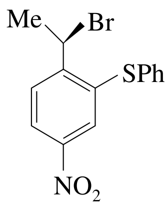
(1) Alcoholic KOH
(2) Alcoholic KOH followed by $NaNH_2$
(3) Aqueous KOH followed by $NaNH_2$
(4) Zn/CH_3OH

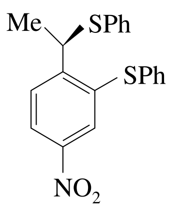
37. The major product of the following reaction is:
[IIT-2008]



(1) 

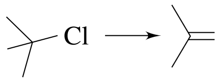
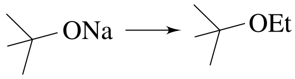
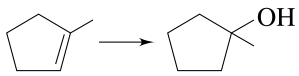
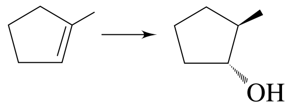
(2) 

(3) 

(4) 

38. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is
[JEE Adv.-2011 (integer type)]

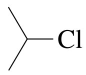
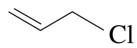
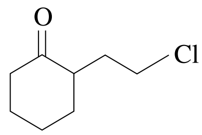
39. Match the chemical conversion in Column-I with the appropriate reagents in Column-II and select the correct answer using the code given below the lists
[JEE Adv.-2013]

Column-I		Column-II
(A)		(p) (I) $Hg(OAc)_2$; (ii) $NaBH_4$
(B)		(q) NaOEt
(C)		(r) Et-Br
(D)		(s) (i) BH_3; (ii) H_2O_2/NaOH

Codes

	A	B	C	D
(1)	q	r	p	s
(2)	r	q	p	s
(3)	r	q	s	p
(4)	r	q	s	p

40. KI in acetone, undergoes S_N2 reaction with each P, Q, R and S. The rates of the reaction vary as **[JEE Adv. Only-2013]**

$H_3C–Cl$   

(P) (Q) (R) (S)

(1) P > Q > R > S (2) S > P > R > Q
(3) P > R > Q > S (4) R > P > S > Q

ANSWER KEY

EXERCISE # 1

1. (4)	2. (3)	3. (1)	4. (4)	5. (1)
6. (1)	7. (4)	8. (3)	9. (4)	10. (2)
11. (3)	12. (1)	13. (1)	14. (3)	15. (3)
16. (4)	17. (1)	18. (1)	19. (3)	20. (1)
21. (2)	22. (2)	23. (3)	24. (1)	25. (2)
26. (2)	27. (2)	28. (3)	29. (2)	30. (1)
31. (1)	32. (3)	33. (2)	34. (4)	35. (3)
36. (4)	37. (1)	38. (1)	39. (2)	40. (1)

EXERCISE # 2

1. (2)	2. (4)	3. (2)	4. (2)	5. (1)
6. (3)	7. (1)	8. (4)	9. (3)	10. (2)
11. (2)	12. (2)	13. (2)	14. (1)	15. (2)
16. (3)	17. (2)	18. (1)	19. (3)	20. (4)
21. (1)	22. (1)	23. (2)	24. (2)	25. (4)
26. (1)	27. (4)	28. (3)	29. (2)	30. (3)
31. (4)	32. (1)	33. (1)	34. (3)	35. (2)

EXERCISE # 3

1. (1,2,4)	2. (1,2,3,4)	3. (1,2,4)	4. (1,3,4)	5. (1,4)
6. (1,3,4)	7. (1,2,3)	8. (1,3)	9. (1,3)	10. (1,2,4)
11. (1,2,4)	12. (2,3,4)	13. (2,3,4)	14. (1,3)	15. (2)
16. (4)	17. (2)	18. (1)	19. (4)	20. (2)
21. (2)	22. (3)	23. (4)	24. (4)	25. (2)
26. (3)	27. (3)	28. (1)	29. (3)	30. (4)
31. (1)	32. (2)	33. (1)	34. (8)	35. (6)
36. (3)	37. (4)	38. (4)		

EXERCISE # 4

1. (1)	2. (2)	3. (3)	4. (4)	5. (1)
6. (3)	7. (2)	8. (2)	9. (4)	10. (2)
11. (3)	12. (4)	13. (3)	14. (3)	15. (2)
16. (3)	17. (2)	18. (4)	19. (1)	20. (2)
21. (2)	22. (2)	23. (3)	24. (3)	25. (1)
26. (3)	27. (3)	28. (3)	29. (4)	30. (3)
31. (4)	32. (4)	33. (2)	34. (1)	35. (1)
36. (2)	37. (1)	38. (5)	39. (1)	40. (2)

HINT AND SOLUTION

EXERCISE # 1

1. [4]

S_N2 Reaction does not involve rearrangement.

Product of (i) and (ii) reaction formed without rearrangement, so that both reaction involve S_N2 mechanism.

2. [3]

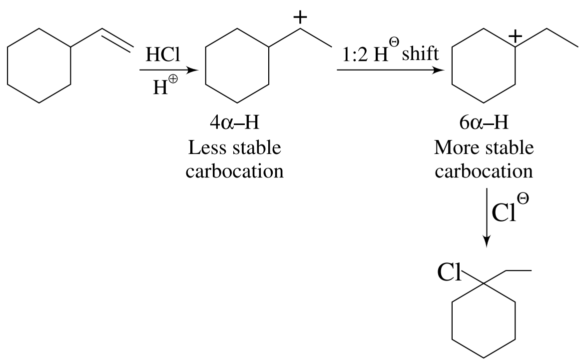
(1) $CH_3CH_2CH_2C\equiv CH \xrightarrow{Cl_2} CH_3-CH_2-CH_2-CCl_2-CHCl_2$

(2) $CH_3CH_2CH_2C\equiv CH \xrightarrow{H_2} [A] \xrightarrow{Cl_2} CH_3-CH_2-CH(Cl)-CH_2Cl$

(3) $CH_3CH_2CH_2C\equiv CH \xrightarrow{2HCl} CH_3-CH_2-CH_2-CCl_2-CH_3$

(4) $CH_3CH_2CH\equiv CHCH_3 \xrightarrow{HCl} CH_3-CH_2-CH(Cl)-CH_2-CH_3$

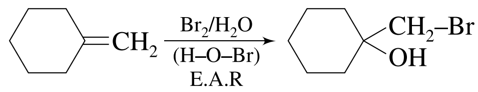
3. [1]



4. [4]

$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Tollens Reagent}]{Ag_2O} CH_3-\overset{O}{\overset{\|}{C}}-O-Ag \xrightarrow{Br_2/CS_2} CH_3-Br$

5. [1]



'Markownikov's rule'

6. [1]

Rate of $S_N1 \propto C^{\oplus}$ stability

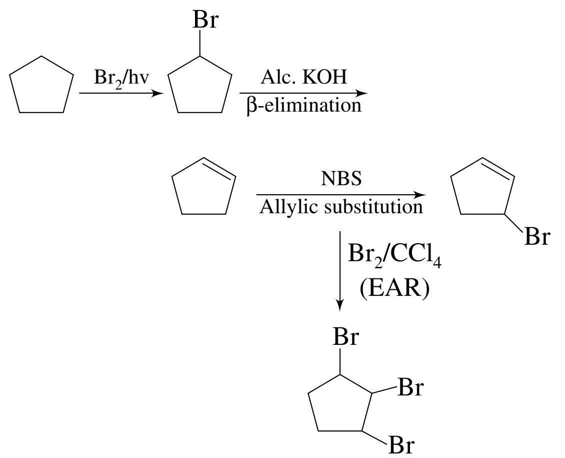
Rate of $S_N2 \propto \dfrac{1}{\text{Steric crowding}}$

7. [4]

Nucleophilic strength $\propto$ size

$$\left.\begin{array}{l} HCl \rightarrow H^+ + Cl^{\ominus} \\ HI \rightarrow H^+ + I^{\ominus} \end{array}\right] \begin{array}{l} \text{Size}\uparrow \\ \text{Base strength}\downarrow \\ \text{Nucleophilic strength}\uparrow \end{array}$$

8. [3]



9. [4]

$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CH(Br)-CH_3$

$CH_2=CH_2 \xrightarrow{HOBr} CH_2(OH)-CH_2(Br)$

$CH_3-CH_2-CH=CH_2 \xrightarrow[H_2O_2]{HBr} CH_3-CH_2-CH_2-CH_2-Br$

$CH_3-CH_2-CH=CH_2 \xrightarrow{HBr} CH_3-CH_2-\overset{*}{C}H(Br)-CH_3$

(chiral C-present)

10. [2]

$$CH_3–CH_2–CH=CH_2 \xrightarrow[C_6H_5–O–O–C_6H_5]{HBr}$$

Antimarkownikoff addition

$$CH_3–CH_2–CH_2–CH_2–Br$$

1-bromobutane

11. [3]

In given reaction configuration of product opposite as reactant, i.e., inversion takes place so that it must be SN_2 reaction.

$$\frac{dx}{dt} = k\ [\text{substrate}]^1\ [OH^-]^1$$

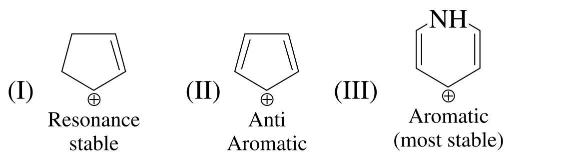
12. [1]

Rate of SN_1 reaction $\propto$ stability of carbocation

$CH_3-\overset{\oplus}{C}H_2$	$CH_3–\overset{\oplus}{C}H–CH_3$	$CH_2=CH–\overset{\oplus}{C}H_2$	$Ph–\overset{\oplus}{C}H–CH_3$
(I)	(II)	(III)	(IV)
(3α–H)	(6α–H)	(Resonance)	(Resonance + H-effect) most stable

13. [1]

Reactivity of SN_1 Reaction $\propto$ Stability of carbocation



III > I > II

14. [3]

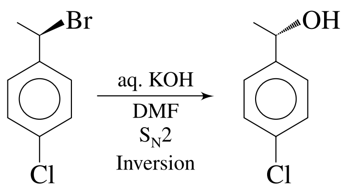
S_N2 reaction of iodide ion converts the alkyl chloride to the more reactive alkyl iodide

$$R–Cl \xrightarrow{NaI} R–I \text{ (Finkeltein reaction)}$$

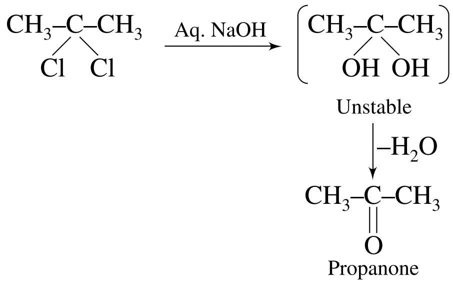
R–I > R–Br > R–Cl > R–F

Reactivity ↓

15. [3]



16. [4]

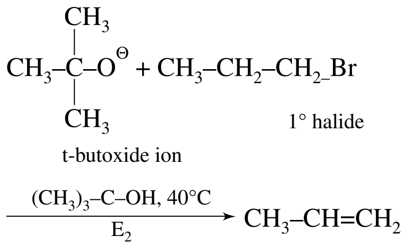


17. [1]

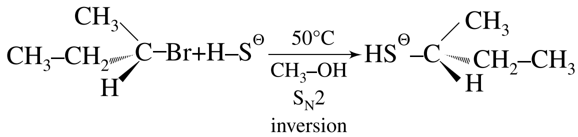
In polar protic solvent 3° halide will give unimolecular substitution (SN_1)

18. [1]

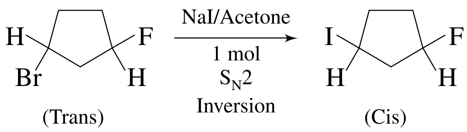
In strangest base (t-Buō) β-elimination predominantly takes place.



19. [3]



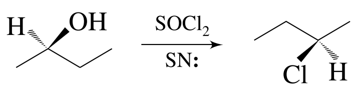
20. [1]



Reactivity of alkyl halides,

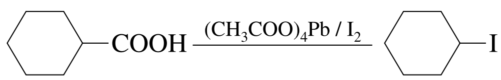
R – I > R – Br > R – Cl > R – F

21. [2]



Retention takes place, i.e., configuration of product and reactant are same.

22. [2]



De-carboxylation followed by iodination takes place.

23. [3]

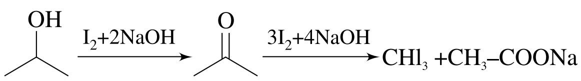
$$CHCl_3 \xrightarrow{\overline{OH}/H_2O} H-C(OH)_3 \xrightarrow{-H_2O} H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{\overline{OH}} H-\underset{\underset{O}{\|}}{C}-O^{\ominus}$$

24. [1]

$$CHCl_3 \xrightarrow[HF]{SbF_5} \underset{(2\ mole)}{CHF_2Cl} \xrightarrow{1070K} CF_2{=}CF_2\,(X) + 2HCl$$

25. [2]

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$
$$\downarrow$$
$$NaI + [O]$$



a = 4, (I_2 molecule used)
b = 6 (NaOH molecule used)

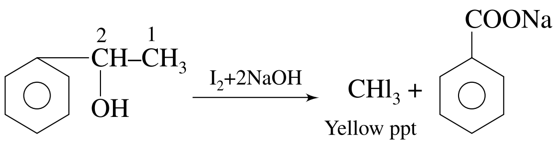
$$\frac{a}{b} = \frac{4}{6} = 2:3$$

26. [2]

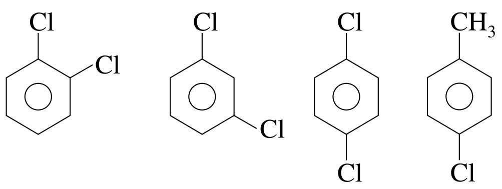
$$CHCl_3 \xrightarrow[\text{Nitration}]{\text{Conc. } HNO_3} \underset{\text{Chloropicrin}}{CNO_2\cdot Cl_3}$$

27. [2]

A will give positive iodoform test, so it must be 2-alkanol of $C_8H_{10}O$.



28. [3]



$\mu \neq 0$ $\mu \neq 0$ $\mu = 0$ $\mu \neq 0$

Magnitude of equal vector at 180°, Cancelled by each other.

29. [2]

Boiling point ∝ molecular weight.

30. [1]

Stability of R–X

$$\xrightarrow[\text{E.N.}\downarrow\ \text{Polarity}\downarrow\ \text{stability}\downarrow]{R{-}F > R{-}Cl > R{-}Br > R{-}I}$$

31. [1]

Bond strength ∝ Electronegativity.

32. [3]

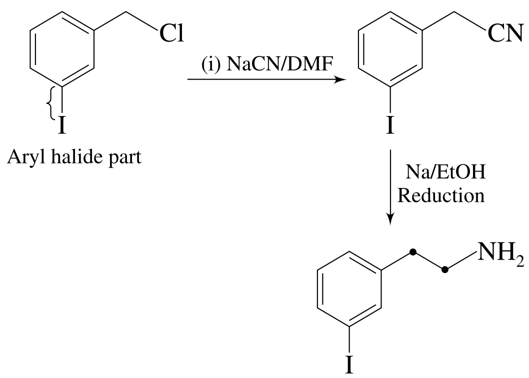
Boling point ∝ Molecular weight

$$\propto \frac{1}{\text{Branching (for isomer)}}$$

33. [2]

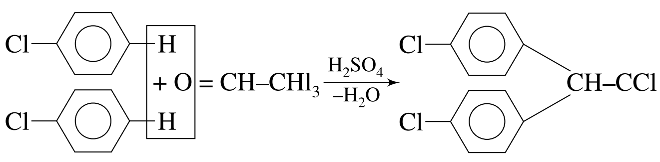
$R{-}X \xrightarrow[\text{Beilstein's test}]{\text{Cu-wire}}$ Green flame (A halogen may be present.)

34. [4]



1° halide undergoes SN reaction but aryl halides do not give SN reaction in ordinary condition.

35. [3]



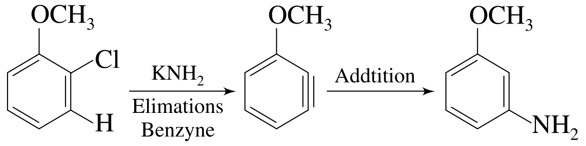
(D.D.T.)

36. [4]

$$\text{Rate of Ar SN} \propto \text{EWG} \propto \frac{1}{\text{ERG}}$$

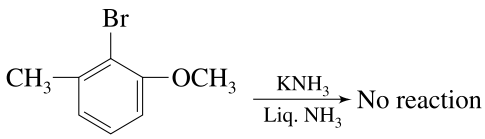
Thus presence of strong EWG increases the rate of hydrolysis.

37. [1]



(Elimination addition reaction
Benzyne mechanism refer keyconcept)

38. [1]

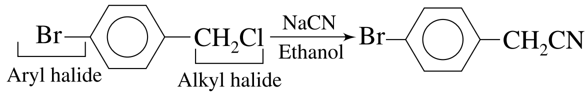


- Aryl substitution reaction takes place by benzyne mechanism; needed H at *ortho* position which is not present in option (1). So no reaction takes place.

39. [2]

Rate of nucleophilic substitution in Ar–Cl < R–Cl

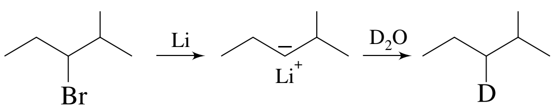
40. [1]



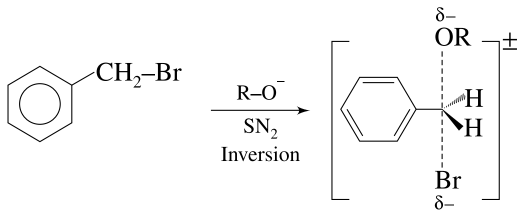
In ordinary condition aryl halide do not give SN reaction

EXERCISE # 2

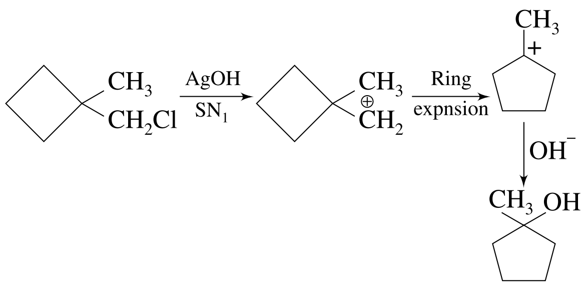
1. [2]



2. [4]



3. [2]



4. [2]

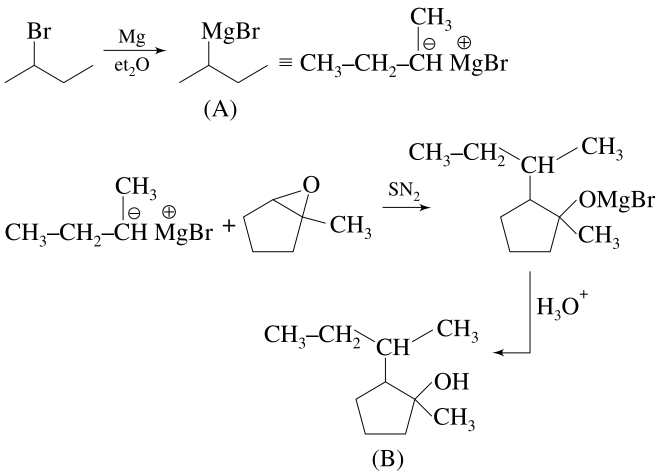
Rate of S_N1 reaction α stability of $-\overset{|}{\underset{|}{C}}{}^{\oplus}$

If carbocation is same, than

R–I > R–Br > R–Cl > R–F

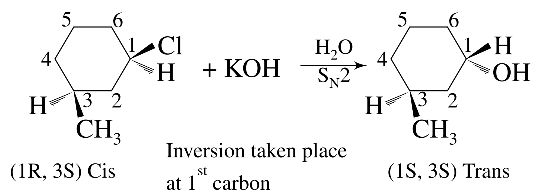
$\therefore$ I > III > II > IV

5. [1]



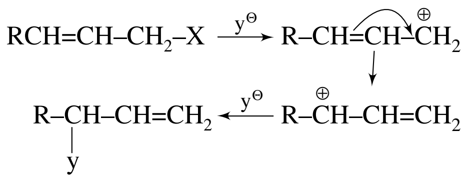
Since breaking of cyclic ether in alkaline media accompanied by SN_2, so that nucleophile added at least stericly hindred position.

6. [3]



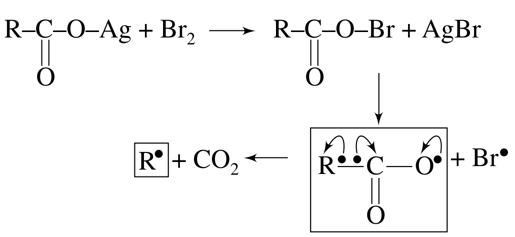
Hence configiration of only 1st carbon will revert.

7. [1]

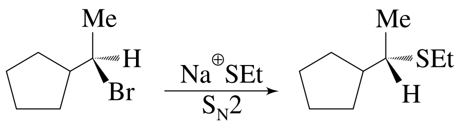


This reaction happened by stable carbocation so it is S_N1 reaction.

8. [4]



9. [3]

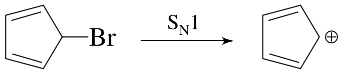


10. [2]

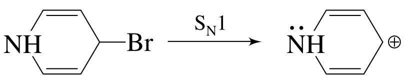
Rate of Ar-SN ∝ – M, – I

→ Lone pair of $\ddot{N}$ atom does not delocalize. So it works as –I group Thus it increases the rate of Ar–SN (aromatic nucleophlilic substitution) reaction.

11. [2]



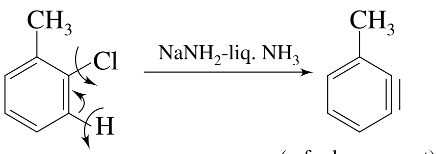
A Antiaromatic



B Aromatic

Rate of S_N1 reaction α stability of carbocation

12. [2]



β-elimination (refer keyconcept)

13. [2]

α-carbon is achiral, hence retention of configuration at β-carbon.

14. [1]

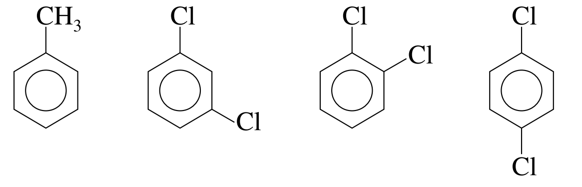
For Cl(1), other two Cl present at either *ortho* or *para* position; so it works as Electron Withdrawing Group.

Rate of Ar–S_N2 ∝ power of EWG

15. [2]

Dipole moment depends upon magnitude as well direction, and also it is calculated by the vector sum of two dipoles.

Angle (θ) ↑ dipole moment (μ) ↓

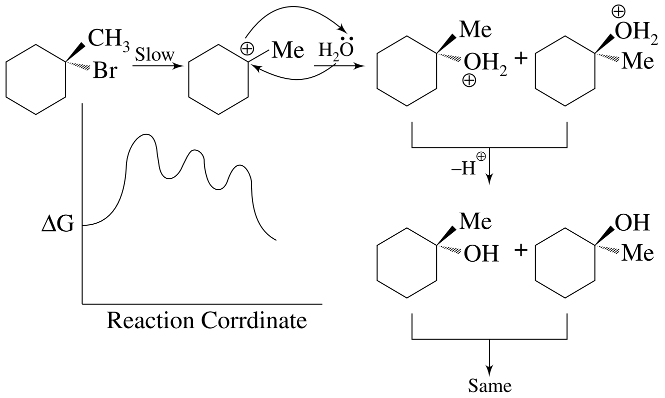


(I) (Polar) (II) (θ = 120) (III) (θ = 60) (IV) (θ = 180)

16. [3]

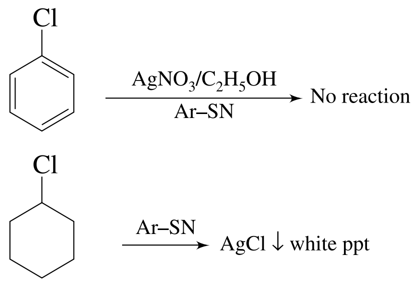
β-H at the bridging carbon is anti to leaving group, lost in E2 reaction

17. [2]



Two intermediate formed carbocation and oxoniumion.

18. [1]

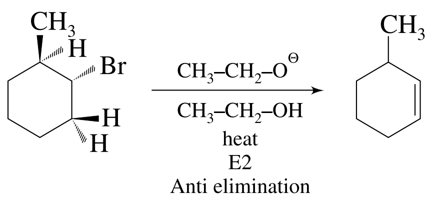


19. [3]

→ 1° halide will gives S_N2 reaction predominantly with $\overset{\ominus}{S}H$ ion.

→ If alkyl halide is same then R–Br is more reactive than R–Cl.

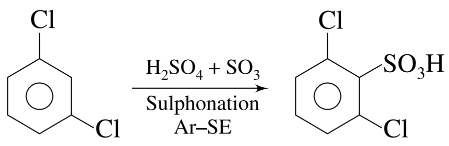
20. [4]



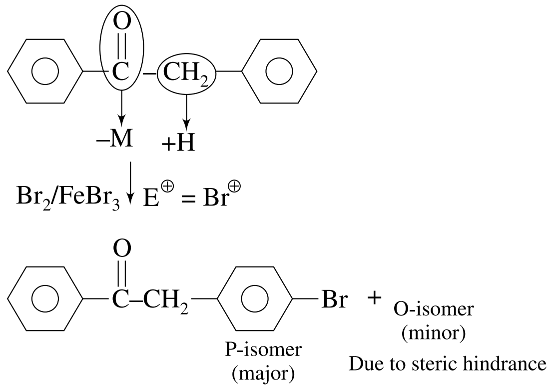
21. [1]

Arylic substitution takes place by benzyne mechanism, for this presence of H-atom at ortho position must be essential which is available only in option (1).

22. [1]



23. [2]



24. [2]

$$C_6H_5–CH_2–\underset{\displaystyle OH}{CH}–CH_3 \xrightarrow[H^{\oplus}]{H–Br} C_6H_5–CH_2–\overset{\oplus}{C}H–CH_3$$

$$\downarrow 1 : 2\ H^{\ominus}\ \text{shift}$$

$$C_6H_5–\overset{\oplus}{C}H–CH_2–CH_3$$

$$\downarrow Br^{\ominus}$$

$$C_6H_5–\underset{\displaystyle Br}{CH}–CH_2–CH_3$$

1-brano-1-phenyl propanea

$$C_6H_5–CH{=}CH–CH_3 \xrightarrow[C_6H_5–O–O–C_6H_5]{H–Br} C_6H_5–\overset{1}{C}H_2–\underset{\displaystyle Br}{\overset{2}{C}H}–\overset{3}{C}H_3$$

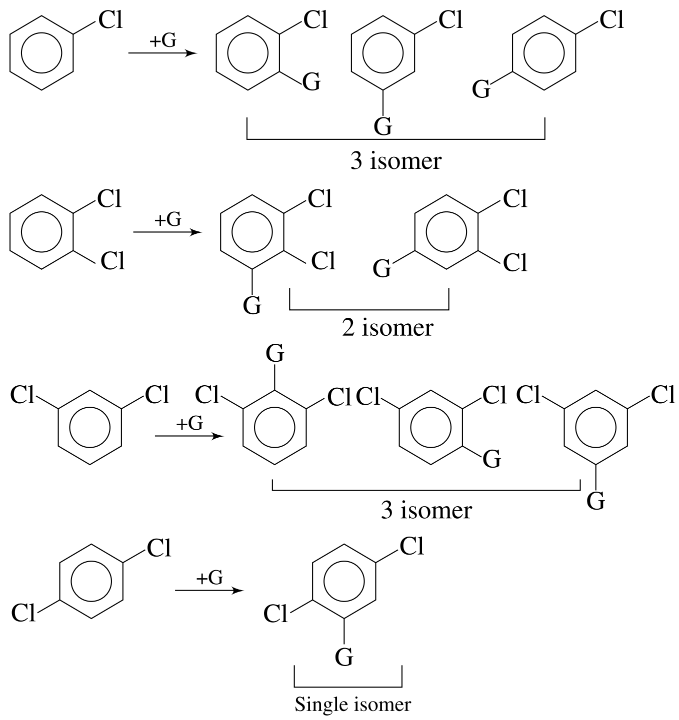
Anti-markownikoff

$$C_6H_5–CH_2–CH_2–CH_3 \xrightarrow[C_6H_5–O–O–C_6H_5]{Br_2/h\nu} C_6H_5–\underset{\displaystyle Br}{CH}–CH_2–CH_3$$

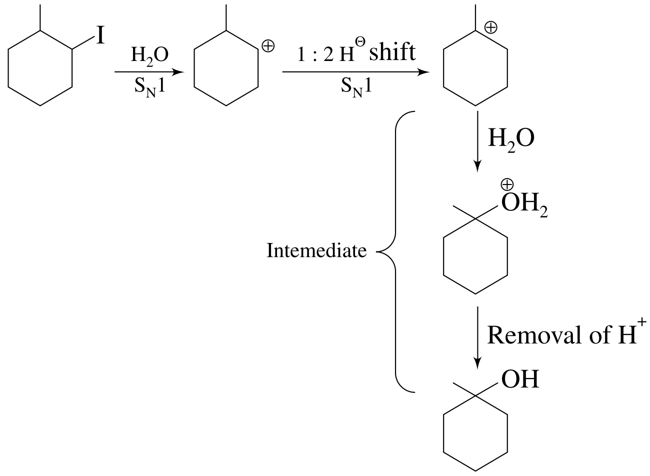
Benzylic substitution

via stable ($C_6H_5–\dot{C}H–CH_2–CH_3$) radical

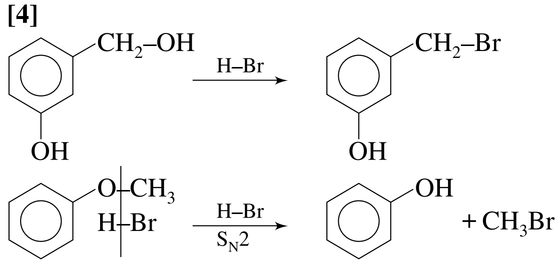
25. [4]



26. [1]



27. [4]



$$CH_3–CH_2–OH \xrightarrow{SOCl_2} CH_3–CH_2–Cl$$

$$CH_3–CH_2–OH \xrightarrow{KBr} \text{no reaction}$$

Poor Leaving group

28. [3]

Allyl bromide (I) is most reactive among the given halides as pi bonds from alylic position stabilizes the transition state. Vinyl iodide (II) is least reactive due double bond character. Electron withdrawing inductive effect of CH_3O^- increase reactivity of (IV) over (III)

29. [2]

HO^- is stronger nucleophile than CH_3COO^-. Hence, lower is the activation energy of (i) than (ii).

30. [3]

(III) forms tertiary carbocation, hence most reactive, (I) is the least reactive as highly unstable carbocation is formed at bridge head carbon of bicyclic compound.

31. [4]

In ordinary condition aryl halide do not give SN reaction.

32. [1]

Rate of Ar–S_N2 $\propto$ Electron Withdrawing Group ($-NO_2$)

33. [1]

Density $\propto$ Molecular weight

34. [3]

Reactivity of S_N1 reaction $\propto$ stability of carbocation

$$\propto \text{ERG}$$

$$\propto \frac{1}{\text{EWG}}$$

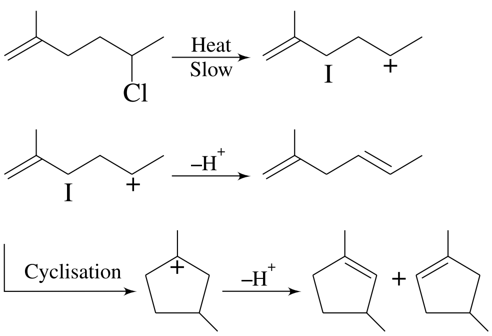
35. [2]

Theory based.

EXERCISE # 3

1. [1, 2, 4]

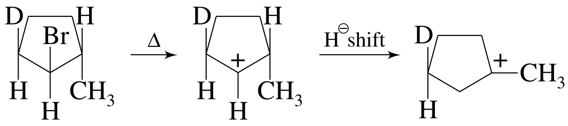
Reaction proceeds by E1 mechanism.



2. [1, 2, 3, 4]

H_2O (Protic Solvent)

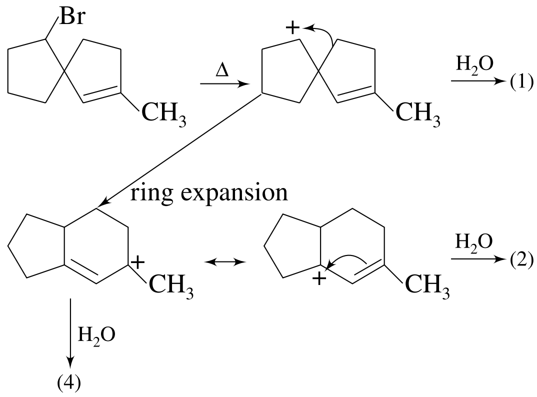
Hence SN_1 reaction takes place



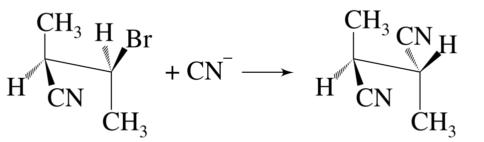
(I) (II)

(I) gives (1) and (2) while (II) gives (3) and (4).

3. [1, 2, 4]



4. [1, 3, 4]



Meso achiral

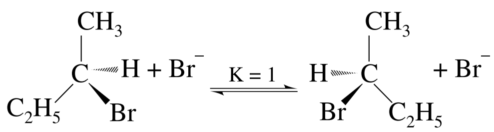
Rest 1, 3, 4 give chiral product

5. [1, 4]

In both option (1) and option (4) α-carbon is chiral, hence S_N2 reaction will lead to inversion of configuration. In option (2), α-carbon is achiral, configuration of chiral β-carbon will not be affected. In option (3) S_N2 reaction occur twice at the same α-carbon hence, double inversion will give not retention of configuration.

6. [1, 3, 4]

In both option (1) and option (4) products have inverted configuration but at α-carbon only. In option (2) product has inverted configuration at both α and β-carbons, hence not true in S_N2 reaction. In case of option (4), an equilibrium will be established with K = 1.



At equilibrium both enantiomers exist in equal amounts giving racemic mixture.

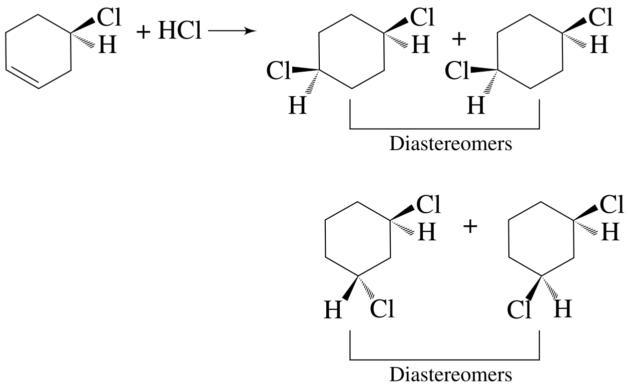
7. [1, 2, 3]

All will react via cyclic sulphonium ion intermediate involving S_N2 reaction twice giving over all retention of configuration.

8. [1, 3]

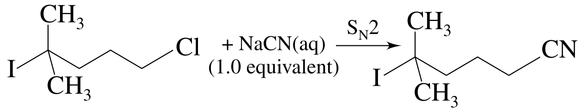
Due to neighbouring group participation, reaction occurs at much faster rate than 2-bromo-3, 3-dimethylpentane. Also it involves S_N2 reaction twice, overall retention of configuration is observed.

9. [1, 3]



10. [1, 3, 4]

Steric hindrance plays the most important role in S_N2 reaction. Hence, although Cl is poorer leaving group than I, Cl is substituted predominantly in the above reaction due to less steric hindrance at α-carbon. Addition of NaI replace Cl by I and substitution becomes easier.



11. [1, 3, 4]

Theory based

12. [2, 3, 4]

Theory based.

13. [2, 3, 4]

(1) $CH_3CH_2OCH_2CH_3 \xrightarrow[h\nu]{Cl_2} C_2Cl_5\text{–O–}C_2Cl_5$

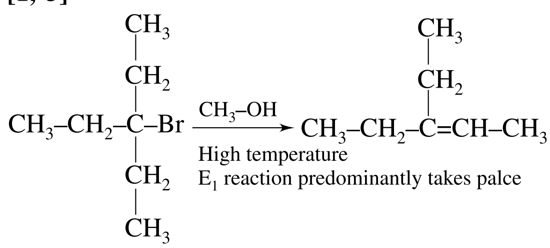
Not alkyl halide

(2) $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{\text{conc. HI}} CH_3\text{–}CH_2\text{–}OH + CH_3\text{–}CH_2\text{–}I$

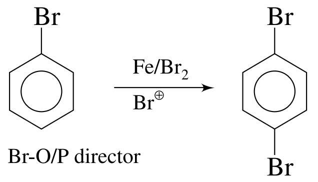
(3) $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{PCl_5} 2CH_3\text{–}CH_2\text{–}Cl + POCl_3$

(4) $CH_3CH_2OH \xrightarrow{SOCl_2} CH_3\text{–}CH_2\text{–}Cl + SO_2 + HCl$

14. [1, 3]



15. [2]



16. [4]

Aryl halide do not give nucleophilic substitution in ordinary condition to because partial double bond character develop due to resonance.

17. [2]

refer key concept.

18. [1]

refer key concept.

19. [4]

Boiling point ∝ molecular weight.

So R–Br has higher b.pt. than R–Cl.

20. [2]

refer key concept.

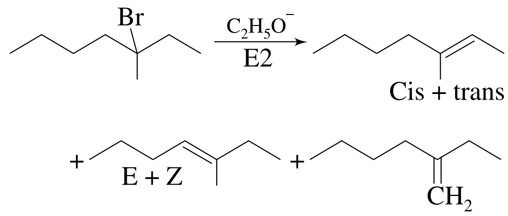
21. [2]

In aryl halide C–X bond have partial double bond character due to resonance, so bond energy increase thus removal of X as leaving group is difficult in ordinary condition. Hence aryl halide do not give substitution reaction easily.

22. [3]

Only deuterium is present at anti position of a β-carbon, it is abstracted by base, although giving less substituted alkene as the major product. On tertiary β-carbon, hydrogen is not available in *anti* position to leaving group.

23. [4]



24. [4]

Bulky base takes β-H from least hindered β-carbon, giving least substituted alkene as the major product.

25. [2]

Products are same in both reaction, hence same potential energies of products are shown, Also I^- is better leaving group, has lower activation energy in S_N2 reaction as indicated by curve-I in diagram.

26. [3]

Since I^- is better leaving group, $k_I > k_{II}$

27. [3]

Following neutralisation is preferred over S_N2 reaction:

$$CH_3—CH_2—OH + NaNH_2 \longrightarrow CH_3— CH_2—O^- Na^+ NH_3$$

28. [1]

(A) $CH_3CH(CH_3)—CH(OH)CH_3 \xrightarrow[\text{Via 1, 2H}^{\ominus}\text{ shift in carbocation}]{HCl} CH_3C(Cl)(CH_3)CH_2CH_3$ (r)

(B) $CH_3CH(CH_3)CH_2CH_2OH \xrightarrow[S_N2]{PCl_5} CH_3CH(CH_3)CH_2CH_2Cl$ (q)

(C) $CH_3CH(CH_3)—CH(OH)CH_3 \xrightarrow[S_N2]{PCl_3} CH_3CH(CH_3)—CH(Cl)CH_3$ (p)

(D) $CH_3CHCH_2CH_3 \xrightarrow[S_Ni]{SOCl_2} CH_3–CH(CH_2Cl)–CH_2CH_3$ (s)

29. [3]

Theory based.

30. [4]

Theory based.

31. [1]

(i) Due to 'S' at β-position, neighbouring group participation occur giving net retention (twice inversion).

(ii) S_N2 at a-carbon gives inversion and product is meso diol.

(iii) Only S_N2 hence inversion

(iv) Show neighbouring group effect

Hence, (i) → (q, s); (ii) → (p, r); (iii) → (p); (iv) → (r, s)

32. [2]

(i) Given halide is a primary, predominantly undergo S_N2 reaction.

(i) → (q)

(ii) Given halide is secondary, can undergo S_N2 reaction. Also, E2 reaction leads to a conjugated system. Also, it any react by E1cb mechanism because it forms resonance stabilised carbanion.

(ii) → (q, r, s)

(iii) It is a 3° halide and in the presence of weak base H_2O, weak nucleophile H_2O, it may undergo unimolecular substitution (S_N1) and elimination (E1) reaction.

(iii) → (p)

(iv) It may form a stable benzylic carbocation after hydride shift, hence any react by $S_N1$mechanism. Also, it is a secondary halide, may undergo S_N2 reaction. It may also react by E2 reaction at it gives conjugated system. Carbanion, formed at β-C will be stabilized by resonance from ring, hence may undergo E1cb mechanism.

(iv) → (p, q, r, s)

33. [1]

(A) $C_2H_5OH + HCl \xrightarrow[\text{Groove reaction}]{ZnCl_2} C_2H_5Cl + H_2O$

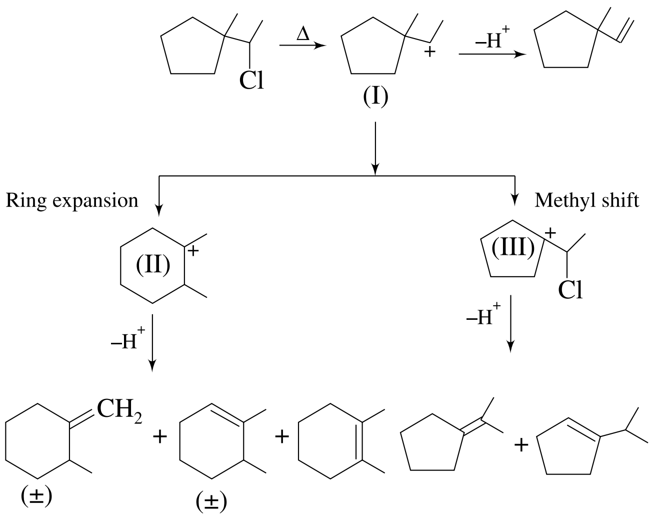
(B) $C_6H_5N_2^+Cl^- + HBr \xrightarrow[\text{Gattermann reaction}]{Cu} C_6H_5Br + N_2 + HCl$

(C) $CH_3CH(Br)CH_2CH_3 \xrightarrow[\text{Elimination reaction}]{\text{alc. KOH}} CH_3–CH = CHCH_3$

(D) $CH_3CH_2CH_2Cl+NaI \xrightarrow[\text{Frenkelstein reaction}]{\text{Acetone}} CH_3CH_2CH_2I + NaCl$

34. [8]

Total 8 alkenes

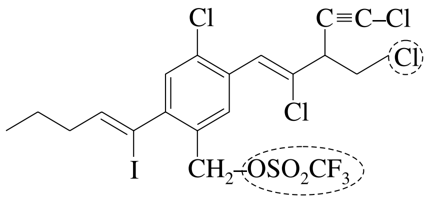


35. [6]

Only (ii), (iv), (vii) and (ix) are less dense than water. Alkyl bromides, alkyl iodides and all alkyl halides containing two or more halogen atoms.

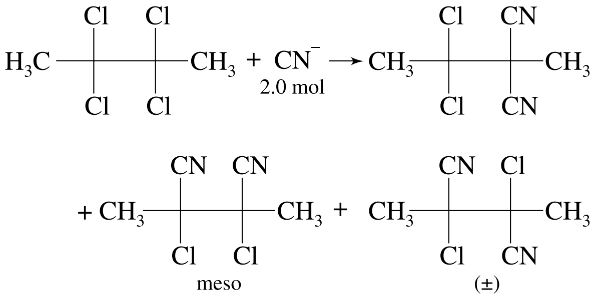
36. [3]

Only the circled groups are substituted in S_N2

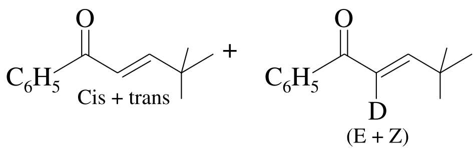


37. [4]

Any of the two Cl can be substituted by CN^- as:



38. [4]



EXERCISE # 4

1. [1]

Replacement of Br by –OH group takes place.

So that it is substitution reaction.

2. [2]

Reactivity of HX is HI > HBr > HCl > HF

3. [3]

$$\text{Reactivity of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

Reactivity order 1° halide > 2° halide > 3° halide.

4. [4]

$R_2CuLi + R'X \longrightarrow R - R' + R - Cu + LiX$

(Dialkyl copper lithium) (alkane)

5. [1]

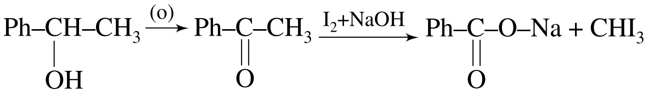
$$CH_3–CH_2–\underset{\displaystyle Br}{\underset{|}{C}H}–CH_3 \xrightarrow[-HBr]{\text{Alc. KOH}}$$

$CH_3–CH=CH–CH_3 + CH_3–CH_2–CH=CH_2$

More substitute (I) Major; Less substitute (II) Minor

Stability of (I) > (II) hence (I) is predominant.

6. [3]



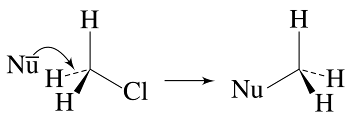
7. [2]

$$\text{Reactivity of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

Reactivity order 1° halide > 2° halide > 3° halide.

8. [3]

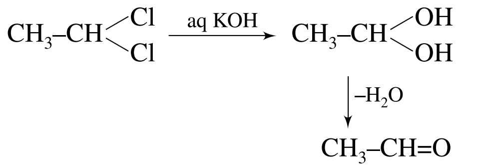
Nucleophilic substitution bimolecular (S_N2) prefers less sterically hindered site to attack. Lesser the steric hindrance, faster is the S_N2 reaction. So ease of reaction is 1° > 2° > 3°.



S_N2 involves inversion of configuration stereo, chemically.

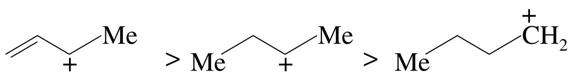
Since 1° alkyl halides are preferred to S_N2 reactions, therefore CH_3Cl undergoes complete stereochemical inversion.

9. [4]



10. [2]

The reactivity of S_N1 reaction depends upon the stability of the intermediate, carbocation formed during these reactions. The stability order of the carbocation formed from the given species is



Allylic carbocation (stabilizes through resonance due to conjugation) > 2° carbocation (stabilizes by hyperconjugation due to 5α-H atoms) > 1° carbocation (stabilizes by hyperconjugation due to 2α-H-atom)

Hence, the reactivity order of the given bromide towards S_N1 reaction is

11. [3]

$$\underset{\text{Ethyl chloride}}{CH_3–CH_2–Cl} \xrightarrow[S_N2]{KCN} \underset{\text{Propane nitrile}}{CH_3–CH_2–CN}$$

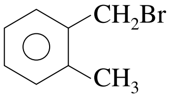
12. [4]

Compound A gives a precipitate with alcoholic $AgNO_3$ (here white is misprinting because the colour of ppt. is light yellow), so it must contain Br in side chain.

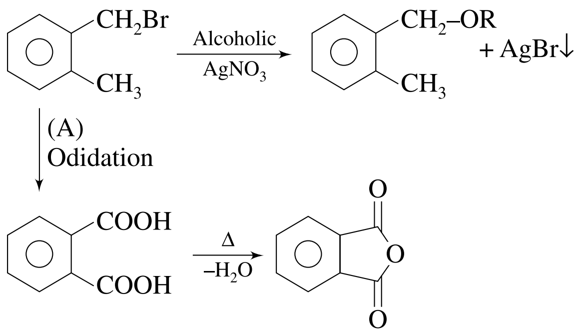
On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus.

Since compound B gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position.

Thus, A must be



And the reactions are as follows



Phthalic anhydride

13. [3]

$$CH_3\text{–}\boxed{CH\text{–}CH_3} \xrightarrow{I_2/KOH} +\text{ve test}$$
with OH on the CH carbon

Isopropyl alcohol 2-alkanol

$$CH_3\text{–}\underset{\displaystyle CH_3}{CH}\text{–}\boxed{\underset{\displaystyle OH}{CH}\text{–}CH_3} \longrightarrow +\text{ve test}$$

$$CH_3\text{–}\underset{\displaystyle CH_3}{CH}\text{–}CH_2\text{–}OH \longrightarrow -\text{ve test}$$

Isobutyl alcohol

$$\boxed{CH_3\text{–}\underset{\displaystyle \| \atop O}{C}}\text{–}CH_2\text{–}CH_3 \longrightarrow +\text{ve test}$$

Ethyl methyl ketone

2-alkanol or methyl ketone will give positive iodoform test, isobutyl alcohol is not 2-alkanol type, hence gives negative iodoform test.

14. [3]

$$CH_3\text{–}CH_2\text{–}Br \xrightarrow[\text{Covalent nature}]{AgCN} CH_3\text{–}CH_2\text{–}N \overrightarrow{\equiv} C$$

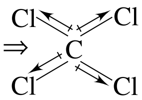
$$\xrightarrow{\text{Reduction Zn–Hg/HCl}} CH_3\text{–}CH_2\text{–}NH\text{–}CH_3$$

Ethyl methyl amine

15. [2]

Copper wire test for halogens is known as Beilstein's Test.

16. [3]

$CCl_4 \Rightarrow$  $\mu = 0$

Equal and opposite dipole cancelled by each other.

17. [2]

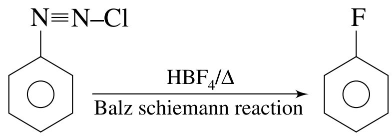
Beilstein test is used for estimation of Cl.

$$R\text{–}\boxed{Cl} \xrightarrow[\text{(Beilstein test)}]{\text{Cu-wire}} \text{Green flame}$$

18. [4]

$$Ph\text{–}N{=}N\text{–}Cl \xrightarrow[\text{Gattermann reaction}]{Cu/HBr} Ph\text{–}Br$$

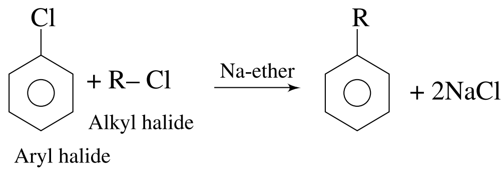
19. [1]



20. [2]

Tertiary alkyl halide mainly give β-elimination reaction so alkene will be formed as major product.

21. [2]



22. [2]

$$R\text{–}NH_2 \xrightarrow{CHCl_3/KOH} R\text{–}N\overrightarrow{\equiv}C$$

$$CHCl_3 + KOH \longrightarrow \ddot{C}Cl_2 + KCl + H_2O$$

α-elimination (dichloro carbene)

23. [3]

The given compound, (–)– chloro-1-phenylethane in the presence of $SbCl_5$ forms a carbocation.

$$Cl\text{–}\underset{\displaystyle Ph}{CH}\text{–}CH_3 \xrightarrow[\text{Toluene}]{SbCl_5} [Ph\text{–}\overset{+}{C}H\text{–}CH_3]\ SbCl_6^-$$

Since, the carbocation is a planar species, therefore it can be attacked by $SbCl_6^-$ either from the front or back side of the carbocation with equal ease. As a result, 50:50 mixture of two enantiomers of 1-choro-1-phenylethane undergoes racemisation due to the formation of a carbocation intermediate.

$$[Ph–CH–CH_3]\ SbCl_6^- \longrightarrow \underset{\underset{\text{Cl}}{|}}{Ph–CH}–CH_3 + SbCl_5$$

[d and *l* forms]

24. [3]

$$R–NH_2 \xrightarrow{CHCl_3/KOH} \underset{\text{Alkyl isocyanide}}{R–N \overset{\rightarrow}{\equiv} C} + KCl + H_2O$$

$$CH–CH_3 + KOH \longrightarrow \ddot{C}Cl_2 + KCl + H_2O$$

α-elimination (dichloro carbene)

25. [1]

Reactivity of $S_N2 \propto \dfrac{1}{\text{steric hindrance}}$

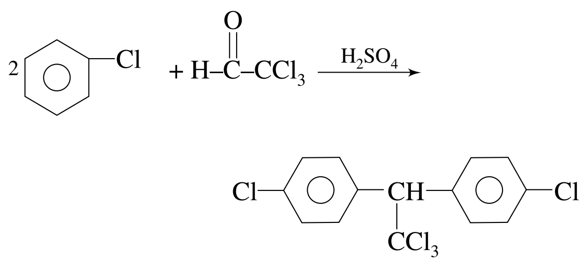
Reactivity order 1° halide > 2° halide > 3° halide.

26. [3]

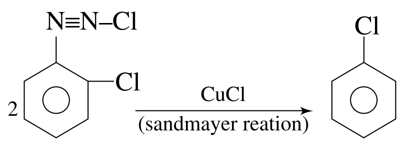
When alkyl halide having chiral carbon then only complete inversion takes place.

In option 3 $C_6H_5–\overset{*}{C}H(Br)–CH_3$ hence it gives complete inversion of configuration

27. [3]



28. [3]



29. [4]

$$CH_3–CH_2–CCl_3 \xrightarrow{\text{aq KOH}} CH_3–CH_2–C(OH)_3$$

$$\xrightarrow{-H_2O} \underset{\text{(Propanoic acid)}}{CH_3–CH_2–\underset{\underset{\text{O}}{\|}}{C}–OH}$$

30. [3]

$$\underset{\text{(1, 1, 1-trichliroethane 2 mole)}}{Cl–\overset{\overset{\text{Cl}}{|}}{\underset{\underset{\text{Cl}}{|}}{C}}–CH_3} \xrightarrow{Ag} \underset{\text{(2 butyne)}}{CH_3–C\equiv C–CH_3}–{}_6AgCl$$

31. [4]

Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. It is known as Swarts reaction.

32. [4]

Reactivity of alkyl halide ∝ power of leaving group.

$$I^{\ominus}\ Br^{\ominus}\ Cl^{\ominus}\ F^{\ominus}$$

size ↓ Base strength ↑ leaving tendency ↓

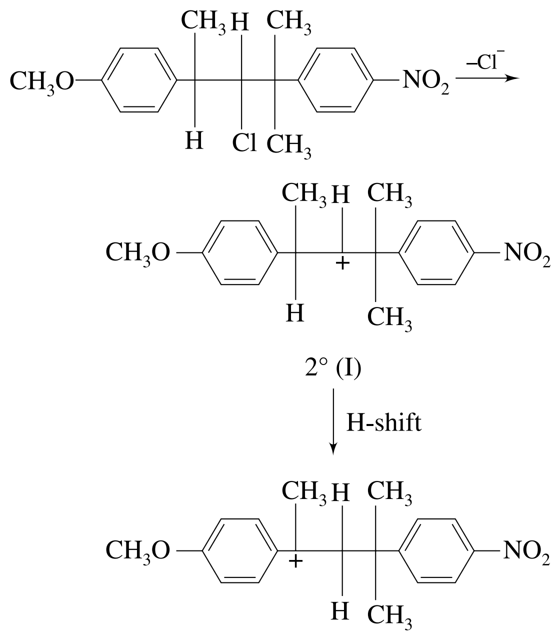
33. [2]

$$CH_3–CH_2–CH_2–Br \xrightarrow[\text{NaOH, 80°C}]{\text{Conc. alc.}} CH_3–CH{=}CH_2$$

β-elimination (x)

$$\xrightarrow[\text{Y}]{\text{HBr/ acetic acid, 20°C}} \underset{\underset{\text{Br}}{|}}{CH_3–CH}–CH_3$$

34. [1]



Stabilized by +R effect of $–OCH_3$

$$\text{(I)} \xrightarrow{H_2O} K$$

$$\text{(II)} \xrightarrow{H_2O} L$$

35. [1]

(A) $CH_3–CHBr–CD_3 \xrightarrow[E2]{\text{Alc. KOH}} CH_2=CH–CD_3$

E2 reaction is a single-step reaction in which both deprotonation from β-C and loss of leaving group from α-C occur simultaneously in the rate-determining step. C–D bond is stronger than C–H bond. C–H is preferably broken in elimination.

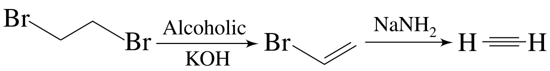
(B) $Ph–CHBr–CH_3$ reacts faster than $Ph–CHBr–CD_3$ in E2 reaction because in latter case, stronger C–D bond is to be broken in the rate determining step.

(C) $Ph–CH_2–CH_2Br \xrightarrow[C_2H_5O^-]{C_2H_5OD} Ph–CD=CH_2$

(D) Both $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ will react at same rate in E1 reaction because C–H bond is broken in fast non-determining.

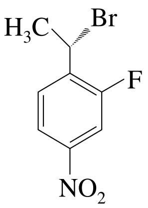
Thus, (A) → q; (B) → q; (C) → r; (D) → p, s

36. [2]



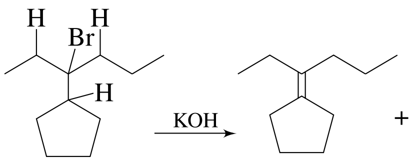
37. [1]

Nucleophile PhS^- substitute the Br^- through S_N2 mechanism with inversion of configuration at α-C

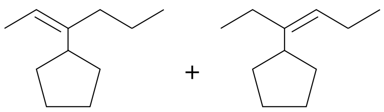


38. [5]

The substrate has three different types of B–H, therefore, first, three structural isomers of alkenes are expected as



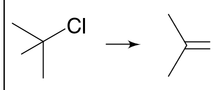
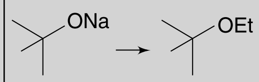
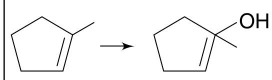
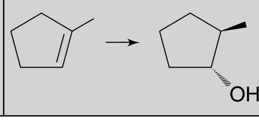
3 type of β-H (I)



(II) (III)

The last two alkenes (II) and (III) are also capable of showing geometrical isomerism; hence, two geometrical isomers for each of them will be counted giving a total of five isomers

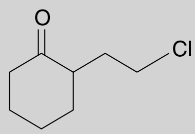
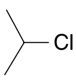
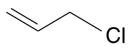
39. [1]

	Column-I	Column-II	Explanation
(A)		NaOEt	$\overline{O}Et$ (strong nucleophile) causes dehydrohalogenation of 3° alkyl halide
(B)		Et-Br	3° butoxide undergoes S_N2 reaction with 1° alkyl halide
(C)		(i) $Hg(OAc)_2$; (ii) $NaBH_4$	Mercuration–demercuration adds H_2O by Markownikoff's rule without rearran-gement
(D)		(i) BH_3; (ii) H_2O_2/NaOH	Hydroboro-oxidation adds H_2O by anti-Markownikoff's rule

40. [2]

Acetone is an aprotic solvent and can dissolve both the nucleophile and the substrate and thus S_N2 reaction is favoured. Also rate of $S_N2 \propto -$ I power. Also

$$S_N2 \xleftarrow{\quad 1° \quad 2° \quad 3° \quad} \text{Alkyl halides}$$
$$\xrightarrow{\qquad\qquad\qquad} S_N1$$

S		1° alkyl halide but (C–Cl). BE is decreased by electron withdrawing $[C_6H_5CO]$ group, (a case of I-effect). Thus, maximum rate in SN2 reaction
Q		2° alkyl halide, rate is minimum
P	$CH_3–Cl$	1° alkyl halide
R		1° allylic halide but allylic 1° carbocation is resonance stabilised in SN1 reaction

Thus, reactivity order is S > P > R > Q

CHAPTER 2

Alcohols, Ethers and Phenol

INTRODUCTION

ALCOHOLS

- Alcohols are organic compounds in which –OH group is directly attached with carbon.
- Alcohols are hydroxy derivatives of alkanes and mono alkyl derivatives of water.
- General formula of alcohols is $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.
- The hybridisation state of carbon, with which – OH group is directly attached, is sp^3. Therefore geometry around this carbon atom is tetrahedral.
- In these compounds C–O bond length is 1.42 Å.
- Depending on the number of –OH groups alcohols are classified into the following:
  - (i) Monohydric alcohol: Contains only one –OH group; example- Ethanol
  - (ii) Dihydric alcohol: Contains two –OH groups; example- Ethylene glycol
  - (iii) Trihydric alcohol: Contains three –OH groups; example- Glycerol
- Alcohols shows chain, position and functional group isomerism. If chiral carbon atom is present, they show optical isomerism.

PHYSICAL PROPERTIES

(I) Nature of alcohol:

- Alcohols are poisonous in nature. Poisonous character increases with increment in molecular mass or branching. Ethanol is exception, which is non-poisonous in nature. Methanol causes blindness.
- Isopropyl alcohol is called as rubbing alcohol.
- Cholesterol is also alcohol, it causes heart attack. Hence it is also called as notorious alcohol.
- Ethanol is liquid while glucose is solid because of more intermolecular H–bonding in glucose.
- Alcohols are neutral substances towards litmus paper.
- Lower members containing upto 12 carbon atoms are liquids.
- The higher members are solids and are almost odourless.
- They have a distinctive smell and a burning taste.

(II) Boiling point:

- $\boxed{\text{Boiling point} \propto \text{Molecular mass} \propto \dfrac{1}{\text{Number of branches}}}$
- Boiling point of alcohols in water increases as the extent of hydrogen bonding increases.
- Boiling point of alcohols are higher than ethers of comparable molecular masses because intermolecular hydrogen bonding is present in alcohols.

- Order of Boiling point:
  (i) $CH_3OH < CH_3CH_2OH < CH_3CH_2CH_2OH$

  (ii) $CH_3CH_2CH_2OH > CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CH_3 > CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$

  (iii) $\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \\ \text{(Max. H-bond)} \end{array} > \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} > CH_3CH_2OH$

(III) Solubility in water:

- Lower alcohols are soluble in water and the solubility diminishes as the molecular mass increases.

$$\boxed{\text{Solubility} \propto \frac{1}{\text{Molecular mass}} \propto \text{number of branches}}$$

- Their solubility in water is to be expected, since the oxygen atom of hydroxyl group in alcohols can form hydrogen bonds with water molecules.
- Solubility of alcohols in water increases as extent of hydrogen bonding increases.
  (i) $CH_3OH > CH_3CH_2OH > CH_3CH_2CH_2OH$
- Order of solubility in water:

  (ii) $CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3 > CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CH_3 > CH_3CH_2CH_2CH_2OH$

  (iii) $\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \\ \text{(Max. H-bond)} \end{array} > \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} > CH_3CH_2OH$

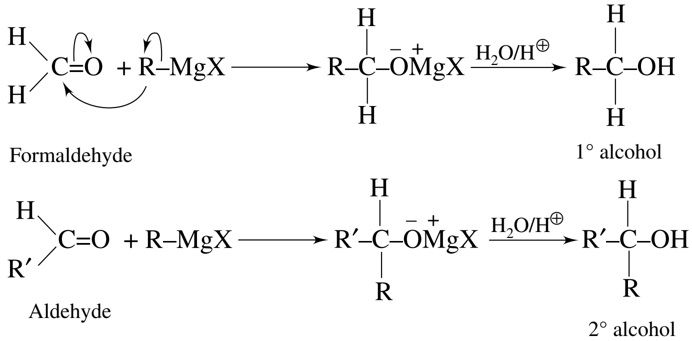
METHODS OF PREPARTION OF ALCOHOL

Grignard Synthesis of Alcohols

(I) Reaction of oxygen with RMgX

$$R-MgX + \frac{1}{2}O_2 \longrightarrow R-O-MgX \xrightarrow{H_2O/H^{\oplus}} \underset{\text{Alcohol}}{R-OH}$$

(II) Reaction of carbonyl compounds with RMgX



$$\underset{\text{Ketone}}{R''R'C{=}O} + R\text{–}MgX \longrightarrow R'\text{–}\overset{R''}{\underset{R}{C}}\text{–}\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O/H^{\oplus}} \underset{3^\circ\ \text{alcohol}}{R'\text{–}\overset{R''}{\underset{R}{C}}\text{–}OH}$$

(III) Reaction of ethylene oxide with RMgX

$$\underset{\diagdown\ O\ \diagup}{CH_2\text{–}CH_2} + RMgX \rightarrow RCH_2CH_2\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O/H^{\oplus}} RCH_2CH_2OH$$

(IV) Reaction of lithium acetylides or alkynyl Grignard Reagents with aldehyde or ketone

$$HC{\equiv}CLi + O = \overset{R}{C}\text{–}R' \rightarrow HC{\equiv}C\text{–}\overset{R}{\underset{OMgBr}{C}}\text{–}R' \xrightarrow{H^+} HC{\equiv}C\text{–}\overset{R}{\underset{OH}{C}}\text{–}R'$$

$$HC{\equiv}CMgBr + O = \overset{R}{C}\text{–}R' \rightarrow HC{\equiv}C\text{–}\overset{R}{\underset{OMgBr}{C}}\text{–}R' \xrightarrow{H^+} HC{\equiv}C\text{–}\overset{R}{\underset{OH}{C}}\text{–}R'$$

Other methods of preparation of alcohols

$$CH_2 = CH_2 \xrightarrow[\text{Acid catalyze Hydration}]{H_2O/H^{\oplus}} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_2 = CH_2 \xrightarrow[\text{Hydroboration-Oxidation Process}]{BH_3/H_2O_2/\overset{\ominus}{O}H} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_2 = CH_2 \xrightarrow[\text{Oxymercuration-Demercuration process}]{(AcO)_2\,Hg/H_2O/NaBH_4} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3CH_2\text{–}Cl \xrightarrow[SN_2\ \text{reaction}]{\text{aq. NaOH}} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3\text{–}CH{=}O \xrightarrow[\text{Reduction}]{H_2/Pd\ \text{or}\ Na/EtOH\ \text{or}\ LiAlH_4/H^{\oplus}} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3\text{–}\underset{\parallel}{\underset{O}{C}}\text{–}Cl \xrightarrow[\text{Reduction}]{LiAlH_4/H^{\oplus}\ \text{or}\ NaBH_4/H^{\oplus}} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3\text{–}\underset{O}{\overset{}{C}}(=O)\text{–}OCH_2CH_3 \xrightarrow[\text{Reduction}]{LiAlH_4/H^{\oplus}} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3\text{–}C(=O)\text{–}OCH_2CH_3 \xrightarrow[SN_2\ \text{reaction}]{NaOH} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3\text{–}C(=O)\text{–}OCH_2CH_3 \xrightarrow[\text{Reversible reaction}]{\text{Dil}\ H_2SO_4\ \text{or}\ H_3O^{\oplus}} \text{CH}_3\text{CH}_2\text{OH}$$

$$CH_3CH_2\text{–}NH_2 \xrightarrow{NaNO_2 + HCl\ \text{or}\ HNO_2} \text{CH}_3\text{CH}_2\text{OH}$$

CH$_3$CH$_2$OH
Ethyl alcohol

CHEMICAL PROPERTIES OF ALCOHOL

The general formula of simple alcohol is ROH. Reactions shown by alcohols may be classified into two categories, namely, cleavage of R….OH bond and cleavage of RO….H bond.

(I) Reactions exhibiting cleavage of RO….H bond

Reaction with active metals

$$RO{-}H + M \rightarrow R{-}\overset{-}{O}\overset{+}{M} + \frac{1}{2}H_2$$

(M = Na, K, Mg, Al, etc.)

Reactivity of alcohol $CH_3OH > 1° > 2° > 3°$

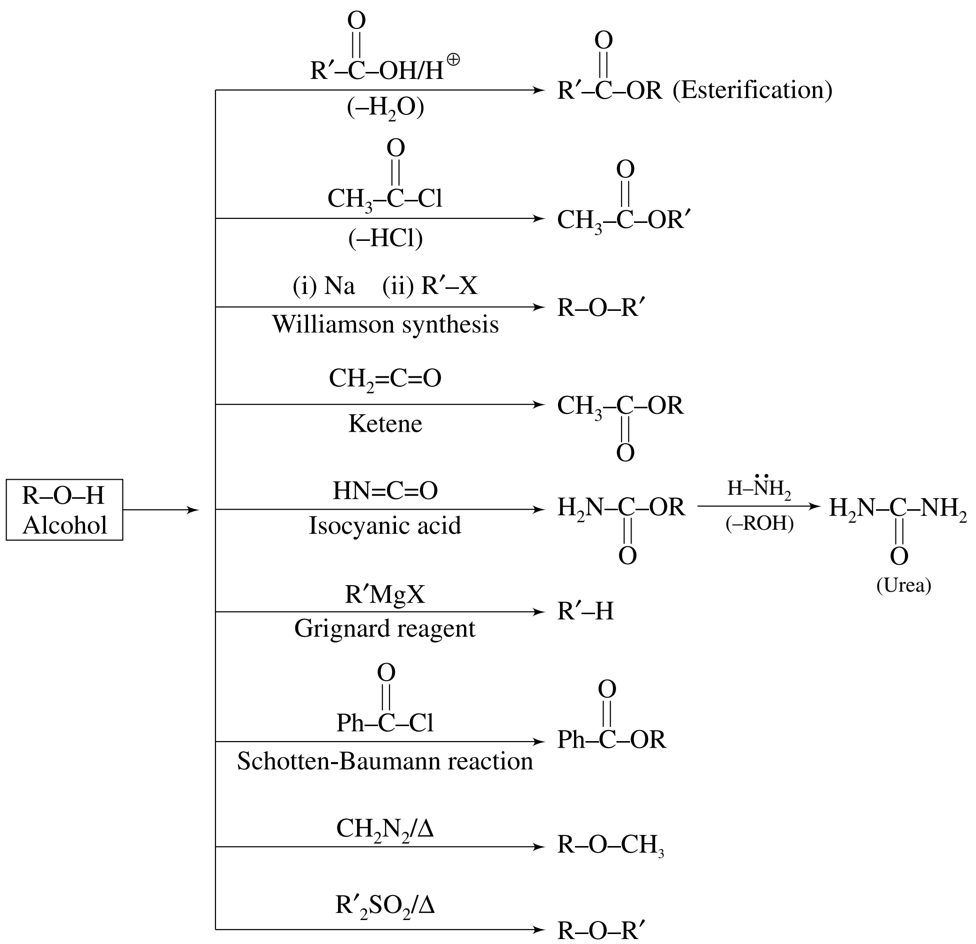
The above reaction shows alcohol as an acid. It is worth comparing the acid strength of alcohol with other species.

$H_2O > ROH > HC \equiv CH > NH_3 > RH$

The relative order of basicity follows the reverse order, i.e.,

$OH^- < OR^- < HC \equiv C^- < NH_2^- < R^-$

Other Reaction



(II) Reactions exhibiting cleavage of R….OH Bond

Reaction with hydrogen halides

$R{-}OH + HX \rightarrow RX + H_2O$

As such –OH is a poor leaving group. But its protonation converts into a good leaving group. There is formation of carbocation as the intermediate and thus the reaction may show rearrangement. The following is the reactivity of HX and ROH.

HI > HBr > HCl; allyl, benzyl > 3° > 2° > 1°

The reagents used are concentrated HBr or NaBr + concentrated H_2SO_4, HCl + $ZnCl_2$, and concentrated HCl.

R–O–H (Alcohol):

$$R\text{–}OH \xrightarrow{PCl_3 \text{ or } PCl_5 \text{ or } SOCl_2} R\text{–}Cl$$

$$R\text{–}OH \xrightarrow[(H\text{–}Cl + ZnCl_2)]{\text{Lucas reagent}} R\text{–}Cl$$

$$R\text{–}OH \xrightarrow[(-H_2O)]{H\text{–}NH_2/Al_2O_3/\Delta} R\text{–}NH_2$$

$$R\text{–}OH \xrightarrow[(-H_2O)]{H\text{–}O\text{–}NO_2/100^\circ C} R\text{–}O\text{–}NO_2 \text{ (Alkyl nitrate)}$$

$$R\text{–}OH \xrightarrow[(-H_2O)]{H_2SO_4/100^\circ C} R\text{–}HSO_4 \text{ (Alkyl hydrogen sulphate)}$$

(Alkyl nitrate and alkyl hydrogen sulphate: Inorganic esters)

$$R\text{–}OH \xrightarrow[\text{reduction}]{HI + \text{red P}} R\text{–}H$$

$$R\text{–}OH \xrightarrow{H_2SO_4/170^\circ C} \text{Alkene}$$

$$R\text{–}OH \xrightarrow{H_2SO_4/140^\circ C} R\text{–}O\text{–}R \text{ (Williamson etherification)}$$

Oxidation Reaction:

- Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohol is resistant to oxidation.
- The oxidation of an alcohol involves the loss of one or more α-hydrogens.
- 1° alcohol is changed to an aldehyde by using the reagent pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$)

$$\underset{1^\circ\text{alcohol}}{RCH_2OH} \xrightarrow[\text{P.C.C.}]{C_5H_5NH^+CrO_3Cl^-} \underset{\text{Aldehyde}}{RCH{=}O}$$

- 1° alcohol is directly converted into a carboxylic acid by the use of potassium permanganate.

$$\underset{1^\circ\text{alcohol}}{RCH_2OH} \xrightarrow{KMnO_4/H^\oplus} \underset{\text{Carbodylic acid}}{RCOOH}$$

- 2° alcohol is changed into a ketone by the use of potassium dichromate or CrO_3 in glacial acetic acid or CrO_3 in pyridine.

$$\underset{2^\circ\text{ alcohol}}{R_2CHOH} \xrightarrow{K_2Cr_2O_7/H^\oplus} \underset{\text{Ketone}}{R_2C{=}O}$$

- 3° alcohol is not oxidisable as it does not contain α-hydrogen.

Summery of Oxidation:

	Reagent/Alcohol	CH_3CH_2OH	$\succ$–OH	$\succ\!\!\!-$–OH
(1)	PCC or PDC	CH_3CHO	$\succ$=O	×
(2)	CrO_3 in CH_2Cl_2 Solvent	CH_3CHO	$\succ$=O	×
(3)	CuO/Δ	CH_3CHO	$\succ$=O	$\succ$=CH_2
(4)	$KMnO_4/H^+$	CH_3COOH	$\succ$=O	×
(5)	$K_2Cr_2O_7/H_2CrO_4$	CH_3COOH	$\succ$=O	×
(6)	CrO_3 in water	CH_3COOH	$\succ$=O	×

Note: MnO_2 is regioselective reagent for oxidation of only allylic and benzylic –OH into carbonyl group.

DIFFERENCE BETWEEN PRIMARY, SECONDARY AND TERITARY ALCOHOLS

(1) Oxidation method:

(A) Dichromate test:

(i) 1°-alcohol $\xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ aldehyde + Cr^{+3} [green colour]

(ii) 2°-alcohol $\xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ ketone + Cr^{+3} [green colour]

(iii) 3°-alcohol $\xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ No oxidation [No green colour]

(B) By catalytical oxidation/dehydrogenation:

When vapours of alcohols are passed over hot metallic Cu at 300°C, limited oxidation takes place.

(i) Primary alcohol gives aldehyde on oxidation
(ii) Secondary alcohol gives ketone, and
(iii) Tertiary alcohol gives alkene (dehydration takes place in tertiary alcohols.)

(2) Lucas Test:

A mixture of (anhydrous $ZnCl_2$ + Conc. H_2SO_4) is called as **Lucas Reagent**

(i) Tertiary alcohol gives white ppt. with Lucas reagent in 2–3 seconds only.
(ii) Secondary alcohol takes 5–10 minutes.
(iii) Primary alcohol does not give white ppt. at room temperature.
(iv) Allyl alcohol reacts as rapidly as tertiary alcohol but remains in the solution.

(3) Victor Meyer Test:

This test is also known as RBC (Red, Blue, Colourless) test.

(i) $R–CH_2–OH \xrightarrow{\text{red P/I}_2} R–CH_2–I \xrightarrow[-AgI]{AgNO_2} R–C\boxed{H_2}–NO_2 \xrightarrow[(-H_2O)]{O=N–OH} \underset{\text{(Nitrolic acid)}}{R(NO_2)C=N–OH} \xrightarrow{NaOH}$ Red solution (salt)

(ii) $R_2CH–OH \xrightarrow{\text{red P/I}_2} R_2CH–I \xrightarrow{AgNO_2} R_2C(NO_2)(H) \xrightarrow{HO–N=O} R_2C(NO_2)(N=O) \xrightarrow{NaOH}$ No reaction

(Pseudo nitrole)
Blue-colour

(iii) $R_3C–OH \xrightarrow{\text{red P/I}_2} R_3C–I \xrightarrow{AgNO_2} \underset{\text{(white)}}{R_3C–NO_2} \xrightarrow{HNO_2}$ No reaction

(4) Characteristic test of CH_3CO- group

An alcohol of the type $R-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$ is oxidised to $R-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$ which gives iodoform test.

The reagent used is iodine and sodium hydroxide (sodium hypoiodite, NaOI)

The reactions involved are

$$R-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-CH_3 + NaOI \rightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + Na + H_2O$$

$$R-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + 3NaOI \rightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-CCl_3 + 3NaOH$$

$$R-\underset{\displaystyle O}{\underset{\|}{C}}-CCl_3 + NaOI \rightarrow RCOO^-Na^+ \underset{\substack{\text{Iodoform}\\ \text{(yellow Ppt.)}}}{CHI_3}$$

(5) Analysis of molecules containing –OH or =O group attached to adjacent carbon atoms

Molecules containing –OH or =O groups attached to adjacent carbon atoms undergo oxidation with cleavage of carbon–carbon bonds when treated with periodic acid. Example:

$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-R' \longrightarrow \left[R\underset{\displaystyle OH}{\underset{|}{CH}}-OH\right] + \left[R'\underset{\displaystyle OH}{\underset{|}{CH}}-OH\right] \longrightarrow RCHO + R'COH$$

$$R\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}-R' \xrightarrow{HIO_4} \left[R\underset{\displaystyle OH}{\underset{|}{CH}}-OH\right] + HO-\underset{\displaystyle O}{\underset{\|}{C}}R' \longrightarrow RCHO + R'COOH$$

$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-R' \xrightarrow{2HIO_4} RCHO + HCOOH + R'CHO$$

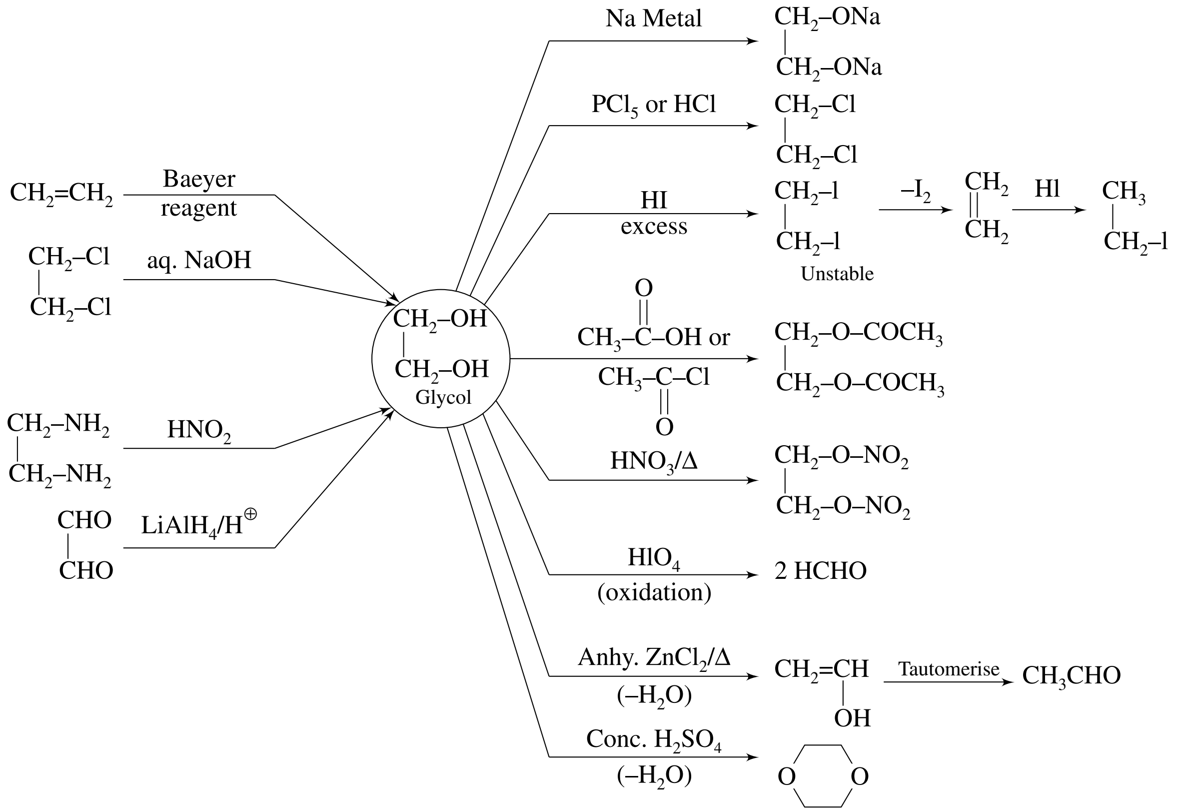
$$R-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-R' \xrightarrow{HIO_4} RCOOH + R'COOH$$

The amount of HIO_4 consumed is equal to the amount of carbon–carbon bond broken in the molecule.

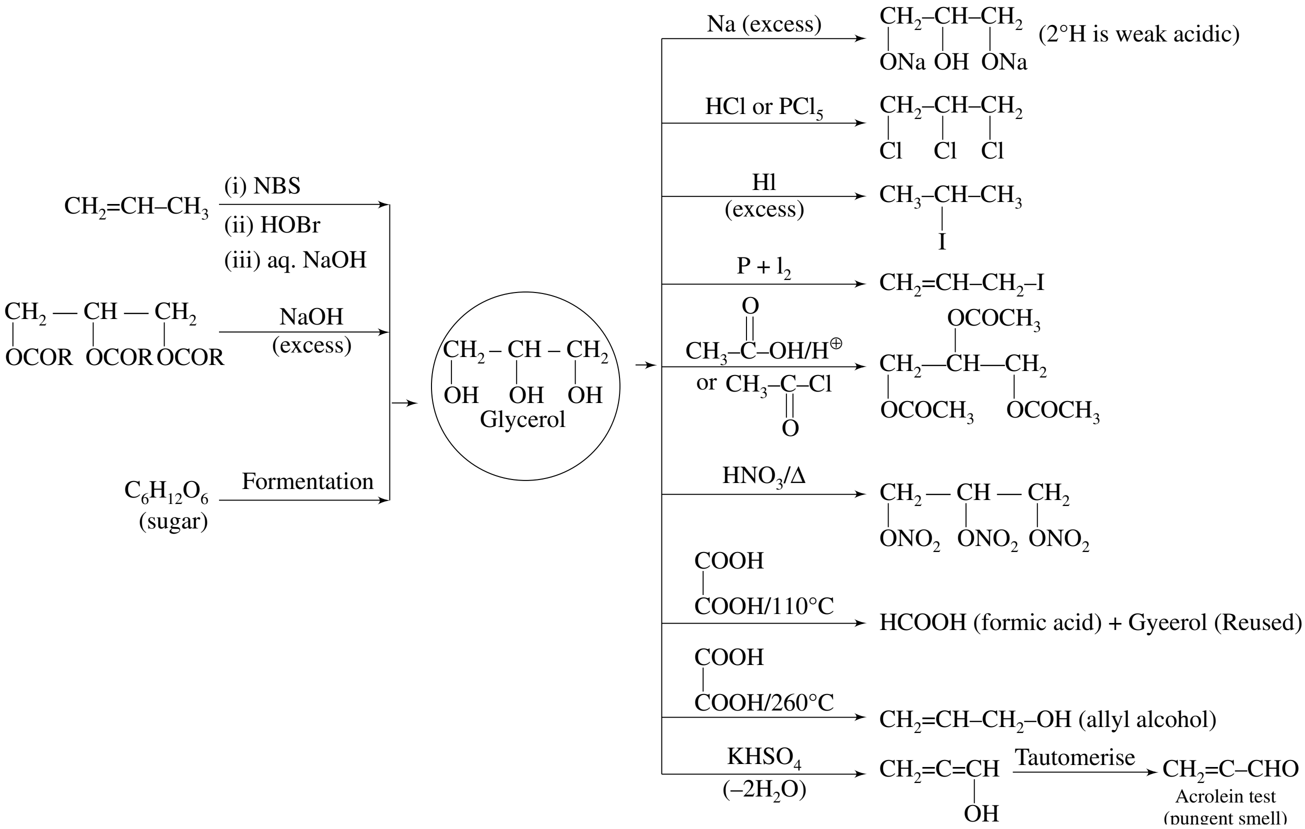
(4) Difference between methanol and ethanol:

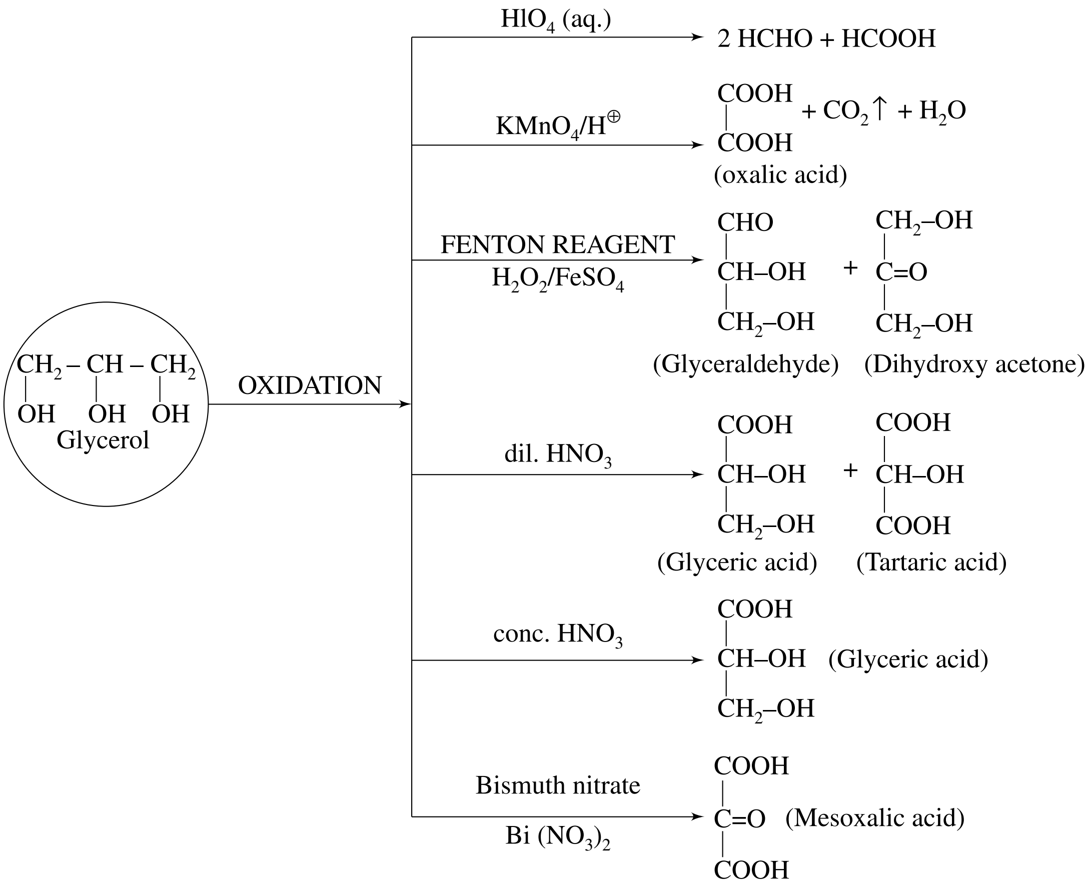
S. N.	Methanol	Ethanol
1.	When CH_3OH is heated on Cu coil it gives formalin like smell.	It does not give formalin like smell.
2.	When CH_3OH is heated with salicylic acid in H_2SO_4 (conc.) then methyl salicylate is formed which has odour like winter green oil	No such odour is given.
3.	It does not give Iodoform test	It gives Iodoform test
4.	Boiling point = 65°C	Boiling point = 78°C

Chemical Properties and Methods of Preparation of Glycol:



Chemical Properties and Methods of Preparation of Glycerol:





Special Points

- Glycol is used as antifreeze for automobile radiators and as a coolant for aeroplane aviation petrol under the name **prestone**.
- Glyceryl trinitrate is an inorganic ester.
- Glyceryl trinitrate is colourless, oily liquid insoluble in water and is called **Nobel’s oil**.
- On detonating it explodes violently giving CO_2, N_2, O_2 as gaseous products.

$$4\begin{array}{l} CH_2\text{–}ONO_2 \\ | \\ CH\text{–}ONO_2 \\ | \\ CH_2\text{–}ONO_2 \end{array} \longrightarrow 12CO_2 + 10\,H_2O + 6N_2 + O_2$$

- It is a safer explosive when adsorbed on keiselguhr and is known as **DYNAMITE.**
- Its mixture with cellulose nitrate is known as **blasting gelatine** or **gelignite**.
- Its mixture with cellulose nitrate (gun cotton) and vaseline is called cordite. It is a smokeless powder.
- Nobel's oil is also used in the treatment of angina pectoris and asthma.
- Dunstan’s test for glycerol: A drop of phenolphthalein is added to approx. 5 mL of borax solution. The pink colour appears. On adding 2–3 drops of glycerol, the pink colour disappears. The pink colour reappears on heating and disappears on cooling again.

INTRODUCTION

ETHERS

- Compounds that contain an oxygen atom bonded to two alkyl groups. R–O–R′, are called ether.

  When R and R′ are same, they are called as symmetrical ethers and when both are different, they are called mixed or unsymmetrical ether.
- Ether have general formula $C_nH_{2n+2}O$. where n = 2, 3...
- These may be considered as dialkyl derivatives of water.
- The oxygen atom in ethers is sp^3 hybridised.
- In IUPAC system ethers are named as alkoxyalkanes.
- Ether shows chain, positional, functional isomerism and metamerism.
- Ether are functional isomers of alcohols.

Physical Properties

(i) Dimethyl ether and ethyl methyl ether are gases. All others are colourless liquids with pleasant smell.

(ii) Ethers are sparingly soluble in water, but readily soluble in organic solvents.

(iii) Ethers are lighter than water. Lower ethers are highly volatile and inflammable.

(iv) Boiling points of ethers show a gradual increase with increase in molecular mass.

(v) Ethers have low boiling points than isomeric alcohols, as there is association between the alcohol molecules due to hydrogen bonding. The boiling points of ethers are close to the boiling points of alkanes.

(vi) Due to bond angle of 110°, ethers are partial polar.

(vii) Lower ethers act as **anaesthetics**.

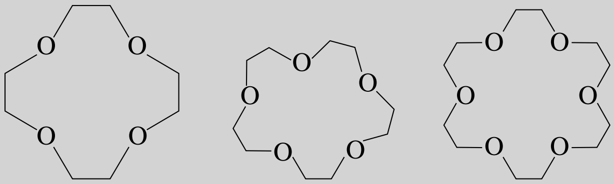
- **Test of ether** before anaesthetic use:

(i) ether (peroxide) + $Fe^{+2} \longrightarrow Fe^{+3} \xrightarrow{KCNS}$ Red colour $[Fe(CNS)_3]$
(ii) ether (peroxide) KI $\xrightarrow{Starch}$ Blue colour $[I_2]$

Use of ether

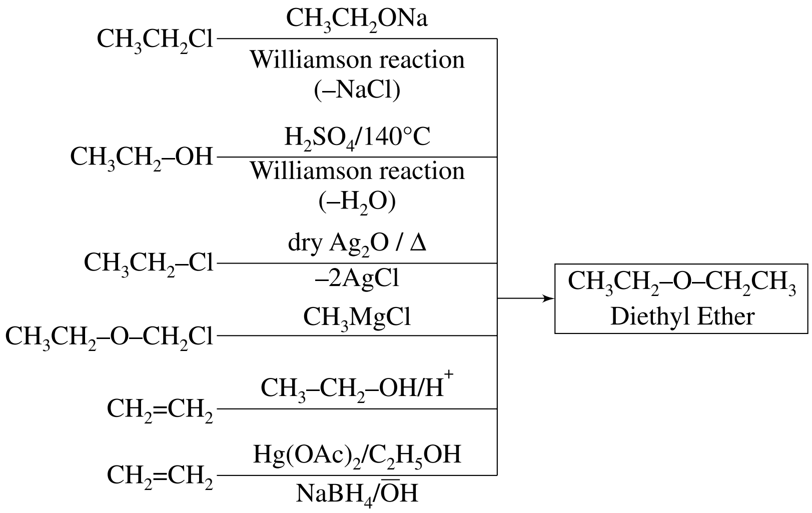
- Reaction of HI with ether is used to estimate alkoxy group (mainly CH_3O-) in organic compound. This method is called **Zeisel method.**
- Mixture of diethyl ether and ethyl alcohol is known as **NATALITE** used in place of petrol.
- **CROWN** ether is the cyclic polyether which has at least four oxygen atoms.
- Crown ethers are mainly used as an antibiotic.

  Examples:

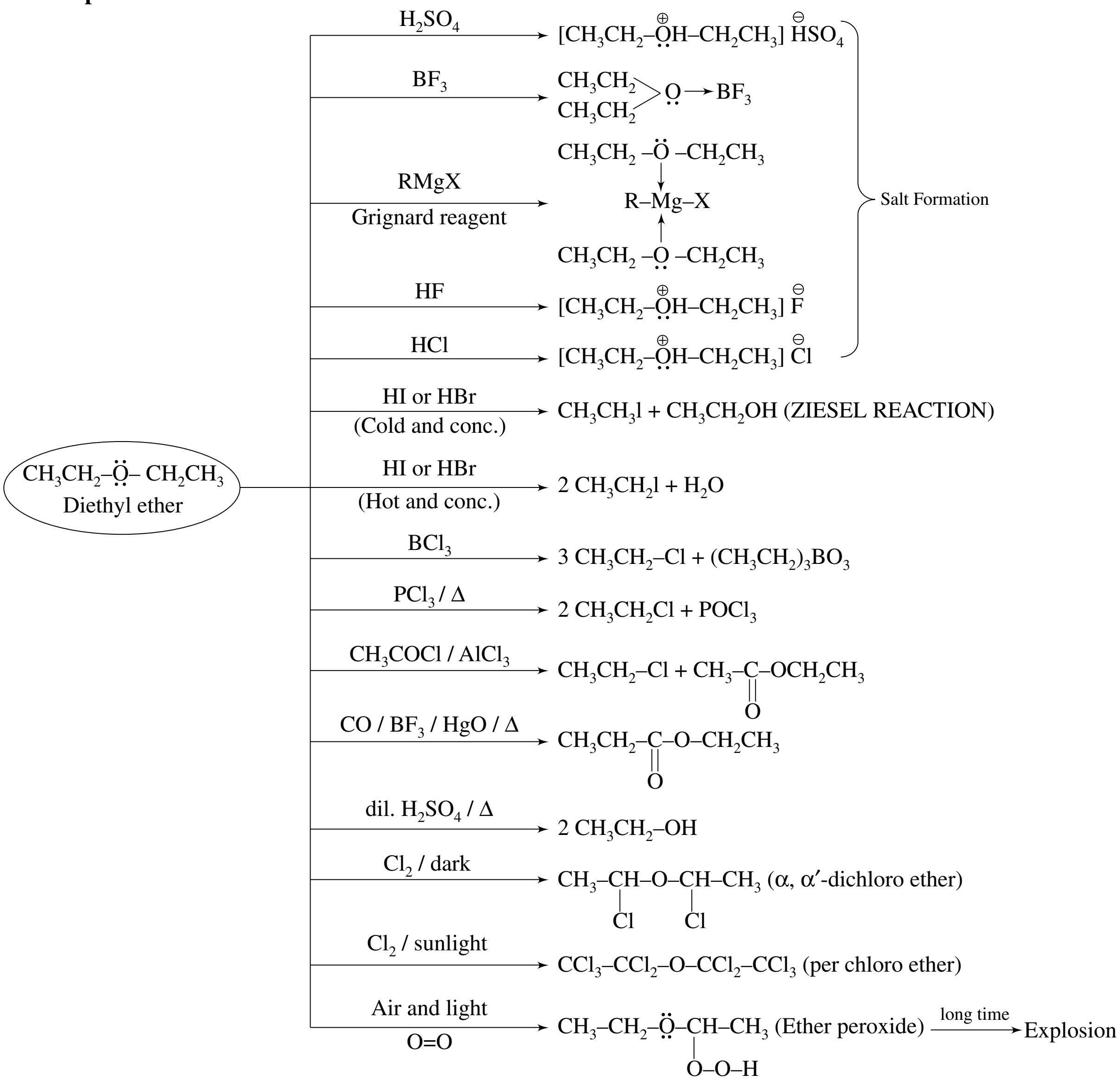


12-Crown-4 15-Crown-5 18-Crown-6

Methods of Preparation of Ether:



Chemical Properties of Ether:

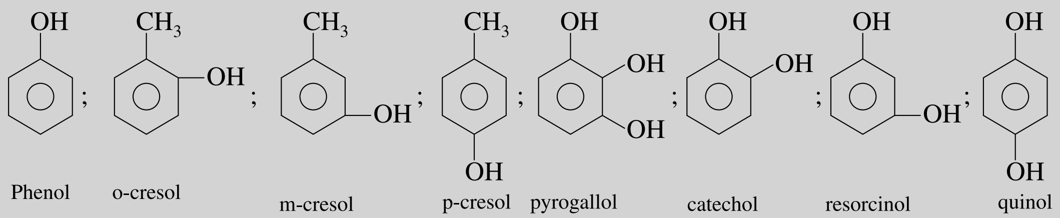


INTRODUCTION

PHENOL

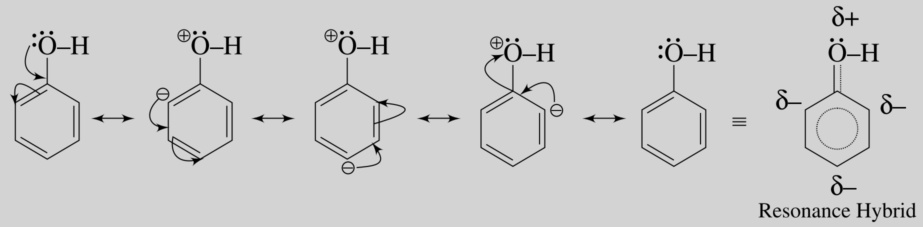
- Phenol is also called as **carbolic acid.**
- Compounds in which —OH group is directly attached with benzene ring are called as Phenols.
- Phenol is discovered by **Runge**
- **Hofmann,** another scientist, prepared it first from 'coal tar'.
- Aromatic hydroxy compounds in which a single –OH group is attached with benzene ring are called phenols.

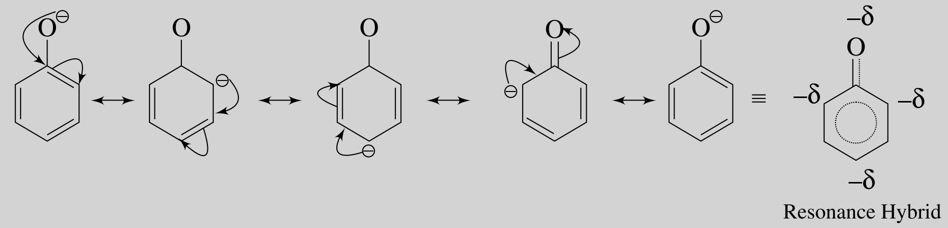
  Examples are:



- Physical properties of phenol are strongly influenced by the hydroxyl group which permits phenols to form hydrogen bond with other phenol molecules as well with water
- Thus, phenols have higher melting points (40°C) and boiling points (132°C).
- Phenols are more soluble in water than arenes and aryl halides of comparable molecular weight.
- Some *ortho*-substituted phenols, such as *ortho*-nitro phenol, have boiling point that are significantly lower than those of the *meta* and *para* isomers.

  Reason: Intermolecular hydrogen bonds that are formed between the hydroxyl group and substituent, partially compensates states for the energy required to go from the liquid state to the vapour.
- **Resonance in phenol and phenoxide ion:**

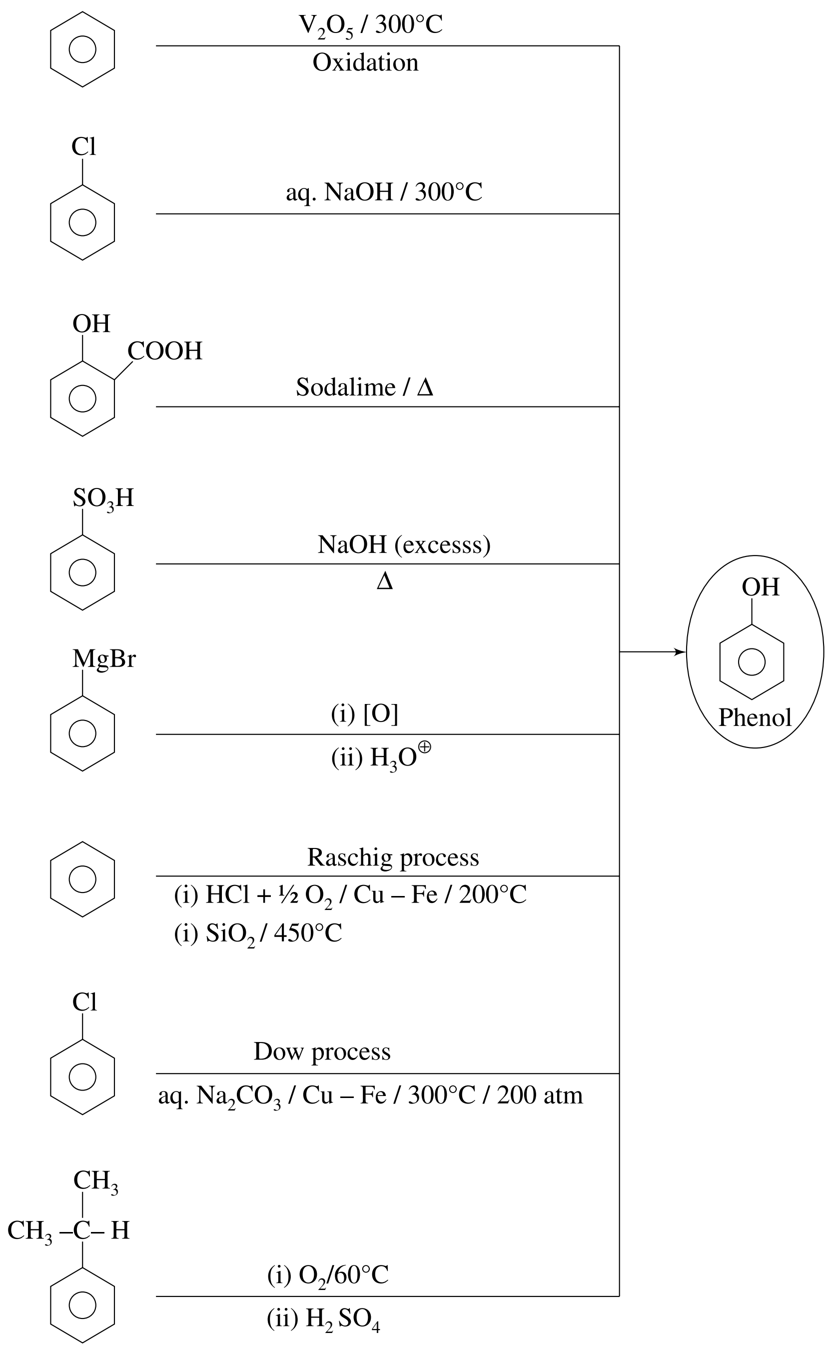




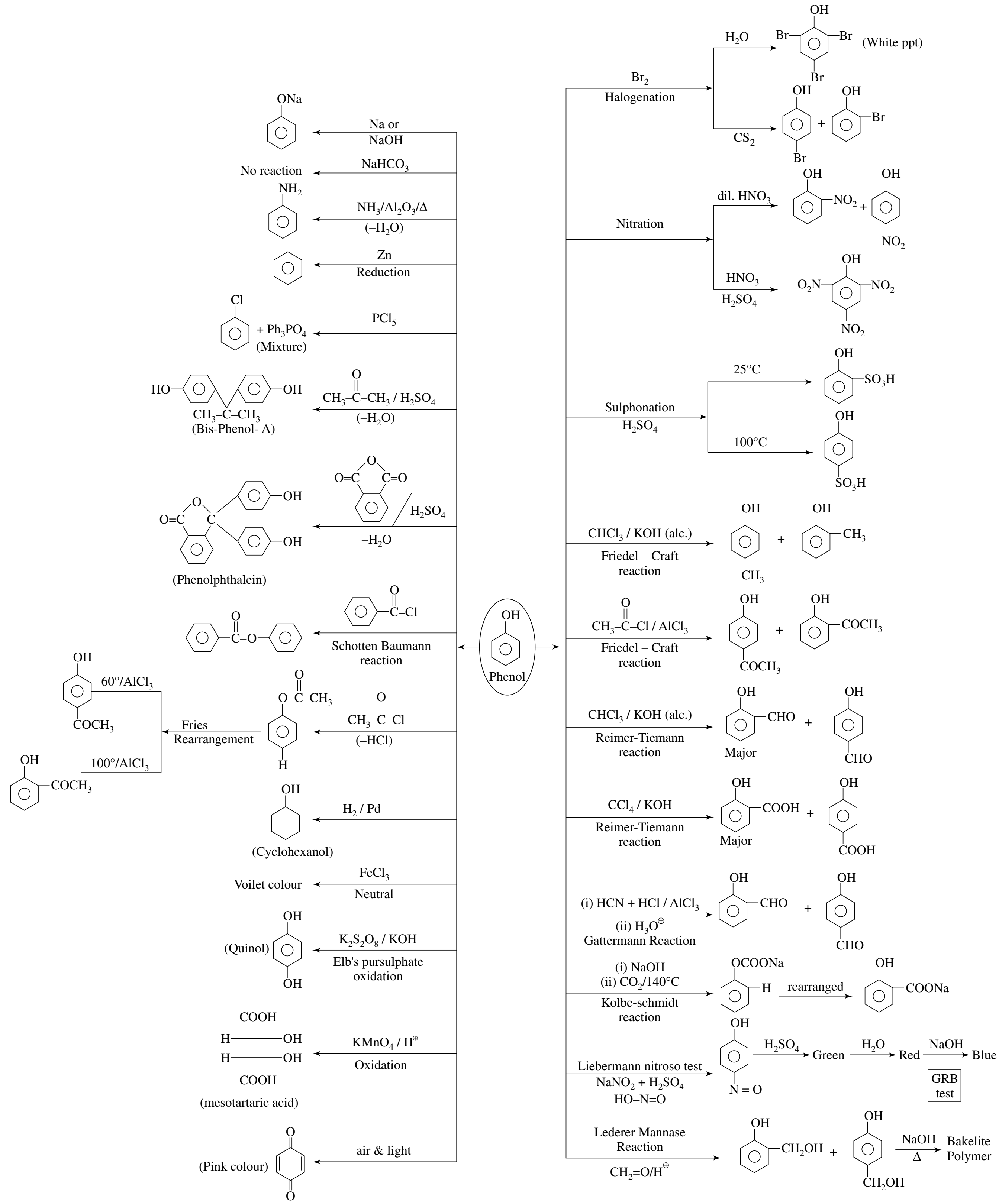
It is evident from the above structures that — OH group of phenol is o- and p-directing, as these are electron richer places; so electrophiles attack at these positions.

- Phenoxide ion is resonance stabilised. That is why phenol shows acidic character.
- The hydroxyl oxygen is less basic, and the hydroxyl proton is more acidic in phenol than in alcohol.

Methods of Preparation of Phenol:

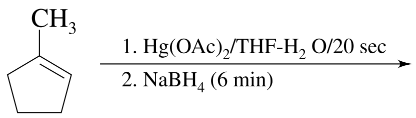


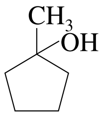
Chemical Properties of Phenol:

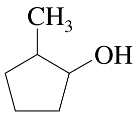


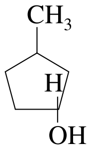
SOLVED EXAMPLE

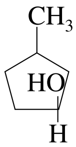
1. The final product obtained in the reaction



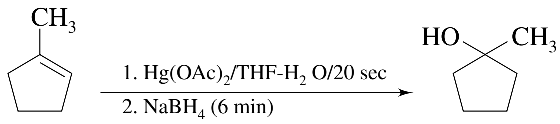
(1) 

(2) 

(3) 

(4) 

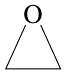
Sol. **[1]**



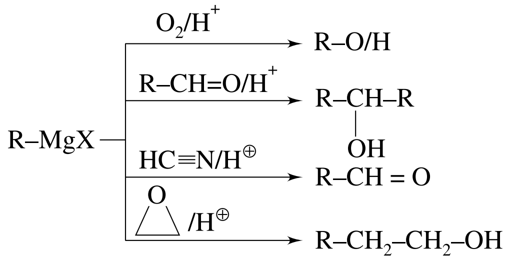
Hydration (addition of H^+/OH^-) takes place according to Markownikoff rule.

2. Which of the following compounds does not give alcohol on reaction with RMgX?

(1) $O_2/H^{\oplus}$ (2) $R-\overset{O}{\overset{\|}{C}}-H/H^{\oplus}$

(3) $HC\equiv N/H^{\oplus}$ (4)  $/H^{\oplus}$

Sol. **[3]**



3. Which one/ones of the following reactions will yield 2-propanol? Choose the right answer from (I), (II), (III) and (IV)

(I) $CH_2 = CH - CH_3 + H_2O \xrightarrow{H^+}$

(II) $CH_3 - CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI}$

(III) $CH_2O \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgI}$

(IV) $CH_2{=}CH{-}CH_3 \xrightarrow{\text{Neutral } KMnO_4}$

(1) I and II (2) II and III

(3) III and I (4) II and IV

Sol. **[1]**

(I) $CH_2{=}CH{-}CH_3 + H_2O \xrightarrow[\text{EAR}]{H^+} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

2-propanol

(II) $CH_3{-}CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

NAR 2-propanol

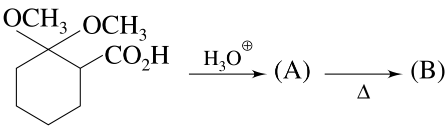
(III) $CH_2O \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgI} CH_3{-}CH_2{-}CH_2{-}OH$

NAR 1-propanol

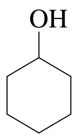
(IV) $CH_2{=}CH{-}CH_3 \xrightarrow[\text{oxidation}]{\text{Neutral } KMnO_4}$

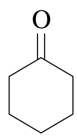
$CH_3{-}COOH + H{-}COOH$

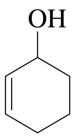
Acetic acid Formic acid

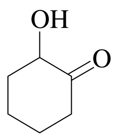
4. 

Product (B is)

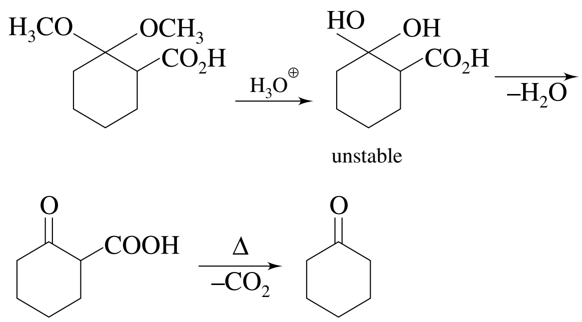
(1) 

(2) 

(3) 

(4) 

Sol. **[2]**



5. Dehydration of alcohol to alkene by heating with conc. H_2SO_4 the initiation step is ____ followed with _____ mechanism.

(1) Elimination of water, free radical
(2) Formation of an ester, free radical
(3) Protonation of alcohol, carbocation
(4) Protonation of alcohol, carbanion

Sol. **[3]**

$$R\text{–}OH \xrightarrow[H^{\oplus}]{\text{Conc. } H_2SO_4} R\text{–}\overset{\oplus}{O}\text{–}H_2 \longrightarrow R^{\oplus}$$

(Protonation) (Carbocation)

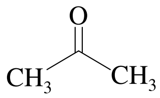
6. Ethylene glycol on treatment with PI_3 mainly gives:

(1) Ethylene (2) Ethylene iodide
(3) Ethyl iodide (4) Ethane

Sol. **[1]**

$$\begin{matrix} CH_2\text{–}OH \\ | \\ CH_2\text{–}OH \end{matrix} \xrightarrow{PI_3} \underset{\text{unstable}}{\begin{matrix} CH_2\text{–}I \\ | \\ CH_2\text{–}I \end{matrix}} \xrightarrow{-I_2} \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}$$

7. In which of the following reactions, alcohol is formed as product gives positive iodoform test?

(1)  $\xrightarrow[\text{(ii) HOH/H}^+]{\text{(i) PhMgBr}}$

(2) $CH_3\text{–}CH_2\text{–}CH{=}O \xrightarrow[\text{(ii) HOH/H}^+]{\text{(i) MeMgBr}}$

(3) $H\text{–}\overset{O}{\overset{\|}{C}}\text{–}OEt \xrightarrow[\text{(ii) HOH/H}^+]{\text{(i) PhMgBr (excess)}}$

(4) $CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}OEt \xrightarrow[\text{(ii) HOH/H}^+]{\text{(i) PhMgBr (excess)}}$

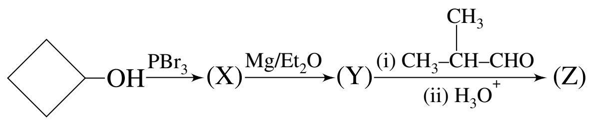
Sol. **[2]**

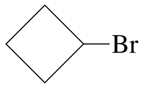
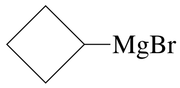
$$CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}CH_3 \xrightarrow[\text{H OH/H}^+]{\text{Ph–MgBr}} \underset{\text{(tertiary alcohol)}}{CH_3\text{–}\underset{OH}{\overset{Ph}{C}}\text{–}CH_3} \xrightarrow{I_2 | KOH} \text{–ve test}$$

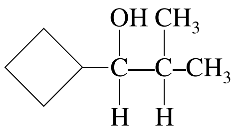
$$CH_3\text{–}CH_2\text{–}CH{=}O \xrightarrow[\text{H OH/H}^+]{\text{MeMgBr}} \underset{\text{(Secondary alkanol)}}{CH_3\text{–}CH_2\text{–}\underset{OH}{CH}\text{–}CH_3} \xrightarrow{I_2 | KOH} \text{+ve test}$$

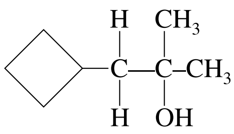
$$H\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}Et \xrightarrow[\text{H OH/H}^+]{\text{Ph–MgBr}} Ph\text{–}CH{=}O \xrightarrow[\text{H OH/H}^+]{\text{Ph–MgBr}} Ph\text{–}\underset{OH}{CH}\text{–}Ph \xrightarrow{I_2 | KOH} \text{–ve test}$$

$$CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}Et \xrightarrow[\text{H OH/H}^+]{\text{Ph–MgBr}} CH_3\text{–}\underset{OH}{\overset{Ph}{C}}\text{–}Ph \xrightarrow{I_2 | KOH} \text{–ve test}$$

8. 

(I) Y is  (II) Y is 

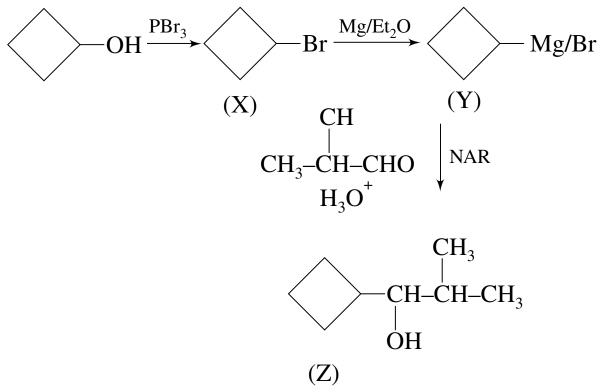
(III) Z is 

(IV) Z is 

Select the correct code for given reaction

(1) I and III (2) II and IV
(3) I and IV (4) II and III

Sol. **[4]**



9. $CH_3\text{–}\overset{18}{O}\text{–}\underset{CH_3}{\overset{CH_3}{C}}\text{–}CH_3 \xrightarrow{\text{conc. HI}}$

Product of above reaction is:

(1) $CH_3\text{–}I + CH_3\text{–}\underset{CH_3}{\overset{CH_3}{C}}\text{–}\overset{18}{O}H$

(2) $CH_3\text{–}\overset{18}{O}H + CH_3\text{–}\underset{CH_3}{\overset{CH_3}{C}}\text{–}I$

(3) $CH_3\text{–}\overset{18}{O}H + CH_3\text{–}\underset{CH_3}{\overset{CH_3}{C}}\text{–}OH$

(4) $CH_3\text{–}I + CH_3\text{–}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}\text{–}I$

Sol. **[2]**

When one of the alkyl of ether is 3° alkyl then breaking of C–O bond takes place by S_N1 path.

In SN_1 reaction, breaking site towards the most stable carbocation

$$CH_3\text{—}\overset{18}{O}\text{—}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}\text{—}CH_3 \xrightarrow[SN_1\text{ Reaction}]{\text{Conc. HI}} CH_3\text{—}\overset{18}{O}H + CH_3\text{—}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}\text{–}I$$

H I

10. Consider the following sequence of reaction

$PhCH_3(\text{excess}) + Cl_2 \xrightarrow{\text{Heat}} A \xrightarrow{\text{aq. KOH}} B \xrightarrow{\text{Na}} C$

$A + C \xrightarrow{\text{Heat}} D$. Product D is:

(1) $PhCH_2OPh$ (2) $PhCH_2OCH_2Ph$

(3) $PhCH_2CH_2Ph$ (4) $Ph\text{–}CH_2\text{–}\overset{\displaystyle O}{\overset{||}{C}}\text{–}Ph$

Sol. **[2]**

$$\underset{}{Ph\text{–}CH_3(\text{excess})} \xrightarrow{Cl_2/\Delta} \underset{(A)}{Ph\text{–}CH_2\text{–}Cl} \xrightarrow{\text{Aq KOH}} \underset{(B)}{Ph\text{–}CH_2\text{–}OH} \xrightarrow{Na/\Delta} \underset{(C)}{Ph\text{–}CH_2\text{–}\overset{\ominus\oplus}{ONa}}$$

$$\underset{(A)}{Ph\text{–}CH_2\text{–}Cl} + \underset{(C)}{Ph\text{–}CH_2\text{–}\overset{\ominus}{O}} \xrightarrow{SN_2} Ph\text{–}CH_2\text{–}O\text{–}CH_2\text{–}Ph$$

Williamson synthesis

11. Identify the product C in the given reaction.

$CH_3\text{–}C\equiv N \xrightarrow{H_2/Pd} A \xrightarrow{HNO_2} B \xrightarrow{I_2/NaOH}$

(1) $CH_3\text{–}COOH$ (2) $CH_3\text{–}CH_2\text{–}NH\text{–}OH$

(3) $CH_3\text{–}\overset{\displaystyle O}{\overset{||}{C}}\text{–}\overset{\ominus}{O}+CHI_3$ (4) CHI_3+HCOO^-

Sol. **[4]**

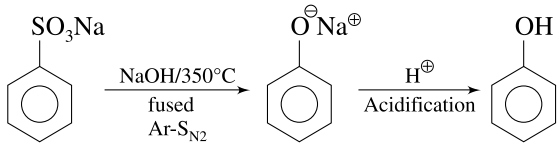
$$CH_3\text{–}CN \xrightarrow{H_2/Pd} CH_3\text{–}CH_2\text{–}NH_2 \xrightarrow{HNO_2} CH_3\text{–}CH_2\text{–}OH \xrightarrow[\text{Iodoform reaction}]{I_2/NaOH} CHI_3 + H\text{–}\underset{\displaystyle O}{\underset{||}{C}}\text{–}O\text{–}Na$$

12. When sodium benzenesulphonate is fused with solid sodium hydroxide and subsequently acidified with dilute sulphuric acid, the product formed is:

(1) benzene (2) sodium phenoxide

(3) thiophenol (4) phenol

Sol. **[4]**



13. $Ph\text{–}\overset{\displaystyle O}{\overset{||}{C}}\text{–}OH + Et\overset{18}{O}H \xrightarrow[\Delta]{H^{\oplus}}$ (P) major product, Product (P) is–

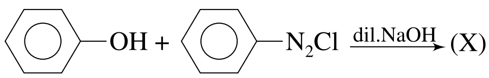
(1) $Ph\text{–}\overset{\displaystyle O^{18}}{\overset{||}{C}}\text{–}O\text{–}Et$ (2) $Ph\text{–}\overset{\displaystyle O}{\overset{||}{C}}\text{–}\overset{18}{O}\text{–}Et$

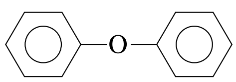
(3) $Ph\text{–}\overset{\displaystyle O}{\overset{||}{C}}\text{–}Et$ (4) $Ph\text{–}\overset{18}{O}\text{–}\overset{\displaystyle O}{\overset{||}{C}}\text{–}Et$

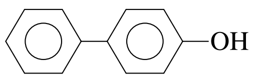
Sol. **[2]**

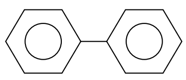
$$Ph\text{–}\underset{\displaystyle O}{\underset{||}{C}}\boxed{\text{–}O\text{–}H + H}\text{–}\overset{18}{O}\text{–}Et \xrightarrow[\text{Estrification}]{} Ph\text{–}\underset{\displaystyle O}{\underset{||}{C}}\text{–}\overset{18}{O}\text{–}Et + H_2O$$

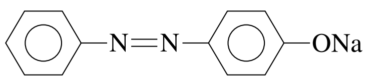
14. Consider the reaction:



(1) 

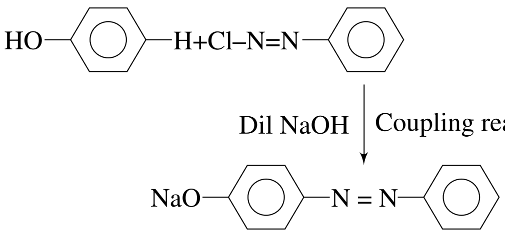
(2) 

(3) 

(4) 

Sol. **[4]**

Coupling reaction predominantly takes place at the *para* position.

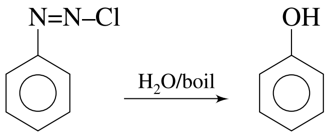


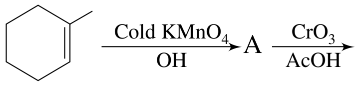
15. Benzenediazonium chloride can be converted into phenol by treating it with

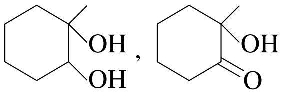
(1) H_3PO_3, H_2O, CuCl (2) H_2O, heat

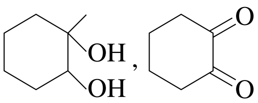
(3) Alcohol, heat (4) HBF_4, and $NaNO_2$/Cu

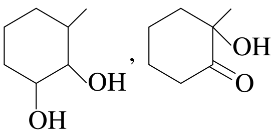
Sol. **[2]**

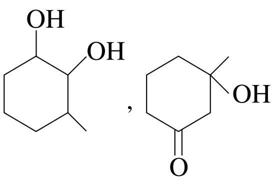


16.  B, A and B are:

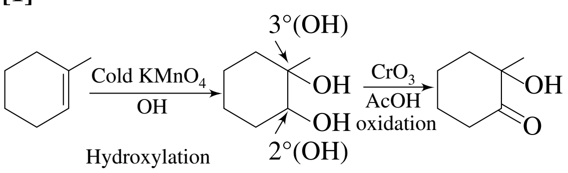
(1) 

(2) 

(3) 

(4) 

Sol. **[1]**



(A) (B)

Oxidation of 3°-alcohol does not take place and 2°-alcohol oxidised into ketone.

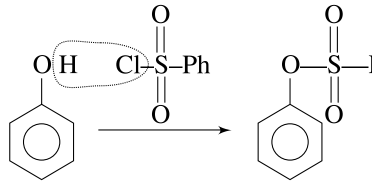
17. Phenol on reacting with Hinsberg's reagent gives:

(1) Sulphone (2) Sulphanilic

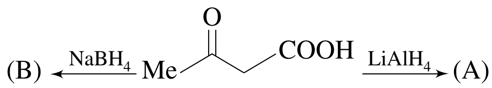
(3) Sulphonic ester (4) Sulphonal

Sol. **[3]**

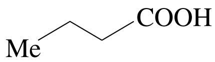
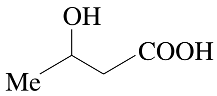
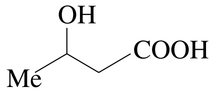
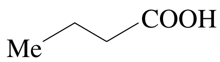
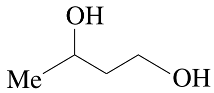
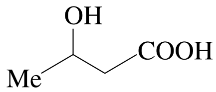
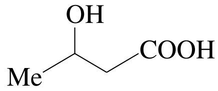
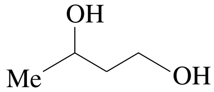
Benzene sulphonyl chloride (Ph–SO_2Cl) is known as Hinsberg reagent.



sulphonic ester

18. 

The products (A) and (B) are:

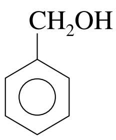
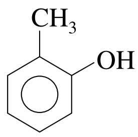
	(A)	**(B)**
(1)		
(2)		
(3)		
(4)		

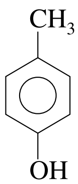
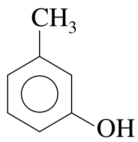
Sol. **[3]**

$NaBH_4$ is a weak reducing reagent. So it reduces only carbonyl group while reduction of –COOH group does not happen and it remains unaffected.

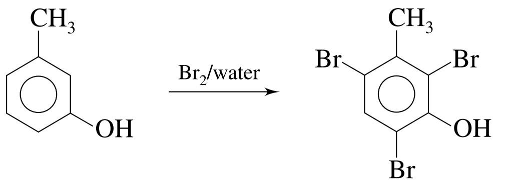
$LiAlH_4$ is strong reducing reagent; so it can reduce both $>C=O$ and –COOH groups.

19. The structure of the compound that gives tribromo derivative on treatment with bromine water is:

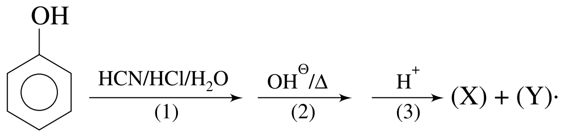
(1)  (2) 

(3)  (4) 

Sol. **[4]**



Tribromo derivative
White ppt

20. 

X gives white turbidity with Lucas reagent instantly. X and Y both turn blue litmus solution red. Y can be:

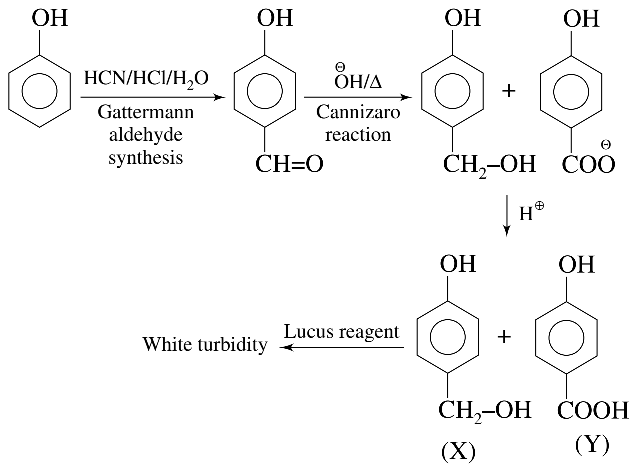
(1) *p*-Hydroxy benzoic acid

(2) *p*-Hydroxy benzaldehyde

(3) *m*-Hydroxy benzoic acid

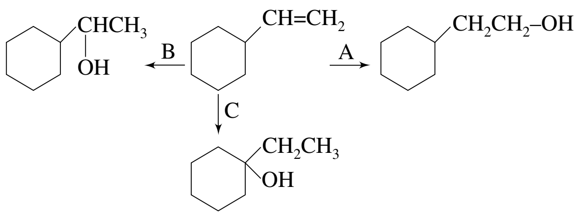
(4) *p*-Hydroxy benzyl alcohol

Sol. **[1]**



Both are phenolic so that (X) and (Y) give litmus test.

EXERCISE 1

1. 

Select schemes A, B, C, respectively, out of

I. Acid catalysed hydration

II. HBO

III. Oxymercuration–demercuration

(1) I in all cases (2) I, II, III

(3) II, III, I (4) III, I, II

2. The reaction

$$CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}OC_2H_5 + n\text{-}C_3H_7OH \xrightarrow{n\text{-}C_2H_7ONa}$$

$CH_3COOC_3H_7(n) + C_2H_5OH$ is known as:

(1) Esterification

(2) Double decomposition

(3) Transesterification

(4) None of these

3. A compound 'X' with molecular formula C_3H_8O can be oxidised to a compound 'Y' with the molecular formula $C_3H_6O_2$, 'X' is most likely to be:

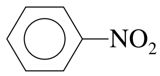
(1) Primary alcohol (2) Secondary alcohol

(3) Aldehyde (4) Ketone

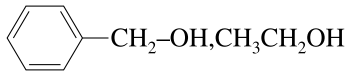
4. Which 'A' gives blue colour in the reaction?

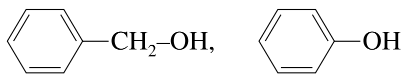
'A' $\xrightarrow[\text{(ii) NaOH}]{\text{(i) HNO}_2}$ blue colour

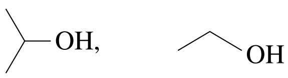
(1) $CH_3CH_2NO_2$ (2) $(CH_3)_2CHNO_2$

(3) $(CH_3)_3CNO_2$ (4) 

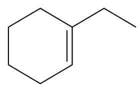
5. Which of the following pairs cannot be distinguished by using Lucas reagent?

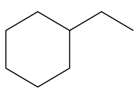
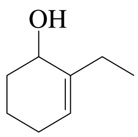
(1) 

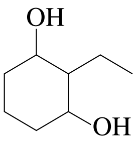
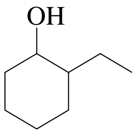
(2) 

(3) 

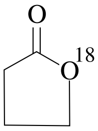
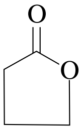
(4) 

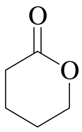
6.  $\xrightarrow{SeO_2}$ A.A is

(1)  (2) 

(3)  (4) 

7. $HO\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}OH$ (O-18 in HO) $\xrightarrow[\text{lactonization reaction}]{H^+/\Delta}$

(1)  (2) 

(3)  (4) None

8. $A + Ac_2O \longrightarrow (B)$
(acetic anhydride)

Molecular formula of A increases by $C_8H_8O_4$. Number of OH group present in A are:

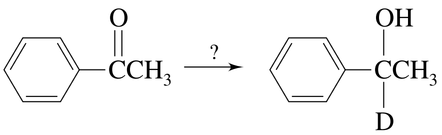
(1) 3 (2) 4
(3) 5 (4) 6

9. $H\text{–}\underset{\underset{O}{\|}}{C}\text{–}OEt \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) MeMgI (excess)}}$ A. A is

(1) $H_3C\text{–}\overset{CH_3}{\underset{OH}{C}}\text{–}CH_3$ (2) $H\text{–}\overset{H}{\underset{OH}{C}}\text{–}CH_3$

(3) $H_3C\text{–}\overset{H}{\underset{OH}{C}}\text{–}CH_3$ (4) $CH_3\text{–}CH\text{=}O$

10. Which of the following reagents would carry out of the following transformation ? (D = ^{2}H)



(1) $NaBD_4$ in CH_3OH (2) $LiAlH_4$, then D_2O
(3) ($NaBD_4$ in CH_3OD (4) $LiAlD_4$, then D_2O

11. Methyl propionate, $CH_3CH_2COOCH_3$, is heated with aqueous H_2SO_4 in ^{18}O labelled water. When the equilibrium is achieved, the labelled oxygen will be present in:

(1) methyl alcohol
(2) Propionic acid
(3) unchanged methyl propionate
(4) both propionic acid and methyl propionate

12. $\underset{\text{Ester(X)}}{C_4H_8O_2} \xrightarrow[\text{(ii) HOH/HCl}]{\text{(i) } CH_3MgBr} \underset{\text{Alcohol(Y)}}{C_4H_{10}O}$

Alcohol (Y) gives Lucas test immediately. Thus, (X) and (Y) are, respectively:

(1) $CH_3COOC_2H_5$; $(CH_3)_3(COH)$
(2) $HCOOC_3H_7$; $C_2H_5CH(CH_3)OH$
(3) $C_2H_5COOCH_3$; $(C_2H_5)_3COH$
(4) $HCOOC_3H_7$; $CH_3(CH_2)_3OH$

13. The enzymes A, B and C in the reaction sequence are:

$$(C_6H_{10}O_5)_n \xrightarrow{A} C_{12}H_{22}O_{11} \xrightarrow{B} C_6H_{12}O_6 \xrightarrow{C} C_2H_5OH$$

(1) Invertase, Maltase, Zymase
(2) Diastase, Maltase, Zymase
(3) Maltase, Zymase, Invertase
(4) Diastase, Zymase, Maltase

14. A carbon compound A forms B with sodium metal and again A forms C with PCl_5, but B and C form diethyl ether. Therefore A, and B and C are:

(1) C_2H_5OH, C_2H_5ONa, C_2H_5Cl
(2) C_2H_5Cl, C_2H_5ONa, C_2H_5OH
(3) C_2H_5OH, C_2H_6, $C_2H_5Cl_2$
(4) C_2H_5OH, C_2H_5Cl, C_2H_5ONa

15. In order to obtain diethyl ether from ethanol and sulphuric acid, the latter is taken:

(1) In equal amount of sulphuric acid
(2) In slightly lesser amount of sulphuric acid
(3) In excess amount of sulphuric acid
(4) In far lesser amount of sulphuric acid

16. The synthesis of $Ph\text{–}\overset{CH_3}{\underset{C_2H_5}{C}}\text{–}OH$ cannot be achieved by:

(1) $PhMgBr + CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}C_2H_5 \xrightarrow{H^{\oplus}/H_2O}$

(2) $C_2H_5MgBr + Ph\text{–}\overset{O}{\overset{\|}{C}}\text{–}CH_3 \xrightarrow{H^{\oplus}/H_2O}$

(3) $CH_3MgBr + Ph\text{–}\overset{O}{\overset{\|}{C}}\text{–}CH_2CH_3 \xrightarrow{H^{\oplus}/H_2O}$

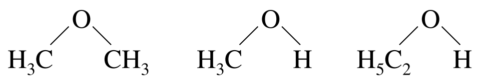
(4) $PhMgBr + CH_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}Cl \xrightarrow{H^{\oplus}/H_2O}$

17. Which of the following is the final product in the reaction between benzoyl chloride and phenyl magnesium bromide?

(1) $C_6H_5\overset{\overset{\large C_6H_5}{|}}{\underset{\underset{\large Cl}{|}}{C}}-OH$ (2) $C_6H_5\overset{\overset{\large C_6H_5}{|}}{\underset{\underset{\large Cl}{|}}{C}}-OMgBr$

(3) C_6H_5COOH (4) $(C_6H_5)_3COH$

18. The order of solubility of

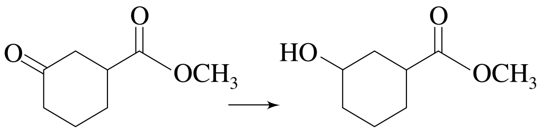


(I) (II) (III)

in water is:

(1) I > II > III (2) I < II < III

(3) II > III > I (4) II > I > III

19. 

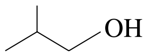
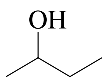
Above conversion can be achieved by–

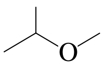
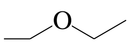
(1) $LiAlH_4$ (2) $NaBH_4$

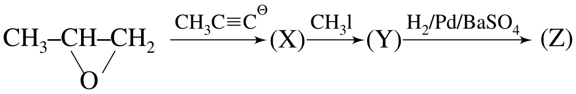
(3) H_3O^+ (4) PCC

20. (A) $\xrightarrow[C_4H_{10}O]{CrO_3/H^{\oplus}}$ (B) $\xrightarrow{NaOI}$ CHI_3+ Salt of acid

Reactant (A) is:

(1)  (2) 

(3)  (4) 

21. 

Which one in not correct

(1) Y is $CH_3-\underset{\underset{\large O-CH_3}{|}}{CH}-CH_2C\equiv CCH_3$

(2) Y is $CH_3-CH_2-\underset{\underset{\large OCH_3}{|}}{CH}C\equiv CCH_3$

(3) Z is $CH_3-\underset{\underset{\large OCH_3}{|}}{CH}-CH_2-\underset{H}{C}=\underset{H}{C}-CH_3$

(4) Z is $CH_3-\underset{\underset{\large OCH_3}{|}}{CH}-CH_2-\underset{H}{C}=C\begin{smallmatrix}H\\ \\ CH_3\end{smallmatrix}$

22. Which of the following is the best method for making isopropyl methyl ether?

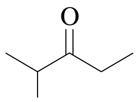
(1) $CH_3I + (CH_3)_2CHOH \longrightarrow$

(2) $CH_3I + (CH_3)_2CHO^- \longrightarrow$

(3) $(CH_3)_2CHI + CH_3O^- \longrightarrow$

(4) $(CH_3)_2CHCl + CH_3OH \longrightarrow$

23. Which sequence of steps describes the best synthesis of 2-methyl-3-pentanone?



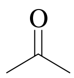
(1) (1) 1-Propanol + $(CH_3)_2CHMgBr$, diethyl ether
(2) H_3O^+
(3) PCC, CH_2Cl_2

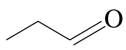
(2) (1) 1-Propanol + $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat
(2) $SOCl_2$
(3) $(CH_3)_2CHCl$, $AlCl_3$

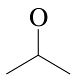
(3) (1) 1-Propanol + PCC, CH_2Cl_2
(2) $(CH_3)_2CHLi$, diethyl ether
(3) H_3O^+
(4) $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat

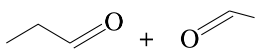
(4) (1) 2-Propanol + $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat
(2) $CH_3CH_2CH_2Li$, diethyl ether
(3) H_3O^+
(4) PCC, CH_2C12

24. $CH_3-CH_2-O-\underset{\underset{\large CH_3}{|}}{C}=CH_2 \xrightarrow{H_3O^{\oplus}}$ Product are

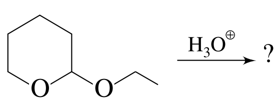
(1)  + EtOH

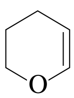
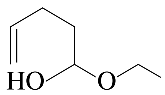
(2)  + EtOH

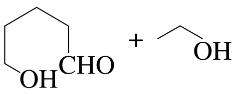
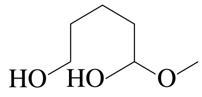
(3)  + EtOH

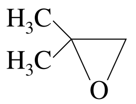
(4) 

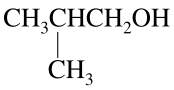
25. The major product formed in the reaction is:

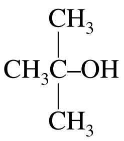


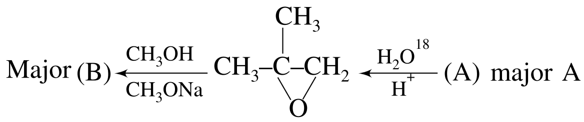
(1)  + CH_3CH_2OH (2) 

(3)  (4) 

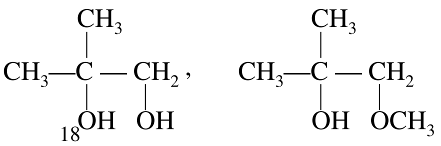
26.  $\xrightarrow{LiAlH_4/H^{\oplus}}$ A, A is

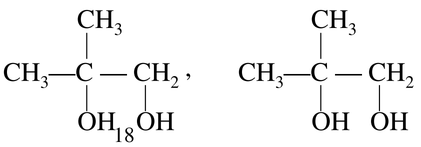
(1)  (2) $CH_3CH_2CH_2CH_2OH$

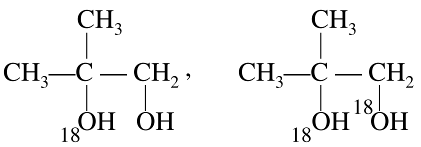
(3)  (4) No reaction

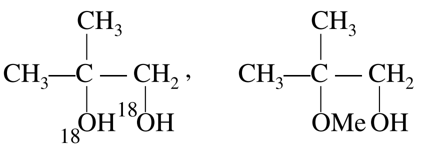
27. 

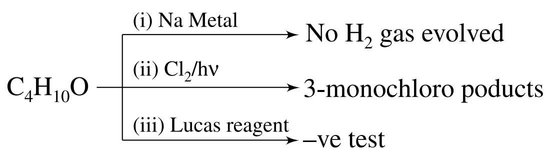
and B are:

(1) 

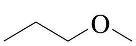
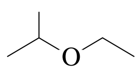
(2) 

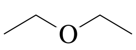
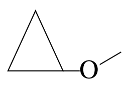
(3) 

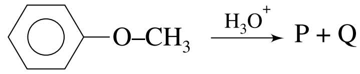
(4) 

28. 

Compound is:

(1)  (2) 

(3)  (4) 

29. 

What is false about this reaction–

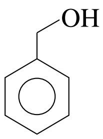
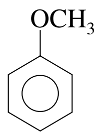
(1) one compound is phenol which is less acidic than other compound

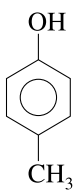
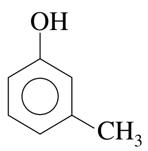
(2) one compound is phenol and other is methanol

(3) reactant is anisole

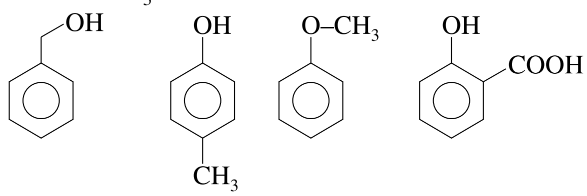
(4) this reaction occur through SN^2 reaction

30. A compound of molecular formula C_7H_8O is insoluble in water and dilutes sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide and gives a characteristic colour with aqueous $FeCl_3$. On treatment with bromine water, it readily gives precipitate of $C_7H_5OBr_3$. The structure of 'A' is:

(1)  (2) 

(3)  (4) 

31. Which of the following can give purple colour with neutral $FeCl_3$?



(I) (II) (III) (IV)

(1) II and IV (2) I and III

(3) II and III (4) III and IV

32. *Ortho*-nitrophenol is steam volatile, whereas *para*-nitrophenol is not. This is due to

(1) the presence of intramolecular hydrogen boding in o-nitrophenol.

(2) the presence of intermolecular hydrogen bonding in o-nitrophenol.

(3) the presence of intermolecular hydrogen bonding in p-nitrophenol.

(4) None of these.

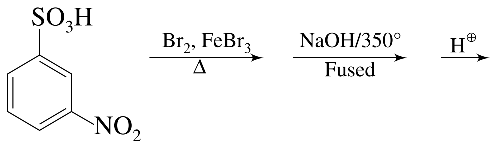
33. Phenol cannot be converted into salicylic acid by heating with:

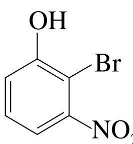
(1) CO_2 (under pressure) and alkali
(2) CCl_4 and alkali
(3) $CHCl_3$ and alkali
(4) HCN/HCl, followed by oxidation

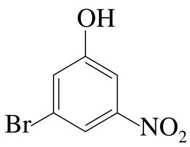
34. 4-Hydroxybenzenesulphonic acid is treated with bromine water. The product formed is:
(1) 2, 4, 6-tribromophenol
(2) 3, 5-dibromo-4-hydroxybenzenesulphonic acid
(3) 3-bromo-4-hydroxybenzenesulphonic acid
(4) 2, 6-dibromophenol

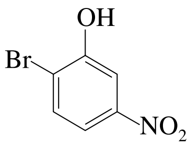
35. In the Liebermann nitroso reaction, changes in the colour of phenol occur as:
(1) Brown or red-green-red-deep blue
(2) Red-deep blue-green
(3) Red-brown-white
(4) White-red-green

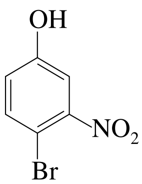
36. Which of the following is the major product from given sequence?



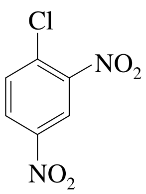
(1) 

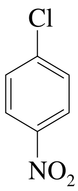
(2) 

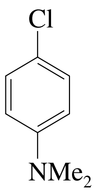
(3) 

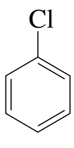
(4) 

37. Which of the following would undergo most rapid hydrolysis with aqueous NaOH to furnish the corresponding hydroxyl derivatives?

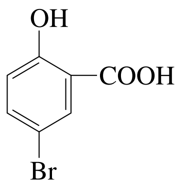
(1) 

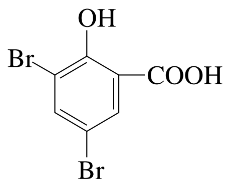
(2) 

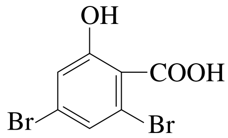
(3) 

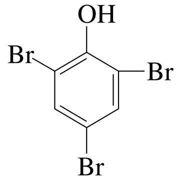
(4) 

38. The bromination of salicylic with bromine water gives

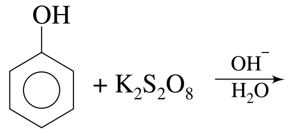
(1) 

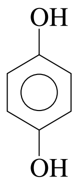
(2) 

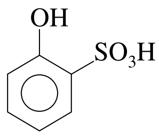
(3) 

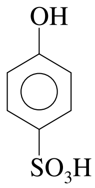
(4) 

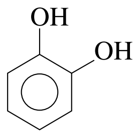
39. Identify the nature of product of in the following reaction:

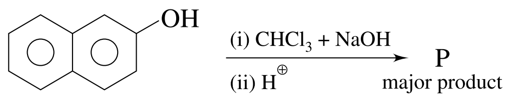


(1) 

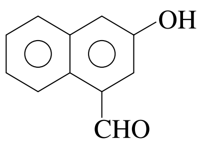
(2) 

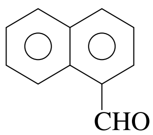
(3) 

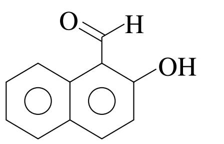
(4) 

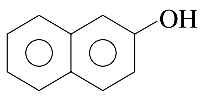
40. 

Identify the structure of 'P'

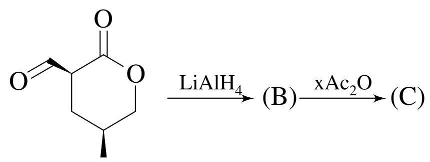
(1) 

(2) 

(3) 

(4) 

EXERCISE 2

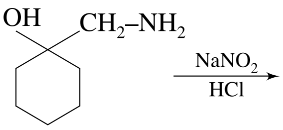
1. 

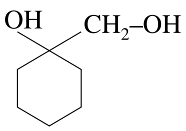
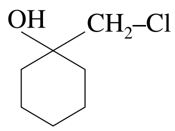
(A)

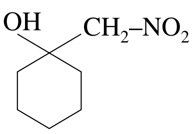
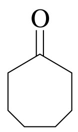
(I) x = 3
(II) A will show geometrical isomerism
(III) B is optically active
(IV) C is optically inactive

Select correct statement

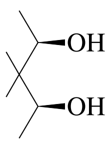
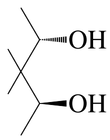
(1) (I), (II), (IV) (2) (I), (II), (III)
(3) (II), (III), (IV) (4) (I), (II), (III), (IV)

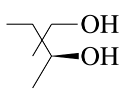
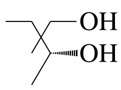
2.  A; A (major product) is:

(1)  (2) 

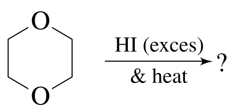
(3)  (4) 

3. A chiral $C_7H_{16}O_2$ diol is oxidised by PCC in CH_2Cl_2 to an achiral $C_7H_{12}O_2$ compound. Which of the following would satisfy these facts?

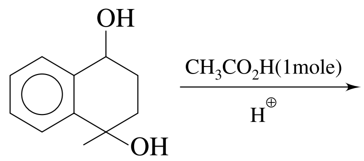
(1)  (2) 

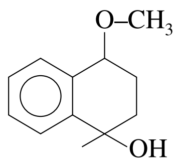
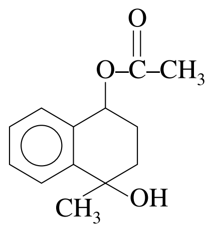
(3)  (4) 

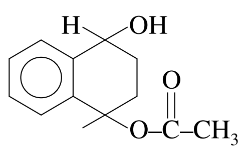
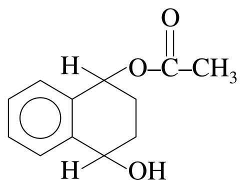
4. What product(s) are expected from the following reaction?

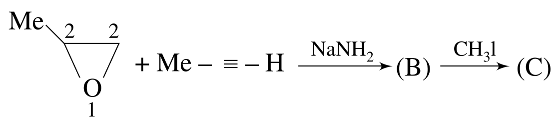


(1) $2CH_3CH_2I$
(2) $2ICH_2CH_2OH$
(3) $2ICH_2CH_2I$
(4) $CH_3CH_2I + CH_3CH_2OH$

5.  (A), Product (A) is:

(1)  (2) 

(3)  (4) 

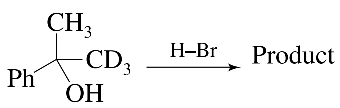
6. 

2-Methyl oxirane

Give the product (C) in the above reaction

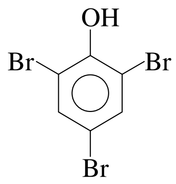
(1) 2-Methoxy hex-4-yne
(2) 4-Methoxy hex-2-yne
(3) 5-Methoxy hex-2-yne
(4) None of these

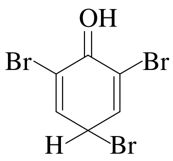
7. Which describes the best stereochemical aspects of the following reaction?

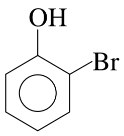


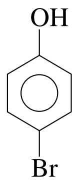
(1) Inversion of configuration occurs at the carbon undergoing substitution.
(2) Retention of configuration occurs at the carbon undergoing substitution.
(3) Racemisation occurs at the carbon undergoing substitution.
(4) The carbon undergoing substitution is not sterogenic.

8. What is the structure of the major product when phenol is treated with bromine water?

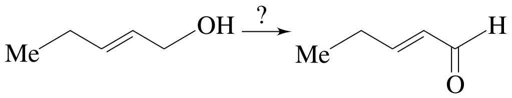
(1) 

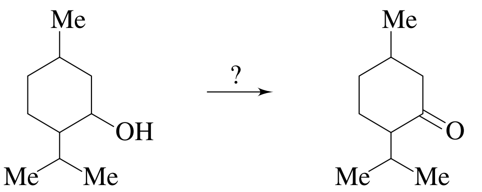
(2) 

(3) 

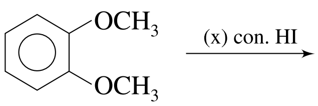
(4) 

9. Suggest a suitable oxidising reagent for the following conversions:

(A) 

(B) 

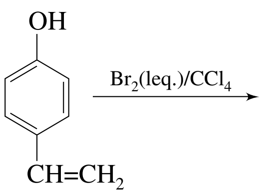
(1) MnO_2 in (A) and CrO_3 (in glacial acetic acid) in (B)
(2) CrO_3 in (A) and MnO_2 in (B)
(3) both are correct
(4) both are incorrect

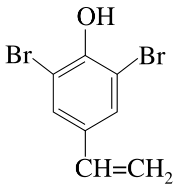
10. 

X = moles of HI consumed.
Value of x is:

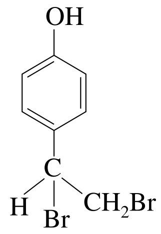
(1) 2 (2) 4
(3) 5 (4) 6

11. Observe the following reaction carefully. Select the correct answer regarding the major product formed and the relative reactivity of compound X with respect to ethene for the following reaction.

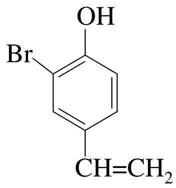
x = 

(1) 

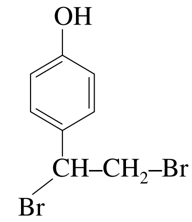
Much less reactive than ethene

(2) 

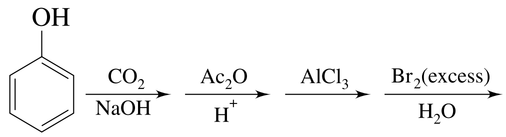
Much more reactive than ethene

(3) 

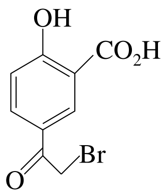
Much less reactive than ethene

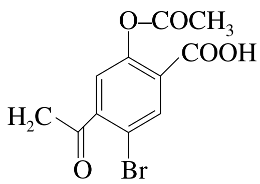
(4) 

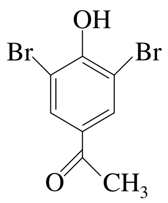
Less more reactive than ethene

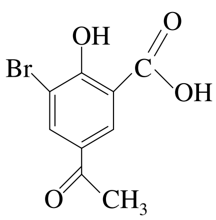
12. 

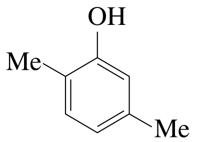
Final product is:

(1) 

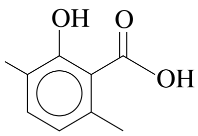
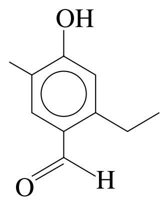
(2) 

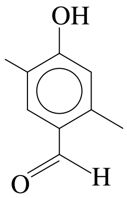
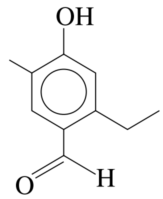
(3) 

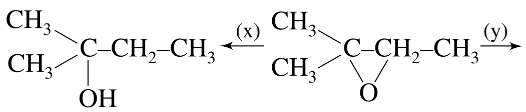
(4) 

13.  $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CHCl_3\text{. KOH}}$ 'P', the product

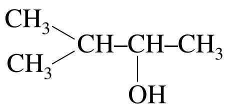
'P' is–

(1)  (2) 

(3)  (4) 

14. 

3° alchol

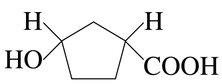


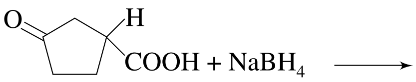
2° alchol

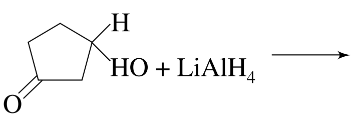
Find missing reagents

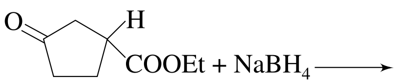
(1) x = $LiAlH_4$, y = $NaBH_4$
(2) x = $LiAlH_4/AlCl_3$, y = $LiAlH_4$
(3) x = $LiAlH_4$, y = $LiAlH_4/AlCl_3$
(4) x = H_2/Ni, y = H_2/Pt

15. The given compound is prepared by–



(1) 

(2) 

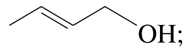
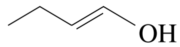
(3) 

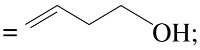
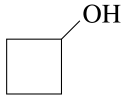
(4) 

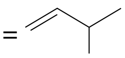
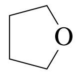
16. Compounds X and Y both have the same molecular formula C_4H_8O, and they give the following results with some characteristic tests:

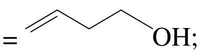
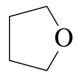
Tests	**Compounds X**	**Compound Y**
Bromine	Decolourise	No reaction
Na Metal	Bubbles	No reaction
Chromic acid	Orange to green	No reaction
Lucas reagent	Slow reaction	No reaction

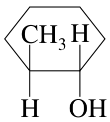
Which of the following structures for X and Y are consistent with the test results?

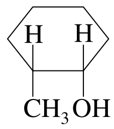
(1) X = ; Y = 

(2) X = ; Y = 

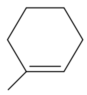
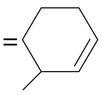
(3) X = ; Y = 

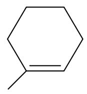
(4) X = ; Y = 

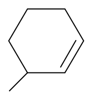
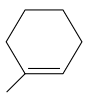
17. Reaction I:  $\xrightarrow{POCl_3}$ A

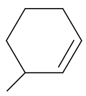
Reaction II:  $\xrightarrow[\text{Pyridine}]{POCl_3}$ B

Products A and B are respectively

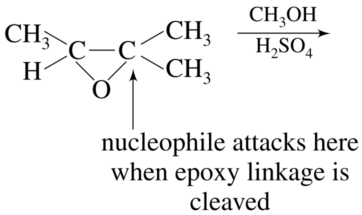
(1) A =  ; B = 

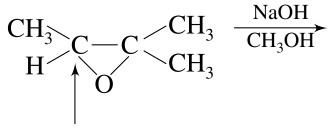
(2) A =  = B

(3) A =  ; B = 

(4) A =  = B

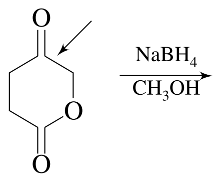
18. Which is/are correct Statements?

(A) 

(B) 

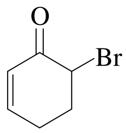
Nucleophile attacks here

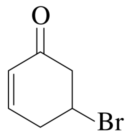
(C) This is only affected in reduction to 2° alcohol

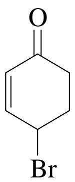


(D) $R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-O-R \xrightarrow{H^+}$ These bonds are affected in esterification

(1) A and D (2) A and B
(3) A, B and C (4) A, B, C and D

19. Reaction (I)  $\xrightarrow{\text{Alc. KOH}}$ (A) (major)

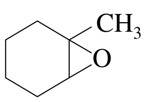
Reaction (II)  $\xrightarrow{\text{Alc. KOH}}$ (B) (major)

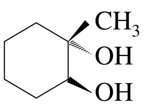
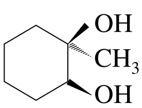
Reaction (III)  $\xrightarrow{\text{Alc. KOH}}$ (C) (major)

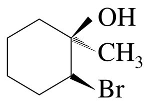
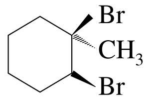
Product obtained in above reactions (I), (II) & (III) is:

(1) A = B, but C is different
(2) A = C, but B is different
(3) B = C, but A is different
(4) A = B = C all product are identical

20. The best choice of reactant(s) for the following conversion is:

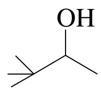
? $\xrightarrow{HO^-}$ 

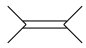
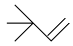
(1)  (2) 

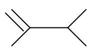
(3)  (4) 

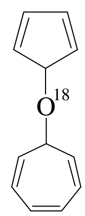
21. In the reaction, $CH_3CH_2ONa + CH_3CH_2OSO_2CH_3 \xrightarrow[\text{heat}]{\text{THF}}$ the product formed is:

(1) $CH_3CH_2OCH_3$
(2) $CH_3CH_2OCH_2CH_3$
(3) $CH_3CH_2OSO_2OCH_2CH_3$
(4) $CH_3CH_2OSO_2OCH_3$

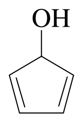
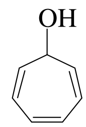
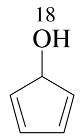
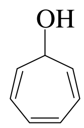
22.  $\xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$ Major product?

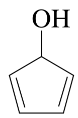
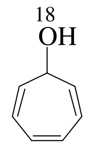
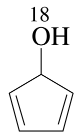
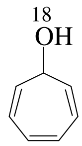
(1)  (2) 

(3)  (4) None of these

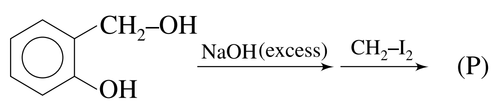
23.  $\xrightarrow{H_3O^{\oplus}}$ X + Y

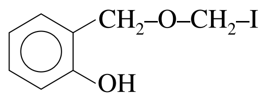
The products X and Y are

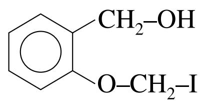
(1)  ,  (2)  , 

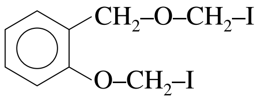
(3)  ,  (4)  , 

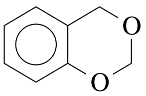
24. The product 'P' of the following reaction is:

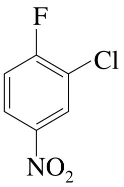


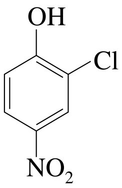
(1) 

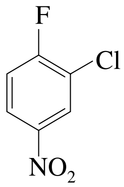
(2) 

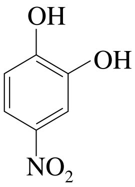
(3) 

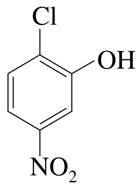
(4) 

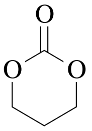
25.  $\xrightarrow[\Delta]{KOH}$ Y; Identify Y in this reaction.

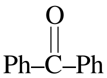
(1) 

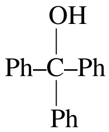
(2) 

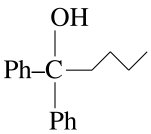
(3) 

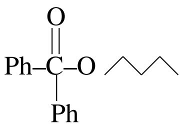
(4) 

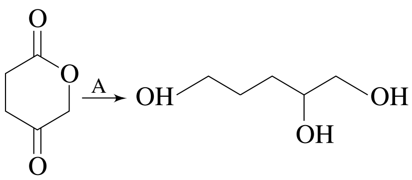
26. PhMgBr + (excess)  $\xrightarrow{H^+}$ (A). Product (A) is:

(1) 

(2) 

(3) 

(4) 

27. 

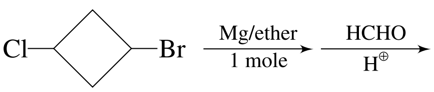
Reagent A used in this change is:

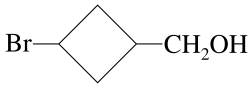
(1) Sn/HCl

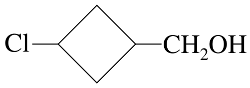
(2) $LiAlH_4$

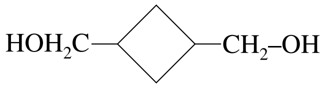
(3) $NaBH_4$

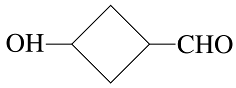
(4) HI/P_4

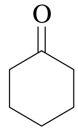
28.  A, A is

(1) 

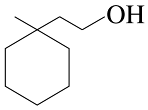
(2) 

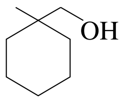
(3) 

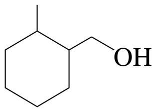
(4) 

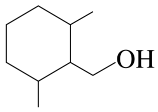
29.  + CH_3MgBr $\xrightarrow{H^{\oplus}/H_2O}$ P $\xrightarrow{KBr+H_2SO_4}$

Q $\xrightarrow[Ether]{Mg}$ R $\xrightarrow[H^{\oplus}/H_2O]{HCHO}$ S, S is

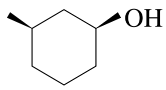
(1) 

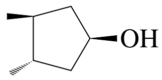
(2) 

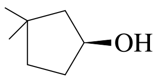
(3) 

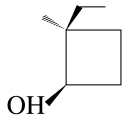
(4) 

30. A $C_7H_{14}O$ optically active alcohol is oxidised by Jones' reagent (H_2CrO_4) to an optically inactive (achiral) ketone. Which of the following compounds meets these facts?

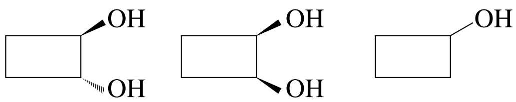
(1) 

(2) 

(3) 

(4) 

31. What is the order of solubility of the following in water?



I II III

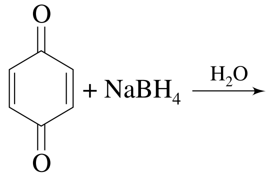
(1) I < II < III

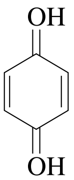
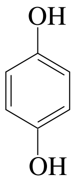
(2) III < II < I

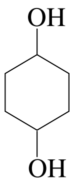
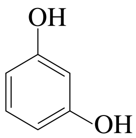
(3) III < I < II

(4) II < I < III

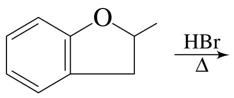
32. What is the major product of the following reaction?

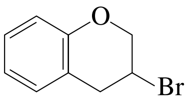
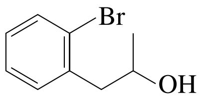


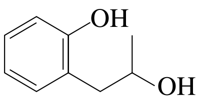
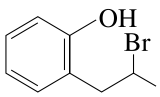
(1)  (2) 

(3)  (4) 

33. The major organic product formed in the following reaction is

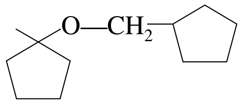


(1)  (2) 

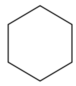
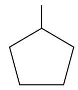
(3)  (4) 

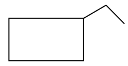
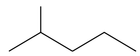
34. Consider the following roadmap reaction:

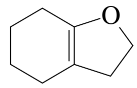
$$\text{X(Hydrocarbon)} \xrightarrow[hv]{Br_2} \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} \text{Y (major)} \xrightarrow[H_2O_2]{HBr} \text{Z}$$

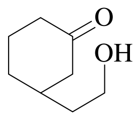
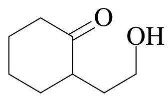
$$\text{Y} \xrightarrow[H_2/\text{Heat}]{H_2SO_4} \xrightarrow[\Delta]{Na} \xrightarrow{Z}$$ 

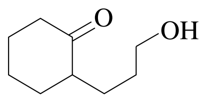
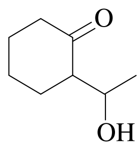
The most probable structure of X is

(1)  (2) 

(3)  (4) 

35.  $\xrightarrow[H_2O]{H^+}$?

(1)  (2) 

(3)  (4) 

EXERCISE 3

One and More Than One Option Correct Type Question

1. C_2H_5Br can be converted into $C_2H_5–O–C_2H_5$ by:

(1) Reacting by C_2H_5ONa

(2) Heating with moist Ag_2O

(3) Heating with dry Ag_2O

(4) Treating with C_2H_5MgBr

2. Which of the following statements is correct about the transesterification reaction, catalysed by

$H_3O^{\oplus}$ (H_2SO_4 or dry HCl) or $RO^{\ominus}$ (EtONa)?

$$\text{Me–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}\overset{*}{O}\text{–Et} + \text{PrOH} \xrightarrow{H_3O^{\oplus}} \text{Me–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–O–Pr} + \text{Et}\overset{*}{O}\text{H}$$

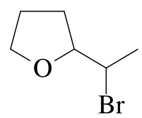
(1) Alcohol (PrOH) is taken in excess to shift the equilibrium to R.H.S.

(2) It involves tetrahedral intermediate in which the hybridisation of C of the (C = O) group changes from sp^2 to sp^3

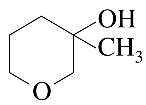
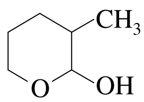
(3) Isotopic oxygen is present in the new alcohol ($Et\overset{*}{O}H$) formed

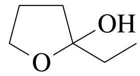
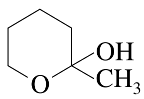
(4) Rate of transesterification is dependent on the concentration of ester only.

3. In the following reaction.

 $+ AgNO_3\,(aq) \xrightarrow{\text{heat}}$

The possible substitution product (s) is/are

(1)  (2) 

(3)  (4) 

4. In the reaction given below,

$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + LiAlD_4 \longrightarrow \xrightarrow{H_3O^+}$$

The correct statement regarding the outcome of the above reaction is/are

(1) A pure enantiomer of alcohol is formed
(2) Racemic mixture of alcohol is formed
(3) Product alcohol has deuterium attached to oxygen
(4) Product alcohol has deuterium attached to carbonyl-carbon atom

5. Which of the following is true statement regarding reaction of *cis* and *trans*-2-hexene with CH_3OH/H^+

(1) Both react at same rate
(2) *Cis* isomer reacts faster than *trans* isomer
(3) Both cis and *trans* isomers give mixture of positional isomers as the major product
(4) No reaction is possible

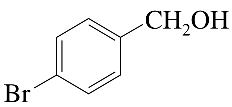
6. Upon treatment with bromine water, allyl bromide gives chiefly primary alcohol $BrCH_2CHBrCH_2OH$. What are the expected primary alcohols in the following reaction?

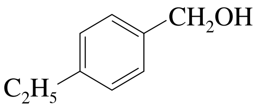
$$\underset{\underset{\displaystyle {}^{82}Br}{|}}{CH_2}-CH=CH_2 \xrightarrow[H_2O]{Br_2} \text{[Normal bromine is } Br^{80}]$$

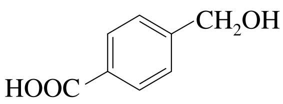
(1) $\underset{\underset{\displaystyle Br}{|}}{CH_2}-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2OH$ (2) $\underset{\underset{\displaystyle {}^{82}Br}{|}}{CH_2}-\overset{\overset{\displaystyle {}^{82}Br}{|}}{CH}-CH_2OH$

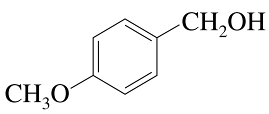
(3) $\underset{\underset{\displaystyle {}^{82}Br}{|}}{CH_2}-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2OH$ (4) $\underset{\underset{\displaystyle Br}{|}}{CH_2}-\overset{\overset{\displaystyle {}^{82}Br}{|}}{CH}-CH_2OH$

7. Alcohols given below that behaves like 1°-aliphatic alcohol in Lucas test is/are

(1) 

(2) 

(3) 

(4) 

8. Consider the following reaction,

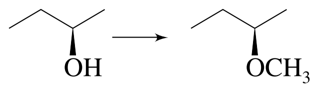
$$X(C_6H_{12}O) \xrightarrow{Na} \text{Gas evolved}$$

$$\underset{\text{Chiral}}{X} \xrightarrow{H_2/Ni} \underset{\text{Achiral}}{Y(C_6H_{14}O)}$$

The correct statement(s) concerning X and Y is/are

(1) Both form immediate turbidity with HCl in the presence of $ZnCl_2$
(2) Both change colour of $CrO_3 - H_2SO_4$
(3) X gives yellow solid with $NaOH/I_2$
(4) X decolourises Br_2-CCl_4 solution forming $C_6H_{12}OBr_2$

9. Consider the following reaction

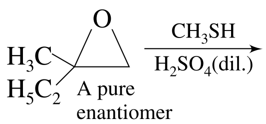


I II

The correct statements(s) concerning the above transformation is/are

(1) If I is treated with Na followed by addition of CH_3I gives II with the retention of configuration
(2) If I is treated with TsCl followed by the addition of CH_3ONa gives II with inversion of configuration
(3) If I is first heated with concentrated H_2SO_4 followed by the addition of CH_3OH in dil. H_2SO_4 gives racemic mixture of II
(4) If I is heated with concentrated H_2SO_4 followed by the treatment with $(CH_3COO)_2Hg—CH_3OH$ and finally reducing the mercurinium intermediate with $NaBH_4$ gives a pure enantiomer of II

10. Consider the reaction given below,



A pure enantiomer

The correct statement regarding the above reaction is/are

(1) The major product is $C_2H_5-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2-S-CH_3$

(2) The major product is $C_2H_5-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle SCH_3}{|}}{C}}-CH_2OH$

(3) The product would be a single enantiomer
(4) The product would consist of a racemic mixture

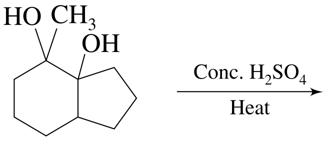
11. In the reaction below,

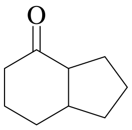
$$CH_3—C\equiv C—CH_3 \xrightarrow[\text{Liq. } NH_3]{Na} X \xrightarrow[\text{Heat}]{Ag_2O} Y \xrightarrow[H_2O]{NaOH} Z$$

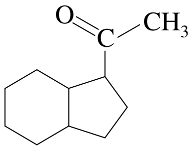
The correct statement concerning the above reaction is/are

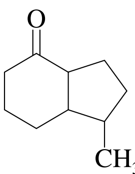
(1) Y is a racemic mixture while Z is achiral
(2) Both Y and Z are racemic mixture
(3) A diastereomer of Y gives racemic Z
(4) X shows diastereomerism but not enantiomerism

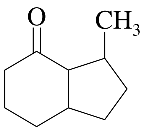
12. In the following rearrangement, possible product(s) is/are



(1) 

(2) 

(3) 

(4) 

13. 3-methyl-3-hexanol can be prepared by the reaction of

(1) CH_3MgBr and 3-hexanone followed by hydrolysis
(2) C_2H_5MgBr and 2-pentanone followed by hydrolysis
(3) propyl-MgBr + 2-butanone followed by hydrolysis
(4) C_4H_9MgBr and propanone followed by hydrolysis

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I
(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

14. **Statement-I:** Phenolic compounds give characteristic colours with neutral $FeCl_3$.

Statement-II: It is the property of all the enolic compounds.

15. **Statement-I:** 3-Methyl-2-butanol is more reactive than 2-butanol in acid catalysed dehydration to alkene.

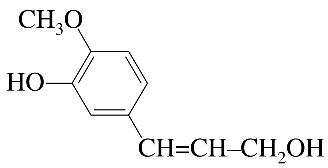
Statement-II: 3-methyl-2-butanol forms more stable carbocation than 2-butanol during dehydration reaction.

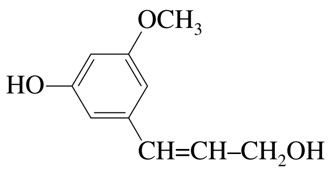
Comprehension Type Question

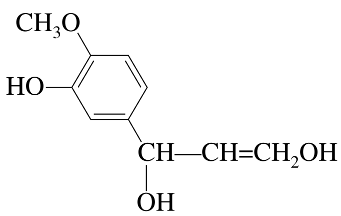
Passage based questions (Q. 16–18)

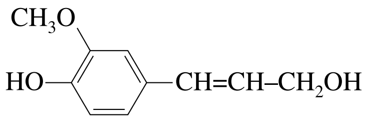
An organic compound $X(C_{10}H_{12}O_3)$ is not soluble in water or $NaHCO_3$. A solution of Br_2 in CCl_4 is decolourised by X forming $C_{10}H_{12}O_3Br_2$. X on controlled ozonolysis followed by the treatment with $(CH_3)_2S$ gives $Y(C_8H_8O_3)$ and $C_2H_4O_2$. Y can also be obtained by reaction between *ortho* methoxy phenol with $CHCl_3$ in KOH solution followed by acid hydrolysis.

16. What is the correct structure of X?

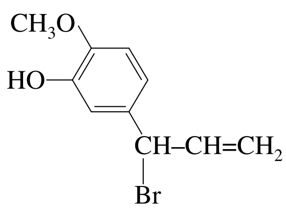
(1) 

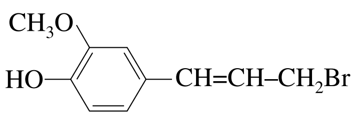
(2) 

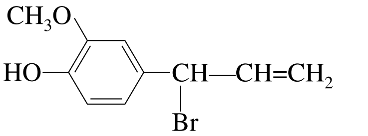
(3) 

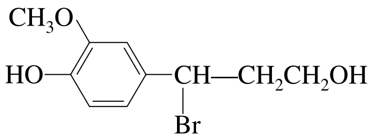
(4) 

17. If X is treated with cold HBr, the major product would be

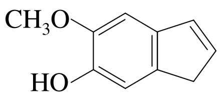
(1) 

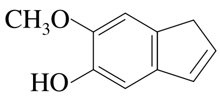
(2) 

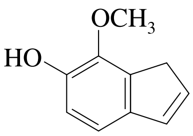
(3) 

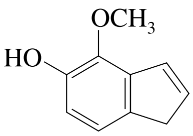
(4) 

18. What would be the major product if X is treated with cold concentrated H_2SO_4?

(1) 

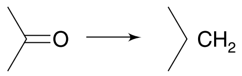
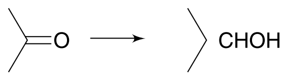
(2) 

(3) 

(4) 

Column Matching Type Questions

19. Match the statements given in Column-I and Column-II

Column-I	Column-II
(a) 	(p) $LiAlH_4$
(b) H–CH = O → CH_3CH_2OH	(q) Zn-Hg/conc. HCl
(c) 	(r) DIBAL-H
(d) $-\overset{O}{\overset{\|}{C}}-O- \longrightarrow -\overset{O}{\overset{\|}{C}}-H-$	(s) CH_3MgBr

(1) a → p; b → q; c → r; d → s
(2) a → q; b → s; c → p; d → r
(3) a → p; b → q; c → s; d → r
(4) a → r; b → s; c → q; d → p

20. Match the reagents given in Column-I with the appropriate items given in Column-II

Column-I	Column-II
(a) Conc. HCl–$ZnCl_2$	(p) Reducing agent
(b) $LiAlH_4$	(q) Grignard reagent
(c) pyridinium chlorochromate	(r) Oxidising agent
(d) Ethyl magnesium bromide	(s) Lucas reagent

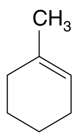
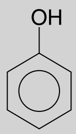
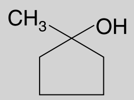
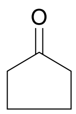
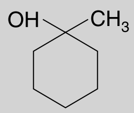
(1) a → s; b → r; c → p; d → q
(2) a → s; b → p; c → r; d → q
(3) a → p; b → s; c → q; d → r
(4) a → s; b → q; c → p; d → r

21. Match the pairs of compounds in Column-I with the appropriate Column-II. Distinguishing test in Column-II

Column-I	Column-II
(a) Methanol and ethane-1, 2-diol	(p) Lucas test
(b) O-cresol and Benzyl alcohol	(q) Iodoform test
(c) n-butyl alcohol and iso-butyl alcohol	(r) Litmus test
(d) 2-Pentanol and 3-pentanol	(s) Periodic acid test

(1) A → r, B → p, C → s; D → q
(2) A → s, B → r, C → q; D → p
(3) A → s, B → r, C → p; D → q
(4) A → r, B → s, C → p; D → q

22. Make the correct match of the following from List-I and List-II.

List-I		List-II	
(A)	 (i) Hg(OAC)$_2$ (ii) NaBH$_4$	(P)	Picric Acid
(B)	 Conc. HNO$_3$	(Q)	
(C)	 CH_3MgBr, $H_3\overset{+}{O}$	(R)	CH_3OH
(D)	$CO + 2H_2 \xrightarrow[\text{High temp}]{Cr_2O_3\text{-}ZnO}$	(S)	

(1) A → P, B → Q, C → R, D → S
(2) A → S, B → P, C → Q, D → R
(3) A → P, B → S, C → Q, D → R
(4) A → S, B → P, C → R, D → Q

23. Make the correct match of the following from List-I and List-II.

List-I		List-II	
(A)	Ethyl alcohol	(P)	$FeCl_3$ Test
(B)	Picric acid	(Q)	Iodoform Test
(C)	Glycerol	(R)	Lucas Test
(D)	Isopropyl alcohol	(S)	HIO_4

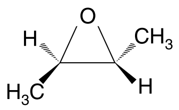
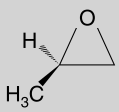
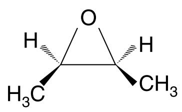
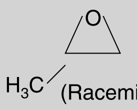
(1) A $\rightarrow$ Q, B $\rightarrow$ P, C $\rightarrow$ S, D $\rightarrow$ R

(2) A $\rightarrow$ P, B $\rightarrow$ Q, C $\rightarrow$ S, D $\rightarrow$ R

(3) A $\rightarrow$ Q, B $\rightarrow$ P, C $\rightarrow$ R, D $\rightarrow$ S

(4) A $\rightarrow$ R, B $\rightarrow$ S, C $\rightarrow$ P, D $\rightarrow$ Q

24. Match the reactant from Column I with the reaction(s) from Column II and mark the correct option from the codes given below.

Column I		Column II	
i.		**p.**	$\xrightarrow[H_2O]{NaOH}$ Racemic mixture
ii.		**q.**	$\xrightarrow[H_2O]{NaOH}$ Pure, single enantiomer
iii.		**r.**	$\xrightarrow[H_2O]{NaOH}$ Meso isomer
iv.	 (Racemic)	**s.**	$\xrightarrow{CH_3MgBr}\ \xrightarrow{H_2O}$ Racemic mixture

Codes:

	i	ii	iii	iv
(1)	r, s	q	p, s	p, s
(2)	p	q	r	s
(3)	q	r	s	p
(4)	q, p	s	p	r

25. Match the column I with Column II and mark the correct option from the codes given below.

Column I		Column II	
i.	1-butanol	**p.**	Treatment with H^+/H_2O gives racemic mixture
ii.	2-butanol	**q.**	Changes the colour of acidic $K_2Cr_2O_7$
iii.	(+)-3-methyl-3-hexanol	**r.**	Gives turbid solution with $ZnCl_2$/Conc. HCl at room temperature
iv.	(–)-2-ethyl oxirane	**s.**	With $LiAlH_4$. gives another compound from column II.

Codes:

	i	ii	iii	iv
(1)	p, q	p, q, r	p, r	s
(2)	q	r	p	q
(3)	p, s	r	p	q
(4)	p, q	r	s	p

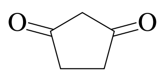
Single Digit Integer Type Question

26. In the reaction given below,

$$CH_3—CH_2–\underset{\underset{CH_3}{|}}{C}=CH—CH_3 + CO + H_2 \xrightarrow{Co_2(CO)_8} \xrightarrow[H_2]{Cu\text{-}Zn}$$

How many different products are expected?

27. In the following reaction how many different diols, are formed?

 $\xrightarrow[\text{(ii) } H_2O]{\text{(i) } NaBH_4}$

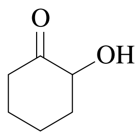
28. An alcohol $X(C_4H_{10}O_3)$ is chiral and absorbs two moles of HIO_4 per mole of X. How many stereoisomers exist for X?

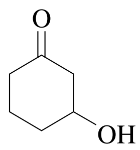
29. When 2-ethyl-3-metyl-1-pentene is treated with CH_3OH in H_2SO_4, how many different methoxy ethers would be formed in significant amount?

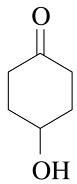
30. An organic compound $A(C_{10}H_{18}O_8)$ on treatment with excess of CH_3COCl gives a fully acetylated product whose molar mass is found to be 518 g/mol. How many hydroxyl functional groups are present in A?

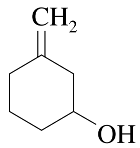
EXERCISE 4

1. Maximum dehydration takes place that of **[AIEEE-2002]**

(1) 

(2) 

(3) 

(4) 

2. An ether is more volatile than an alcohol having the same molecular formula. This is due to **[AIEEE-2003]**

(1) Dipolar character of ethers
(2) Alcohols having resonance structures
(3) Intermolecular hydrogen bonding in ethers
(4) Intermolecular hydrogen bonding in alcohols

3. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 the initiation step is **[AIEEE-2003]**

(1) Protonation of alcohol molecule
(2) Formation of carbocation
(3) Elimination of water
(4) Formation of an ester

4. Among the following compounds which can be dehydrated very easily is **[AIEEE-2004]**

(1) $CH_3CH_2CH_2CH_2CH_2OH$

(2) $CH_3CH_2CH_2\overset{\overset{\large OH}{|}}{C}HCH_3$

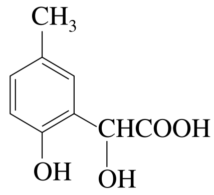
(3) $CH_3CH_2\underset{\underset{\large OH}{|}}{\overset{\overset{\large CH_3}{|}}{C}}CH_2CH_3$

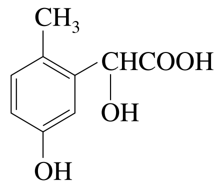
(4) $CH_3CH_2\underset{\underset{\large CH_3}{|}}{C}HCH_2CH_2OH$

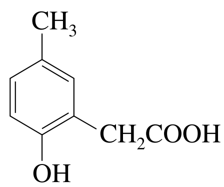
5. For which of the following parameters the structural isomer C_2H_5OH and CH_3OCH_3 would be expected to have the same values? **[AIEEE-2004]**

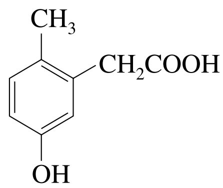
(1) Heat of vaporisation
(2) Vapour pressure at the same temperature
(3) Boiling points
(4) Gaseous densities at the same temperature and pressure

6. p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is **[AIEEE-2005]**

(1) 

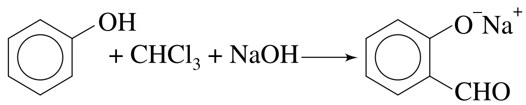
(2) 

(3) 

(4) 

7. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give– **[AIEEE-2005]**

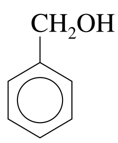
(1) $BrCH_2CHO$ and CH_3OH
(2) $BrCH_2–CH_2–OCH_3$
(3) $H_3C–CHBr–OCH_3$
(4) CH_3CHO and CH_3Br

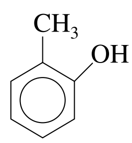
8. 

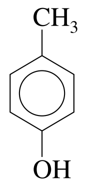
The electrophile involved in the above reaction is **[AIEEE-2006]**

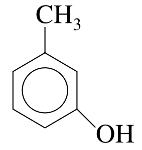
(1) dichlorocarbene $(:CCl_2)$
(2) trichloromethyl anion $\overset{\ominus}{C}Cl_3$
(3) formyl cation $(\overset{\oplus}{C}HO)$
(4) dichloromethyl cation $(\overset{\oplus}{C}HCH_2)$

9. The structure of the compound that gives a tribromo derivative on treatment with bromine water :is: **[AIEEE-2006]**

(1) 

(2) 

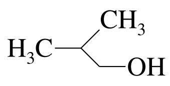
(3) 

(4) 

10. Among the following the one that gives positive iodoform test upon reaction with I_2 NaOH is **[AIEEE-2006]**

(1) $CH_3CH_2CH(OH)CH_2CH_3$

(2) $C_6H_5CH_2CH_2OH$

(3) 

(4) $PhCHOHCH_3$

11. Acid catalysed hydration of alkenes except ethene leads to the formation of **[AIEEE-2006]**

(1) mixture of secondary and tertiary alcohols

(2) mixture of primary and secondary alcohols

(3) secondary or tertiary alcohol

(4) primary alcohol

12. In the following sequence of reactions, **[AIEEE-2007]**

$$CH_3CH_2OH \xrightarrow{P + I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is

(1) butanol (2) n-butyl alcohol

(3) n-propyl alcohol (4) propanol

13. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives **[AIEEE-2008]**

(1) *o*-nitrophenol (2) *p*-nitrophenol

(3) nitrobenzene (4) 2, 4, 6-trinitrophenol

14. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **[AIEEE-2009]**

(1) HCHO (2) CH_3COCH_3

(3) CH_3COOH (4) CH_3OH

15. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is– **[AIEEE-2009]**

(1) Salicyladehyde (2) Salicyclic acid

(3) Phthalic acid (4) Benzoic acid

16. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is– **[AIEEE-2010]**

(1) 1-Butanol (2) 2-Butanol

(3) 2-Methylpropan-2-ol (4) 2-Methylpropanol

17. Consider the following reaction **[AIEEE-2011]**

$C_2H_5OH + H_2SO_4 \rightarrow$ Product

Among the following, which one cannot be formed as a product under any conditions?

(1) Ethylene (2) Acetylene

(3) Diethyl ether (4) Ethyl-hydrogen sulphate

18. Thermosetting polymer, Bakelite is formed by the reaction of phenol with **[AIEEE-2011]**

(1) CH_3CHO (2) HCHO

(3) HCOOH (4) CH_3CH_2CHO

19. Reagent used to convert allyl alcohol to acrolein is: **[JEE Main Online-2012]**

(1) MnO_2 (2) $KMnO_4$

(3) OsO_4 (4) H_2O_2

20. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism- **[JEE Main-2013]**

(1) secondary alcohol by S_N2

(2) Tertiary alcohol by S_N2

(3) Secondary alcohol by S_N1

(4) Tertiary alcohol by S_N1

21. Rate of dehydration of alcohols follows the order- **[JEE Main Online-2013]**

(1) $2° > 1° > CH_3OH > 3°$

(2) $3° > 2° > 1° > CH_3OH$

(3) $2° > 3° > 1° > CH_3OH$

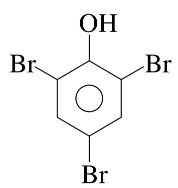
(4) $CH_3OH > 12° > 2° > 3°$

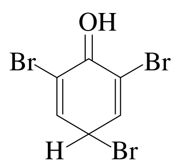
22. An ether (A), $C_5H_{12}O$, when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (B) and (C). Oxidation of (B) and (C) gave a propanone and an ethanoic acid respectively. The IUPAC name of the ether (A) is- **[JEE Main Online-2013]**

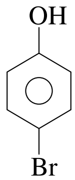
(1) 2-ethoxypropane (2) ethoxypropane

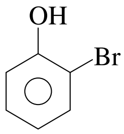
(3) methoxybutane (4) 2-methoxybutane

23. What is the structure of the major product when phenol is treated with bromine water: **[JEE Main Online-2013]**

(1) 

(2) 

(3) 

(4) 

24. Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$?

[JEE Main Online-2013]

(1) Pentanol (2) 2-Methylbutanol

(3) 2-Pentanol (4) 2-Methyl butan-2-ol

25. The reaction of phenol with benzoyl chloride to give phenyl benzoate is known as:

[JEE Main Online-2013]

(1) Claisen reaction

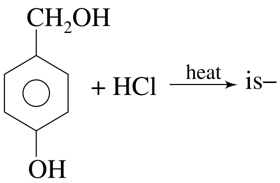
(2) Schotten–Baumann reaction

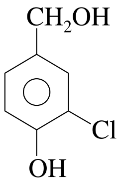
(3) Reimer–Tiemann reaction

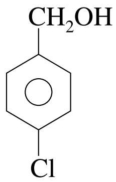
(4) Gatterman–Koch reaction

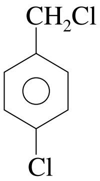
26. The major product in the following reaction

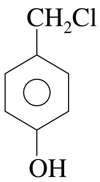
[JEE Main Online-2013]



(1) 

(2) 

(3) 

(4) 

27. Phenol on heating with $CHCl_3$ and NaOH gives salicylaldehyde. The reaction is called

[JEE main Online-2013]

(1) Reimer–Tiemann reaction

(2) Claisen reaction

(3) Cannizzaro reaction

(4) Hell-Volhard-Zelinsky reaction

28. The most suitable reagent of the conversion of $R—CH_2—OH \longrightarrow R—CHO$ is

(1) $KMnO_4$

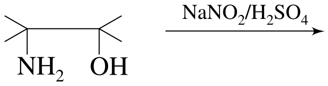
(2) $K_2Cr_2O_7$

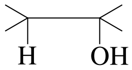
(3) CrO_3

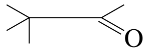
(4) PCC (Pyridinium chlorochromate)

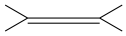
29. The major product of reaction

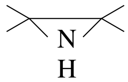
[JEE main Online-2014]



(1) 

(2) 

(3) 

(4) 

30. Allyl phenyl ether can be prepared by heating:

[JEE main Online-2014]

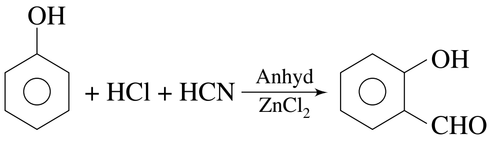
(1) $C_6H_5Br + CH_2{=}CH–CH_2–ONa$

(2) $CH_2{=}CH–CH_2–Br + C_6H_5ONa$

(3) $C_6H_5–CH{=}CH–Br + CH_3–ONa$

(4) $CH_2{=}CH–Br + C_6H_5–CH_2–ONa$

31. The following reaction **[JEE main Online-2014]**



Is known as:

(1) Perkin reaction

(2) Gattermann–Koch formylation

(3) Kolbe's reaction

(4) Gattermann reaction

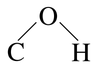
32. Which one of the following statements is not correct? **[JEE main Online-2014]**

(1) Alcohols are weaker acids than water

(2) Acid strength of alcohols decrease in the following order

$RCH_2OH > R_2CHOH > R_3COH$

(3) Carbon–oxygen bond length in methanol, CH_3OH is shorter than that of C–O bond length in phenol

(4) The bond angle  in methanol is 108.9°

33. In the Victor–Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively:

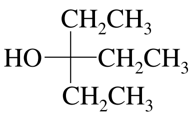
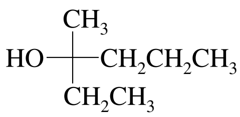
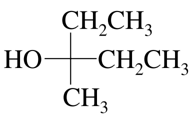
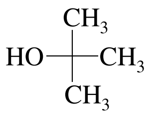
[JEE main Online-2014]

(1) Red, colourless, blue (2) Red, blue, colourless
(3) Colourless, red, blue (4) Red, blue, violet

34. Phthalic acid reacts with resorcinol in the presence of concentrated H_2SO_4 to give: **[JEE main Online-2014]**
(1) Phenolphthalein (2) Alizarin
(3) Coumarin (4) Fluorescein

35. Williamson synthesis of ether is an example of: **[JEE main Online-2014]**
(1) Nucleophilic addition
(2) Electrophilic addition
(3) Electrophilic substitution
(4) Nucleophilic substitution

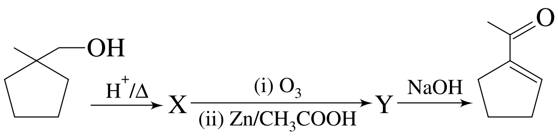
36. CH_3MgBr (excess) + Ethyl ester $\rightarrow$ which can be formed as product **[IIT-2003]**

(1) 
(2) 
(3) 
(4) 

37. The best method to prepare cyclohexene from cyclohexanol is by using **[IIT-2005]**
(1) Conc. HCl + $ZnCl_2$ (2) Conc. H_3PO_4
(3) HBr (4) Conc. HCl

38. When phenyl magnesium bromide reacts with tert. butanol, which of the following is formed? **[IIT-2005]**
(1) Tert. butyl methyl ether
(2) Benzene
(3) Tert. butyl benzene
(4) Phenol

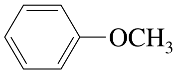
39. Consider the given reaction, **[IIT-2005]**

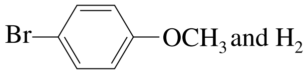
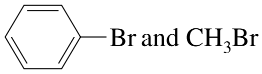
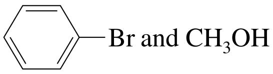
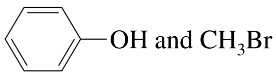


Identify X and Y.

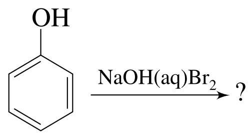
40. The increasing order of boiling points of the following mentioned alcohols is **[IIT-2006]**
I. 1, 2-dihydroxy benzene
II. 1, 3-dihydroxy benzene
III. 1, 4-dihyroxy benzene
IV. Hydroxy benzene

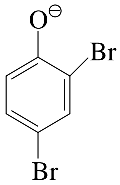
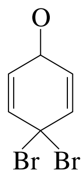
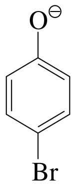
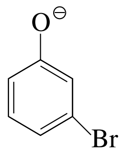
(1) I < II < III < IV (2) I < II < IV < III
(3) IV < I < II < III (4) IV < II < I < III

41. In the reaction  $\xrightarrow{HBr}$ the products are- **[IIT-2010]**

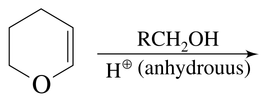
(1) 
(2) 
(3) 
(4) 

42. In the reaction intermediate (s) is (are) **[IIT-2010]**



(1) 
(2) 
(3) 
(4) 

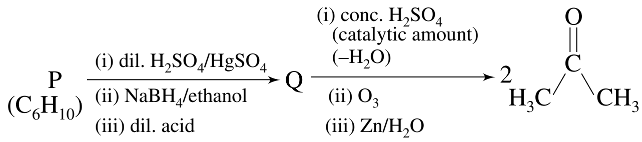
43. The major product of the following reaction is **[IIT-2011]**



(1) A hemiacetal (2) An acetal
(3) An ether (4) An ester

Passage: (Q.44 to Q.45)

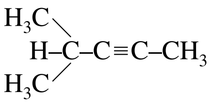
An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound, **[IIT-2011]**

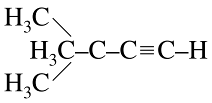


44. The structure of compound P is–

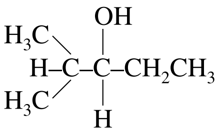
(1) $CH_3CH_2CH_2CH_2–C≡C–H$

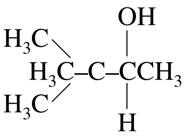
(2) $H_3CH_2C–C≡C–CH_2CH_3$

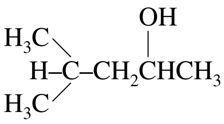
(3) 

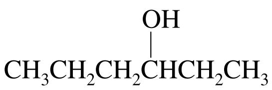
(4) 

45. The structure of compound Q is

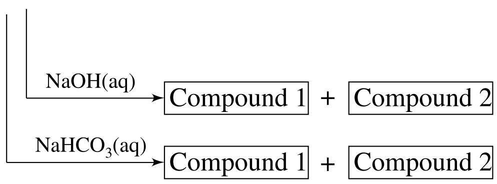
(1) 

(2) 

(3) 

(4) 

46. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. **[IIT-2012]**



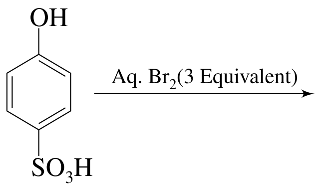
(1) C_6H_5OH and C_6H_5COOH

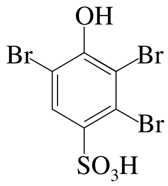
(2) C_6H_5COOH and $C_6H_5CH_2OH$

(3) $C_6H_5CH_2OH$ and C_6H_5OH

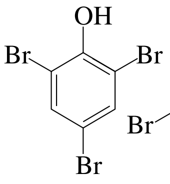
(4) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

47. The major product(s) of the following reaction is (are) **[JEE Advance-2013]**

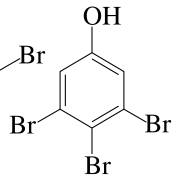




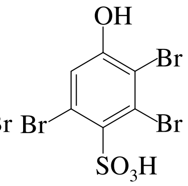
(P)



(Q)



(R)

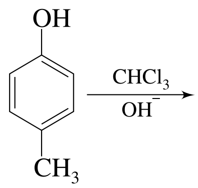


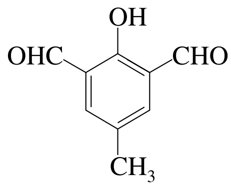
(S)

(1) P (2) Q

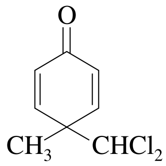
(3) R (4) S

48. In the following reaction, the product(s) formed **[JEE Advance-2013]**

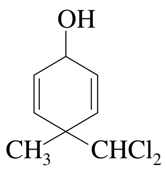




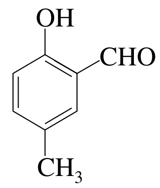
(P)



(Q)



(R)

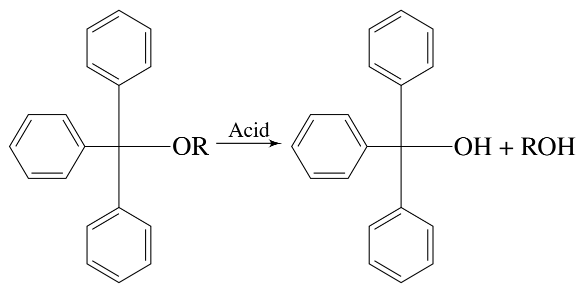


(S)

(1) P (major) (2) Q (minor)

(3) R (minor) (4) S (major)

49. The acidic hydrolysis of ether x shown below is fastest when **[IIT-2014]**



X

(1) One phenyl group is replaced by a methyl group

(2) One phenyl group is replaced by a *para*-methoxyphenyl group

(3) Two phenyl groups are replaced by two *para*-methoxyphenyl groups

(4) No structural change is made of X

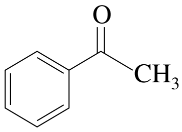
Passage for Q. Nos. (50 and 51)

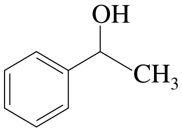
$$C_8H_6 \xrightarrow[H_2]{Pd\text{-}BaSO_4} C_3H_8 \xrightarrow[(ii)\ H_2O_2,\ NaOH,\ H_2O]{(i)\ B_2H_6} X$$

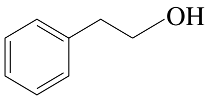
$$C_8H_6 \xrightarrow{H_2O,\ HgSO_4,\ H_2SO_4} C_8H_6O \xrightarrow[(ii)\ H^+,\ Heat]{(i)\ EtMgBr,\ H_2O} Y$$

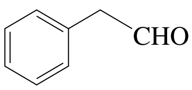
[IIT-2015]

50. Compound X is

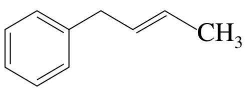
(1) 

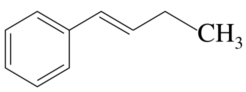
(2) 

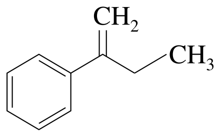
(3) 

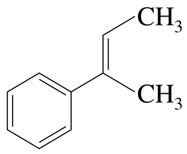
(4) 

51. The major compound Y is

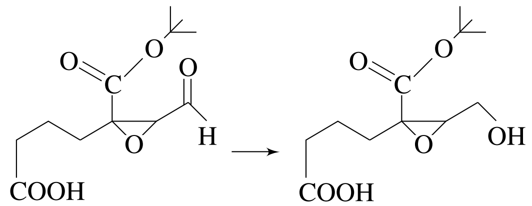
(1) 

(2) 

(3) 

(4) 

52. Reagent(s) which can be used to bring about the following transformation is (are)



(1) $LiAlH_4$ in $(C_2H_5)_2O$ (2) BH_3 in C_2H_5OH

(3) $NaBH_4$ in C_2H_5OH (4) Raney Ni/H_2 in THF

53. The correct statement(s) about the following reaction sequence is (are) Cummene (C_9H_{12})

$$\xrightarrow[(ii)\ H_3O^+]{(i)\ O_2} P \xrightarrow{CHCl_3/NaOH} Q(\text{major}) + R(\text{minor}),\ Q \xrightarrow[PhCH_2Br]{NaOH} S$$

(1) R is steam volatile

(2) Q gives dark violet colouration with 1% aqueous $FeCl_3$ solution

(3) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine

(4) S gives dark violet colouration with 1% aqueous $FeCl_3$ solution

ANSWER KEY

EXERCISE # 1

1. (3)	2. (3)	3. (1)	4. (2)	5. (4)
6. (2)	7. (1)	8. (2)	9. (3)	10. (1)
11. (2)	12. (1)	13. (2)	14. (1)	15. (3)
16. (4)	17. (4)	18. (3)	19. (2)	20. (2)
21. (2)	22. (2)	23. (3)	24. (1)	25. (3)
26. (3)	27. (1)	28. (2)	29. (1)	30. (4)
31. (1)	32. (1)	33. (3)	34. (1)	35. (2)
36. (2)	37. (2)	38. (4)	39. (1)	40. (2)

EXERCISE # 2

1. (2)	2. (4)	3. (2)	4. (1)	5. (2)
6. (3)	7. (3)	8. (1)	9. (1)	10. (3)
11. (2)	12. (3)	13. (3)	14. (3)	15. (1)
16. (4)	17. (3)	18. (4)	19. (4)	20. (3)
21. (2)	22. (1)	23. (2)	24. (4)	25. (1)
26. (2)	27. (2)	28. (2)	29. (2)	30. (3)
31. (2)	32. (2)	33. (4)	34. (2)	35. (2)

EXERCISE # 3

1. (1,3)	2. (1,2,3)	3. (2,3)	4. (2,4)	5. (1,3)
6. (3,4)	7. (1,3)	8. (1,4)	9. (1,2,3)	10. (2,3)
11. (1,3,4)	12. (1,2)	13. (1,2,3)	14. (1)	15. (1)
16. (*)	17. (*)	18. (*)	19. (*)	20. (*)
21. (*)	22. (*)	23. (*)	24. (1)	25. (*)
26. (*)	27. (*)	28. (*)	29. (*)	30. (*)

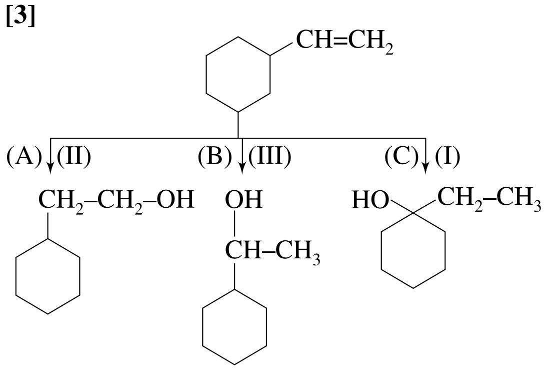
EXERCISE # 4

1. (2)	2. (4)	3. (1)	4. (3)	5. (4)
6. (3)	7. (4)	8. (1)	9. (4)	10. (4)
11. (3)	12. (3)	13. (4)	14. (3)	15. (2)
16. (3)	17. (2)	18. (2)	19. (1)	20. (4)
21. (2)	22. (1)	23. (1)	24. (4)	25. (2)
26. (4)	27. (1)	28. (4)	29. (2)	30. (2)
31. (4)	32. (3)	33. (2)	34. (4)	35. (4)
36. (4)	37. (2)	38. (2)	39. (*)	40. (3)
41. (4)	42. (1,2,3)	43. (2)	44. (4)	45. (2)
46. (2,4)	47. (2)	48. (2,4)	49. (3)	50. (3)
51. (4)	52. (3)	53. (2,3)		

HINT AND SOLUTION

EXERCISE # 1

1. [3]



2. [3]

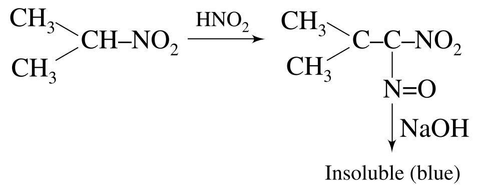
Fact

3. [1]

$$\underset{\text{Primary alcohol (X)}}{C_3H_8O} \xrightarrow{[O]} \underset{\text{carboxylic acid (Y)}}{C_3H_6O_2}$$

4. [2]

Victor Mayer test



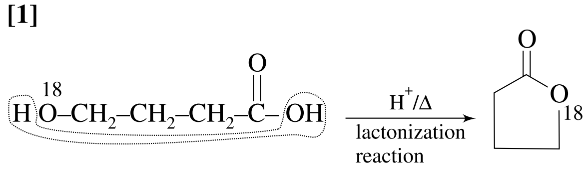
5. [4]

Both enol and 1° alcohol gives negative test with Lucas reagent at room temprature.

6. [2]

With SeO_2, oxidation at allylic position takes place

7. [1]



Intramolecular esterification

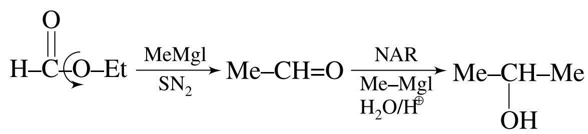
8. [2]

$$-O-H \xrightarrow{Al_2O_3} -O-\overset{\overset{\large O}{||}}{C}-CH_3$$

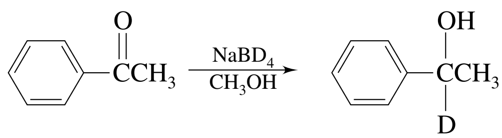
1 OH increase molecular formula $\rightarrow C_2H_2O$

$$\text{No of } -OH = \frac{C_8H_8O}{C_2H_2O} = 4$$

9. [3]

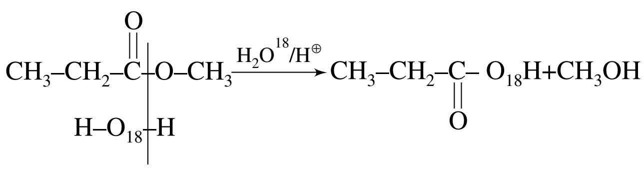


10. [1]



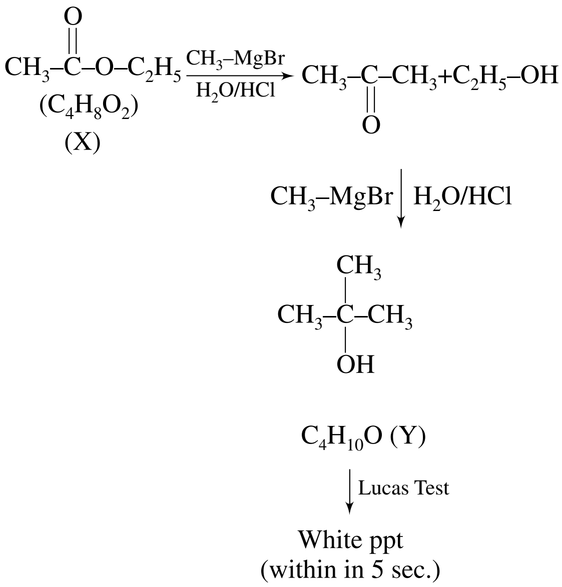
(Nucleophilic addition takes place)

11. [2]



12. [1]

Since Y will give white ppt immediately with Lucas reagent, hence it must be 3° alcohol so that (X) is alkyl alkanoate.



13. **[2]**

Theory based

14. **[1]**

(A) $C_2H_5\text{–}OH \xrightarrow{Na/\Delta} C_2H_5\text{–}O\text{–}Na$ (B)

$C_2H_5\text{–}OH \xrightarrow{PCl_5} C_2H_5Cl$ (C)

$C_2H_5\text{–}\overset{\ominus}{O}\text{–}\overset{\oplus}{Na} + C_2H_5\text{–}Cl \xrightarrow[SN_2]{} C_2H_5\text{–}O\text{–}C_2H_5$ Diethylether

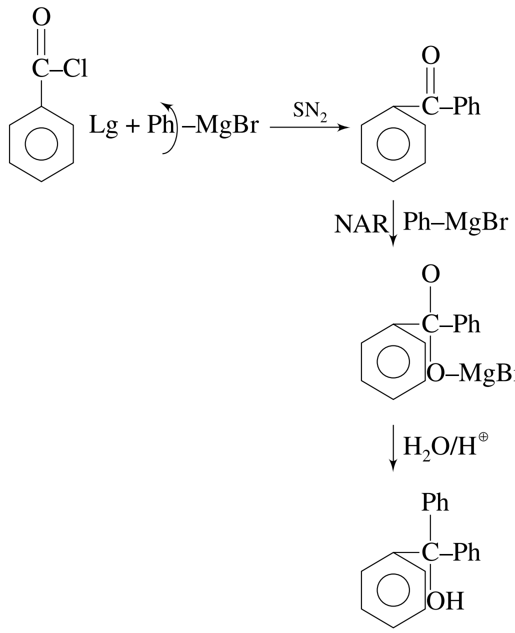
15. **[3]**

$\underset{\substack{\text{2 mole}\\\text{(excess)}}}{C_2H_5\text{–}OH} \xrightarrow[\substack{SN_2\\\text{(lesser)}}]{H_2SO_4} C_2H_5\text{–}O\text{–}C_2H_5$

16. **[4]**

$Ph\text{–}MgBr + CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}Cl \xrightarrow{H^+/H_2O} CH_3\text{–}\underset{OH}{\overset{Ph}{C}}\text{–}Ph$

17. **[4]**



18. **[3]**

(Refer key concept)

19. **[2]**

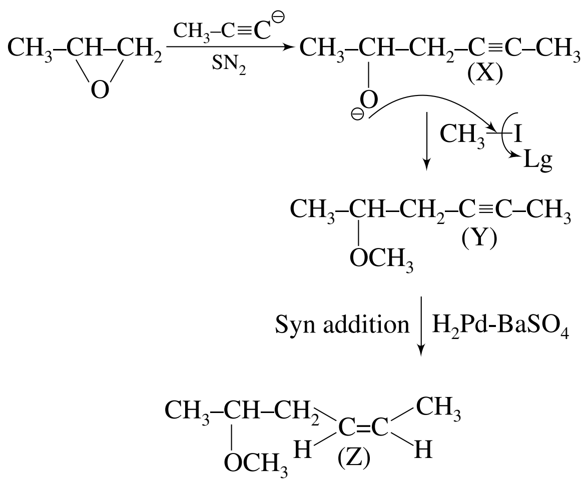
$NaBH_4$ do not reduce ester. It reduces only > C=O in > CH –OH.

20. **[2]**

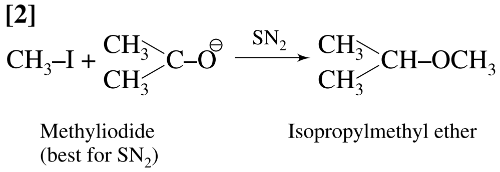
Formation of CHI_3 with NaOI, proves that (B) must be methyl ketone like $R\text{–}\overset{}{\underset{\underset{O}{\|}}{C}}\text{–}CH_3$

$CH_3\text{–}CH_2\text{–}\underset{OH}{CH}\text{–}CH_3 \xrightarrow[|O|]{CrO_3/H^{\oplus}} CH_3\text{–}CH_2\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3 \xrightarrow{NaOI} CHI_3 + CH_3\text{–}CH_2COONa$

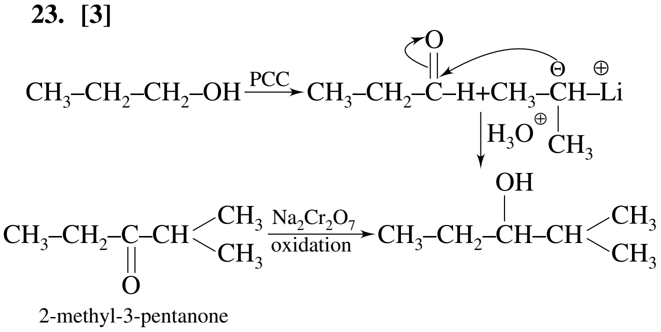
21. **[2]**



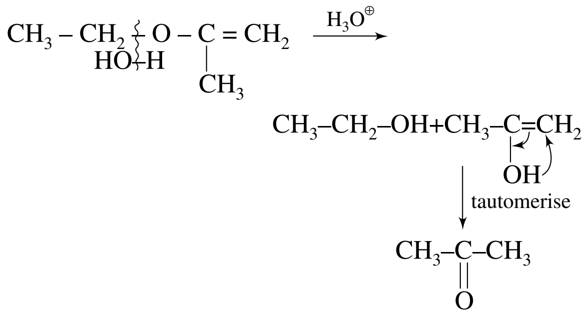
22. [2]



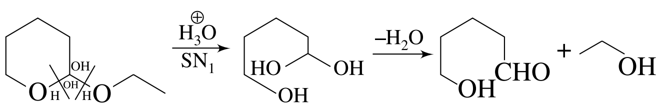
23. [3]



24. [1]



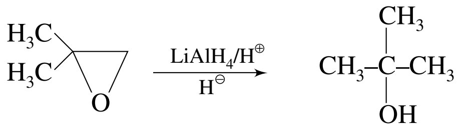
25. [3]



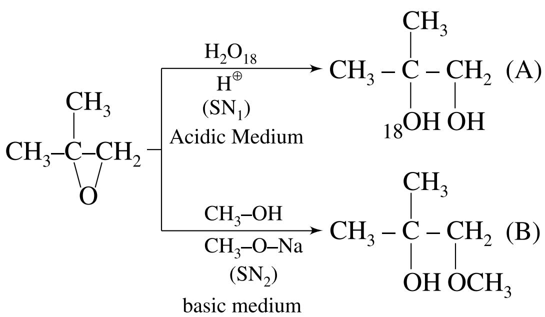
26. [3]

$LiAlH_4 \rightarrow Li^+ + \overset{\oplus}{AlH_4} \rightarrow AlH_3 + H^{\ominus}$

In alkaline medium nucleophilic attack from less steric side takes plance.



27. [1]



→ In acidic medium, SN_1 reaction is favoured, i.e., nucleophile approach towards most sterically hindered site

→ In alkaline media, SN_2 reaction is favoured, i.e., Nucleophile approach towards least sterically hindered site

28. [2]

$C_4H_{10}O \Rightarrow C_nH_{2n+2}O$ (alcohol/ether)

The given reaction indicates that

(i) no alcohol, i.e., only ether

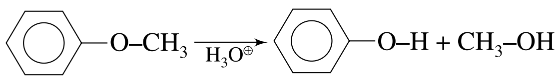
(ii) type of H = 3

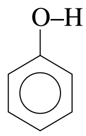
(iii) no alcohol

Thus $CH_3-\overset{\overset{CH_3}{|}}{CH}-O-CH_3$

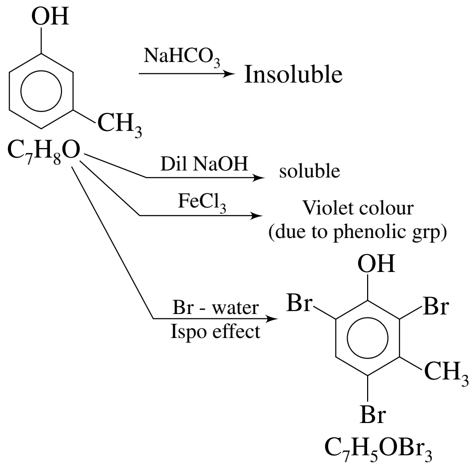
(Type of H = 3)

29. [1]



Acidic strength  > CH_3-O-H

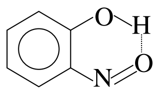
30. [4]



31. [1]

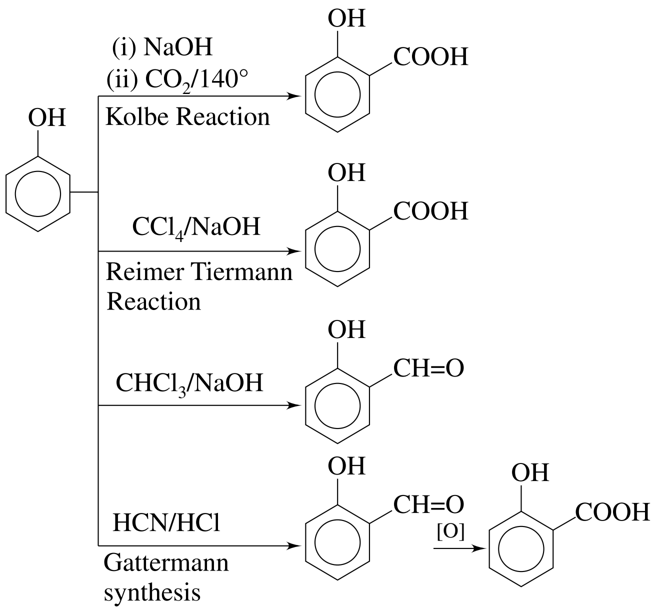
Substances containing phenolic group give purple colour with $FeCl_3$

32. [1]

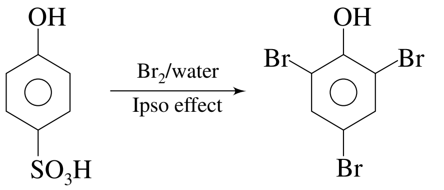


Intramolecular H-bond boiling point ↓ volatile nature

33. [3]



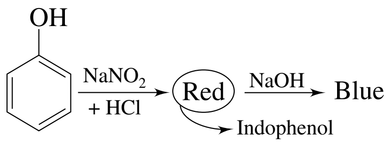
34. [1]

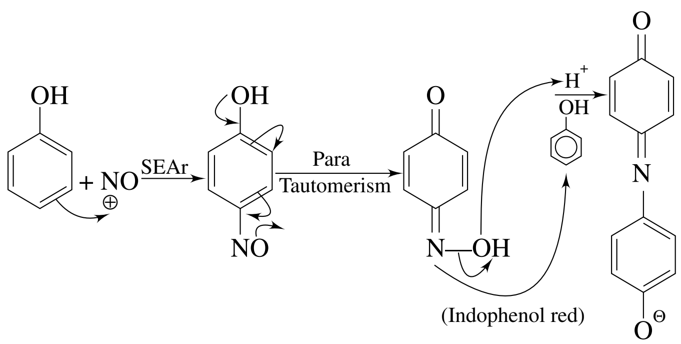


2, 4, 6-tribromophenol

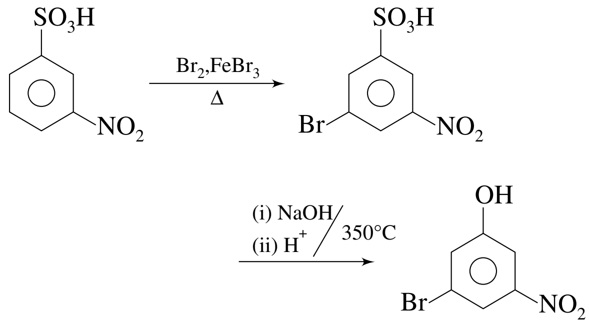
Ipso substitution means replacement of any functional group (good leaving group) which already exist in benzene.

35. [2]





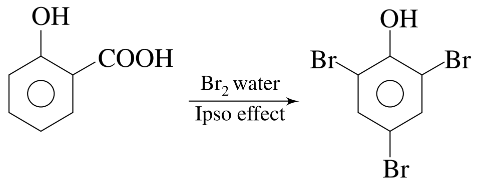
36. [2]



37. [1]

Rate of Ar–SN_2 reaction ∝ (EWG) De-activating power

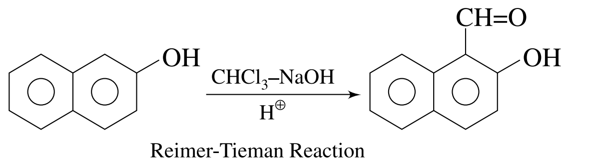
38. [4]



39. [1]

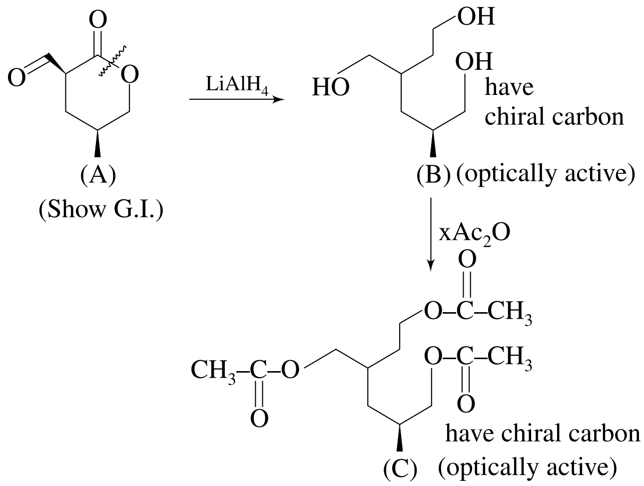
Elb's persulphate oxidation reaction

40. [2]



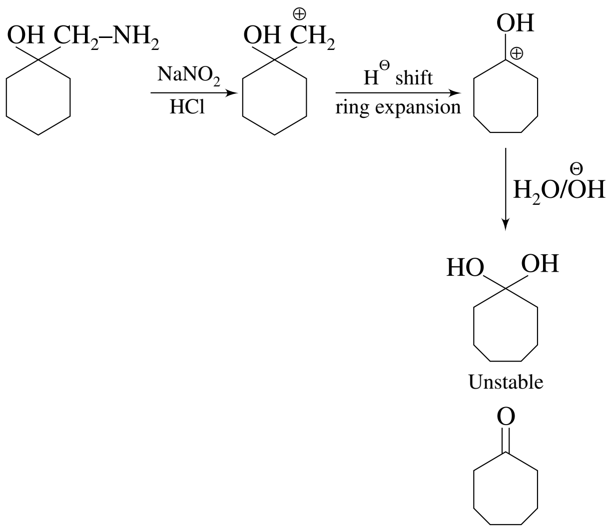
EXERCISE # 2

1. [2]

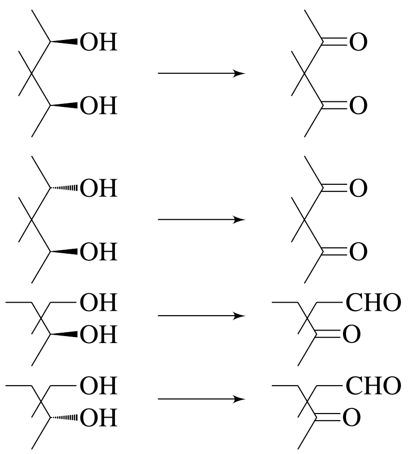


→ x = 3(because 3 OH group present)

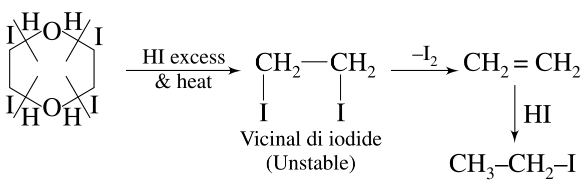
2. [4]



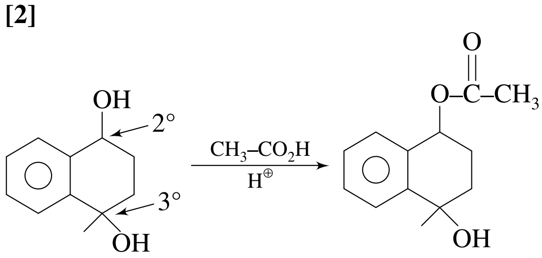
3. [2]



4. [1]

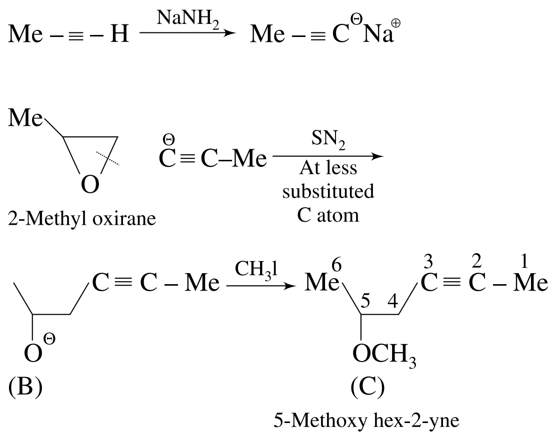


5. [2]

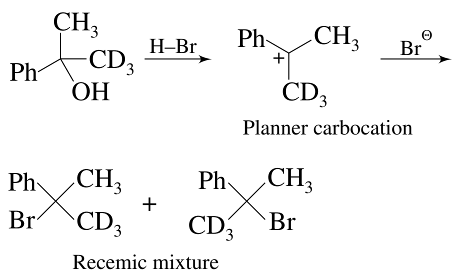


Rate of esterification $\propto \dfrac{1}{\text{steric hindrance}}$

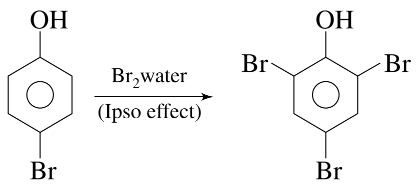
6. [3]



7. [3]



8. [1]

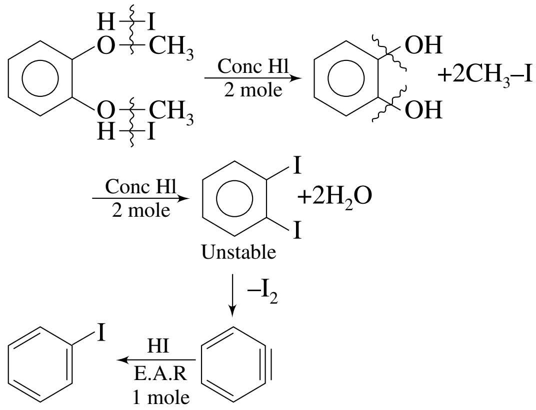


9. [1]

→ Oxidation at allylic position achieved by MnO_2

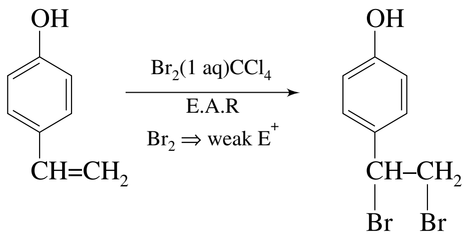
→ Oxidation of ordinary alcohol achieved by CrO_3

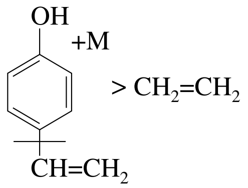
10. [3]



Total mole HI (consumed) = 5

11. [2]

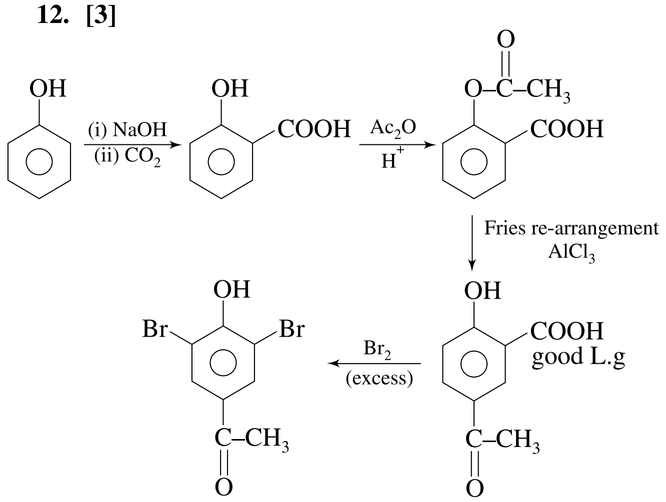




Due of +M and –I effect of –OH, e-density of C = C increases at para position.

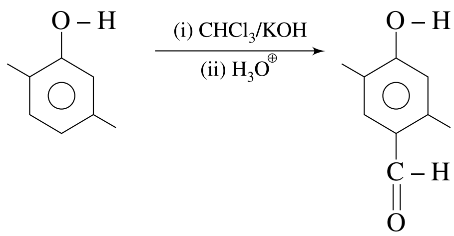
Hence (x) more reactive than ethene.

12. [3]

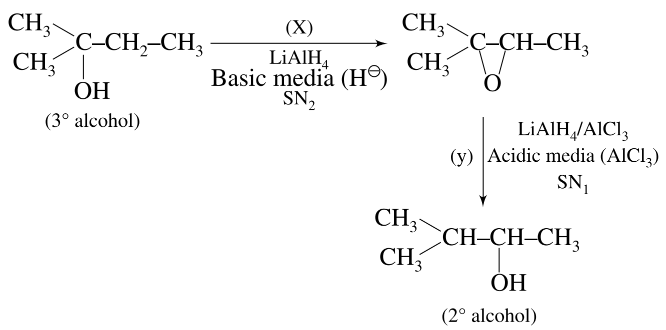


13. [3]

This is Riemer–Tiemann reaction



14. [3]



15. [1]

$NaBH_4$ is weak reducing agent so that only carbonyl group will be reduced.

16. [4]

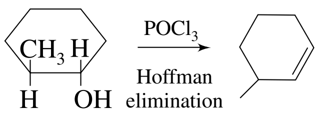
Test	**x**	**y**
Br_2	Unsaturated	Saturated
Na Metal	alcohol	ether
Chromic acid	oxidation	no oxidation
Lucas reagent	1°alcohol	ether

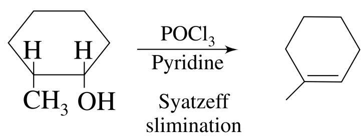
with the above reactions possible structure of

X $\Rightarrow$ Unsaturated primary alcohol &

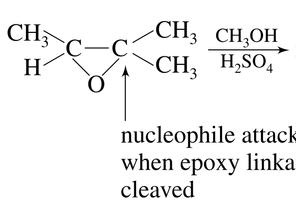
Y $\Rightarrow$ Saturated ether

17. [3]

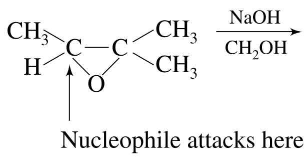
Reaction I: 

Reaction II: 

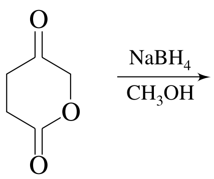
18. [4]

(A) 

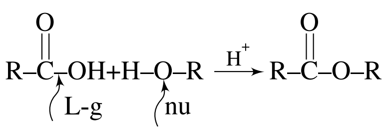
In acidic media SN_1 reaction takes plce at more stericly hindred C

(B) 

In alkaline media SN_2 reaction takes place at stericly less indred C

(C) 

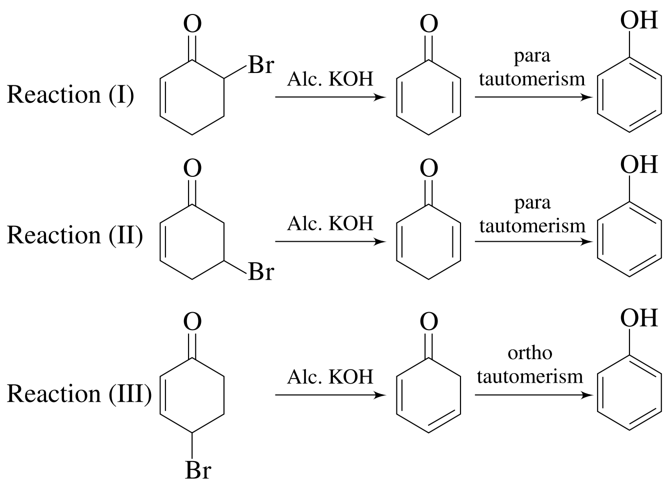
, $NaBH_4$ weak reducing agent so only carbonyl group will be reduced

(D) 

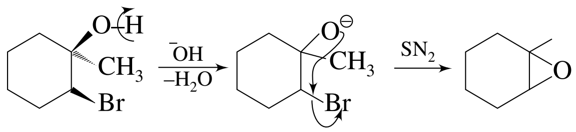
These bonds are affected in esterification

Thus, all four statements are correct

19. [4]



20. [3]



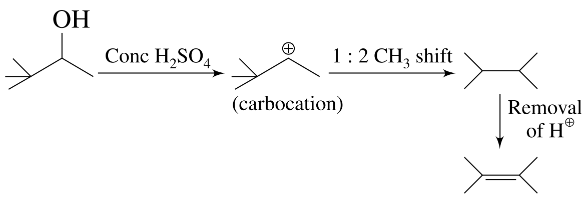
21. [2]

$$C_2H_5-O-Na+CH_3-CH_2\underbrace{-O-SO_2-CH_3}_{Lg}$$

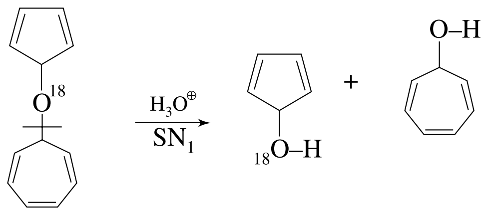
$$\Big\downarrow \text{THF, heat}$$

$$C_2H_5-O-C_2H_5$$

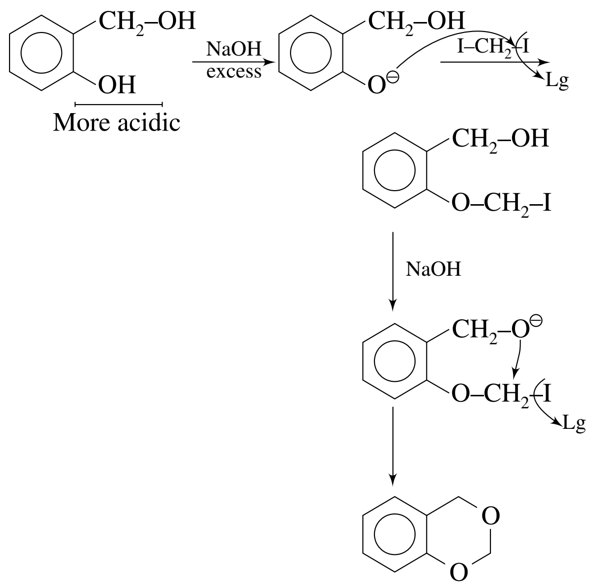
22. [1]



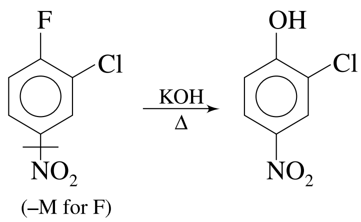
23. [2]



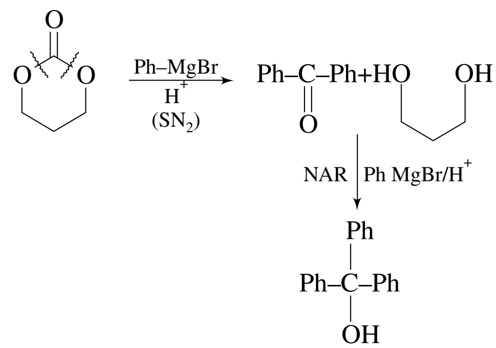
24. [4]



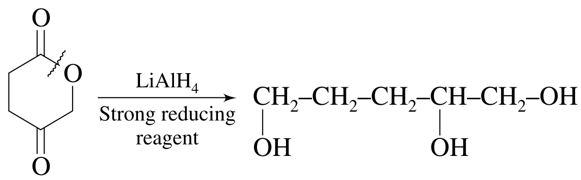
25. [1]



26. [2]

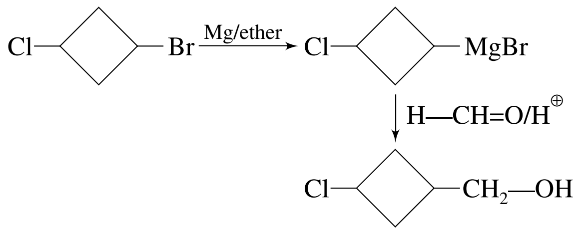


27. [2]

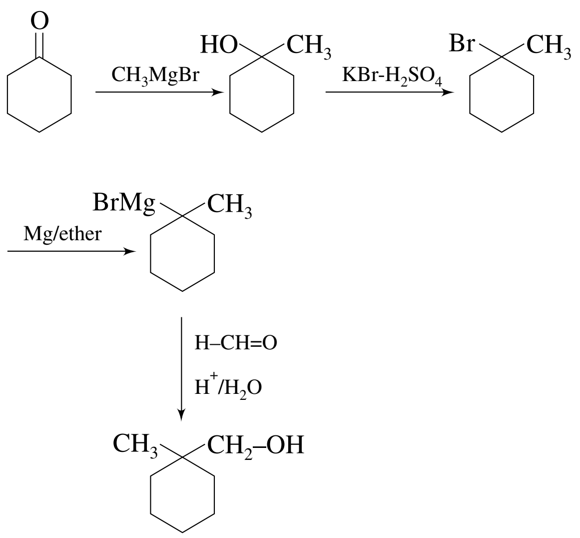


28. [2]

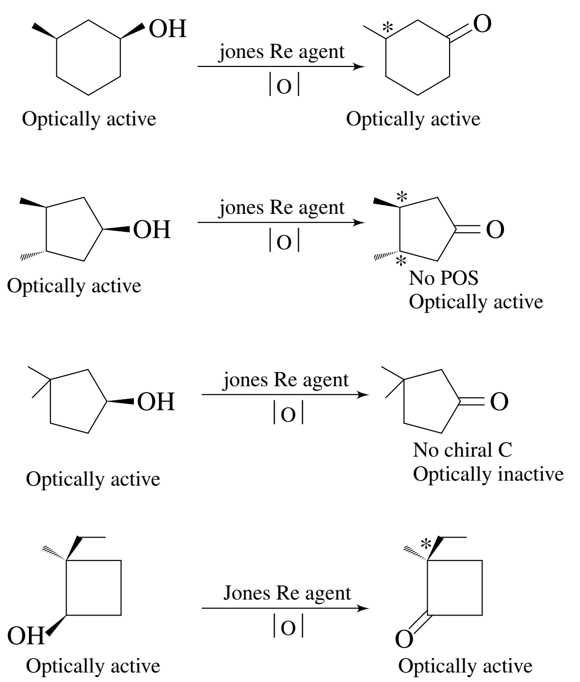
→ R Br more reactive than R Cl



29. [2]



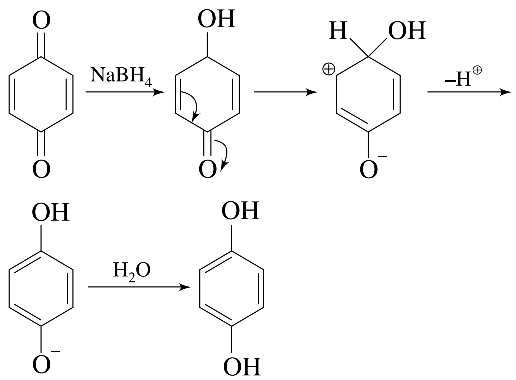
30. [3]



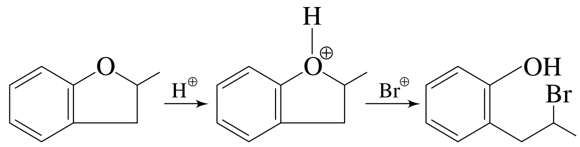
31. [2]

Dihydric alcohols are always more soluble in water than monohydric alcohol. Between (I) and (II), (I) is more soluble as it forms intermolecular H-bonds with water while (II) forms intramolecular H-bonds which decreases its ability to form intermolecular H-bonds with water.

32. [2]

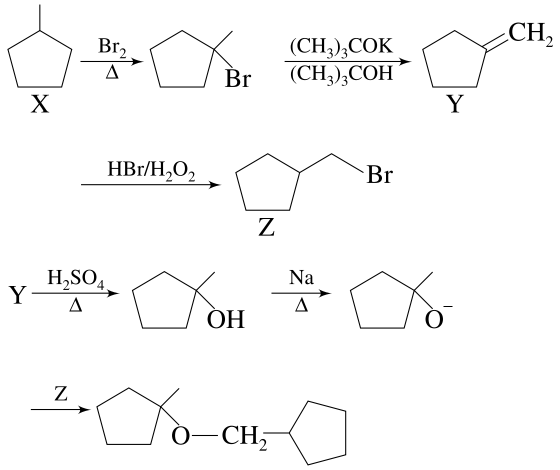


33. [4]

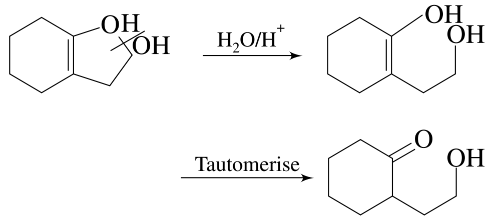


Phenolic —OH does not undergo further substitution.

34. [2]



35. [2]



EXERCISE # 3

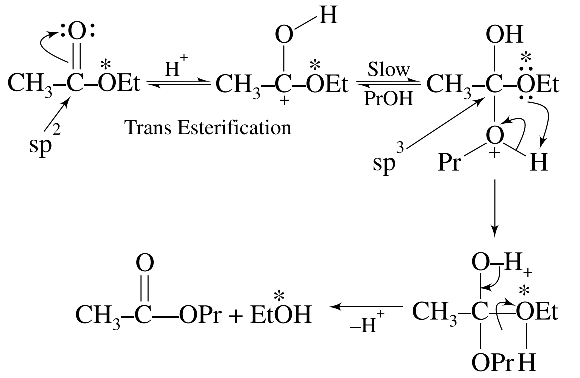
1. [1,3]

$$C_2H_5–Br \xrightarrow{C_2H_5ONa} C_2H_5–O–C_2H_5$$

$$C_2H_5–Br \xrightarrow{\text{dry } Ag_2O} C_2H_5–O–C_2H_5 + 2AgBr$$

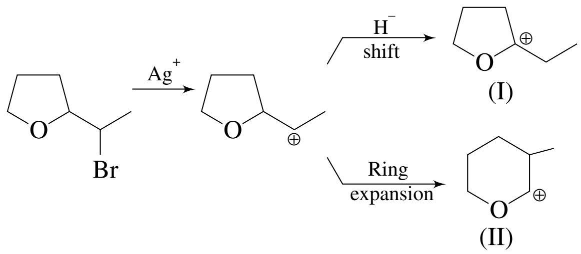
2 Mole

2. [1,2,3]



Trans Esterification follow Le-chaterlier principle in which for forward reaction PrOH is taken in excess and for backward reaction EtOH is taken in excess. In the slow step formation of tetrahedral intermediate it means it having vanderwall repulsion.

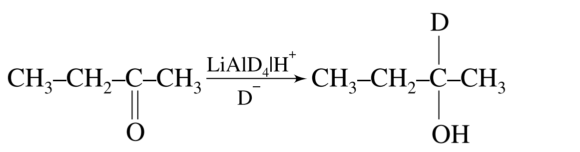
3. [2,3]



(I) and (II) undergo nucleophilic attack by H_2O giving the desired products.

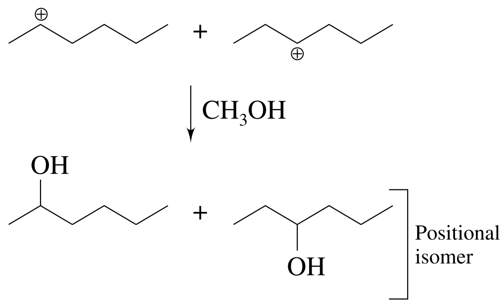
4. [2,4]

Deutride (D^-) addition at planar carbonyl carbon occur from both side of plane with equal probability giving racemic mixture of alcohols, Also, deuterium is attached to carbonyl carbon atom only.

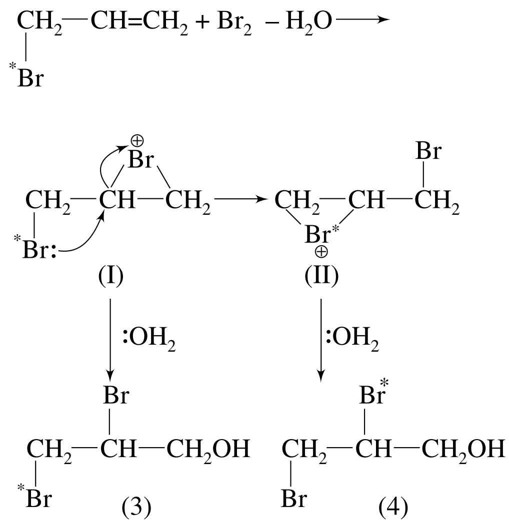


5. [1,3]

Both *cis* and *trans* 2-hexene forms the same carbocation, hence react at same rate.



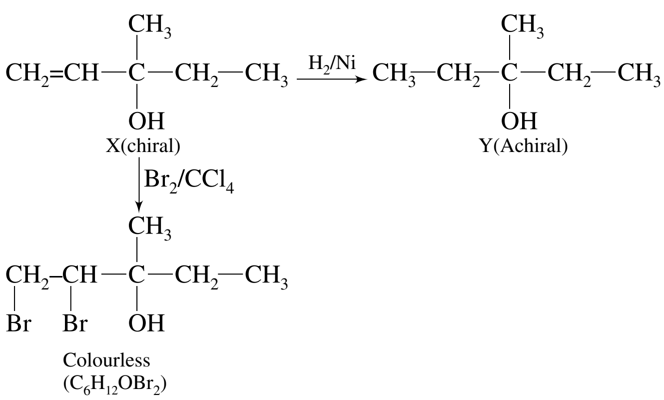
6. [3, 4]



7. [1, 3]

Option (1) and (3) have electron withdrawing groups, destabilises carbocation, do not form turbidity with Lucas reagent at room temperature like primary alcohols. Option (2) and option (4) have electron donating groups, stabilise benzylic carbocation, form immediate turbidity with Lucas reagent like 2° and 3° alcohols.

8. [1, 4]



X neither oxidised by chromic acid nor gives iodoform.

9. [1, 2, 3]

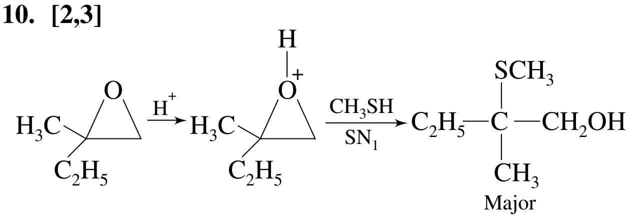
(1) Reaction does not involve breaking of bonds to chiral carbon, hence retention of configuration.

(2) With TsCl, —OTs is formed with retention of configuration. Subsequent reaction with CH_3O-Na involves S_N2 reaction, hence inversion of configuration takes place.

(3) With conc. H_2SO_4, alkene is formed. Alkene in the next step reacts via carbocation intermediate, hence racemic product is obtained.

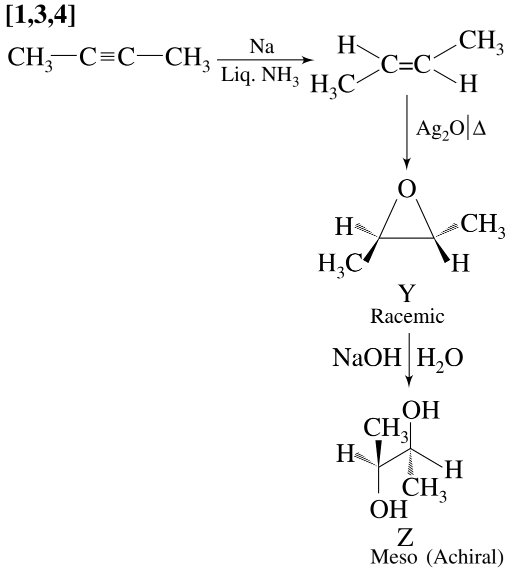
(4) Racemic mixture would be obtained.

10. [2,3]

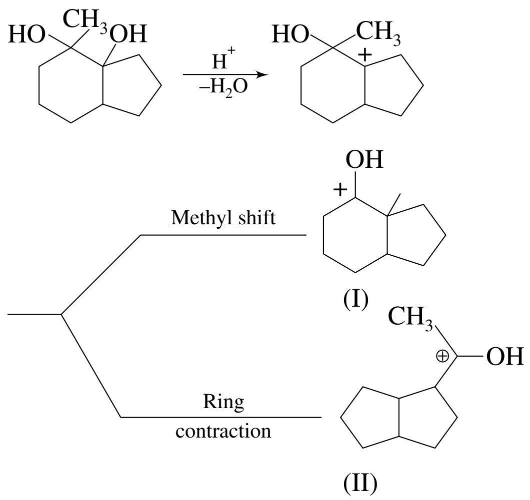


In acidic medium, SN_1 reaction favourable

11. [1,3,4]

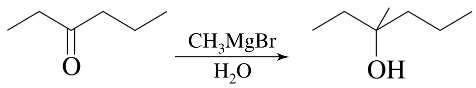


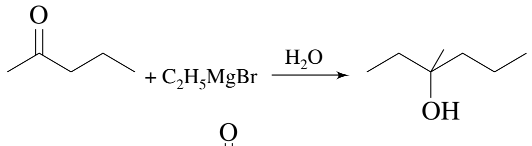
12. [1,2]

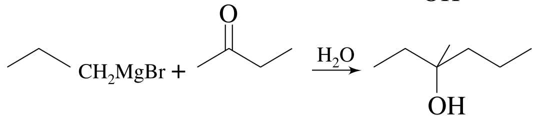


(I) on deprotonation gives (1) while (II) on deprotonation (2)

13. [1,2,3]

(1) 

(2) 

(3) 

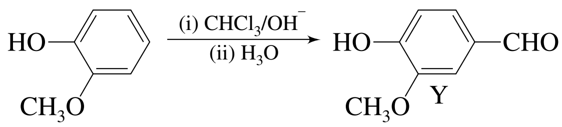
14. [1]

Theory based

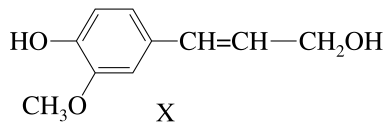
15. [1]

Acid catalysed dehydration of alcohols proceeds via carbocation intermediates. Hence, greater the stability of carbocation, greater is the reactivity of corresponding alcohols.

16. [4]

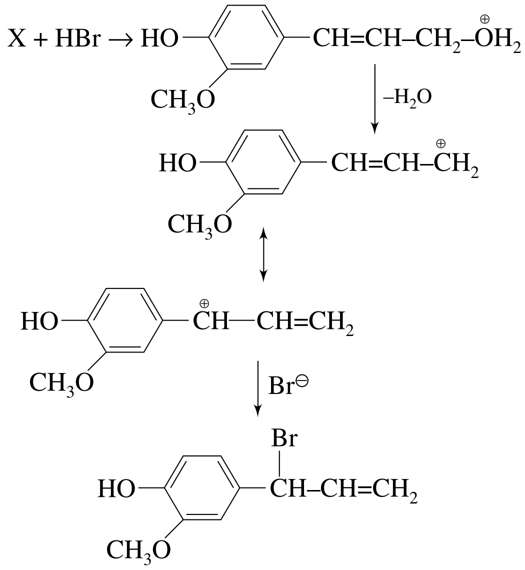


Also, Y is an ozonolysis product of X.

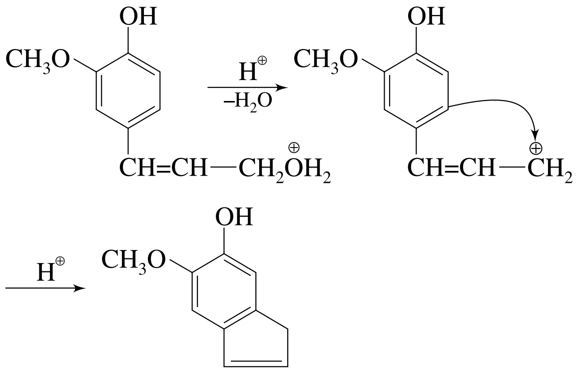


$\xrightarrow[(CH_3)_2S]{O_3}$ Y + OHC—CH_2OH

17. [3]



18. [1]



19. [2]

a → q (Clemmenson reduction)
b → s (NAR)
c → p (reduction by $LiAlH_4$)
d → r (specific reduction of ester)

20. [2]

Theory based

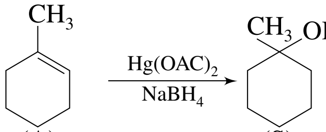
21. [3]

(A) Vicinal diol cleaved by HIO_4
(B) Benzyl alcohol is neutral towards litmus paper
(C) Lucas test achieved via SN1,

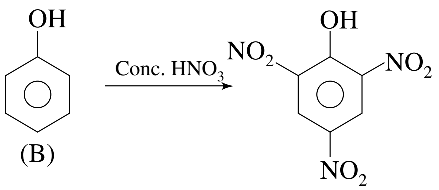
reactivity of SN1 $\propto$ stability of $-\overset{|}{\underset{|}{C}}{}^{+}$

(D) Only $R\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}CH_3$ type gives positive iodoform test

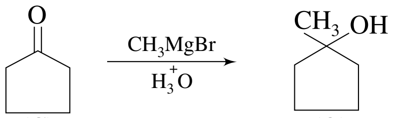
22. [2]



(A) (S)



(B) (P) (Picric acid)



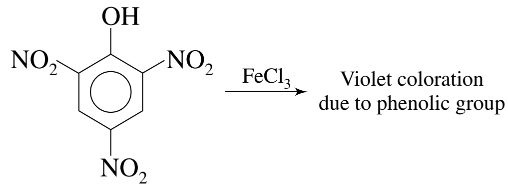
(C) (Q)

$$CO + 2H_2 \xrightarrow{Cr_2O_3\text{–}ZnO} CH_3\text{–}OH$$

(D) (R)

23. [1]

$$CH_3\text{–}CH_2\text{–}OH \xrightarrow{I_2/KOH} +\text{ ve iodoform test}$$



Phenol gives a violet-coloured water soluble complex with ferric chloride. The complex formed is a coordination compound in which iron is hexavalent.

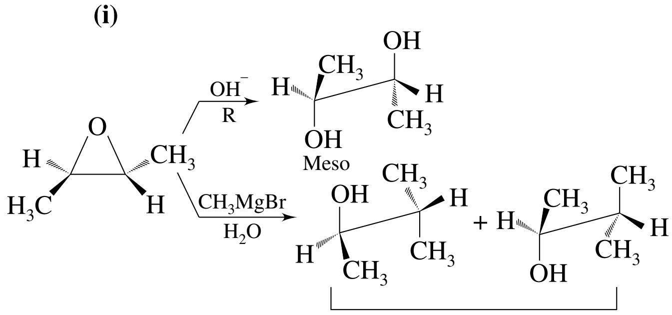
$$6C_6H_5OH + FeCl_3 \rightarrow \underset{\text{violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

$$\begin{array}{l} CH_2\text{–}OH \\ | \\ CH\text{–}OH \\ | \\ CH_2\text{–}OH \end{array} \xrightarrow{2HIO_4} 2HCH{=}O + HCOOH$$

$$CH_3\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}CH_3 \xrightarrow[\text{Conc.HCl+Anhy.ZnCl}_2]{\text{Lucas test}} \text{White turbidity within 5 min}$$

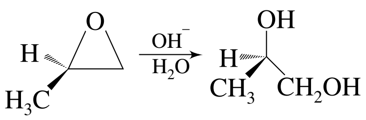
24. [1]

(i)



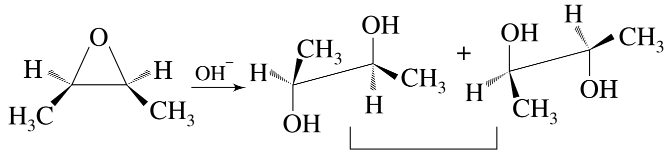
Racemic

(ii)

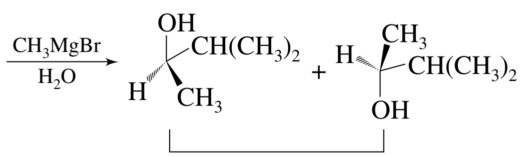


Pure enantiomer   Pure enantiomer

(iii)

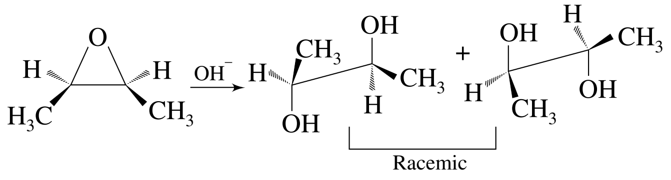


Racemic



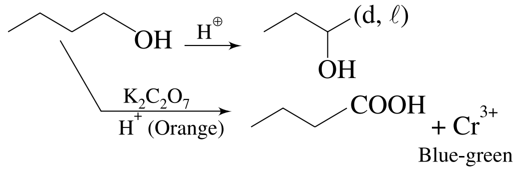
Racemic

(iv)

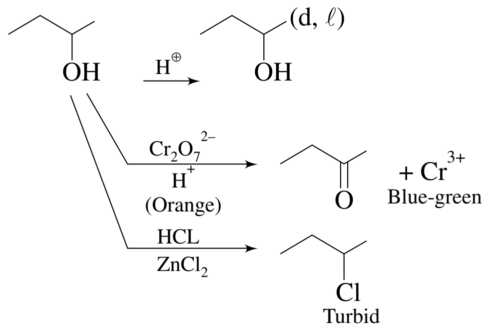


25. [1]

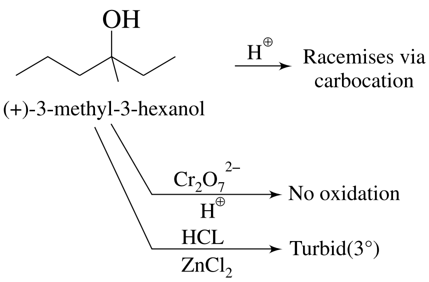
(i)



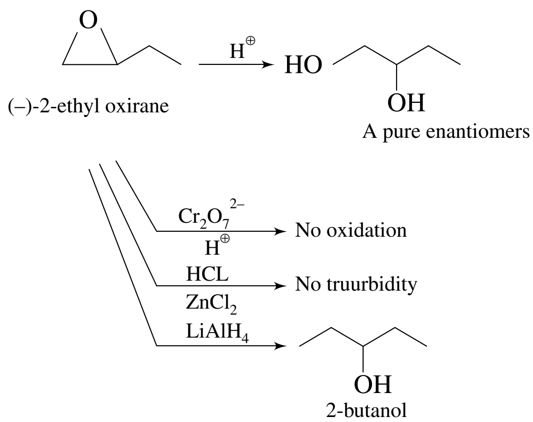
(ii)



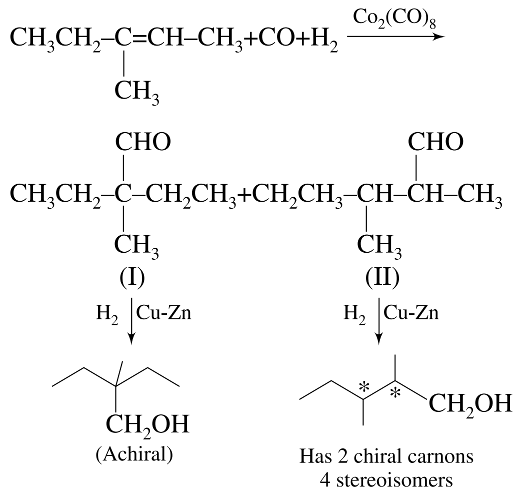
(iii)



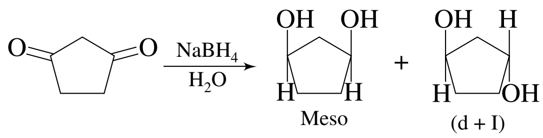
(iv)



26. [5]



27. [3]



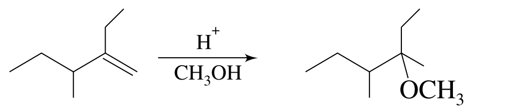
28. [4]

X satisfying the given criteria is

$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH}-CH_3 + 2HIO_4 \rightarrow CH_2O + CO_2 + CH_3CHO$$

Since, X has two chiral carbon so that four optically active isomers exist.

29. [4]



Has two chiral carbons, here total four stereoisomers

30. [6]

$$\underset{17}{\text{(-OH)}} + CH_3COCl \longrightarrow \left(\underset{59}{-O-\overset{O}{\overset{\|}{C}}-CH_3}\right) + HCl$$

Mass gain due to incorporation of one acetyl group $= 59 - 17 = 42$

Net mass gain due to acetylation $= 518 - 266 = 252$

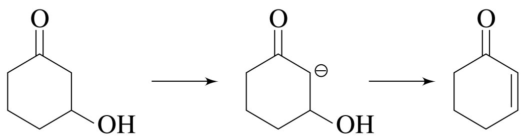
Hence, six hydroxyl groups ($6 \times 42 = 252$) were present.

EXERCISE # 4

1. [2]

In Presence of > C = O group dehydration takes places according to E_{1CB} reaction

Rate of $E_{1CB} \propto$ stability of carbanion



Resonance stable carboanion

2. [4]

Alcohol has polar H which makes intermolecular H-bonding possible. Ether is non-polar, hence has no H-bonding. Lack of H-bonding in ether makes it more volatile than alcohol.

3. [1]

Protonation of —OH is first step. It involves conversion of poor leaving group (—OH) into good leaving group ($-\overset{+}{O}H_2$).

4. [3]

Rate of dehydration $\propto$ stability of carbocation

5. [4]

Gas equation

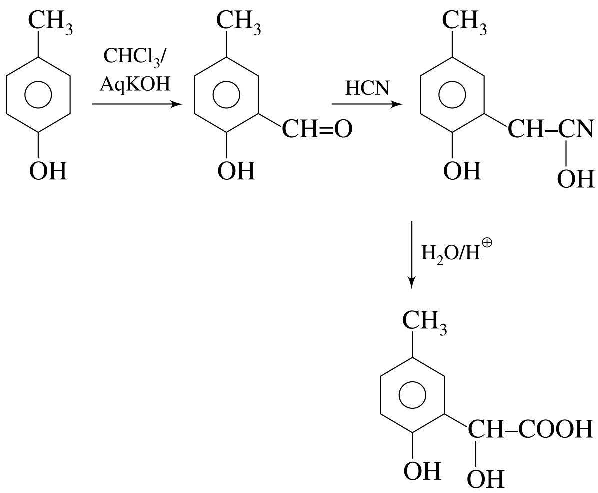
$PV = nRT$

$P = \frac{w}{mv} RT$

$P = \frac{\rho}{m} RT$

$\because P \propto \rho$

6. [3]



7. [4]

$$CH_2{=}CH{-}O{-}CH_3 \xrightarrow[HBr]{\text{Anhydrous}} CH_2{=}CH{-}OH + CH_3{-}Br$$

$$\downarrow \text{Toutomerise}$$

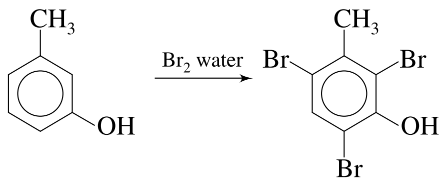
$$CH_3{-}CH{=}O + CH_3{-}Br$$

8. [1]

$$CHCl_3 + KOH \rightarrow \ddot{C}Cl_2 + KCl + H2O$$

Dichlorocarbene

9. [4]



Tri bromo derivative

10. [4]

For positive iodoform test, alcohol molecule must have $CH_3-\underset{OH}{\underset{|}{CH}}-$ group

Thus, iodoform test is given by only (4) $Ph-\underset{OH}{\underset{|}{CH}}-CH_3$

while others will not give this test.

$$Ph-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{I_2 + NaOH} CHI_3 + Ph-COO^-$$

11. [3]

Hydration of ethane gives 1° alcohol (ethanol) while all other alkenes give either 2° or 3° alcohols.

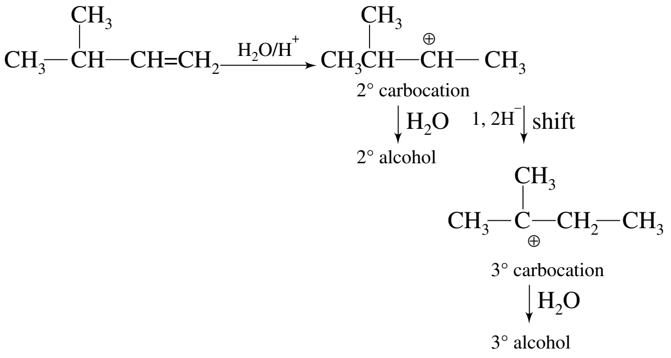
$$\underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow{H_2O/H^+} CH_3CH_2OH$$

$$CH_3-CH{=}CH_2 \xrightarrow{H_2O/H^+} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2$$

[(2° alcohol through 2° carbocation $CH_3\overset{\oplus}{C}HCH_3$)]

$$CH_3-\underset{\substack{|\\CH_3}}{C}=CH_2 \xrightarrow{H_2O/H^+} (CH_3)_3COH$$

[(3° alcohol through 2° carbocation $(CH_3)_3\overset{\oplus}{C}$]

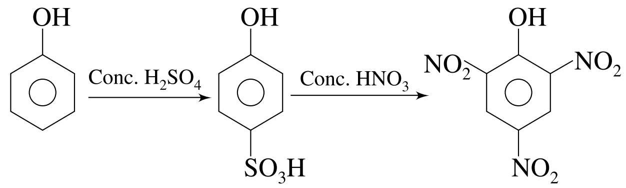


12. [3]

$$\underset{}{CH_3CH_2OH} \xrightarrow[-H_3PO_3]{P + I_2} \underset{(A)}{CH_3CH_2-I} \xrightarrow{Mg,\ ether} \underset{(B)}{CH_3CH_2MgI}$$

$$\xrightarrow{H-\overset{O}{\overset{\|}{C}}-H} \underset{(C)}{CH_3CH_2-\underset{OMgI}{CH_2}} \xrightarrow{H_2O} \underset{\text{n-propyl alcohol (D)}}{CH_3CH_2\overset{OH}{CH_2}} + Mg(OH)I$$

13. [4]



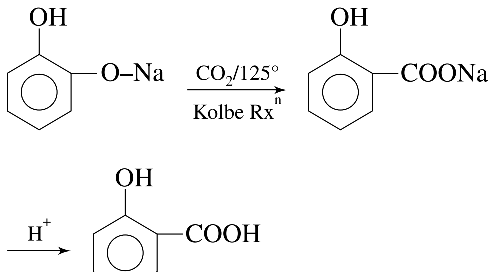
2, 4, 6-trinitrophenol

14. [3]

$$CH_3-COOH+C_2H_5-OH \xrightarrow{Conc.\ H_2SO_4} CH_3-COO-C_2H_5+H_2O$$

Ethyl ester (fruity smell)

15. [2]



Salicyclic acid

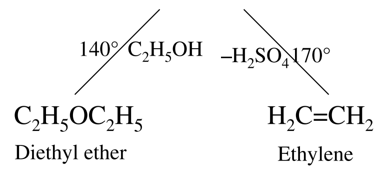
16. [3]

The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed faster sis the reaction 2-methylpropan-2-ol gives 3° carbocation. Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

17. [2]

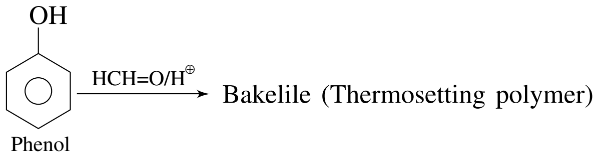
$$C_2H_5OH + H_2SO_4 \xrightarrow{\text{Room temp}} C_2H_5HSO_4$$

Ethyl hydrogen sulphate



Option (1), (3) and (4) may be formed but option (2) is never formed.

18. [2]



19. [1]

By the use of MnO_2 oxidation of only allylic alcohol takes place.

$$CH_2=CH-CH_2-OH \xrightarrow{MnO_2} CH_2=CH-CH=O$$

20. [4]

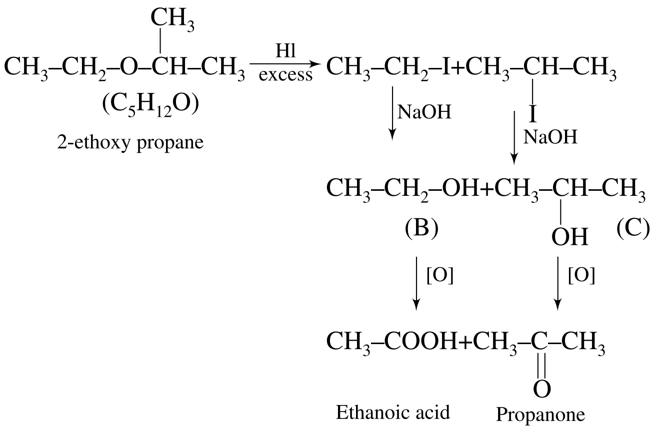
The reaction of alcohol with Lucas reagent is mostly S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction.

Since, 3° R—OH forms 3° carbocation (most stable) hence, it will react fastest by S_N1 reaction.

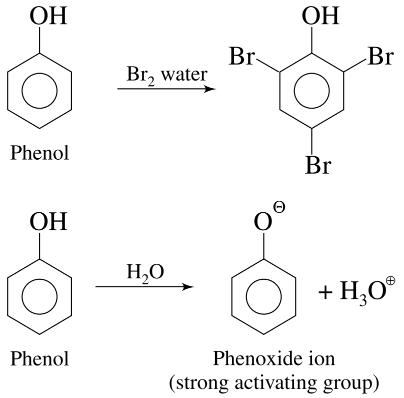
21. [2]

Rate of dehydration ∝ stability of carbocation

22. [1]



23. [1]

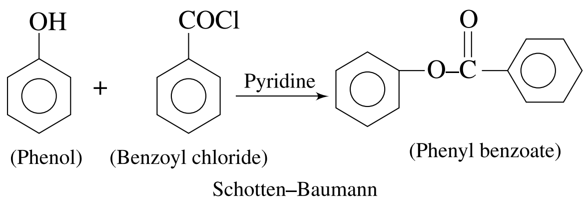


So that Ar-SE reaction takes places at all *o*/*p* position.

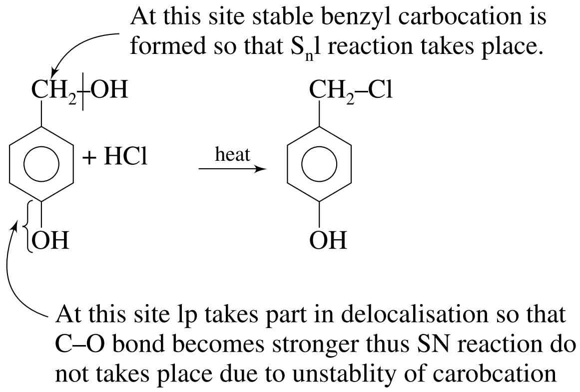
24. [4]

The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed faster sis the reaction 2-methyl butan-2-ol gives 3° carbocation. Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

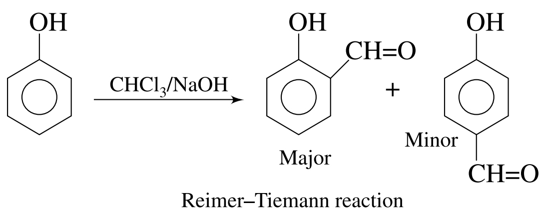
25. [2]



26. [4]



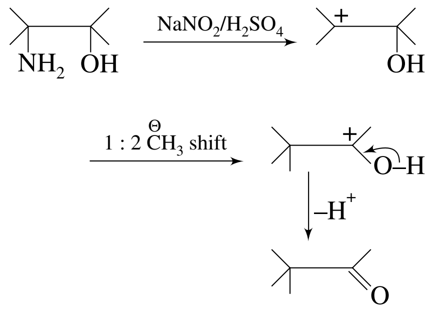
27. [1]



28. [4]

Mild oxidising agents like PCC (Pyridinium chlorochromate are particularly used for the conversion of $R—CH_2OH \longrightarrow R—CHO$

29. [2]



30. [2]

$CH_2{=}CH–CH_2–Br + C_6H_5ONa \longrightarrow$

$CH_2{=}CH–CH_2– O–C_6H_5$

Allyl bromide gives resonating stable allyl carbocation so it easily gives SN reaction.

31. [4]

Given reaction is known as Gattermann reaction.

32. [3]

Acidic strength $\propto -I \propto \dfrac{1}{+I}$

- $\underset{+I}{R}$–OH < H–OH So option (1) is correct
- +I Power ($R_3C– > R_2CH– > R–CH_2–$) So option (2) is correct.
- Bond length of single bond $\propto \dfrac{1}{\text{Resonance}}$

  C–O bond of phenol involve in resonance bond length decreases.

  So that C–O (CH_3–OH) > C–O(Ph–OH) hence option (3) is incorrect.
- Bond angle of sp^3 hybridised atom ≈ 109°.

33. [2]

34. [4]

35. [4]

$$R–X + R'–O^{\ominus} \xrightarrow{S_N2} R–O–R'$$

Nucleophilic substitution

36. [4]

$$CH_3–\underset{\underset{O}{\|}}{C}–O–C_2H_5 + CH_3–MgBr \xrightarrow{S_N2}$$

$$CH_3–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow[\text{NAR}]{CH_3MgBr} CH_3–\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}–CH_3$$

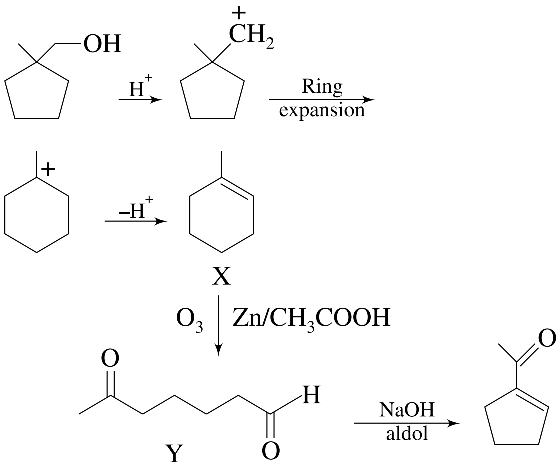
37. [2]

Concentrated H_3PO_4 solution does not involve any substitution product while with others, substitution product are also formed

38. [2]

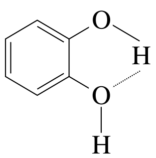
$$C_6H_5MgBr + (CH_3)_3COH \longrightarrow \underset{\text{(Benzene)}}{C_6H_6} + Mg\ [(CH_3)_3CO]Br$$

39.



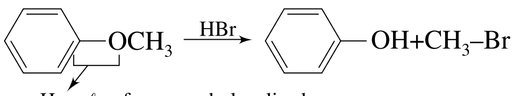
40. [3]

All dihydroxy benzene will have higher boiling points than monohydroxy benzene Also, among dihydroxy benzenes, 1, 2-di-hydroxy benzene has lowest boiling point due to intramolecular H-bonding.



Intramolecular H-bonding in

41. [4]



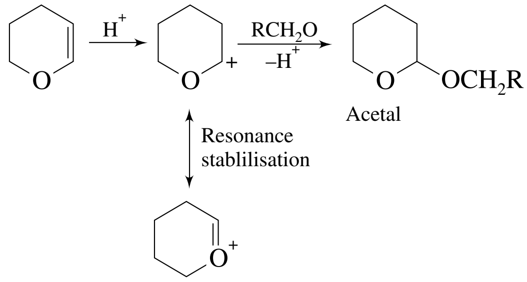
Here ℓp of oxygen de-localised so S_N2 reaction do not takes place

42. [1,2,3]

Since OH group is activating group so that negative charge is developed at *ortho* and para position during resonance.

Hence (1), (2) and (3) are the intermediate obtained during mechanism.

43. [2]

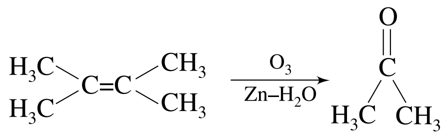


44. [4]

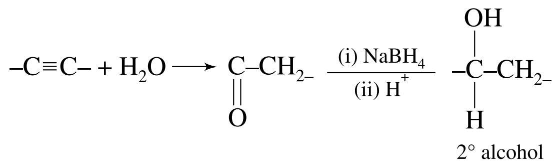
45. [2]

(44 to 45)

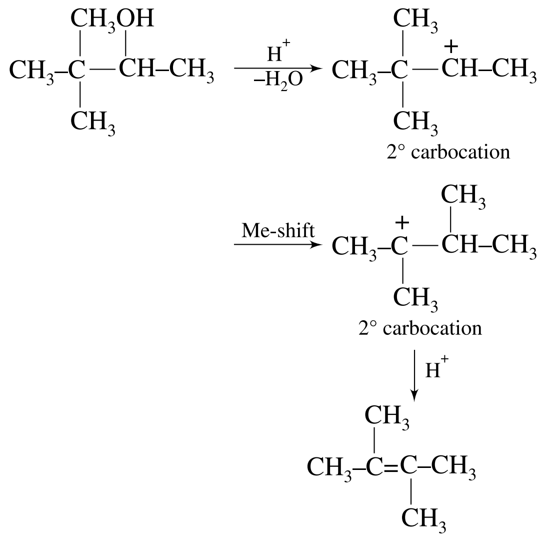
The final ozonolysis product indicates that the alkene before ozonolysis is



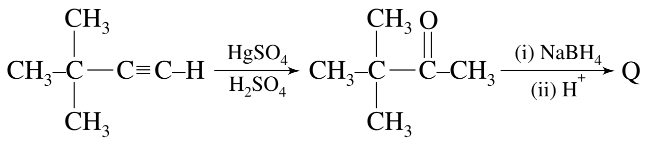
Also P(C_6H_{16}) has two degree of unsaturation and oxymercuration–demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with $NaBH_4$ gives a 2° alcohol.



The secondary alcohol that can give above shown alkene on acid catalysed dehydration is



44.



45. Explained in the beginning.

46. **[2,4]**

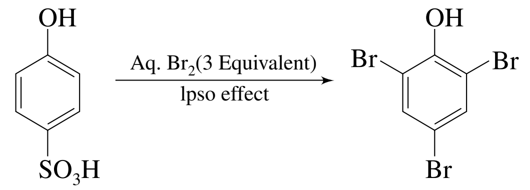
(1) Both phenol and benzoic acid forms salt with NaOH, hence this mixture can't be separated.

(2) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also, benzoic acid forms salt with $NaHCO_3$ but benzyl alcohol does not, hence $NaHCO_3$ can be used for separation.

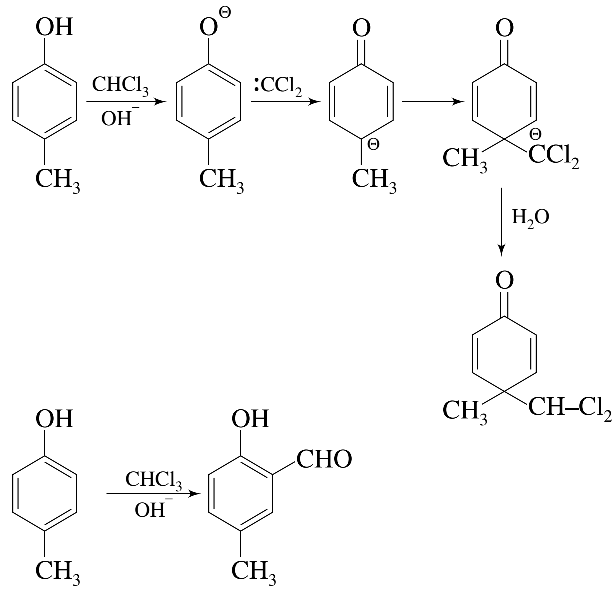
(3) Neither benzyl alcohol nor phenol forms salt with $NaHCO_3$, mixture cannot be separated using $NaHCO_3$.

(4) $C_6H_5CH_2COOH$ forms salt with NaOH, C_6H_5-CH_2OH does not, hence NaOH. $C_6H_5CH_2COOH$ forms salt with $NaHCO_3$. $C_6H_5CH_2OH$ does not, hence mixture can be separated using $NaHCO_3$.

47. **[2]**



48. **[2,4]**

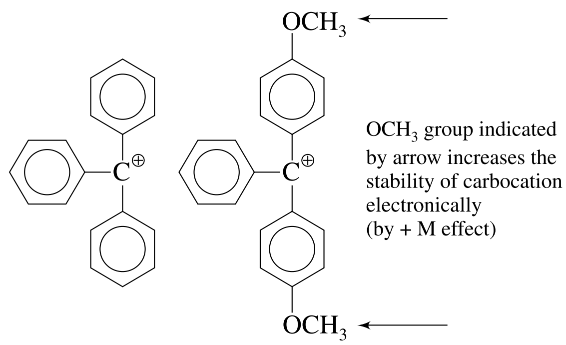


49. **[3]**

This problem can be solved by using the concept of stability of carbocation and S_N1 reaction.

When two phenyl groups are replaced by two para methoxy group, carbocation formed will be more stable.

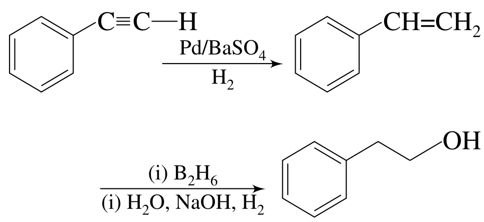
As the stability of carbocation formed increases, rate of acidic hydrolysis increases.



More stable carbocation

50. **[3]**

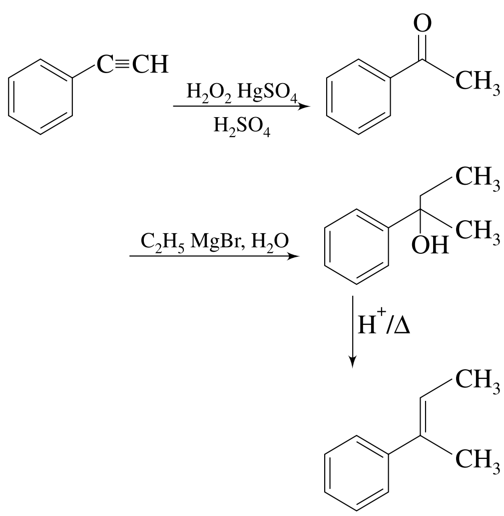
The reaction condition indicates that starting compound is phenyl acetylene.



(2-Phenyl ethanol)
(X)

Hydroboration oxidation brings about anti-Markownikoff's hydration of alkene.

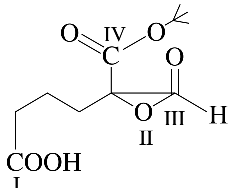
51. **[4]**



52. [3]

Only –CHO group is to be reduced to –CH_2OH

It can be done using $NaBH_4$ in C_2H_5OH.



(1) LiAlH4/$(C_2H_5)_2O$ reduces I, II and III into –CH_2OH, and IV into diol.

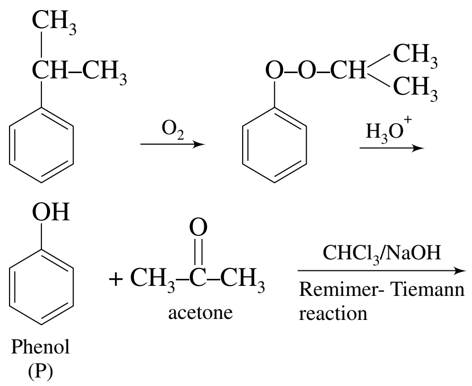
(2) BH_3/THF show same properties as (1).

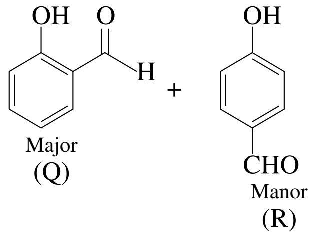
(3) $NaBH_4/C_2H_5OH$ reduces III into –CH_2OH

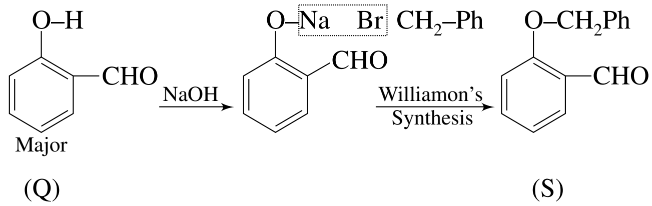
(4) Raney nickel, same as (1) and (2),

Thus (3) is correct reagent.

53. [2, 3]







(1) R is not steam volatile, but Q is steam volatile thus, incorrect.

(2) Q has enolic group; thus it gives violet colour with 1% aqueous $FeCl_3$ solution thus, correct.

(3) S has Carbonyl group hence, gives yellow precipitate with 2,4-DNP thus, correct.

(4) S does not give colour with $FeCl_3$ thus, incorrect

CHAPTER 3

Carbonyl Compounds

INTRODUCTION

- Organic compounds in which $-\underset{\underset{O}{\|}}{C}-$ group is present, are called '**Aldehyde and Ketone**'.
- The group, $-\underset{\underset{O}{\|}}{C}-$ is called as carbonyl group. So the compounds containing this group are also called carbonyl compounds.
- If H atom is attached with this carbonyl group, then compound is called **aldehyde**, and if alkyl group is present on both sides then compound is called **Ketone**.
- In ketone if both alkyl groups are same then they are called simple ketone, if different then the compound is called mixed ketone.
- The general formula of carbonyl compounds is $C_nH_{2n}O$. Hybridisation state of carbon is sp^2 and C=O bond length is 1.23 Å.
- The ratio of C, H, and O in formaldehyde is 1:2:1 (CH_2O).
- Aldehyde shows chain and functional isomerism.
- Ketone shows chain, position, functional isomerism, and also metamerism.
- Aldehyde and ketone both are functional isomer with each other.

PHYSICAL PROPERTIES

- Aldehydes are colourless liquid with pungent smell, while ketones are pleasant smelling liquids; but formaldehyde is gaseous in nature.
- Lower carbonyl compounds are soluble in water. It is due to polarity in carbonyl group.
- Higher carbonyl compounds are insoluble in water due to more covalent character.
- $\boxed{\text{Boiling point} \propto \text{Molecular mass} \propto \dfrac{1}{\text{Number of branches}}}$
- Aldehydes and ketones have higher boiling points than those of non-polar compounds of comparable molar mass, but have lower boiling points than those of alcohols and carboxylic acids due to the absence of H-bonding.

Order of boiling point

(a) Aldehyde < Ketone

(b) The boiling point of unbranched aldehydes increases with the increase in the molecular weight.

Methanal < ethanal < propanal

(c) Order of boiling point of methyl ketones.

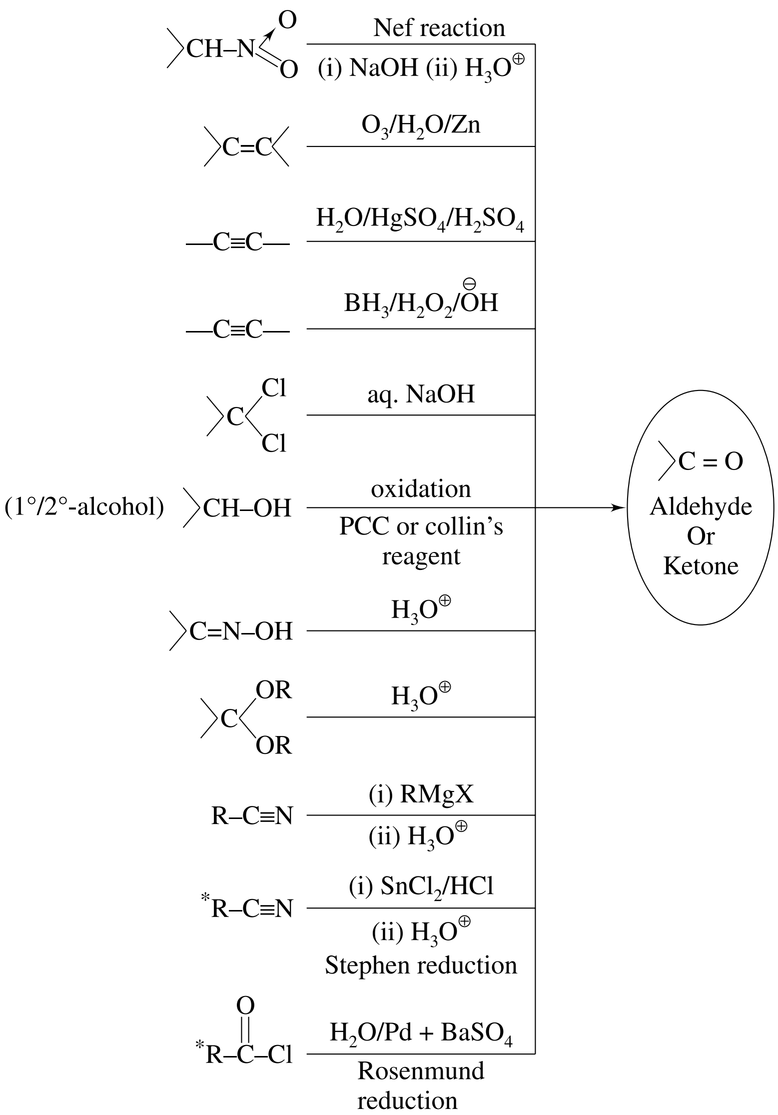
Propanone < butanone < 2-pentanone

(d) Branched carbonyl compounds < unbranched carbonyl compounds
3-methyl butanal < Pentanal
2-pentanone > 3-methyl-2-butanone

- 40% solution of formaldehyde is known as '**FORMALIN**' (40% HCHO, 54–56% H_2O, 4–6% methanol). It is used in preserving dead bodies.
- Mixture of formaldehyde and lactose sugar is called '**FORMAMINT**' which is used in medicine of throat infection.
- Boiling point of carbonyl compounds is as under:

S. No.	Compound	Boiling Point
1.	Formaldehyde	−21°C
2.	Acetaldehyde	+21°C
3.	Acetone	+56°C

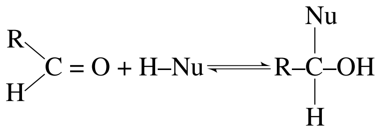
METHODS OF PREPARATION OF CARBONYL COMPOUDNS



*only used for prepration of aldehyde.

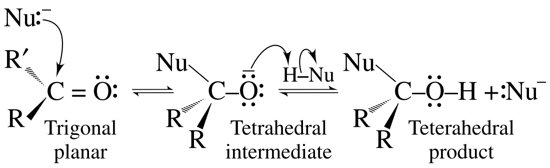
NUCLEOPHILIC ADDITION TO THE CARBON–OXYGEN DOUBLE BOND

The most characteristic reaction of aldehydes and ketones is nucleophilic addition to the carbon–oxygen double bond.



When the reagent is a strong nucleophile (Nu), addition usually takes place in the following way, converting the trigonal planar aldehyde or ketone into a tetrahedral product.

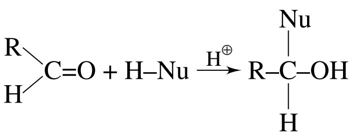
If the nucleophile attacks the carbonyl group, the hybridisation state of carbon changes from sp^2 to sp^3.



Nucleophilic addition can take place either under acidic or basic conditions.

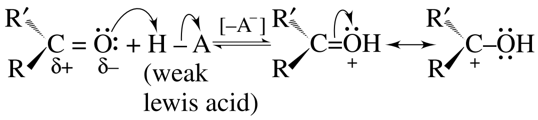
(1) Acid catalysed mechanism of nucleophilic additions to the carbon–oxygen double bonds:

A poor nucleophile requires an acid catalyst to make the nucleophilic addition reaction occur at a reasonable rate. The acid protonates the carbonyl oxygen, which increases the susceptibility of the carbonyl carbon to the nucleophilic attack.

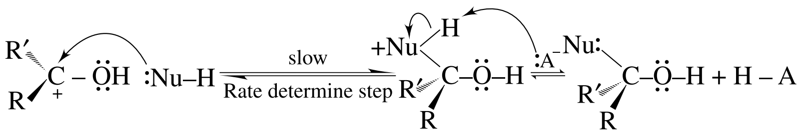


The mechanism of **acid-catalysed** reaction is as follows:

Step-I

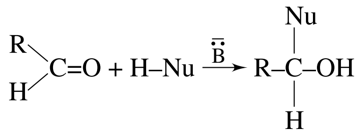


Step-II



(2) Base catalysed mechanism of nucleophilic additions to the carbon–oxygen double bonds:

If the attacking atom of the nucleophile (such as Oxygen nucleophile and nitrogen nucleophile) has a pair of nonbonding electrons in the addition product, water will be eliminated from the addition product. This is called a **nucleophilic addition–elimination** reaction.

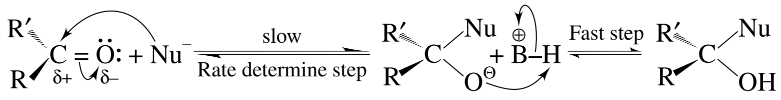


The mechanism for **base-catalysed** reaction is as follows:

Step-I

$$\ddot{B} + H{-}Nu^{-} \rightleftharpoons \overset{\oplus}{B}H + \overset{\ominus}{Nu}$$

Step-II



Intermediate

Reactivity of Aldehydes and Ketones for Nucleophilic Addition Reactions

The reactivity of the carbonyl group for nucleophilic addition depends mainly on three factors.

(1) Ability of carbonyl oxygen to carry a negative charge

(2) Nature of the groups attached to the carbonyl carbon atom

(3) Size of the substituent groups (steric factor).

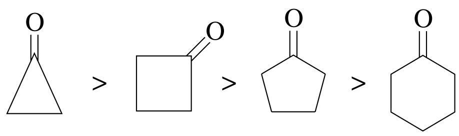
Reactivity of different carbonyl compounds in decreasing order is as follows:

$$\underrightarrow{HCHO > C_6H_5{-}CH_2{-}CHO > RCHO > C_6H_5{-}CHO > R{-}\overset{\overset{O}{\|}}{C}{-}R > R{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5 > C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5}$$

Reactivity in decreasing order

Reactivity of Cyclic Ketones

In case of cyclic ketones the reactivity order is as follows:



Thus more is the angle strain in the cyclic ketones more is their reactivity for nucleophilic addition reaction.

Conclusion

(i) Steric hindrance and more alkyl substituents make carbonyl compounds less reactive towards any nucleophile.

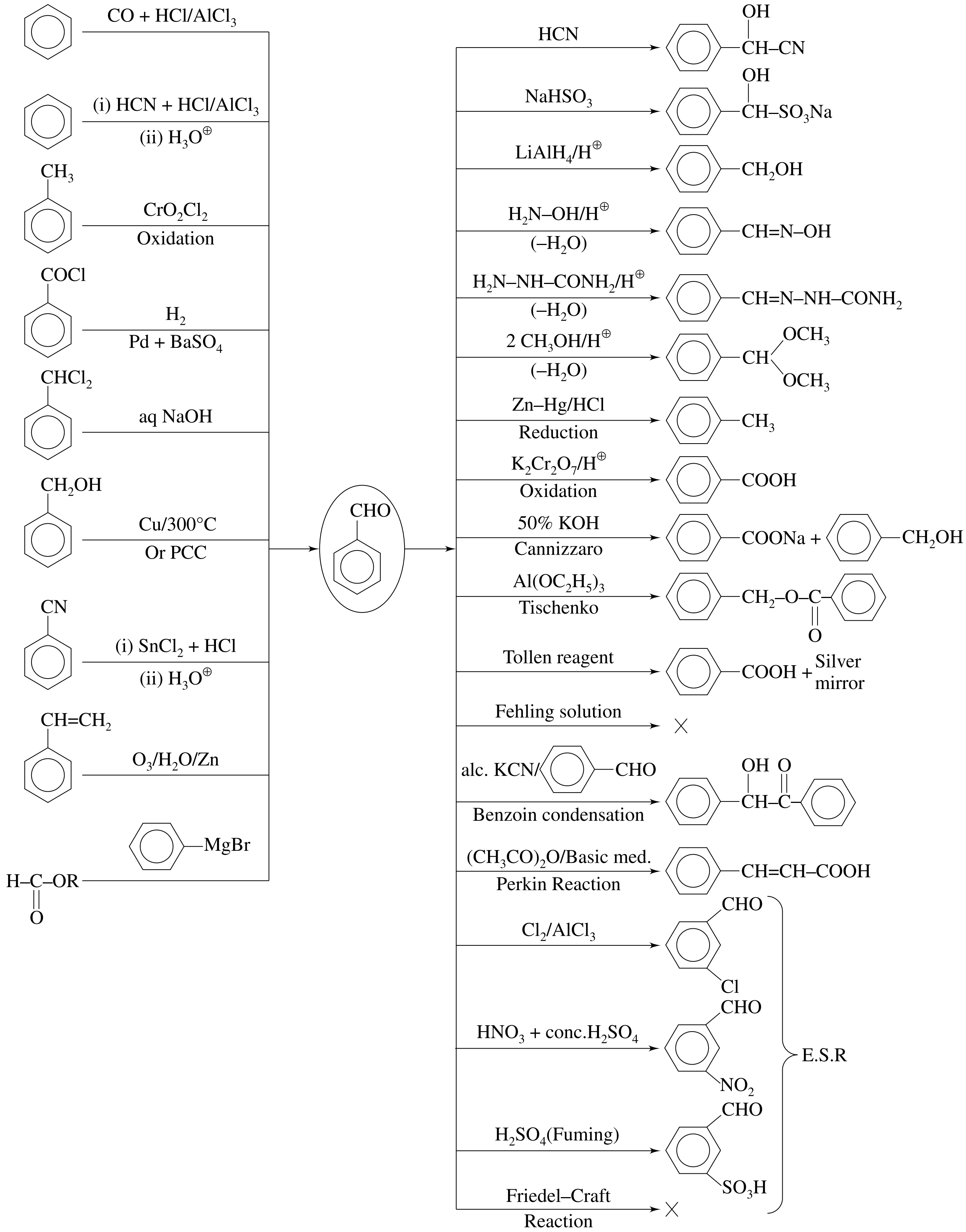
(ii) Electron-withdrawing groups and small rings make carbonyl compounds more reactive towards any nucleophile.

CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

$>C=O$ Aldehyle or Ketone

- $>C=O \xrightarrow{\text{H–CN}/\bar{O}\text{H cat.}} >C(OH)(CN)$ (Cyanohydrin)
- $>C=O \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) R–MgX}} >C(OH)(R)$ (alcohols)
- $>C=O \xrightarrow[\text{(ii) } H_2O]{\text{(i) Br Zn } CH_2 \text{ COOR}} >C(OH)(CH_2\text{–COOR})$ (Reformatsky reaction)
- $>C=O \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) R–C≡C Na}} >C(OH)(C \equiv C\text{–R})$ (Acetylinic alcohol)
- $>C=O \xrightarrow{NaHSO_3} >C(OH)(SO_3Na)$ (White Crystal)
- $>C=O \xrightarrow{H_2O / H^{\oplus}} >C(OH)(OH)$ (Unstable)
- $>C=O \xrightarrow[(-H_2O)]{2\text{ RO–H} / H^{\oplus}} >C(OR)(OR)$ (Acetal or Ketal)
- $>C=O \xrightarrow[(-H_2O)]{2\text{ RS–H} / H^{\oplus}} >C(SR)(SR)$ Thioacetal or Thiketal
- $>C=O \xrightarrow[(-H_2O)]{\text{H–O–}CH_2\text{–}CH_2\text{–O–H} / H^{\oplus}} >C(\text{O–}CH_2)(\text{O–}CH_2)$ (Cyclic acetal or ketal)
- $>C=O \xrightarrow[(-H_2O)]{H_2\ddot{N}\text{–Z} / H^{\oplus}} >C=\ddot{N}\text{–Z}(Z \Rightarrow CH_3, NH_2, OH, NH\text{–Ph...})$
- $>C=O \xrightarrow[\text{dil. NaOH}]{\text{aldol reaction}}$ β–Hydroxy aldehyde / Ketone
- $>C=O \xrightarrow[\text{(ii) } H_3O^{\oplus} / \Delta]{\text{(i) } H_2C(COOR)_2 / \text{Pyridine}} >C=CH\text{–COOH}$ (Knoevenagel reaction)
- $>C=O \xrightarrow[Ph_3P=CH_2]{\text{Witting reaction}} >C=CH_2 + Ph_3P=O$
- Reduction:
  - $>C=O \xrightarrow{H_2 /\text{Pd or } LiAlH_4 / H} >CH\text{–OH}$
  - $>C=O \xrightarrow{\text{Zn–Hg} / HCl} >CH_2$
  - $>C=O \xrightarrow[\Delta]{NH_2\text{–}NH_2 / KOH} >CH_2$

METHODS OF PREPARATION AND CHEMICAL PROPERTIES OF BENZALDEHYDE: (OIL OF BITER ALMONDS)



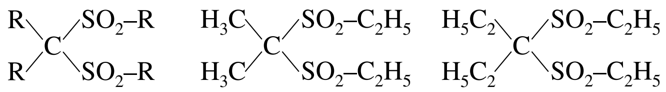
SPECIAL POINTS

1. Distinction between formaldehyde, acetaldehyde and acetone:

S. No.	Reagent/Test	HCHO	CH_3CHO	CH_3COCH_3
1	Brady reagent/DNP	Coloured crystal	Coloured crystal	Coloured Crystal
2	Tollen's reagent	Silver mirror	Silver mirror	×
3	Fehling's solution	Red	Red	×
4	Benedict's solution	Red	Red	×
5	Corrosive sublimate ($HgCl_2$)	Black	Black	×
6	Schiff's reagent	Pink	Pink	×
7	Iodoform test	×	Yellow	Yellow
8	Pyrogallol test	White	×	×
9	Legal test (Sodium nitroprusside/NaOH)	×	Red	Red
10	m-dinitrobenzaldehyde test	×	×	Blue

2. **Chloral** (CCl_3CHO) is an important intermediate in the manufacture of chloroform and D.D.T.
3. **Popoff's rule:** Oxidation of unsymmetrical ketones largely take place in such a way that the smaller alkyl group remains attached to the CO group during the formation of two molecules of acids.

   e.g., $CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_2\text{–}CH_3 \xrightarrow{[O]} CH_3\text{–}COOH + CH_3\text{–}COOH$
4. Formaldehyde is used in preparation of urotropine (Hexamethylene tetramine), a urinary antiseptic and bakelite (phenol–formaldehyde resin) polymer, formamint, throat lozenges (formalin + lactose).
5. Formaldehyde is used as disinfectant and preservative for biological specimens in the form of **formalin.**
6. Acetaldehyde is used in preparation of polymers and dyes; metaldehyde is used as solid fuel and paraldehyde as mild hypnotic. Some more hypnotics are.



sulphonal trional tetronal

7. Acetaldehyde is used as an antiseptic.
8. Acetone is used as a solvent for cellulose, nail polish, varnish and silk.

SOLVED EXAMPLE

1. Which of the following will not be formed when calcium formate is distilled with calcium acetate?
   (1) Propanone (2) Propanal
   (3) Ethanal (4) Methanal

Sol. **[2]**

$(CH_3\text{–}COO)_2Ca + (H\text{–}COO)_2Ca \rightarrow CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3$ (Propanone), $H\text{–}\underset{\underset{O}{\|}}{C}\text{–}H$ (Methanal) } Self product

$CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}H$ (Ethanal) } Cross product

Thus, propanal is not formed.

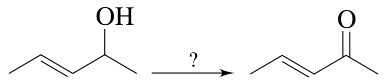
2. When diethyl cadmium [$(C_2H_5)_2Cd$] is treated with acetyl chloride [CH_3COCl], the main product is likely to be:
   (1) acetone (2) methyl ethyl ketone
   (3) diethyl ketone (4) acetaldehyde

Sol. **[2]**

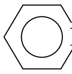
$(C_2H_5)_2\text{–}Cd + CH_3\text{–}\overset{\overset{O}{\|}}{C}\text{–}Cl \xrightarrow{SN_2} CH_3\text{–}CH_2\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3$

Methly ethyl ketone

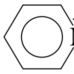
3. Which one among the following is the best reagent for the conversion of pent-3-en-2-ol into pent-3-en-2-one?



(1) $KMnO_4/H_2SO_4$ (2) $K_2Cr_2O_7/H_2SO_4$

(3) CrO_3/CH_3COOH (4)  $\overset{+}{N}H\ ClCrO_3^-$

Sol. **[4]**

 $\overset{+}{N}H\ ClCrO_3^-$

P.C.C. is selective oxidising agent which does not affect the oxidation of $>C=C<$

4. Consider the following sequence of reactions

$$\underset{(C_4H_8O_3)}{A} \xrightarrow{CrO_3} B \xrightarrow{Warm} CH_3\overset{O}{\overset{||}{C}}CH_3 + CO_2$$

The compound (A) is:

(1) $HOCH_2CH_2CH_2COOH$

(2) $CH_3CH(OH)CH_2COOH$

(3) $CH_3CH_2CH(OH)COOH$

(4) $(CH_3)_2C(OH)COOH$

Sol. **[2]**

$$\underset{(C_4H_8O_3)}{CH_3\text{–}\underset{OH}{\underset{|}{CH}}\text{–}CH_2\text{–}COOH}\ (A) \xrightarrow[oxidation]{CrO_3} CH_3\text{–}\underset{O}{\underset{||}{C}}\text{–}CH_2\text{–}COOH\ (B)$$

β-keto acid

$$\downarrow -CO_2,\ Warm$$

$$CH_3\text{–}\underset{O}{\underset{||}{C}}\text{–}CH_3$$

5. Which of the following compounds does not react with sodium bisulphate?

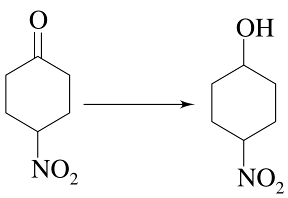
(1) Propanone (2) Propionaldehyde

(3) 3-pentanone (4) 2-pentanone

Sol. **[3]**

All aldehydes and only aliphatic methyl ketones give white precipitate with $NaHSO_3$

3-pentanone, $CH_3\text{–}CH_2\text{–}CO\text{–}CH_2\text{–}CH_3$, does not give white precipitate because it is not methyl ketone.

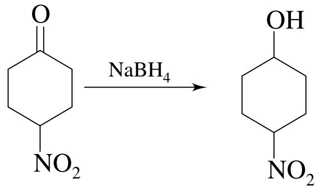
6. 

Above conversion can be achieved by

(1) $LiAlH_4$ (2) H_2,Ni

(3) $NaBH_4$ (4) All

Sol. **[3]**



$\rightarrow$ $-NO_2$ group not reduced by $NaBH_4$

7. A hydrocarbon reacts with HI to give (X) which on being treated with aqueous KOH gives (Y). Oxidation of (Y) gives 3-methyl-2-butanone. The hydrocarbon is

(1) $CH_3CH{=}C(CH_3)_2$ (2) $CH_2 = CHCH(CH_3)_2$

(3) $CH_3CH_2\underset{CH_3}{\underset{|}{C}} = CH_2$ (4) $HC \equiv C\text{–}CH(CH_3)_2$

Sol. **[2]**

$$CH_2{=}CH\text{–}\overset{CH_3}{\overset{|}{CH}}\text{–}CH_3 \xrightarrow{HI} CH_3\text{–}\underset{I}{\underset{|}{CH}}\text{–}\overset{CH_3}{\overset{|}{CH}}\text{–}CH_3 \text{ (one of product)}$$

$$\xrightarrow{Aq\ KOH} CH_3\text{–}\underset{OH}{\underset{|}{CH}}\text{–}\overset{CH_3}{\overset{|}{CH}}\text{–}CH_3 \xrightarrow{(O)} CH_3\text{–}\underset{O}{\underset{||}{C}}\text{–}\overset{CH_3}{\overset{|}{CH}}\text{–}CH_3$$

3-methyl-2-butanone

8. A compound $A(C_5H_{10}Cl_2)$ on hydrolysis gives $C_5H_{10}O$ which reacts with NH_2OH, forms iodoform but does not give Fehling test A is

(1) $CH_3\text{–}\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}\text{–}CH_2\text{–}CH_2\text{–}CH_3$

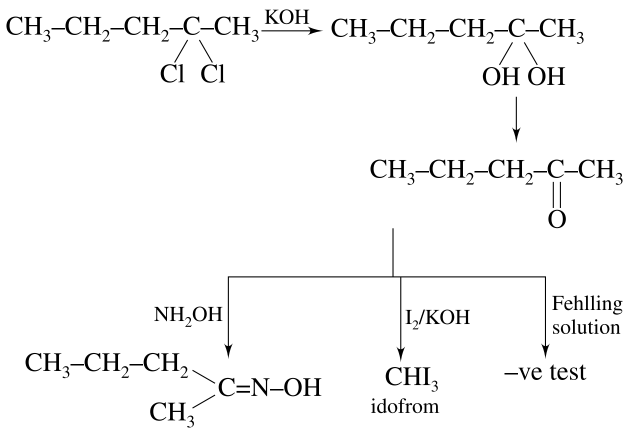
(2) $CH_3CH_2\text{–}\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}\text{–}CH_2CH_3$

(3) $CH_3CH_2CH_2CH_2\overset{Cl}{\overset{|}{CH}}\text{–}Cl$

(4) $CH_3\text{–}\overset{Cl}{\overset{|}{CH}}\text{–}\overset{Cl}{\overset{|}{CH}}\text{–}CH_2CH_3$

Sol. **[1]**

$C_5H_{10}O$ must be methyl ketone because it gives iodoform. Also ketone does not answer Fehling's solution.

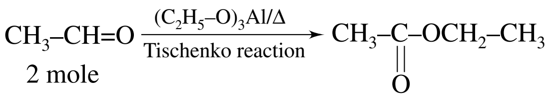


9. Acetaldehyde on being treated with aluminium ethoxide forms

(1) $CH_3CHOHCH_2CHO$ (2) $CH_3COCH_2CH_3$

(3) $CH_3COCH_2COOC_2H_5$ (4) $CH_3COOC_2H_5$

Sol. **[4]**



Ethyl acetate

10. Which of the following cannot be used to convert RCHO into RCH_2OH?

(1) H_2/Pd

(2) $LiAlH_4$

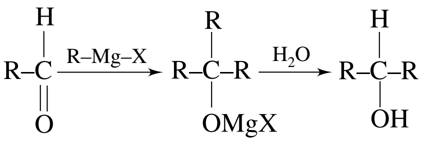
(3) $NaBH_4$

(4) Reaction with RMgX followed by hydrolysis

Sol. **[4]**

H_2/Pd, $LiAlH_4$, $NaBH_4$ will convert R–CH=O into R–CH_2OH by reduction.

Aldehyde is converted into 2° alcohol with Grignard reagent.



2° alcohol

11. A compound (X) of molecular formula C_3H_6O forms bisulphate complex, gives iodoform test but does not reduce Tollens reagent. (X) on reaction with CH_3MgBr/H_3O^+ gives a compound (Y) that cannot

(1) give red colour with CAN

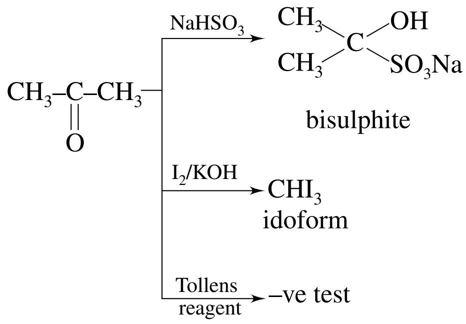
(2) give white turbidity immediately with Lucas reagent

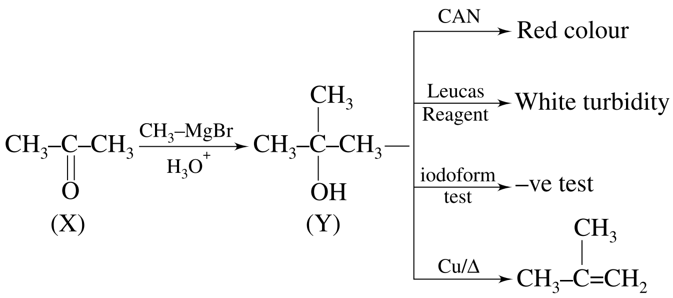
(3) give iodoform test

(4) be dehydrated to alkene on reaction with heated Cu

Sol. **[3]**

In given condition X(C_3H_6O) should be methyl ketone.





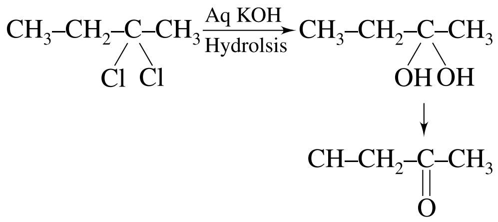
12. A compound (A), $C_4H_8Cl_2$, on hydrolysis gives a product (B) which forms a 2, 4-DNP derivative but does not reduce Tollens reagent. The compound (A) has the structure

(1) $CH_3CH_2CHClCH_2Cl$ (2) $CH_3CH_2CCl_2CH_3$

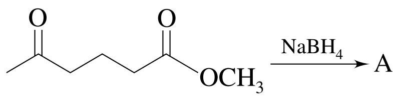
(3) $CH_3CH_2CH_2CHCl_2$ (4) $CH_3CHClCHClCH_3$

Sol. **[2]**

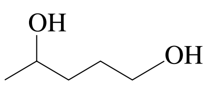
Ketone group forms 2, 4, DNP derivative but do not reduces Tollens' reagent. Hence A($C_4H_8Cl_2$) must be non-terminal geminal di chloride.

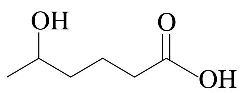


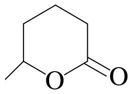
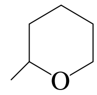
13. Consider the following reaction:



The product (A) is:

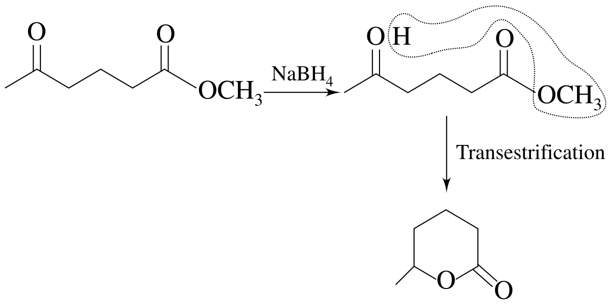
(1) 

(2) 

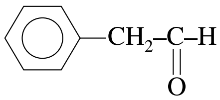
(3)  (4) 

Sol. **[3]**

Reduction of ester group is not affected by weak reducing agent $NaBH_4$



14. Which of the following gives Cannizzaro reaction?

(1) CH_3–C(=O)–H (2) 

(3) CCl_3–C(=O)–H (4) Ph–CH=O

Sol. **[4]**

Aldehydes having no α-H give Cannizzaro reaction. Chloral gives nucleophilic substitution reaction so that derivative of formic acid is formed. Thus only Ph–C(=O)–H no –H (gives Cannizzaro reaction)

15. A water soluble $C_6H_{14}O_2$ compound is oxidised by lead tetraacetate (or periodic acid) to a single C_3H_6O carbonyl compound. Which of the following would satisfy this fact?

(1) meso-2, 3-dimethoxybutane
(2) 1, 2-diethoxyethane
(3) meso-2, 5-hexanediol
(4) meso-3, 4-hexanediol

Sol. **[4]**

Only vicinal diol cleaved by periodic acid

CH_3–CH_2–CH(OH) | CH(OH)–CH_2–CH_3 $\xrightarrow{HIO_4}$ CH_3–CH_2–CH=O (C_3H_6O)

Meso 3,4 hexane diol

16. Which of the following would undergo aldol condensation?

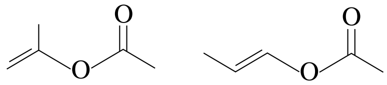
(1) HCHO (2) CH_3–CH_2–C(CH_3)(CH_2CH_3)–CHO

(3) CCl_3CHO (4) CH_3–C(CH_3)$_2$–CH_2–CHO

Sol. **[4]**

Only α-H containing substances undergo aldol condensation.

17. Consider the structures (P) and (Q)

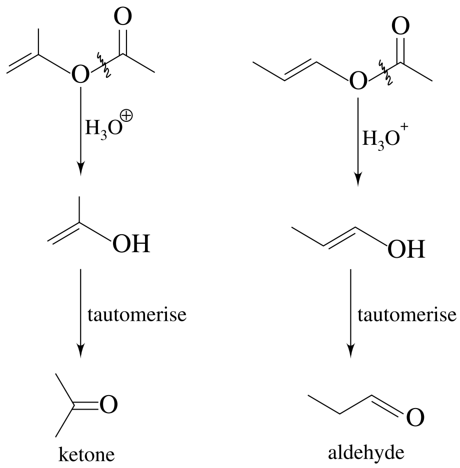


(P) (Q)

The products of acid-catalysed hydrolysis of (P) and (Q) can be distinguished by

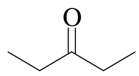
(1) Lucas reagent (2) 2,4-DNP
(3) Fehling's solution (4) $NaHSO_3$

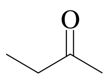
Sol. **[3]**



(Negative test with Fehling's solution) (Postivie test with Fehling's solution)

18. Compound 'A' give positive test with 2,4-DNP and with I_2/NaOH. Compound 'A' may be:

(1) Ph–CHO (2) 

(3) Ph–C(=O)–Ph (4) 

Sol. **[4]**

- positive DNP test indicating that compound (A) must have carbonyl group
- positive iodoform test indicating that (A) must be methyl ketone

19. Which of the following reduce Fehling's solution?

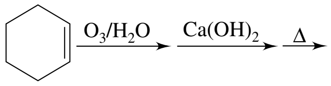
(1) Fructose (2) Benzaldehyde
(3) Sucrose (4) Amylose

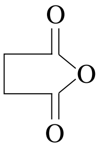
Sol. **[1]**

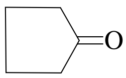
$\text{Fructose} \xrightarrow[\text{Solution}]{\text{Fehling's}} \text{positive test}$

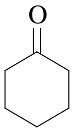
α-Hydroxy ketone will also reduce Fehling's solution.

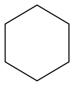
20. End product in the following sequence of reaction is:



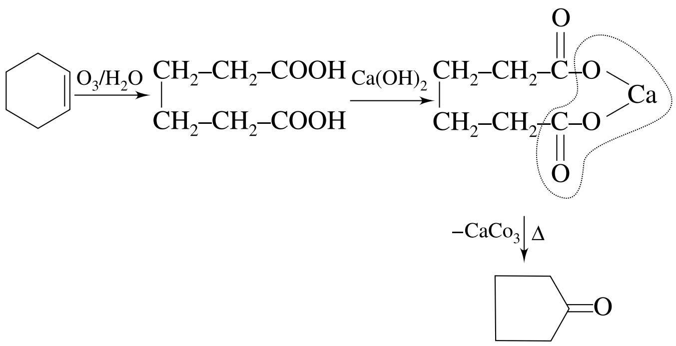
(1) 

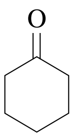
(2) 

(3) 

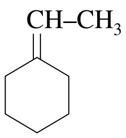
(4) 

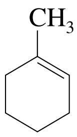
Sol. **[2]**

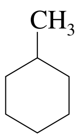


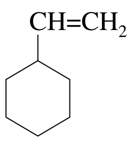
21.  $+ Ph_3P = CH–CH_3 \longrightarrow A$

A is:

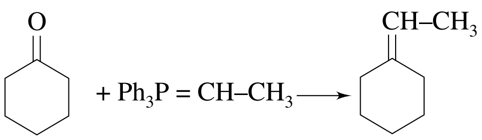
(1) 

(2) 

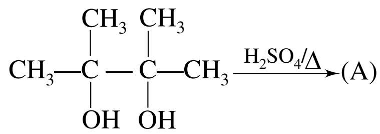
(3) 

(4) 

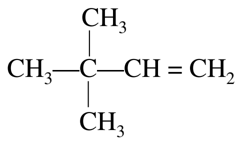
Sol. **[1]**

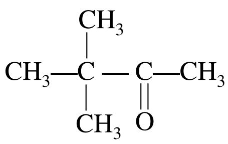


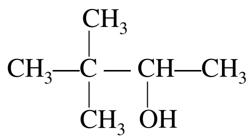
Wittig reaction

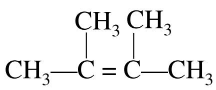
22. 

Product A is:

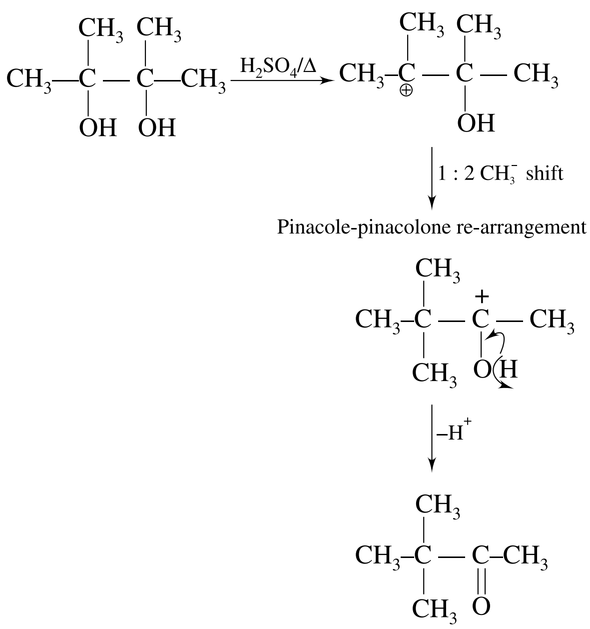
(1) 

(2) 

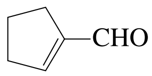
(3) 

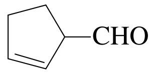
(4) 

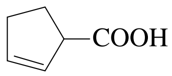
Sol. **[2]**

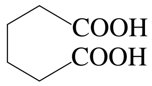


23. Cyclohexene on treatment with O_3, followed by reaction with zinc dust and water gives a compound (E). The compound (E) on further treatment with aqueous KOH yields a compound (F). The compound (F) is

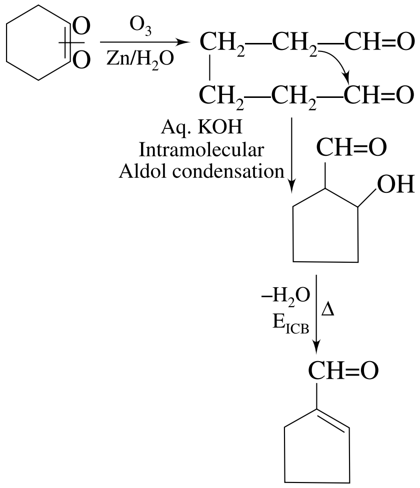
(1) 

(2) 

(3) 

(4) 

Sol. **[1]**

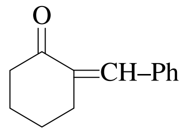


24. $(A) \xrightarrow[\text{Tollens' test}]{\text{Positive}}$

$C_3H_6O \xrightarrow[{}^{-}OH/\Delta]{Ph–CH=O} (B)$

Product (B) is:

(1) $Ph–CH=C(CH_3)–CH_3$

(2) 

(3) $Ph–C(CH_3)=CH–Ph$

(4) Ph–CH=CH–CH=O

Sol. **[4]**

(A) must be aldehyde,

$$CH_3–CH=O \xrightarrow[OH^-/\Delta]{Ph–CH=O} Ph–CH=CH–CH=O$$

(positive Tollens' test)

Claisen condensation

25. Propanone on reaction with magnesium amalgam in benzene and subsequent hydrolysis forms:

(1) $CH_3CHOHCH_3$

(2) $(CH_3)_2C(OH)CH_2COCH_3$

(3) $(CH_3)_2C=CHCOCH_3$

(4) $(CH_3)_2C(OH)—C(OH)(CH_3)_2$

Sol. **[4]**

$$CH_3–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) Mg-Hg benzene}} CH_3–\underset{OH}{\overset{CH_3}{C}}—\underset{OH}{\overset{CH_3}{C}}–CH_3$$

(Reductive Dimerisation)

EXERCISE 1

1. Consider the following sequence of reactions

$$CH_3CH_2I \xrightarrow[\text{2. CuI}]{\text{1. Li/Et}_2\text{O}} A$$

$$(CH_3)_3CCOCl + A \longrightarrow B$$

The final product (B) is:

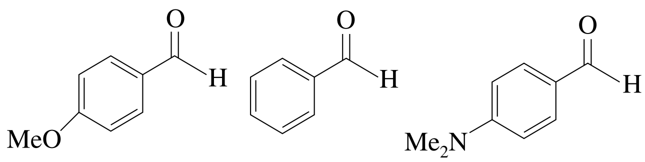
(1) $(CH_3)_3CCOCH_2–CH_3$

(2) $(CH_3)_3CCH(OH)CH_2–CH_3$

(3) $(CH_3)_3C\underset{OH}{\overset{CH_3}{C}}CH_2–CH_3$

(4) $(CH_3)_3CCOOCH_2–CH_3$

2. The $K_{eq.}$ values in HCN addition to following aldehydes are in the order:



I II III

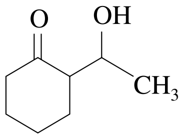
(1) I > II > III
(2) II > III > I
(3) III > I > II
(4) II > I > III

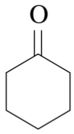
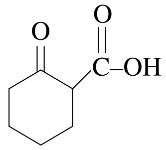
3. Consider the following sequence of reactions:

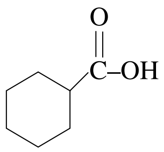
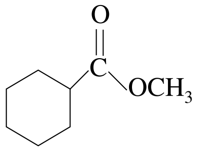
$$CH_3CHO + HCN \rightarrow CH_3CHOHCN \xrightarrow[\text{heat}]{H_3OA^+} CH_3CHOHCOOH$$

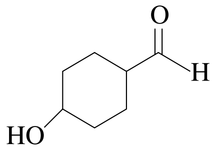
The acid formed as the final product will be obtained as:

(1) an L-isomer
(2) a D-isomer
(3) 20% D-isomer and 80% L-isomer
(4) 50% D-isomer and 50% L-isomer

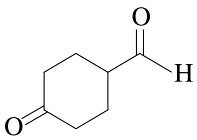
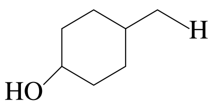
4.  $\xrightarrow[\Delta]{NaOI} \xrightarrow{H^+} \xrightarrow{\Delta}$ A, A is

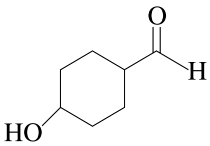
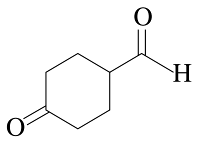
(1) 
(2) 

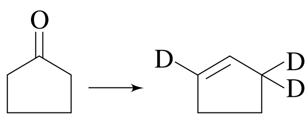
(3) 
(4) 

5.  $\xrightarrow[LiAlH_4]{Ag_2O,\ NH_4OH}$ (P)

Product (P) is:

(1) 
(2) 

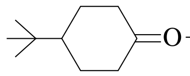
(3) 
(4) 

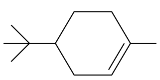
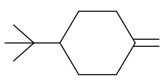
6. 

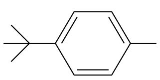
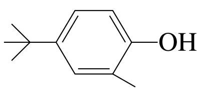
Arrange the follwing reagent in the correct order in which above transformation is carried out:

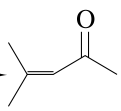
(1) KOD/D_2O, H^+/Δ, $LiAlH_4$
(2) H^+/Δ, KOD/D_2O, $LiAlH_4$
(3) KOD/D_2O, $LiAlH_4$, H^+/Δ
(4) $LiAlH_4$, H^+/Δ, KOD/D_2O

7. Identify the major product in the following reaction.

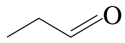
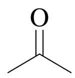
 $\xrightarrow[\text{2. } H_3O^+ \quad \text{3. } H_2SO_4]{\text{1. MeMgBr}}$

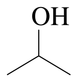
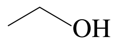
(1) 
(2) 

(3) 
(4) 

8. (X) $\xrightarrow[\Delta]{\text{dil. KOH}}$ 

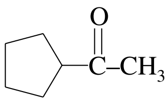
Structure of (X) is

(1) 
(2) 

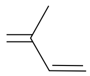
(3) 
(4) 

9. Which of the following ketones/aldehydes can undergo haloform reaction?

(1) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
(2) CH_3-CHO

(3) 
(4) All of these

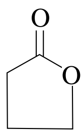
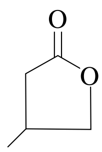
10. Monomer of trioxane is

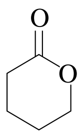
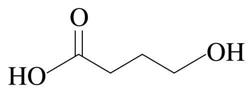
(1) 
(2) $H_2C = O$

(3) $Me(H)C = O$
(4) $Me_2C = O$

11. $HO-\overset{\overset{O}{\|}}{C}-CH_2CH_2-CHO \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4} (A) \xrightarrow{\Delta} (B)$

Structure of B will be:

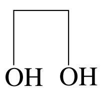
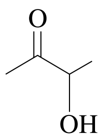
(1) 
(2) 

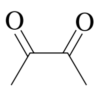
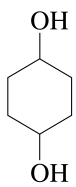
(3) 
(4) 

12. $CH_3-C \equiv N \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) DIBAL-H}} X \xrightarrow[\Delta]{SeO_2} Y \xrightarrow[\Delta]{\overset{\ominus}{O}H} Z$, Z is:

(1) $CH_2(OH)-COO^{\ominus}$
(2) $CH_3-COO^{\ominus}$
(3) $HOOC-COO^{\ominus}$
(4) $CH_2(OH)-CH_2(OH)$

13. Which of the following compound not reacts with HIO_4?

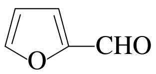
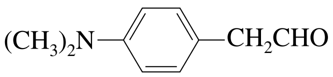
(1) 
(2) 

(3) 
(4) 

14. $CH_3CH=CH_2 \xrightarrow{X} \xrightarrow{Y} CH_3CH_2\overset{\overset{O}{\|}}{C}H$

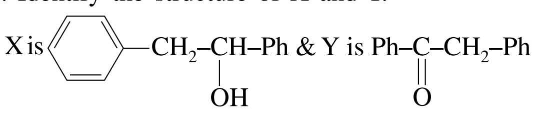
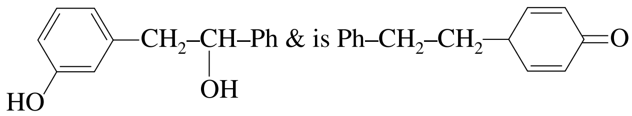
X and Y are, respectively:
(1) H_3O^+, MnO_4^-/H^+
(2) H_3O^+, CrO_3/Pyridine
(3) BH_3. THF/H_2O_2, OH^-, CrO_3/pyridine
(4) BH_3. THF/H_2O_2, OH^-,$Cr2O_7^{2-}/H_3O^+$

15. Which type of reaction in the reduction of carbonyl compound with LAH and $NaBH_4$ occurs, and which nucleophile takes part in the reaction?
(1) Nucleophilic addition and $AlH_4^\ominus$ or $BH_4^\ominus$
(2) Nucleophilic addition and $H^\ominus$
(3) Nucleophilic substitution and $AlH_4^\ominus$ or $BH_4^\ominus$
(4) Nucleophilic substitution and $H^\ominus$

16. Which of the following aldehydes does not undergo a Cannizzaro reaction?
(1) C_6H_5–CHO
(2) 
(3) $(CH_3)_2$–CH–CHO
(4) 

17. Reagent that can distinguish a set of benzaldehyde and formaldehyde is
(1) I_2/NaOH (2) Tollens' reagent
(3) Fehling's solution (4) Baeyer's reagent

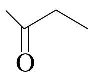
18. In the reaction $PhCN \xrightarrow[\text{2. } H_2O\text{. heat}]{\text{1. } SnCl_2/HCl}$ the modification of the functional group and the change in hybridisation of the functional carbon are, respectively
(1) –CN to –CH_2NH_2, sp^2 to sp^3
(2) –CN to –$CONH_2$, sp to sp^2
(3) –CN to –COOH, sp^2 to sp^3
(4) –CN to –CHO, sp to sp^2

19. A compound 'X' ($C_{14}H_{14}O$) on mild oxidation yields $C_{14}H_{12}O$ (Y). If X is treated with a dehydrating agent, it loses a molecule of H_2O and resulting product on vigorous oxidation yield two molecule of benzoic acid. Identify the structure of X and Y.
(1) 
(2) X is Ph–C(OH)(Ph)–CH_3 & Y is Ph–C(Ph)=CH_2
(3) X is Ph–CH(Ph)–CH_2–OH & Y is Ph–CH(Ph)–CH = O
(4) X is 

20. Consider the following reaction sequence.

$$\begin{matrix} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{matrix} \xrightarrow{\text{MnO/Heat}} (X) \xrightarrow[\text{heat}]{HI/P_4} (Y)$$

The product (Y) is–
(1) cyclobutane (2) cyclopentane
(3) cyclopentanone (4) cyclobutanone

21. Which of the following pairs is differentiated by iodoform and Tollens' reagent?
(1) $PhCOCH_3$; Ph–CHO
(2) H–C(=O)–CH_3 ; CH_3–CH_2–CHO
(3)  ; CH_3–CH_2–CHO
(4) H–C(=O)–H ; Ph – CH = O

22. Schiff's reagent is used for the differentiation between:
(1) HCHO and CH_3CHO
(2) CH_3COCH_3 and CH_3CHO
(3) C_6H_5–CH_2–C(=O)–CH_3 and C_6H_5–C(=O)–CH_2–CH_3
(4) HCHO and C_6H_5CHO

23. CH_2=CHCH(OH)$CH_2CH_2OH \xrightarrow{MnO_2}$ A. A is
(1) CH_2=CHC(=O)CH_2CH_2OH
(2) CH_2=CHCH(OH)CH_2CHO
(3) CH_2=CHC(=O)CH_2CHO
(4) CH_2=CHC(=O)CH_2C(=O)OH

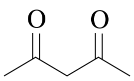
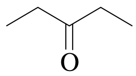
24. In the reaction $PhCOCH_3 \xrightarrow{CH_3CO_3H}$ A, the product (A) is:
(1) $PhCOOCH_3$ (2) CH_3COOPh
(3) $PhCO_2H$ (4) $PhCOOCOCH_3$

25. Aniline undergoes condensation reaction with benzaldehyde to from benzalaniline. The latter is known as:

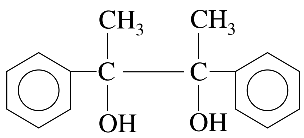
(1) a Mannich base (2) a Schiff base
(3) Schiff reagent (4) Benedict's reagent

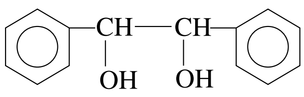
26. Which of the following will give negative Tollens' but positive iodoform test?

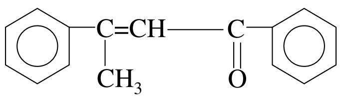
(1) $H-\overset{\overset{O}{\|}}{C}-H$ (2) $CH_3-\overset{\overset{O}{\|}}{C}-H$

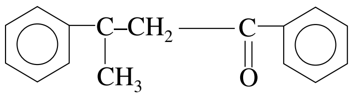
(3)  (4) 

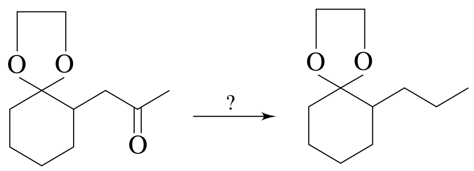
27. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure:

(1) 

(2) 

(3) 

(4) 

28. 

Above conversion can be carried out by:

(1) Clemmensen reduction
(2) Wolff–Kishner reduction
(3) $LiAlH_4$
(4) $NaBH_4$

29. When a nucleophile encounters a ketone, the site of attack is:

(1) The carbon atom of the carbonyl
(2) The oxygen atom of the carbonyl
(3) Both the carbon and oxygen atoms, with equal probability
(4) No attack occurs as ketones do not react with nucleophiles

30. $R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{R-NH_2} R-CH=R$. This reaction gives the best yield at:

(1) pH 1–2 (2) pH 4–5
(3) pH 10–11 (4) pH 13–14

31. $Ph-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{SOCl_2} (A) \xrightarrow[Pd\text{-}BaSO_4]{H_2} (B)$

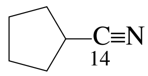
Product (B) is:

(1) $Ph-\overset{\overset{O}{\|}}{C}-H$ (2) $Ph—CH_2—OH$
(3) $Ph—CH_2—Cl$ (4) $Ph—CH=CH_2$

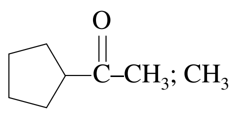
32. $Ph-CH_3 \xrightarrow{CrO_2Cl_2} (A) \xrightarrow{\text{conc. KOH}} Ph-CH_2OH + (B)$

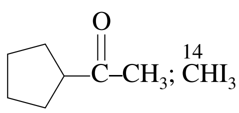
Product (B) of above the reaction is:

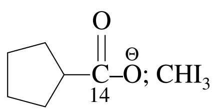
(1) $Ph—CO_2H$ (2) $Ph—CO_2^-$
(3) $Ph—CHO$ (4) $Ph—CH_3$

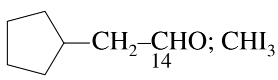
33.  $+ CH_3MgBr \xrightarrow[H_3O^{\oplus}]{} (A) \xrightarrow{NaOI} (B) + (C)$

Products (A) and (C) are:

(1) 

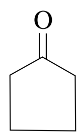
(2) 

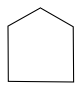
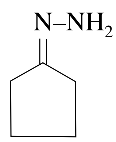
(3) 

(4) 

34. $\begin{matrix} CH_2-CH_2-CO_2H \\ | \\ CH_2-CH_2-CO_2H \end{matrix} \xrightarrow[BaCO_3]{\Delta} (A) \xrightarrow{NH_2-NH_2} (B) \xrightarrow[KOH]{heat} (C),$

Product (C) obtained is:

(1) $CH_3—CH=CH—CH_2$ (2) 

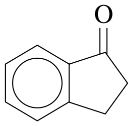
(3)  (4) 

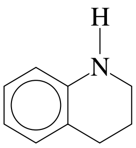
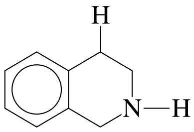
35. $(A) \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4} (B) \xrightarrow{LiAlH_4} \underset{\text{Racemic mixture}}{(C)}$

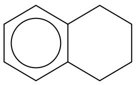
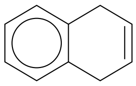
Reactant (A) is:

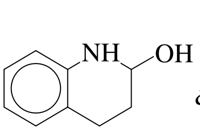
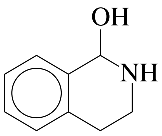
(1) $CH_3—C≡CH$ (2) $HC≡CH$
(3) $CH_3—C≡C—CH_3$ (4) $Ph—CH=CH_2$

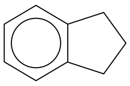
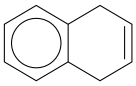
EXERCISE 2

1.  $\xrightarrow[\text{(2) } H^+, D \quad \text{(3) } LiAlH_4]{\text{(1) } NH_2OH}$ (A) + (B). Product (A) & (B) are:

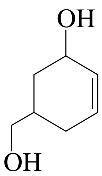
(1)  & 

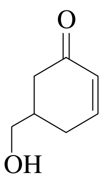
(2)  & 

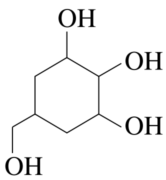
(3)  & 

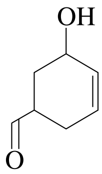
(4)  & 

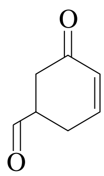
2. Give the major product of the following reaction–

 $\xrightarrow{MnO_2}$ Major product

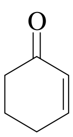
(1) 

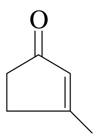
(2) 

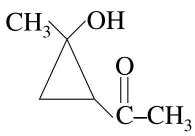
(3) 

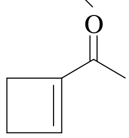
(4) 

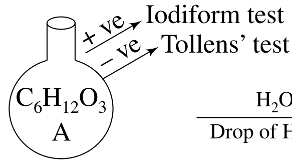
3. $CH_3\text{–}\overset{\overset{\large O}{\|}}{C}\text{–}CH_2\text{–}CH_2\text{–}\overset{\overset{\large O}{\|}}{C}\text{–}CH_3 \xrightarrow[\text{(ii) } \Delta]{\text{(i) dil. NaOH}}$ Major product will be–

(1) 

(2) 

(3) 

(4) 

4. 

$\xrightarrow[\text{Drop of } H_2SO_4]{H_2O}$ Positive Tollens' test

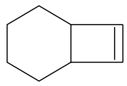
Compound (A is):

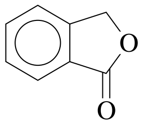
(1) $CH_3\text{—}\overset{\overset{\large O}{\|}}{C}\text{—}\underset{OCH_3}{CH}\text{—}\underset{OCH_3}{CH_2}$

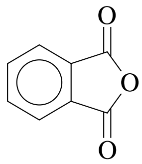
(2) $CH_3\text{—}\overset{\overset{\large O}{\|}}{C}\text{—}\overset{OCH_3}{\underset{OCH_3}{C}}\text{—}CH_3$

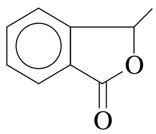
(3) $CH_3\text{—}\overset{\overset{\large O}{\|}}{C}\text{—}CH_2\text{—}\underset{OCH_3}{CH}\text{—}OCH_3$

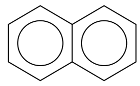
(4) $CH_3\text{—}\overset{\overset{\large O}{\|}}{C}\text{—}CH_2\text{—}CH_2\text{—}\underset{OCH_3}{CH}\text{—}OCH_3$

5.  $\xrightarrow[Zn]{O_3}$ (A) $\xrightarrow{\text{Conc. KOH}}$ (B) $\xrightarrow[\Delta]{H^+}$ (C); Product (C) is

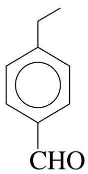
(1) 

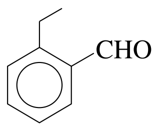
(2) 

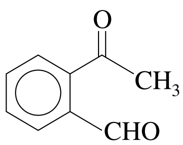
(3) 

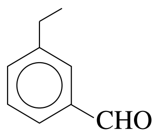
(4) 

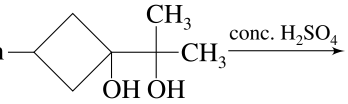
6. An organic compound with the molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction, on $KMnO_4$ oxidation it gives 1, 2-benzenedicarboxylic acid. Structure of organic compound is

(1) 

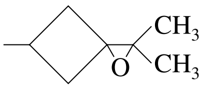
(2) 

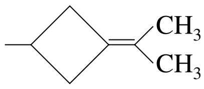
(3) 

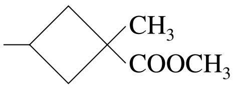
(4) 

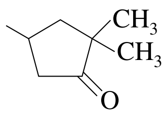
7. In the given reaction  A.

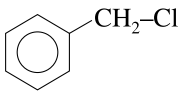
The product A is

(1) 

(2) 

(3) 

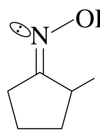
(4) 

8.  $\xrightarrow{KCN}$ (A) $\xrightarrow[\text{(i) Ph–C(=O)–H}]{\text{(i) EtO}^-/\Delta}$ (B).

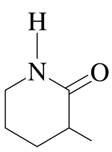
Product (B) of the reaction is

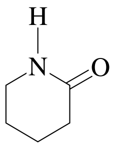
(1) $Ph–CH_2–CH=CH–Ph$ (2) $Ph–CH=\underset{CN}{\underset{|}{C}}–Ph$

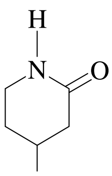
(3) $Ph–\underset{CN}{\underset{|}{C}}=CH–CH_2–Ph$ (4) $Ph–CH=\underset{CN}{\underset{|}{C}}–CH_2–Ph$

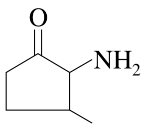
9.  $\xrightarrow{H^+}$ P
major product

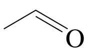
Identify the structure of 'P'

(1) 

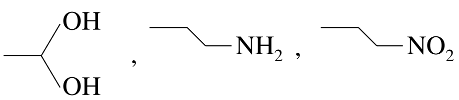
(2) 

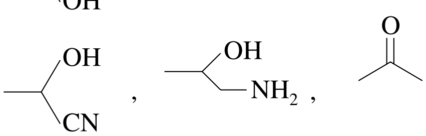
(3) 

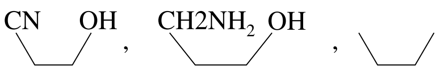
(4) 

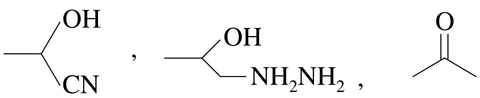
10.  $\xrightarrow[H^+]{KCN}$ (A) $\xrightarrow{LiAlH_4}$ (B) $\xrightarrow{HNO_2}$ (C)

The products A, B and C, respectively, are:

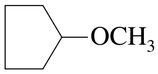
(1) 

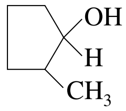
(2) 

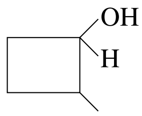
(3) 

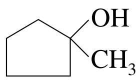
(4) 

11. An organic compound A (molecular formula $C_6H_{12}O$) does not change the colour of acidic dichromate solution. Compound A on treatment with H_2SO_4 produces alkene, which on oxidative ozonolysis gives a molecule ($C_6H_{10}O_3$) which gives positive iodoform test. Find the structure of A

(1) 

(2) 

(3) 

(4) 

12. Acetaldehyde on being heated with malonic acid in the presence of pyridine produces

(1) $CH_3CH=C(COOH)_2$

(2) CH_3COOH

(3) $CH_3CH=CHCOOH$

(4) $HOOCCH_2\underset{CH_3}{\underset{|}{C}}HCH_2COOH$

13. $CH_3—\overset{O}{\overset{\|}{C}}—H \xrightarrow{HCN} (A) \xrightarrow{H_3O^{\oplus}} (B) \xrightarrow[\Delta]{} (C) \xrightarrow{LiAlH_4} (D)$

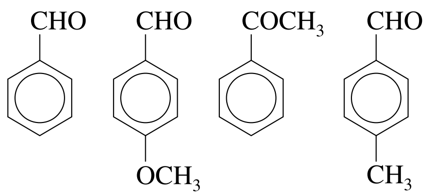
$\xrightarrow{HIO_4} HCHO + (E)$

Compound (C) can show geometrical isomerism. Product (E) of the reaction will be:

(1) $CH_3—\overset{O}{\overset{\|}{C}}—CH_3$ (2) $CH_3—CH_2—\overset{O}{\overset{\|}{C}}—H$

(3) $CH_3—CHO$ (4) HCHO

14. Arrange the following carbonyl compounds in decreasing order of their reactivity in nucleophilic addition reaction.



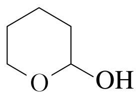
(i) (ii) (iii) (iv)

(1) ii > iii > i > iv (2) ii > i > iv > iii

(3) iii > ii > i > iv (4) i > iv > ii > iii

15. Which of the following compounds will not give positive Tollens' test?

(1) CH_3CHO

(2) 

(3) $CH_3CH_2CH_2CH_2CH(OH)–OCH_3$

(4) $CH_3–CH(OCH_3)_2$

16. The compound A gives following reactions:

$A(C_6H_8O_2) \xrightarrow{\text{Na metal}} H_2 \text{ gas} \uparrow$

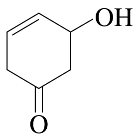
$A(C_6H_8O_2) \xrightarrow{\text{2, 4-DNP}} \text{yellow orange ppt}$

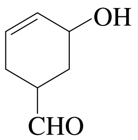
$A(C_6H_8O_2) \xrightarrow{O_3} B(C_6H_8O_4)$

Its structure can be:

(1) $CH_2=CH–(CH_2)_2–C(=O)–CH_2OH$

(2) $OHC–(H_2C_2)_2–HC–COOH$

(3) 

(4) 

17. Consider the following reactions:

I. $CH_3CHO \xrightarrow[H^+]{[Ag(NH_3)_2]^+,\ OH^-}$

II. $CH_3CCl_3 \xrightarrow{OH^-}$

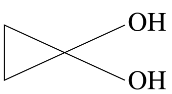
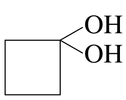
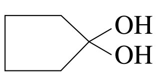
III. $CH_3C(=O)OC_2H_5 \xrightarrow{OH^-}$

The final product is acid in:

(1) I, II, III (2) I, III

(3) I, II (4) I

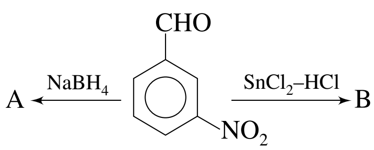
18. Arrange their stabilities of given gem-diols in decreasing order.

(I)  (II)  (III) 

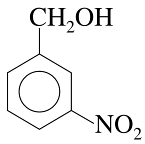
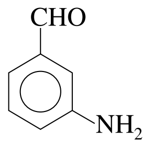
(1) I > II > III (2) III > II > I

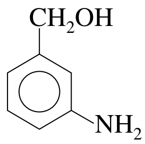
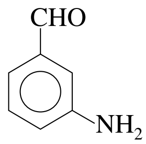
(3) I > III > II (4) III > I > II

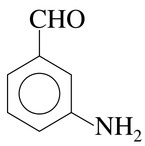
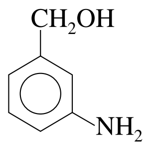
19. Consider the following two reactions:

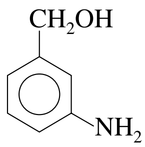
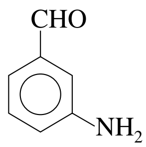


The two major products (A) and (B) are, respectively:

(1)  and 

(2)  and 

(3)  and 

(4)  and 

20. Consider the following sequence of reactions

$ClCH_2COCH_2Cl \xrightarrow{HCN} A \xrightarrow{KCN(\text{excess})} B \xrightarrow{H_3O^+} C$

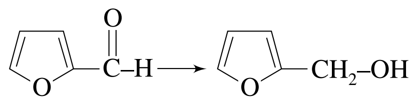
The end product (C) is

(1) $CNCH_2C(OH)(COOH)CH_2CN$

(2) $HOOCCH_2C(OH)(COOH)CH_2COOH$

(3) $CNCH_2COCH_2CN$

(4) $HOOCCH_2COCH_2COOH$

21. 

Identify the reagents that can perform this conversion successfully

(I) H_2, Raney Ni, Δ (II) HI/P_4

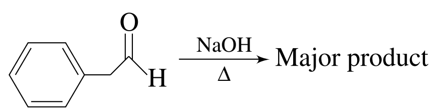
(III) $NaBH_4$, H_2O (IV) $H–C(=O)–H$, $\overset{\ominus}{O}H$

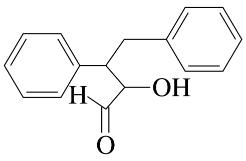
Select the correct code

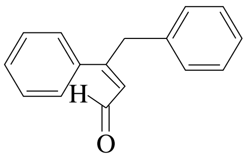
(1) I and II (2) II and III

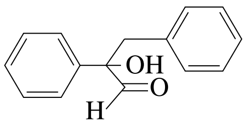
(3) III and IV (4) II and IV

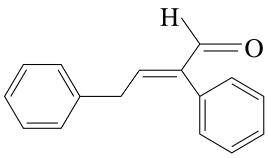
22. Give the major product of the following reaction:

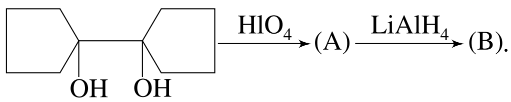


(1) 

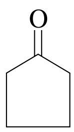
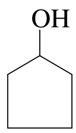
(2) 

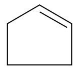
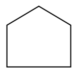
(3) 

(4) 

23. 

Product (B) is

(1)  (2) 

(3)  (4) 

24. In which of the following reactions, an aldehyde is not formed as major product?

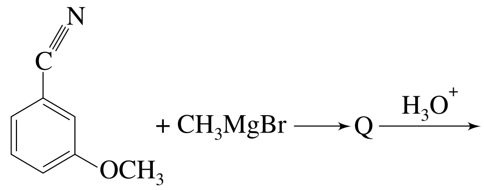
(1) $CH_3—C{\equiv}CH + (CH_3—CH(CH_3)—CH(CH_3))_2BH \xrightarrow[NaOH]{H_2O_2}$

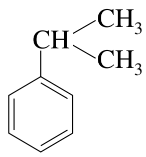
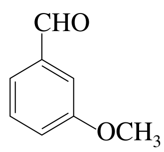
(2) $CH_3—CH_2—C{\equiv}CH + KMnO_4 \xrightarrow[Cold]{H_2O}$

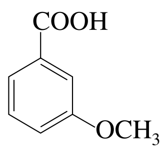
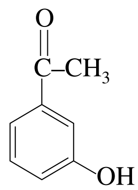
(3) $CH_3—CH_2CH_2CH_2—OH + Cu \xrightarrow{\Delta}$

(4) $CH_3—CH_2CH_2CH_2—COOH + HCOOH \xrightarrow[Heat]{MnO}$

25. The product P in the reaction:



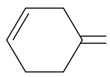
(1)  (2) 

(3)  (4) 

EXERCISE 3

One and More Than One Option Correct Type Question

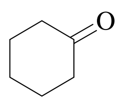
1. Consider the reaction given below:

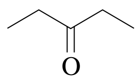
 $=O + NaHSO_3(aq) \longrightarrow$

The correct observation regarding the above reaction is/are:

(1) Precipitate formation takes place
(2) Racemic mixture of salts are formed
(3) Salts on acid hydrolysis give back the original reactant
(4) If $NaHSO_3$ is in limited amount, no precipitation occurs

2. Which of the following form enamine on heating with a secondary amine in weakly acidic medium?

(1) $CH_3—C(CH_3)_2—CHO$ (2) 

(3)  (4) $C_6H_5CH_2–CH{=}O$

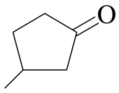
3. In the Cannizzaro reaction mentioned below

$$H—\overset{\overset{\large O}{\|}}{C}—H + NaOD \xrightarrow{D_2O} \xrightarrow{H_3O^+}$$

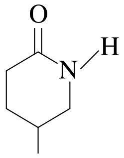
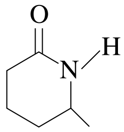
the possible product(s) is/are

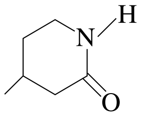
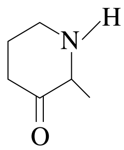
(1) CH_3OH (2) CH_3OD
(3) $HCOOD$ (4) H_2CDOH

4. In the reaction given below

 + H_2N—OH $\xrightarrow{H^{\oplus}}$

expected product(s) is/are

(1)  (2) 

(3)  (4) 

5. Consider the reaction sequence give below.

$$H_3C—CH_2Cl \xrightarrow[\text{(ii) } C_4H_9Li]{\text{(i) } Ph_3P} X \xrightarrow{CH_3CHO} Y$$

The correct statements regarding the above reaction is/are:

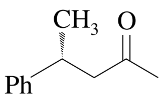
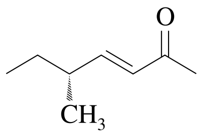
(1) X is CH_3—CH=PPh_3

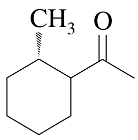
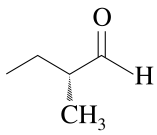
(2) Y is CH_3—CH=CH—CH_3

(3) Y is CH_3—CH_2—CH=CH_2

(4) Y is a mixture of diastereomers

6. The carbonyl compound(s) that will undergo racemisation on treatment with aqueous KOH is (are):

(1)  (2) 

(3)  (4) 

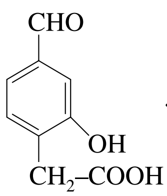
7. Which of the following are correct statements?

(1) Acetophenone does not give a red colour precipitate with Fehling's solution

(2) Benzaldehyde gives a red coloured precipitate with Fehling's solution

(3) Benzaldehyde gives silver mirror with Tollens' reagent

(4) Benzaldehyde gives a black grey precipitate with mercuric chloride solution

8. An organic compound has the structure  .

It will give

(1) ceric ammonium nitrate test

(2) give brisk effervescence with sodium bicarbonate

(3) it will give a characteristic colouration with neutral ferric chloride after decarboxylation and reduction by Clemmensen's method

(4) It will give silver mirror test

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

9. **Statement-I:** Fehling solution can oxidise aliphatic aldehyde but cannot oxidise aromatic aldehyde.

Statement-II: Tollens' reagent can oxidise aliphatic and aromatic aldehyde both.

10. **Statement I:** When a mixture of ethanal and propanal is treated with aqueous Na_2CO_3, four aldol (excluding stereoisomers) compounds are formed.

Statement-II: In mixed aldol condensation, two self and two cross condensation products are always formed.

11. **Statement-I:** Consider the reaction given below,

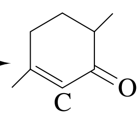
$$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3 + H_2N—\overset{\overset{\displaystyle O}{\|}}{C}—NH\cdot HNCH_3 \longrightarrow$$

$$CH_3—\underset{\underset{\displaystyle CH_3}{|}}{C}=N—\overset{\overset{\displaystyle O}{\|}}{C}—NH.HNCH_3$$

Statement-II: Aldehydes and ketones react with semicarbazide to form semicarbazone.

Comprehension Type Question

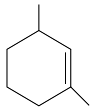
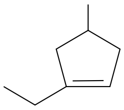
Passage Based Questions (Q. 12–14)

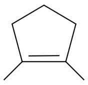
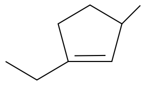
$A(C_8H_{14}) \xrightarrow[(CH_3)S]{O_3} B(C_8H_{14}O_2) \xrightarrow{\text{Dil.NaOH}}$ 

C

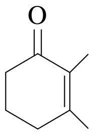
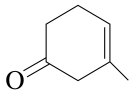
A is optically active and C is one of the several aldol possible in the above reaction.

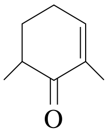
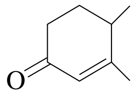
12. The structure of A satisfying above criteria is

(1) 
(2) 

(3) 
(4) 

13. Besides C, the other six membered cyclic aldol formed in the above reaction is

(1) 
(2) 

(3) 
(4) 

14. The product B is stereomeric. If a mixture containing all stereoisomers of B is treated with excess of $LiAlH_4$ followed by the acidification will give how many different isomeric diols?

(1) 2
(2) 4
(3) 6
(4) 8

Column Matching Type Question

15.

Column-I	**Column-II**
(A) –COOH	(p) Tollens' reagent
(B) –CHO	(q) Sodium bisulphite
(C) $CH_3–\overset{\overset{O}{\|\|}}{C}–$	(r) Sodium bicarbonate
(D) $–\overset{\overset{O}{\|\|}}{C}–$	(s) Sodium hypo iodite
(E) $–COOCH_3$	(t) Sodium hydroxide

(1) A→r; B→p; C→s; D→q; E→t
(2) A→p; B→s; C→t; D→q; E→r
(3) A→s; B→q; C→p; D→r; E→t
(4) A→q; B→t; C→s; D→p; E→r

Sol. **[1]**

16.

Column-(I)	**Column-(II)**
(a) PhMgBr + $Cl–NH_2$	(P) Ph–CN
(b) PhMgBr + Cl–CN	(Q) $Ph–NH_2$
(c) PhMgBr + $H_3C–\overset{\overset{O}{\|\|}}{C}–Cl$	(R) $Ph–\overset{\overset{O}{\|\|}}{C}–CH_2CH_3$
(d) PhMgBr + $CH_3–\overset{\overset{O}{\|\|}}{C}–OC_2H_5$	(S) $Ph–\overset{\overset{O}{\|\|}}{C}–CH_3$

(1) a→Q; b→P; c→S; d→R
(2) a→Q; b→P; c→R; d→S
(3) a→P; b→Q; c→R; d→S
(4) a→Q; b→P; c→R; d→S

Sol. **[1]**

$$Ph–Mg – Br + Cl–NH_2 \longrightarrow Ph – NH_2$$

$$Ph–Mg–Br + Cl–C{\equiv}N \longrightarrow Ph–CN$$

$$Ph–Mg–Br + CH_3–\underset{\underset{O}{\|\|}}{C}–Cl \longrightarrow Ph–\underset{\underset{O}{\|\|}}{C}–CH_3$$

$$Ph–Mg–Br + C_2H_5–\overset{\overset{O}{\|\|}}{C}–O–C_2H_5 \longrightarrow Ph–\overset{\overset{O}{\|\|}}{C}–C_2H_5$$

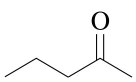
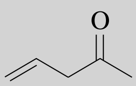
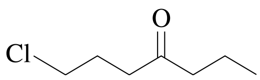
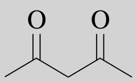
17. Match the compounds given in List-I with those in List-II and select the suitable option using the code given blow:

	List-I		**List-II**
(a)	Benzaldehyde	(i)	Phenolphthalein
(b)	Phthalic anhydride	(ii)	Benzoin condensation
(c)	Phenyl benzoate	(iii)	Oil of wintergreen
(d)	Methyl salicylate	(iv)	Fries rearrangement

Code:

	a	**b**	**c**	**d**
(1)	(ii)	(i)	(iv)	(ii)
(2)	(iv)	(i)	(iii)	(ii)
(3)	(iv)	(ii)	(iii)	(i)
(4)	(ii)	(iii)	(iv)	(i)

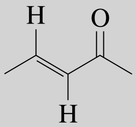
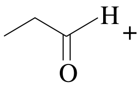
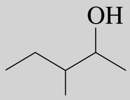
18. Match the reactants from Column I with the reagents and expected outcomes from Column II. Mark the correct option form the codes given below.

	Column I		**Column II**
i.		p.	$LiAlH_4$-racemic mixture of products.
ii.		q.	$[(CH_3)_2CHO]_3$ Al-racemic mixture of products.
iii.		r.	Zn(Hg)–HCl- suitable for selective reduction of carbonyl group
iv.		s.	N_2H_4/NaOH/Heat- suitable for selective reduction of carbonyl group.

Codes:

	i	ii	iii	iv
(1)	p, q, r, s	p, q, s	q, r	p, q, r, s
(2)	p, r	q, r	s	r, r
(3)	q, r	r, s	p, s	s
(4)	p, r	q	r, s	s

19. Match the reaction from Column I with the properties of products from Column II. Mark the correct option form the codes given below.

	Column I		Column II
i.	$\underset{\text{CHO}}{\overset{\text{CHO}}{\vert}}$ + HCN $\xrightarrow{+\text{NaCN}}$ Excess	p.	Racemic mixture
ii.	 + $NaHSO_3$(aq.) ⟶	q.	Pair of diastereomers
iii.	 + CH_3MgBr ⟶ $\xrightarrow{H_3O^+}$	r.	Meso isomer
iv.	 $\xrightarrow[H^+]{K_2Cr_2O_7}$ $\xrightarrow{NaBH_4}$ $\xrightarrow{H_3O^+}$ (+) 3-methyl-2pentanol	s.	Product mixture can be separated into two fractions by chromatography

Codes

	i	ii	iii	iv
(1)	p, q, r, s	q, s	p	q, s
(2)	q, s	p, s	p, q	r, q
(3)	p, q	q	r, q	s
(4)	p, q, r	r, s	r	p

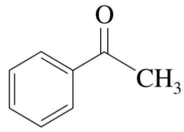
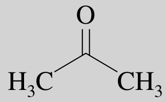
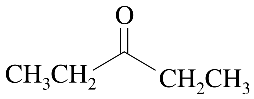
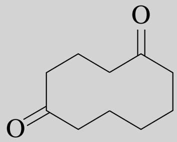
20. Match the reactions of Column I with the type of reactions from Column II. Mark the correct option form the codes given below.

	Column I		Column II
i.	$CH_3CHO + CH_2O$ (excess) $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc. NaOH}}$	p.	Aldol condensation
ii.	F—CHO + Conc. NaOH $\xrightarrow{H_3O^+}$	q.	Cannizzaro reaction
iii.	$(CH_3)_2CH$—CHO $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc. NaOH}}$	r.	Claisen reaction
iv.	$CH_3CHO + C_6H_5CHO$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Conc. NaOH}}$	s.	Tischenko reaction

Codes:

	i	ii	iii	iv
(1)	p, q	s	r	p
(2)	p, q	q	p, q	p, q, r
(3)	p	q	r	s
(4)	p	q	r	s

21. Match the Column I with Column II and mark the correct option form the codes given below.

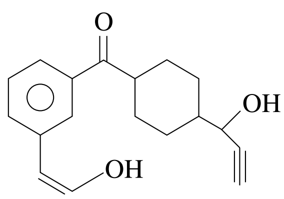
	Column I		Column II
i.		p.	Gives just one aldol only
ii.		q.	Gives yellow precipitate with I_2/NaOH
iii.		r.	Produces isomeric oximes with $HONH_2$
iv.		s.	more than 4 u in molar mass on treatment with NaOD/D_2O
		t.	Gives more than one aldol.

Codes:

	i	ii	iii	iv
(1)	p, q	q	r, t	s, t
(2)	q, r, t	p, q, s	t	r, s, t
(3)	t, r, q	p, q, s	p, r	q
(4)	q, s, t	p, r	r, s, q	s, r, t

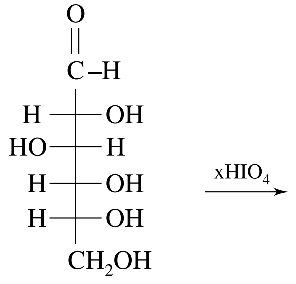
Single Digit Integer Type Question

22. How many reagents (i to viii) are successively reacted with the following it compound



(i) $NaHCO_3$	(ii) 2, 4, DNP
(iii) Na metal	(iv) $AgNO_3$ + OH
(v) Fehling's solution	(vi) Cu_2Cl_2 + HCl
(vii) Br_2/H_2O	(viii) $NaNO_2$ + HCl

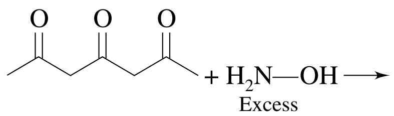
23. How many moles of HIO_4 are consumed by given compound when it reacts with HIO_4?



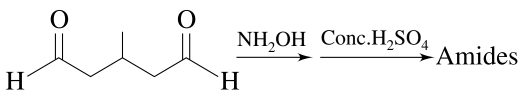
(D-Glucose)

24. How many different alcohol isomers with molecular formula $C_5H_{12}O$ can be oxidised to ketones using $K_2Cr_2O_7$–H_2SO_4?

25. In the following reaction, how many isomers of tri-oximes are formed?

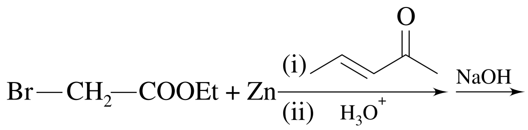


26. In the reaction



How many different amides are expected?

27. Consider the following two step synthesis:



A cyclic diketone X

If x is finally treated with excess of $NaBH_4$ followed by acid work-up, how many different isomers of diols would be formed?

28. In reaction of $C_6H_5COCH_3$ with KOH-I_2 to form iodoform, how many moles of KOH are consumed per mole of ketone?

29. In the reaction given below, how many different oximes would be formed?

$$CH_3CH{=}CH—\overset{\overset{\displaystyle O}{\|}}{C}—CH{=}CHCH_3 + H_2NOH \rightarrow \text{Oximes}$$

30. If all the aldehyde isomers of $C_5H_{10}O$ is independently treated with HCN/NaCN solution, how many of them will of them will give racemic mixture of cyanohydrin?

EXERCISE 4

1. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? **[AIEEE-2004]**

(1) Phenol (2) Benzaldehyde
(3) Butanal (4) Benzoic acid

2. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is **[AIEEE-2005]**

(1) Acidic dichromate
(2) Acidic permanganate
(3) Pyridinium chloro-chromate
(4) Chromic anhydride in glacial acetic acid

3. The increasing order of the rate of HCN addition to compounds A–D is **[AIEEE-2006]**

(a) HCHO (b) CH_3COCH_3
(c) $PhCOCH_3$ (d) $PhCOC_6H_5$
(1) d < b < c < a (2) d < c < b < a
(3) c < d < b < a (4) a < b < c < d

4. Which of the following on heating with aqueous KOH produces acetaldehyde? **[AIEEE-2009]**

(1) CH_3COCl (2) CH_3CH_2Cl
(3) CH_2ClCH_2Cl (4) CH_3CHCl_2

5. Among the following the order of reactivity toward nucleophilic addition is **[JEE-Main Online-2012]**

(1) HCHO > CH_3CHO > CH_3COCH_3
(2) CH_3CHO > HCHO > CH_3COCH_3
(3) CH_3CHO > CH_3COCH_3 > CH_3COCH_3
(4) CH_3COCH_3 > CH_3CHO > HCHO

6. The reaction **[JEE-Main Online-2012]**

$$CH_3CHO \xrightarrow[\text{Zn(Hg/Conc. HCl)}]{[H]} CH_3CH_3 \text{ is:}$$

(1) Cannizzaro reaction
(2) Wolf–Kishner reduction
(3) Rosenmund reduction
(4) Clemmensen reduction

7. Formaldehyde can be distinguished from acetaldehyde by the use of **[JEE-Main Online-2013]**

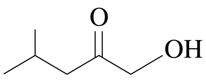
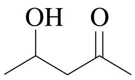
(1) Schiff's reagent (2) Tollens' reagent
(3) I_2/Alkali (4) Fehling's solution

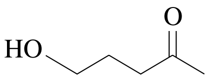
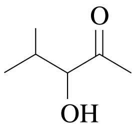
8. Clemmensen reduction of a ketone is carried out in the presence of:– **[JEE-Main Online-2013]**

(1) $LiAlH_4$
(2) Zn–Hg with HCl

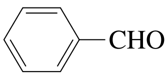
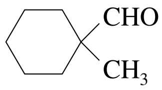
(3) Glycol with KOH
(4) H_2 with Pt as catalyst

9. Which of the following is the product of aldol condensation? **[JEE-Main Online-2013]**

(1)  (2) 

(3)  (4) 

10. Cannizzaro reaction is not given by– **[JEE-Main Online-2013]**

(1)  (2) 

(3) CH_3CHO (4) HCHO

11. Which is the major product formed when acetone is heated with iodine and potassium hydroxide? **[JEE-Main Online-2014]**

(1) Iodoacetone (2) Acetic acid
(3) Iodoform (4) Acetophenone

12. Tishchenko reaction is a modification of: **[JEE-Main Online-2014]**

(1) Aldol
(2) Claisen condensation
(3) Cannizzaro reaction
(4) Pinacol–pinacolone reaction

13. In the following sequence of reactions **[JEE-Main-2015]**

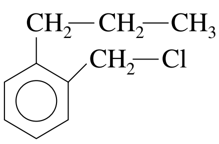
$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C,$$

The product C is:

(1) C_6H_5COOH (2) $C_6H_5CH_3$
(3) $C_6H_5CH_2OH$ (4) C_6H_5CHO

14. A compound A with molecular formula $C_{10}H_{13}Cl$ gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizzaro reaction but not aldol condensation. D gives aldol condensation but not Cannizzaro reaction. A is: **[JEE-Main Online-2015]**

(1) $CH–CH_2–CH_2–\underset{|}{\underset{Cl}{CH}}–CH_3$

(2) 

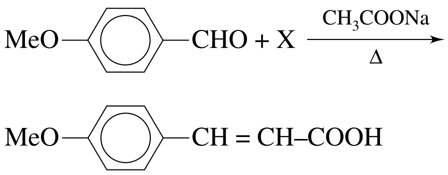
(3) $C_6H_5–CH_2–CH_2–CH_2–CH_2–Cl$

(4) $C_6H_5–CH_2–\underset{|}{\underset{Cl}{C}}(CH_3)_2$

15. In the reaction sequence **[JEE-Main Online-2015]**

$2\ CH_3CHO \xrightarrow{OH^-} A \xrightarrow{\Delta} B$, the product B is

(1) $CH_3–\overset{\overset{O}{||}}{C}–CH_3$
(2) $CH_3–CH_2–CH_2–CH_3$
(3) $CH_3–CH=CH–CHO$
(4) $CH_3–CH_2–CH_2–CH_2–OH$

16.  **[IIT-2005]**

The X in the given reaction is

(1) CH_3COOH (2) $BrCH_2–COOH$
(3) $\underset{\underset{CHO}{|}}{COOH}(CH_3CO)_2O$ (4) $(CH_3CO)_2O$

17. How will you convert butan-2-one to propanoic acid? **[IIT-2005]**

(1) Tollens' reagent (2) Fehling's solution
(3) $NaOH/I_2/H^+$ (4) $NaOH/NaI/H^+$

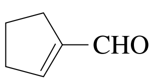
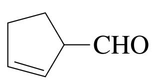
18. Butan-2-one can be converted to propanoic acid by which of the following? **(2006, Only One Option Correct Type)**

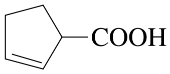
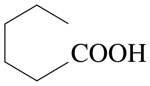
(1) NaOH, NaI/H^+ (2) Fehling's solution
(3) NaOH, I_2/H^+ (4) Tollens' reagent

19. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime **(2006, Only One Option Correct Type)**

(1) Two different oximes are formed
(2) Three different oximes are formed
(3) Two oximes are optically active
(4) All oximes are optically active

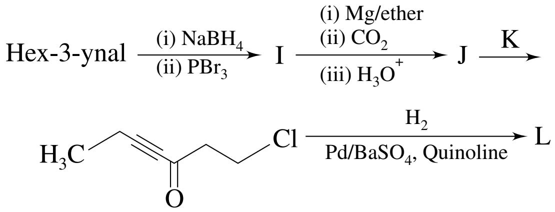
20. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is **(2007, Only One Option Correct Type)**

(1)  (2) 

(3)  (4) 

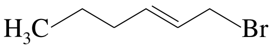
Passage Based Questions: (Q. 21–23)

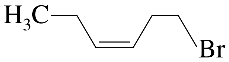
In the following sequence, product I, J and L are formed. K represents a reagent.

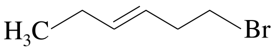


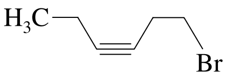
(2008 Comprehension Type)

21. The structure of the product I is

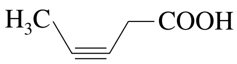
(1) 

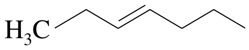
(2) 

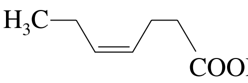
(3) 

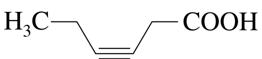
(4) 

22. The structure of compounds J and K, respectively, are

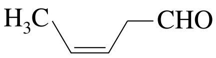
(1)  and $SOCl_2$

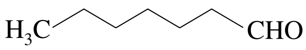
(2)  and $SOCl_2$

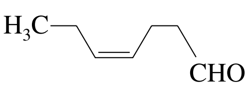
(3)  and SO_2Cl_2

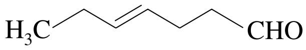
(4)  and CH_3SO_2Cl

23. The structure of product L is

(1) 

(2) 

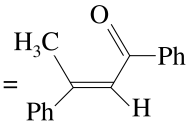
(3) 

(4) 

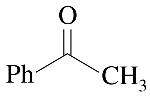
Passage Based Questions: (Q. 24 and 25)

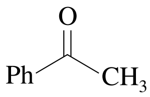
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on react ion with KOH gives only M.

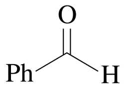
(2008 Comprehension Type)

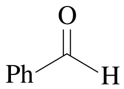
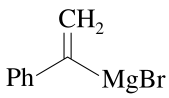
M = 

24. Compound H is formed by the react ion of

(1)  ; PhMgBr

(2)  ; $PhCH_2MgBr$

(3)  ; $PhCH_2MgBr$

(4)  ; 

25. The structures of compounds J, K and L, respectively, are

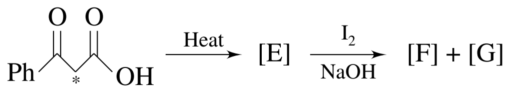
(1) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$

(2) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$

(3) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

(4) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

26. In the following reaction sequence, the correct structures of E, F and G are **[IIT-2008]**



(* implies ^{13}C labeled carbon)

	E	F	G

(1)  CHI_3

(2)  CHI_3

(3)  CHI_3

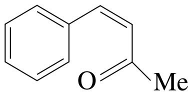
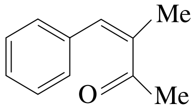
(4)  $\overset{*}{C}H_3I$

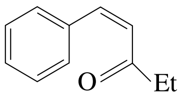
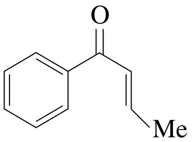
Passage Based Questions: (Q. 27–29)

A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to a dicarbonyl compound R, which undergoes intramolecular aldol reaction to give predominantly S. **(2009 Comprehension Type)**

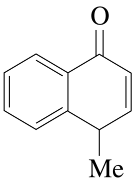
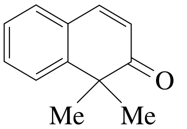
$$P \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4/\text{Heat}}]{1.\ \text{MeMgBr}} Q \xrightarrow{O_3/\text{Zn-}H_2O} R \xrightarrow[\text{Heat}]{OH^-} S$$

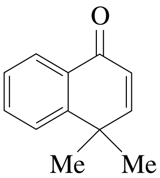
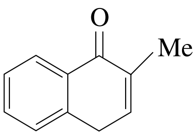
27. The structure of the carbonyl compound P, is

(1) 
(2) 

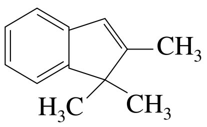
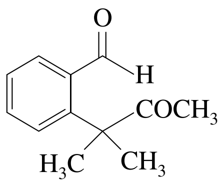
(3) 
(4) 

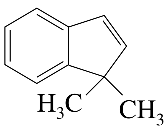
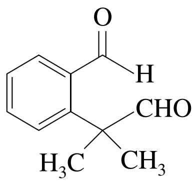
28. The structure of the product S, is

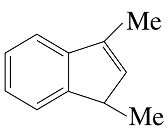
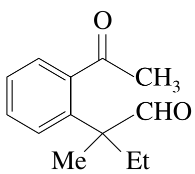
(1) 
(2) 

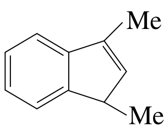
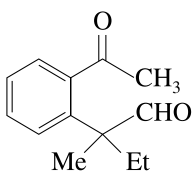
(3) 
(4) 

29. The structures of the products Q and R, respectively, are

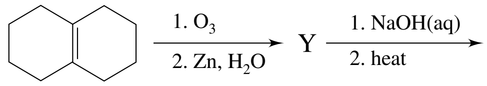
(1)  

(2)  

(3)  

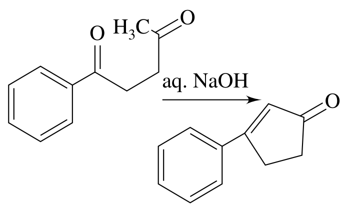
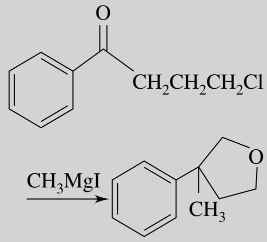
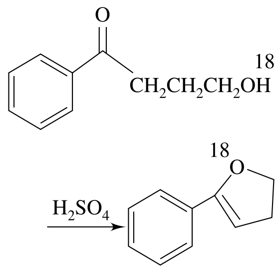
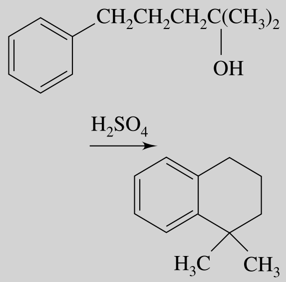
(4)  

30. In the scheme given below, the total number of intra-molecular aldol condensation products form (Y) is **[IIT-2010]**



(1) 1 (2) 2
(3) 3 (4) 4

31. Match the reactions in column I with appropriate type of steps/reactive intermediate involved in these reactions as given in column II and give a correct answer **[IIT-2011]**

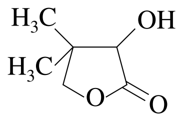
	Column-I		Column-II
(A)		(p)	Nucleophilic substitution
(B)		(q)	Electrophilic Substitution
(C)		(r)	Dehydration
(D)		(s)	Nucleophilic addition
		(t)	Carbanion

(1) A → r, t, s; B → p, s, t; C → r, s; D → r, q
(2) A → r, t, s; B → r, s; C → p, s; D → r, s
(3) A → p, s, t; B → r, s, t; C → r, s; D → q, r
(4) A → q, r, ; B → p, s, t; C → q, t; D → r, s

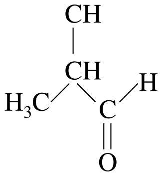
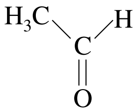
Passage Based Questions: (Q. 32–34)

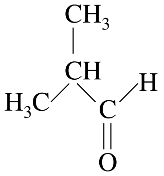
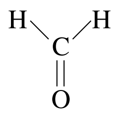
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below.

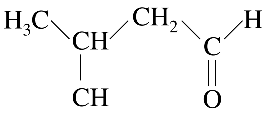
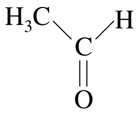
(2012 Comprehension Type)

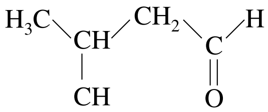
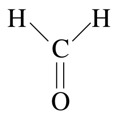


32. The compounds P and Q, respectively, are

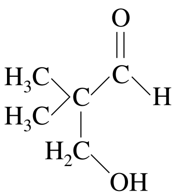
(1)  and 

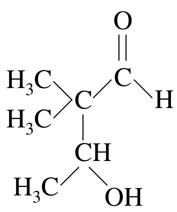
(2)  and 

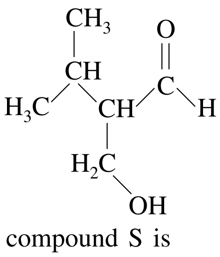
(3)  and 

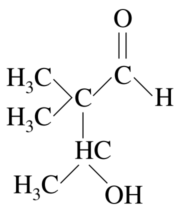
(4)  and 

33. The compound R is

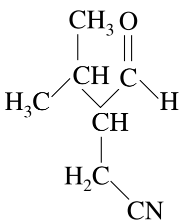
(1) 

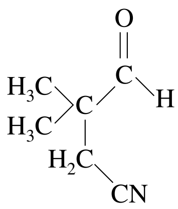
(2) 

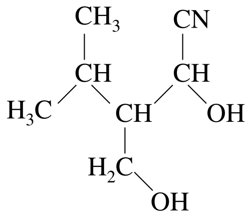
(3) 

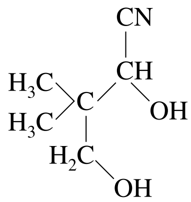
(4) 

34. The compound S is

(1) 

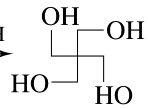
(2) 

(3) 

(4) 

35. The number of aldol reaction (s) that occurs in the given transformation is

(2012 Only One Option Correct Type)

$CH_3CHO + 4HCHO \xrightarrow{\text{Conc. aq. NaOH}}$ 

(1) 1 (2) 2

(3) 3 (4) 4

36. The major product H in the given reaction sequence is

(2012 Only One Option Correct Type)

$CH_3-CH_2-CO-CH_3 \xrightarrow{^{-}CN} G \xrightarrow{95\%\ H_2SO_4} H$

(1) $CH_3-CH{=}\underset{CH_3}{\underset{|}{C}}-COOH$

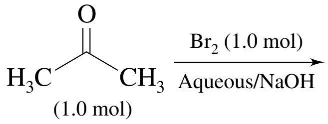
(2) $CH_3-CH{=}\underset{CH_3}{\underset{|}{C}}-CN$

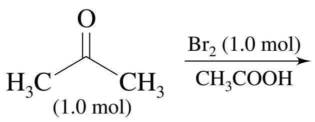
(3) $CH_3-CH_2-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COOH$

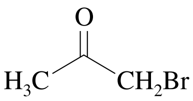
(4) $CH_3-CH{=}\underset{CH_3}{\underset{|}{C}}-CO-NH_2$

37. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

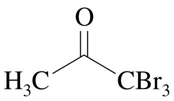
(JEE Adv.-2013)

Reaction-I: 

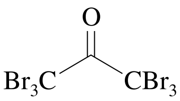
Reaction-II: 



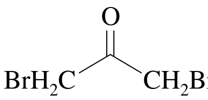
(P)



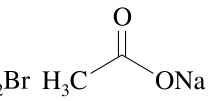
(Q)



(R)



(S)



(T)

$CHBr_3$

(U)

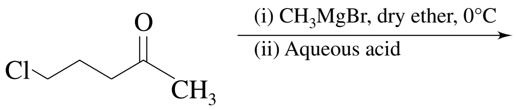
(1) Reaction I: P and Reaction II : P
(2) Reaction I: U, acetone and Reaction II: Q, acetone
(3) Reaction I: T, U, acetone and Reaction II: P
(4) Reaction I: R, acetone and Reaction II: S, acetone

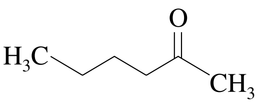
38. Consider all possible isomeric ketones including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$. The total number of ketones that give a racemic product(s) is/are

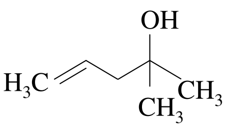
(2014 Adv., Integer Type)

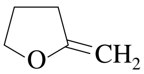
39. The major product in the following reaction is

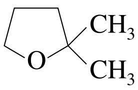
(2014 Adv., Only One Option Correct Type)



(1) 

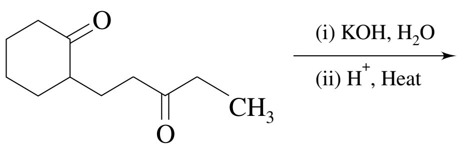
(2) 

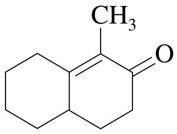
(3) 

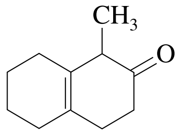
(4) 

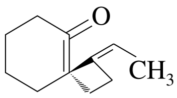
40. The major product of the following reaction is

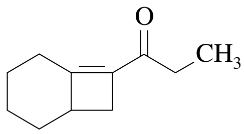
(2014 Adv., Only One Option Correct Type)



(1) 

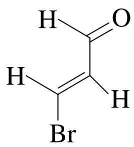
(2) 

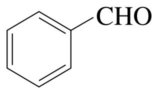
(3) 

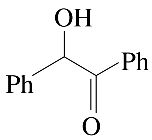
(4) 

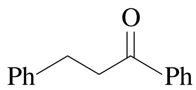
41. Positive Tollens' test is observed for

[IIT Adv.-2016]

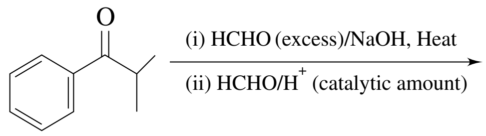
(1) 

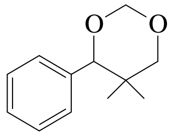
(2) 

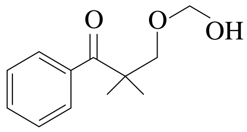
(3) 

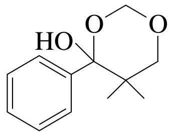
(4) 

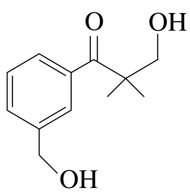
42. The major product of the following reaction sequence is **[IIT Adv.-2016]**



(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

1. (1)	2. (4)	3. (4)	4. (1)	5. (2)
6. (3)	7. (1)	8. (2)	9. (4)	10. (2)
11. (1)	12. (1)	13. (4)	14. (3)	15. (2)
16. (4)	17. (3)	18. (4)	19. (1)	20. (2)
21. (3)	22. (2)	23. (1)	24. (2)	25. (2)
26. (3)	27. (3)	28. (2)	29. (1)	30. (2)
31. (1)	32. (2)	33. (3)	34. (3)	35. (3)

EXERCISE # 2

1. (1)	2. (1)	3. (2)	4. (3)	5. (1)
6. (2)	7. (4)	8. (2)	9. (1)	10. (2)
11. (4)	12. (3)	13. (3)	14. (4)	15. (4)
16. (3)	17. (4)	18. (1)	19. (1)	20. (2)
21. (3)	22. (4)	23. (2)	24. (2)	25. (4)

EXERCISE # 3

1. (1,2,3,4)	2. (2,3,4)	3. (1,2,3)	4. (1,3)	5. (1,2,4)
6. (2,4)	7. (1,3,4)	8. (2,3,4)	9. (2)	10. (3)
11. (4)	12. (3)	13. (4)	14. (4)	15. (1)
16. (2)	17. (1)	18. (1)	19. (1)	20. (2)
21. (2)	22. (6)	23. (5)	24. (5)	25. (6)
26. (4)	27. (4)	28. (4)	29. (6)	30. (3)

EXERCISE # 4

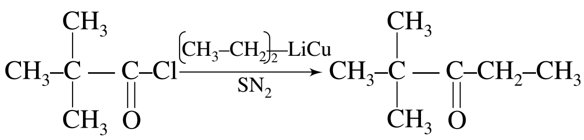
1. (2)	2. (4)	3. (2)	4. (4)	5. (1)
6. (4)	7. (3)	8. (2)	9. (2)	10. (3)
11. (3)	12. (3)	13. (4)	14. (3)	15. (3)
16. (4)	17. (3)	18. (3)	19. (2)	20. (2)
21. (4)	22. (1)	23. (3)	24. (2)	25. (4)
26. (4)	27. (2)	28. (2)	29. (1)	30. (1)
31. (1)	32. (2)	33. (1)	34. (4)	35. (3)
36. (1)	37. (3)	38. (5)	39. (4)	40. (1)
41. (1,2,3)	42. (1)			

HINT AND SOLUTION

EXERCISE # 1

1. [1]

$$CH_3{-}CH_2{-}I \xrightarrow[\text{(ii) CuI}]{\text{(i) Li/Et}_2\text{O}} (CH_3{-}CH_2)_2LiCu$$



2. [4]

Rate of nucleophilic addition or HCN addition $\propto$ EWG. $\propto \dfrac{1}{\text{ERG}}$

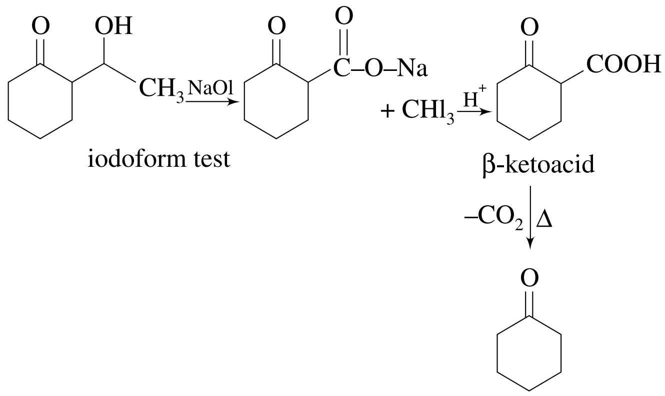
ERG $(-NMe_2)$ > ERG$(-OMe)$

3. [4]

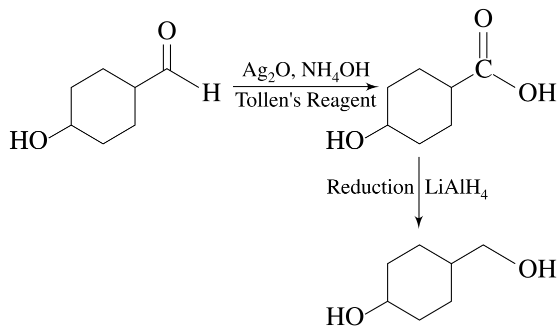
⇒ Final product has chiral C

⇒ So that equal amount of d and l isomer is present

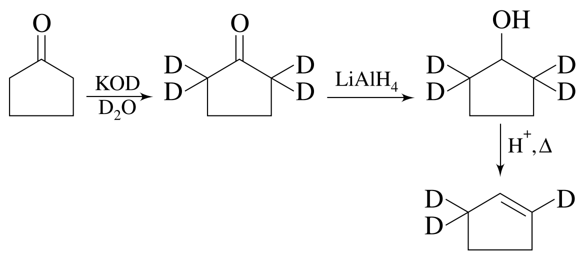
4. [1]



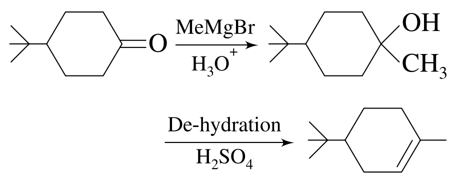
5. [2]



6. [3]

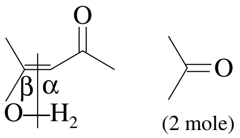


7. [1]



8. [2]

Given product is α, β unsaturated ketone so it is formed by aldol condensation reaction.



9. [4]

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{I_2/KOH} CHI_3 + RCOOK$$

R=H, alkyl, etc.

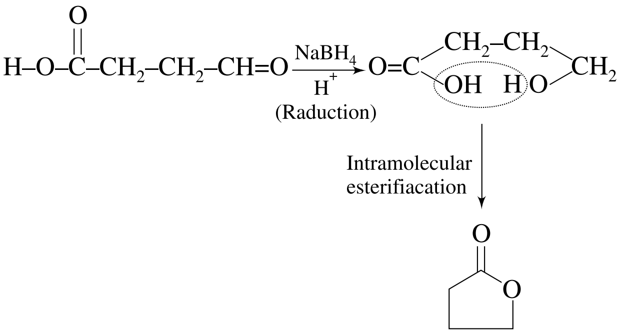
10. [2]

$$3CH_2=O \longrightarrow CH_2\begin{matrix} \diagup O-CH_2 \diagdown \\ \diagdown O-CH_2 \diagup \end{matrix}O$$

(formaldehyde) (Trioxane)

11. [1]

By using $NaBH_4$ reduction of only aldehyde group takes place.



12. [1]

$$CH_3-C\equiv N \xrightarrow[\text{Reduction}]{\text{DIBAL-H}} CH_3-CH=O \xrightarrow{SeO_2} \underset{\underset{O}{\|}}{CH}-\underset{\underset{O}{\|}}{CH}$$

Intramolecular Cannizzaro reaction $\downarrow OH^-/\Delta$

$$\underset{\underset{OH}{|}}{CH_2}-COO^-$$

13. [4]

1, 4 diol not cleaved by HIO_4

14. [3]

$$CH_3-CH=CH_2 \xrightarrow[H_2O_2]{BH_3/T.H.F} CH_3-CH_2-CH_2-OH$$

Hydration by anti-Markovnikoff rule takes place (X)

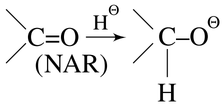
(Y) Mod $\downarrow$ CrO_3/Pyridine oxidation

$$CH_3-CH_2-CH=O$$

15. [2]

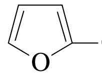
$$LiAlH_4\ (LAH) \rightarrow \overset{\oplus}{Li} + \overset{\oplus}{AlH_4} + \rightarrow AlH_3 + \overset{\oplus}{H}$$

$$NaBH_4 \rightarrow Na^+ + \overset{\ominus}{BH_4} \rightarrow BH_3 + \overset{\ominus}{H}$$

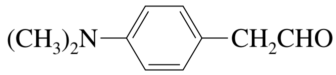


16. [4]

Compound having no α-H undergoes Cannizzaro reaction.

- C_6H_5-CHO and  CHO

no α-H undergoes Cannizzaro reaction.

- $(CH_3)_2CH-CH=O$ gives both Cannizzaro reaction and aldol condensation reaction.
- 

It have α-H so that gives only aldol condensation reaction.

17. [3]

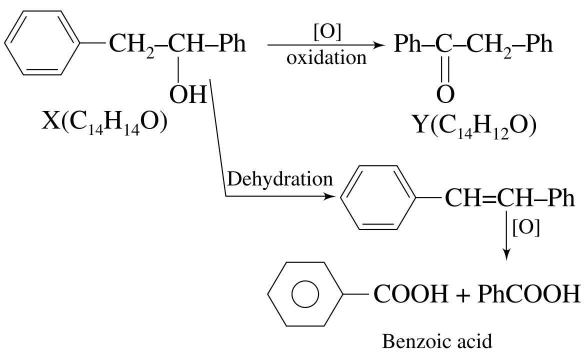
$$Ph-CH=O \xrightarrow{\text{Fehling solution}} -\text{ve test}$$

$$H-CH=O \xrightarrow{\text{Fehling solution}} +\text{ve test}$$

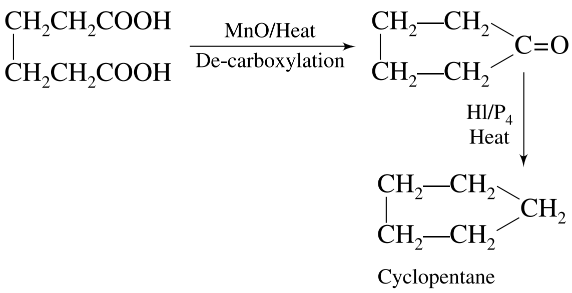
18. [4]

$$\underset{sp}{PhCN} \xrightarrow[2.\ H_2O,\ heat]{1.\ SnCl_2/HCl} \underset{sp^2}{Ph-CH=O}$$

19. [1]



20. [2]



21. [3]

(methyl ketone) Positive Iodoform Negative Tollens' reagent

(aldehyde) Negative Iodoform Positive Tollens' reagent

22. [2]

By Shiff reagent distinction between aldehyde (–CHO) & ketone $\left(\rangle CO\right)$ group takes place.

23. [1]

With MnO_2, oxidation of only allyllic alcohol takes place.

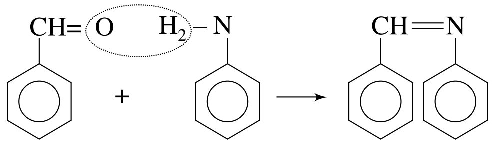
24. [2]

$$Ph\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3 \xrightarrow{CH_3\text{–}CO_3H} Ph\text{–}O\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3$$

Baeyer–Villegar oxidation, migration aptitude order for oxygen atom.

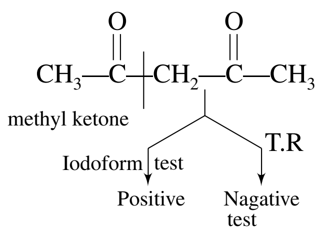
3° > Ph > 2° > 1°

25. [2]



(Shiff base)

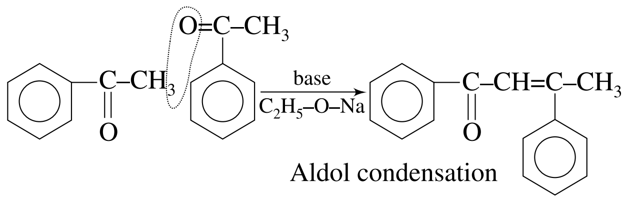
26. [3]



→ Negative Tollens' test indicating that compound have ketone group.

→ Positive iodoform test indicating that A must be methyl ketone or having acidic CH.

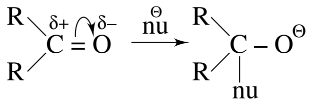
27. [3]



28. [2]

Geminal ethers are stable in basic medium. Hence give conversion carried in basic medium so that NH_2–NH_2 on reagent is most suitable (wolf krishner reduction).

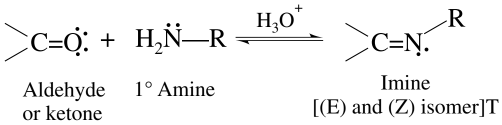
29. [1]



nucleophilic attack on the +vely charged carbon of carbonly group.

30. [2]

A general equation for the formation of an imine from a primary amine and an aldehyde or ketone is shown here. Imine formation is acid catalysed, and the product can from as a mixture of (*E*) and (*Z*) isomers.



Imine formation generally takes place fastest between **pH 4 and 5** and is slow at very low or very high pH. We can understand why an acid catalyst is necessary if we consider the mechanism that has been proposed for imine formation. The important step is the step in which the protonated amino alcohol loses a molecule of water to become an iminium ion. By protonating the alcohol group, the acid converts a poor leaving group (an —OH group into a good one (an $—OH_2^+$ group.).

31. [1]

$$Ph\text{—}\overset{\overset{O}{\|}}{C}\text{—}OH \xrightarrow[S_{N1}]{SOCl_2} Ph\text{—}\overset{\overset{O}{\|}}{C}\text{—}Cl \xrightarrow[\text{Pd-BaSO}_4]{H_2} Ph\text{—}\overset{\overset{O}{\|}}{C}\text{—}H$$

Lindlar catalyst

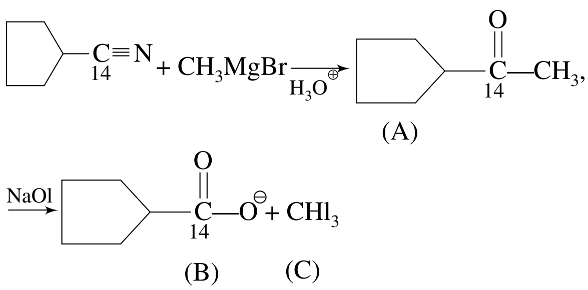
Rosenmund's reduction

32. [2]

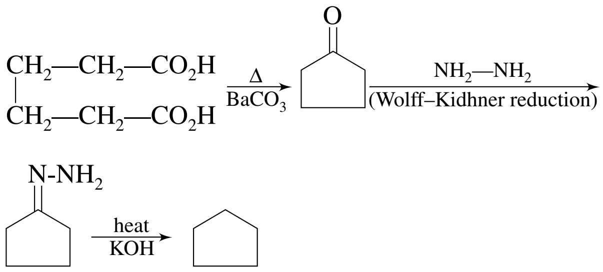
$$Ph\text{—}CH_3 \xrightarrow[\substack{\text{Mild oxidation}\\ \text{Etard reaction}}]{CrO_2Cl_2} \underset{(A)}{Ph\text{–}CH{=}O} \xrightarrow[\substack{\text{Cannizzaro}\\ \text{reaction}}]{\text{Conc. KOH}}$$

$$Ph\text{—}CH_2OH + \underset{(B)}{Ph\text{–}COO^-}$$

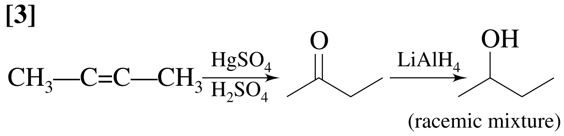
33. [3]



34. [3]

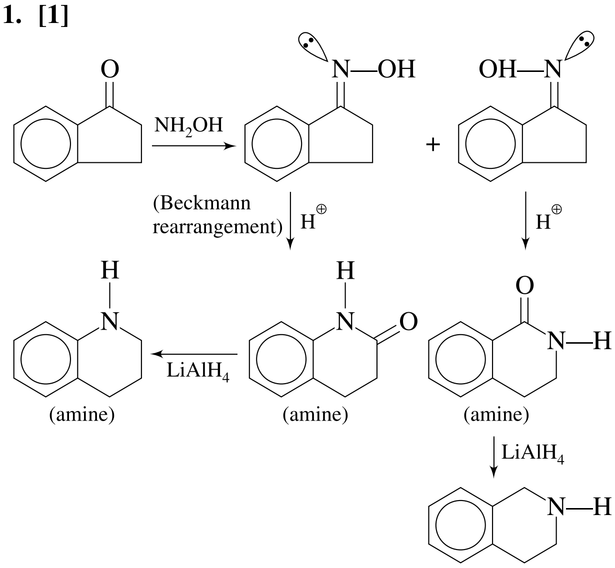


35. [3]

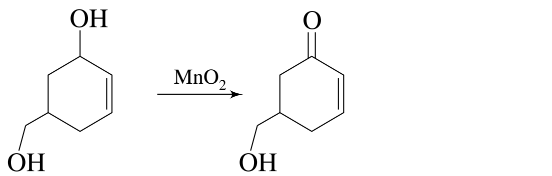


EXERCISE # 2

1. [1]

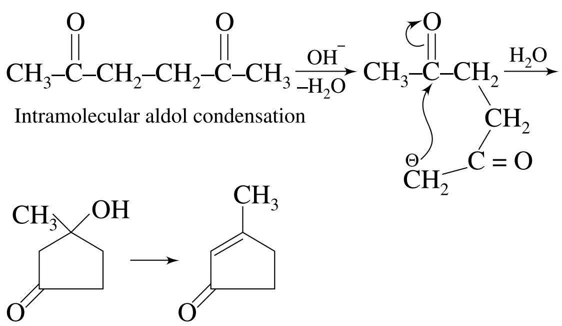


2. [1]

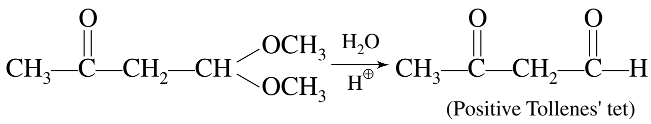


MnO_2 oxidises only allylic and Benzyllic alcohol

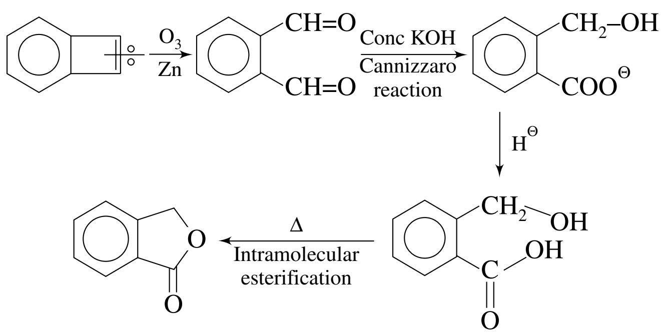
3. [2]



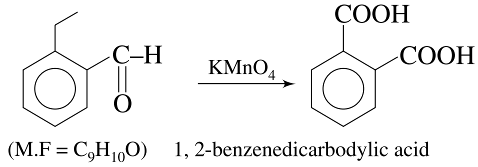
4. [3]



5. [1]

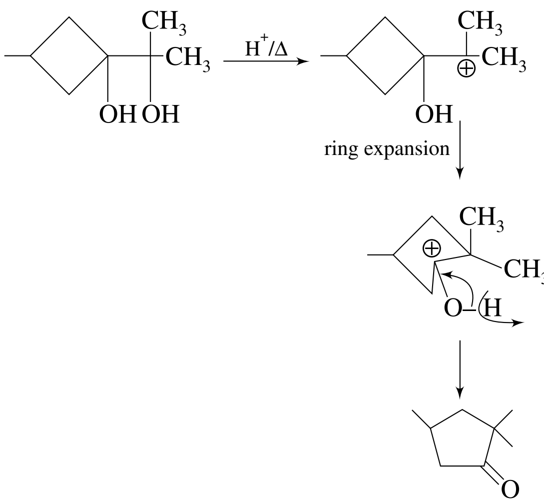


6. [2]



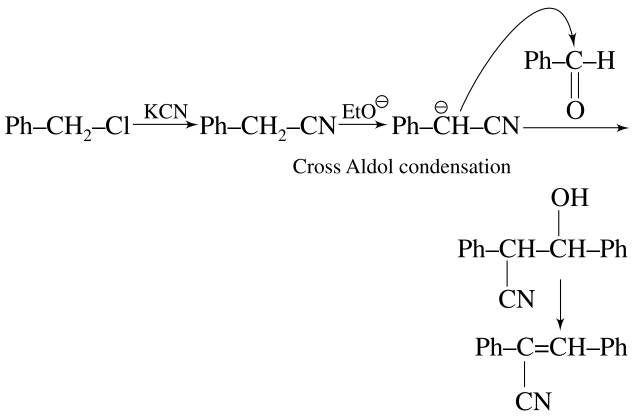
given strueture have CH = O group hence will give 2, 4 DNP test, Tollen's reagent and Cannizzaro reaction

7. [4]

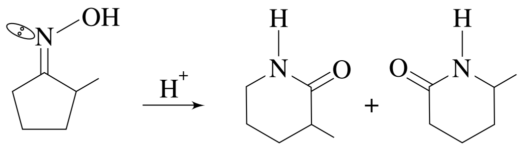


This is pinacole–pinacolone rearrangement

8. [2]

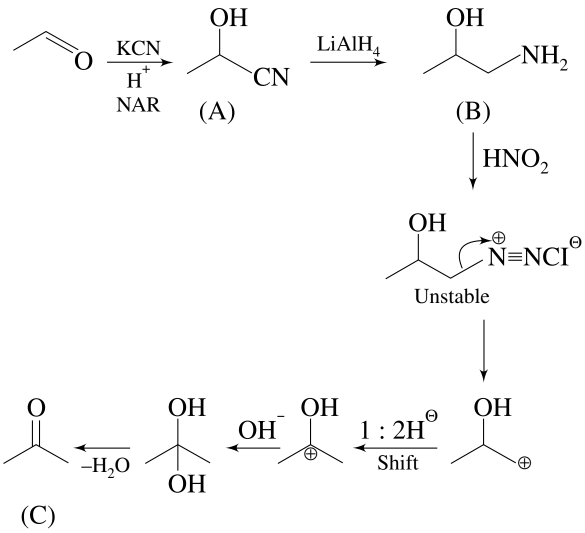


9. [1]



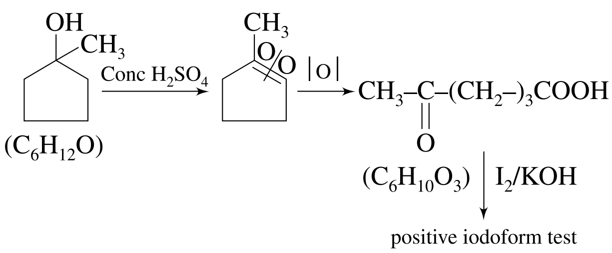
Beckmann re-arrangement (refer mechanism)

10. [2]



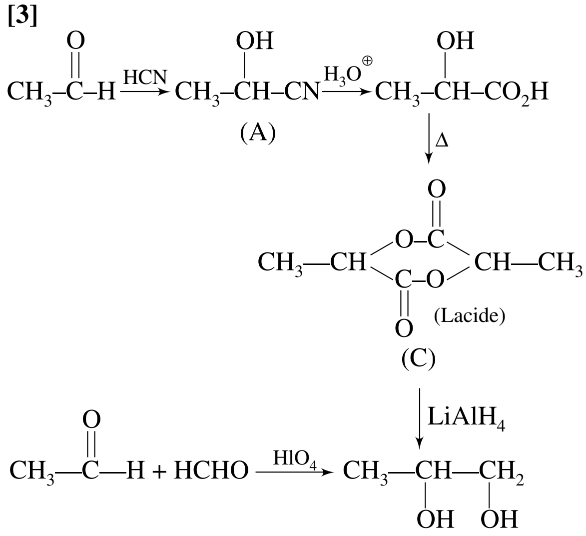
11. [4]

A→Must be 3° alcohol because dichromate test do not given by 3° alcohol



12. [3]

13. [3]



14. [4]

(i) Reactivity in NAR $\propto \xrightarrow[\text{Steric hindrance}]{1}$

Thus aldehyde is more reactive than ketone.

(ii) Reactivity in NAR $\propto$ +ve charge at the carbon of $>$C=O group $\propto$ EWG $\propto \xrightarrow[\text{ERG}]{1}$

We know that ERG Power (—O—CH$_3$) > (—CH$_3$) ERG

Hence order of reactivity in NAR (i) > (iv) > (ii) > (iii)

15. [4]

Aldehyde and hemiacetal gives positive test with Tollens' reagent.

R–CH(OCH$_3$)(OH) type substance known as hemiacetal, they will convert into corresponding aldehyde in basic medium, Hence also give positive test with tollen's reagent.

16. [3]

A ($C_6H_8O_2$) $\xrightarrow{\text{Na/metal}}$ H_2 gas

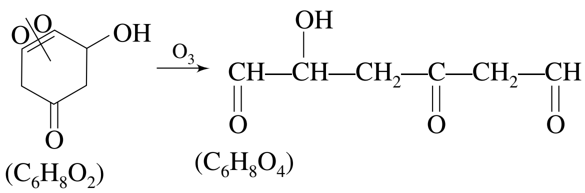
It indicates presence of –OH group.

A ($C_6H_8O_2$) $\xrightarrow{\text{2, 4 DNP}}$ yellow orange solution

It indicates presence Carbonyl group ($>$C=O)

A ($C_6H_8O_2$) $\xrightarrow{O_3}$ B ($C_6H_8O_4$)

No loss of carbon atom indicating that, A must have double bond around the ring.



17. [4]

I. $CH_3—CH{=}O \xrightarrow[H^+]{[Ag(NH_3)_2]^+,\ OH^-} CH_3—COOH$ (Acid)

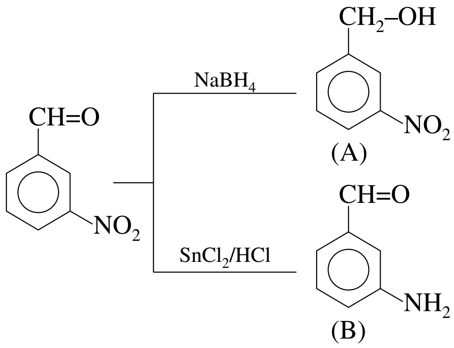
II. $CH_3—CCl_3 \xrightarrow{OH^-} CH_3—COO^{\ominus}$

III. $CH_3—\overset{O}{\overset{||}{C}}—OC_2H_5 \xrightarrow{OH^-} CH_3—COO^{\ominus} + C_2H_5OH$

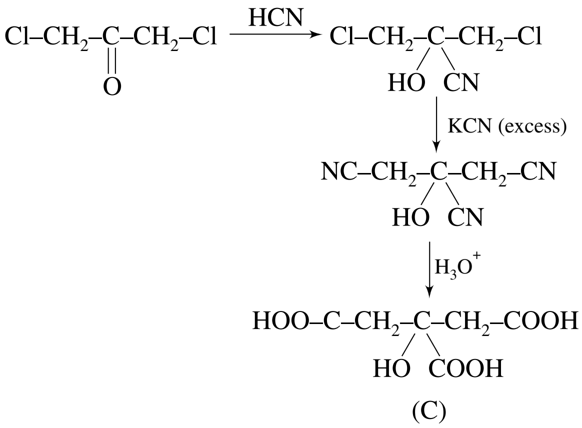
18. [1]

Refer angle strain.

19. [1]



20. [2]



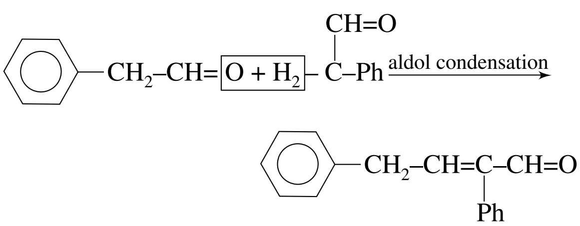
21. [3]

The given conversion is achieved by

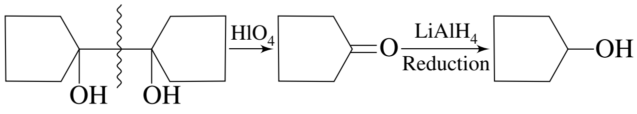
$NaBH_4/H_2O \longrightarrow$ Reduction

$HCH = O/OH^- \longrightarrow$ Intermolecular Cannizzaro reaction

22. [4]



23. [2]



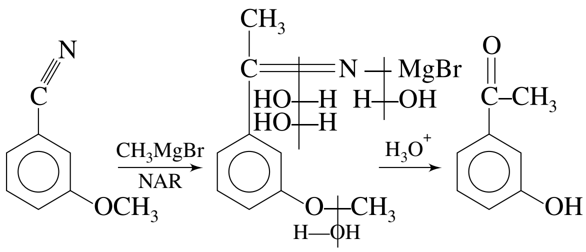
Cleavage of vicinal diol takes place

24. [2]

In option (2), aldehyde is not formed. When a terminal alkyne is oxidised with $KMnO_4$ formation of carboxylic acid is always formed.

All options are preparation of aldehydes.

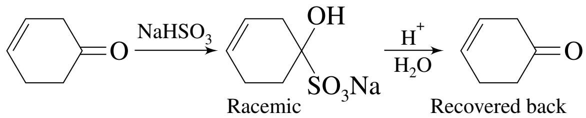
25. [4]



EXERCISE # 3

1. [1,2,3,4]

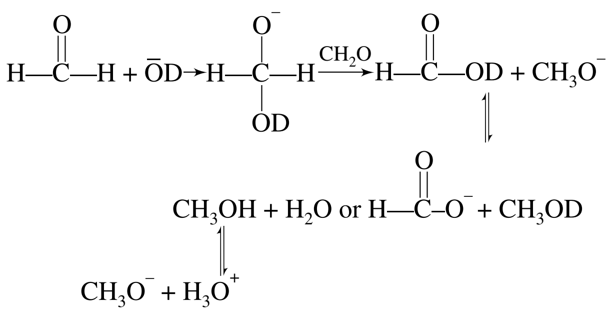
Aldehydes and ketones form bisulphite salt with $NaHSO_3$ which is insoluble in concentrated $NaHSO_3$ solution due to common ion effect. Hence, if $NaHSO_3$ is in limited quantity, precipitation may not take place.



2. [2,3,4]

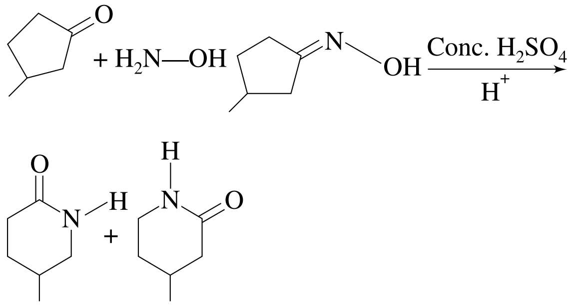
Aldehydes and ketones containing α-H form enamines when treated with secondary amine in slightly acidic medium.

3. [1,2,3]



However, C—D bond is not formed in this reaction.

4. [1,3]



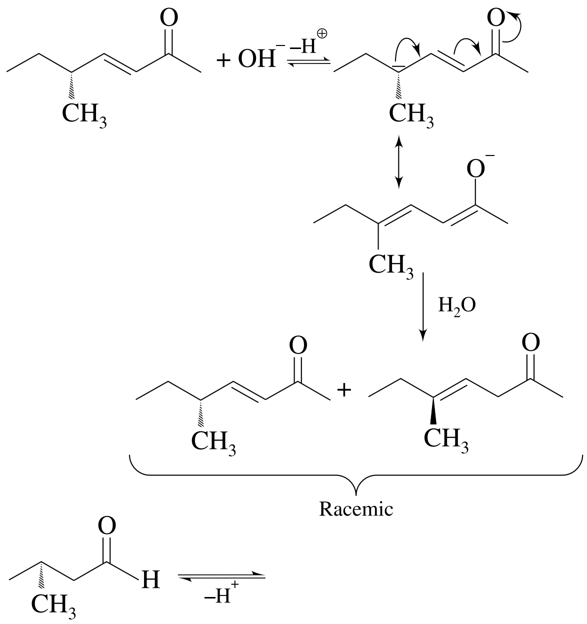
5. [1, 2, 4]

Wittig reaction

$$CH_3\text{—}CH_2Cl \xrightarrow{Ph_3P} \xrightarrow{BuLi} \underset{X}{CH_3\text{—}CH{=}PPh_3} \xrightarrow{CH_3CHO} \underset{Y}{CH_3\text{—}CH{=}CH\text{—}CH_3}$$

Both diastereomers (*cis* and *trans*) of Y are formed.

6. [2,4]



7. [1,3,4]

8. [2,3,4]

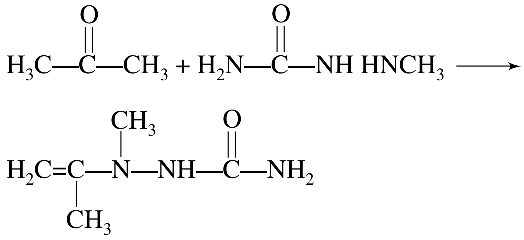
9. [2]

10. [3]

Statement I is correct but Statement II is false, It would be true only if both carbonyls are capable of forming enolates, i.e., if both possess α-H

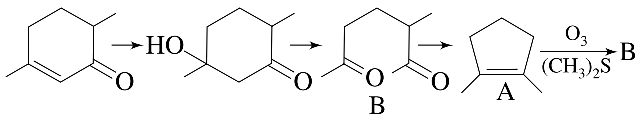
11. [4]

Nucleophilic attack occurs from aminic nitrogen not from amidic nitrogen.

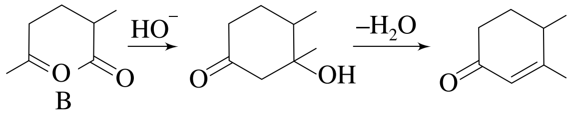


12. [3]

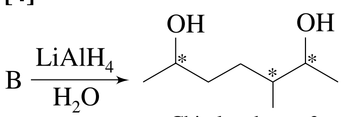
Reversing the final product gives



13. [4]



14. [4]



Chiral carbon = 3

So O.I = 2^3 = 8

15. [1]

16. [2]

$$Ph\text{–}Mg - Br + Cl\ \text{–}NH_2 \longrightarrow Ph - NH_2$$

$$Ph\text{–}Mg\text{–}Br + Cl - C{\equiv}N \longrightarrow Ph\text{–}CN$$

$$Ph\text{–}Mg\text{–}Br + CH_3\text{–}\underset{\underset{O}{\|}}{C}\text{–}Cl \longrightarrow Ph\text{–}\underset{\underset{O}{\|}}{C}\text{–}CH_3$$

$$Ph\text{–}Mg\text{–}Br + C_2H_5\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}C_2H_5 \longrightarrow Ph\text{–}\overset{\overset{O}{\|}}{C}\text{–}C_2H_5$$

17. [1]

18. [1]

(i) It has carbonyl carbon that turns chiral on reduction with hydrides. Hence, with $LiAlH_4$ or aluminium isopropoxide, gives racemic mixture. Also, it has no other functional groups, either Clemmensen reduction or Wolf–Kishner reduction can be used.

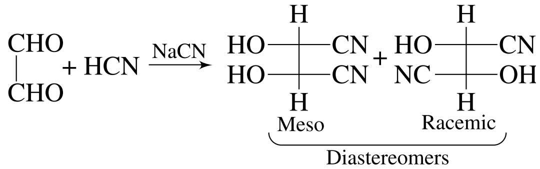
(ii) It has an olefinic double bond. Clemmensen reduction would not be suitable for selective reduction of carbonyl group.

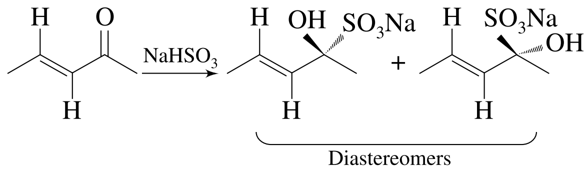
(iii) $LiAlH_4$ also reduces primary halide but aluminium isopropoxide does not. Wolf–Kishner reduction would not be suitable because HO^- reacts with halide group (S_N2 or E2).

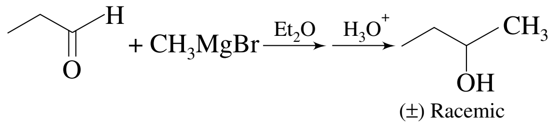
(iv) Same reasons as in (i).

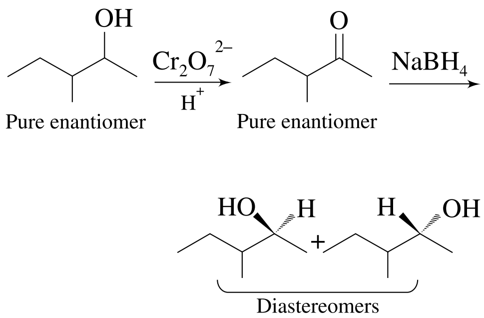
Hence, (i) → (p, q, r, s); (ii) → (p, q, s); (iii) → (q, r); (iv) → (p, q, r, s)

19. [1]

(i) 

(ii) 

(iii) 

(iv) 

Hence, (i) → (p, q, r, s); (ii) → (q, s); (iii) → (p); (iv) → (q, s)

20. [2]

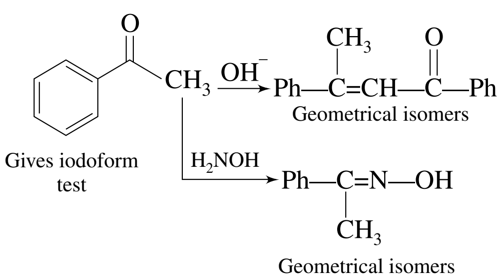
(i) Initially, aldol reaction followed by Cannizzaro reaction gives $C(CH_2OH)_4$ + HCOOH.

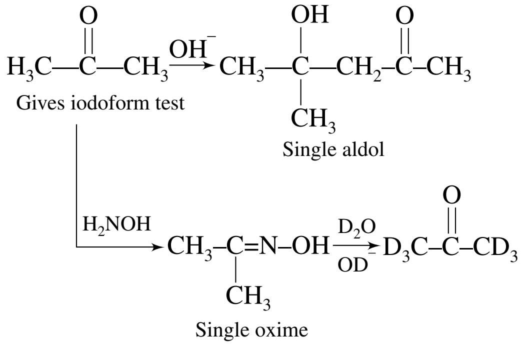
(ii) F—CHO undergoes Cannizzaro reaction due to absence of α-H.

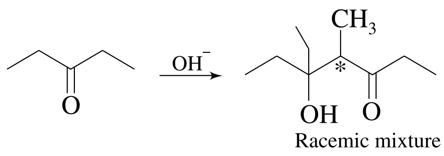
(iii) It has difficulty ion aldol condensation, hence undergo Cannizzaro reaction predominantly.

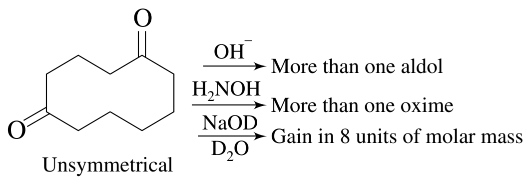
(iv) All aldol, Cannizzaro and Claisen reaction occur.

21. [2]

(i) 

(ii) 

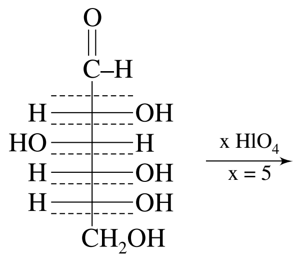
(iii) 

(iv) 

Hence (i) → (q, r, t); (ii) → (p, q, s); (ii) → (t); (iv) → (r, s, t)

22. [6]

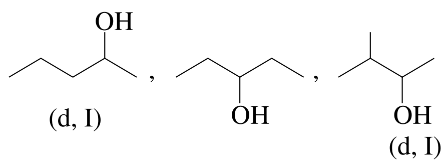
23. [5]



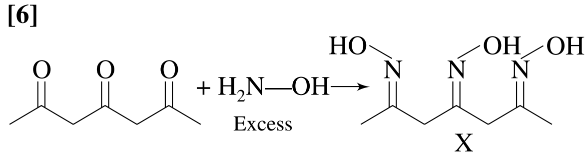
Each C–C bond cleavage requires 1 mole HIO_4

24. [5]

All secondary alcohol isomers can be oxidised to ketones.

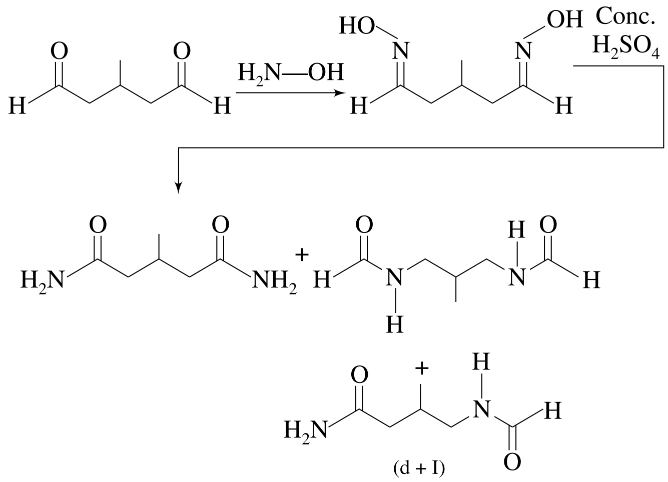


25. [6]

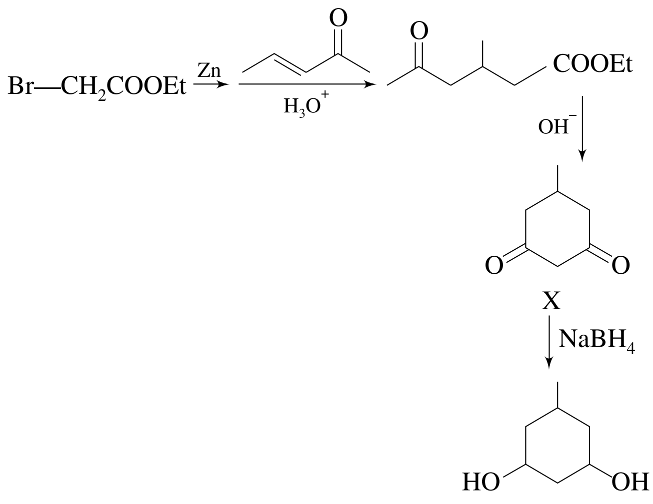


Six isomers (stereoisomers) are possible for X.

26. [4]



27. [4]

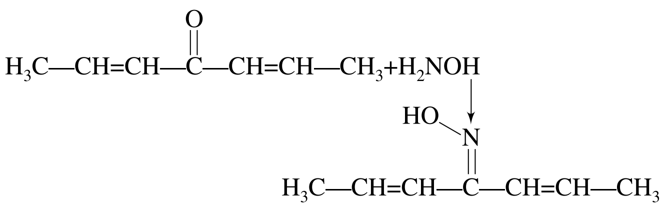


Has two chiral carbons

28. [4]

$$Ph-\overset{O}{\overset{\|}{C}}-CH_3 + 4KOH\ \ 3I_2 \rightarrow Ph-COOK + CHI_3 + 3KI + 3H_2O$$

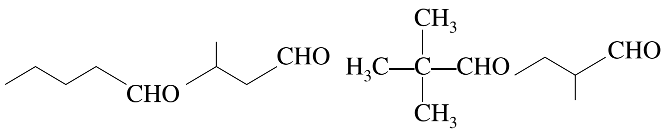
29. [6]



(I)

Four stereoisomers exist for 1, *cis-cis*, *trans-trans* and *cis-trans* with OH *syn* to *cis* and OH *anti* to *cis*.

30. [3]

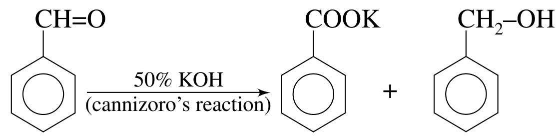


(I) (II) (III) (IV)

IV is enantiomeric, its pure enantiomer, with HCN/NaCN, would produce pair of diastereomers.

EXERCISE # 4

1. [2]



Benzaldehyde Acid salt Alcohol

2. [4]

Only suitable reagent is chromic anhydride in glacial acetic acid.

Option (1) and (2) will also affect (C=C) bond.

Option (3) is more suitable reagent for preparation of aldehyde.

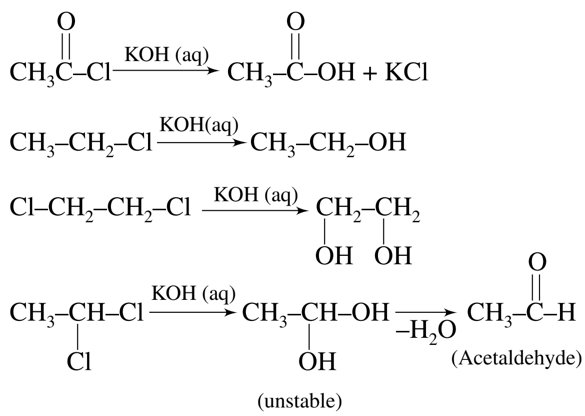
3. [2]

Reactivity towards nucleophilic substitution ∝ positive charge at the carbon of carbonyl group

$$\propto \frac{1}{\text{Steric hidrance}}$$

$PhCOC_6H_5 < PhCOCH_3 < CH_3COCH_3 < HCHO$

4. [4]



5. [1]

Reactivity towards nucleophilic substitution ∝ positive charge at the carbon of carbonyl group

$$\propto \frac{1}{\text{Steric hidrance}}$$

$\therefore$ H–CH=O > $\underset{+1}{CH_3}$–CH = O > $\underset{+1}{CH_3}$–$\underset{\|}{\overset{}{C}}$–$CH_3$ (C=O)

6. [4]

It is Clemmensen reduction

7. [3]

$$H–CH{=}O \xrightarrow{I_2/KOH} \text{–ve test}$$

$$CH_3–CH{=}O \xrightarrow{I_2/KOH} \text{+ve test } (CHI_3)$$

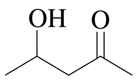
Hence I_2/alkali is suitable reagent.

8. [2]

Zn–Hg/HCl

9. [2]

Compound having α-H gives aldol condensation and β-hydroxy carbonyl Compound is formed.

In option (2) 

β-hydroxy ketone

10. [3]

CH_3–CH=O has α-H so it does not give Cannizzaro reaction.

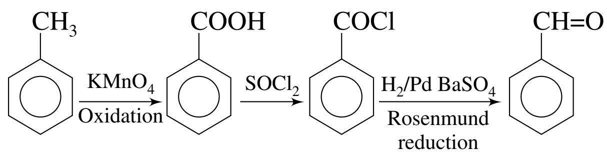
11. [3]

$$CH_3–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow{I_2/KOH} \underset{\text{(iodoform)}}{CHI_3} + CH_3–COOK$$

12. [3]

Tishchenko reaction is a modification of Cannizzaro reaction.

13. [4]



Benzaldehyde

14. [3]

$$\underset{\underset{(C_{10}H_{13}Cl)}{(A)}}{C_6H_5–CH_2–CH_2–CH_2–CH_2–Cl} \xrightarrow{\text{Alc. KOH}}$$

$$\underset{(B)}{C_6H_5–CH_2–CH_2–CH{=}CH_2}$$

$$\downarrow \text{ozonolysis } O_3Zn/H_2O$$

$$\underset{(C)}{H–CH = O} + \underset{(D)}{C_6H_5–CH_2–CH_2–CH{=}O}$$

(C) no α-H
It gives Cannizaro but not aldol condensation

(D) α-H present
It gives aldol condensation not Cannizaro

15. [3]

$$2CH_3–CH{=}O \xrightarrow[\text{Aldol formation}]{\overset{\ominus}{O}H} CH_3–\underset{\underset{OH}{|}}{CH}–CH_2–CH{=}O$$

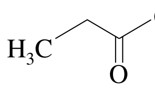
$$\downarrow \Delta \;\; E_{1CB}\text{, dehydration}$$

$$CH_3–CH{=}CH–CH{=}O$$

16. [4]

It is Perkin condensation reaction.

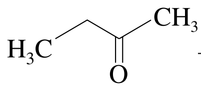
17. [3]

 $\xrightarrow[I_2/H_2O]{NaOH}$ $CHI_3 + CH_3CH_2COONa$

$\downarrow H^+$

CH_3CH_2COOH

18. [3]

 $\xrightarrow[I_2/H_2O]{NaOH}$ $CHI_3 + CH_3CH_2COONa$

$\downarrow H^+$

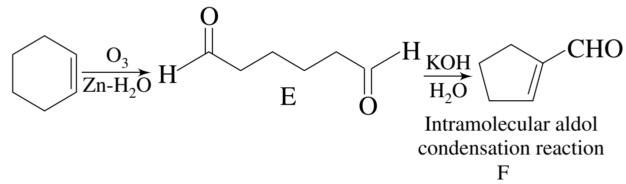
CH_3CH_2COOH

19. [2]

$$H_2C{=}O + H_2N—OH \longrightarrow \begin{matrix}H \\ H\end{matrix}\!\!>C{=}N—OH \text{ (single)}$$

$$CH_3—\overset{\overset{O}{\|}}{C}—H + H_2NOH \rightarrow \begin{matrix}H_3C \\ H\end{matrix}\!\!>C{=}N\!\!<\!\!\begin{matrix}OH \\ \ddot{}\end{matrix} + \begin{matrix}H_3C \\ H\end{matrix}\!\!>C{=}N\!\!<\!\!\begin{matrix}\ddot{} \\ OH\end{matrix} \text{ (two)}$$

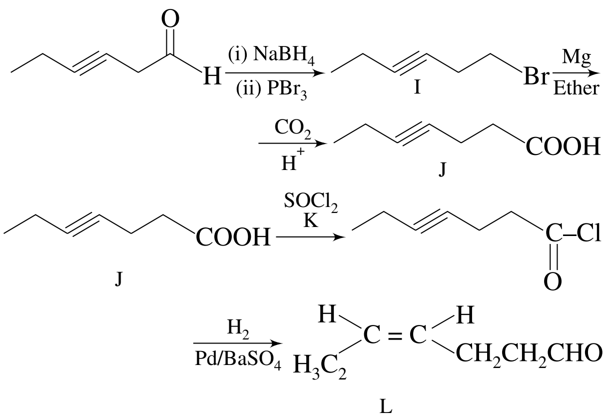
20. [2]



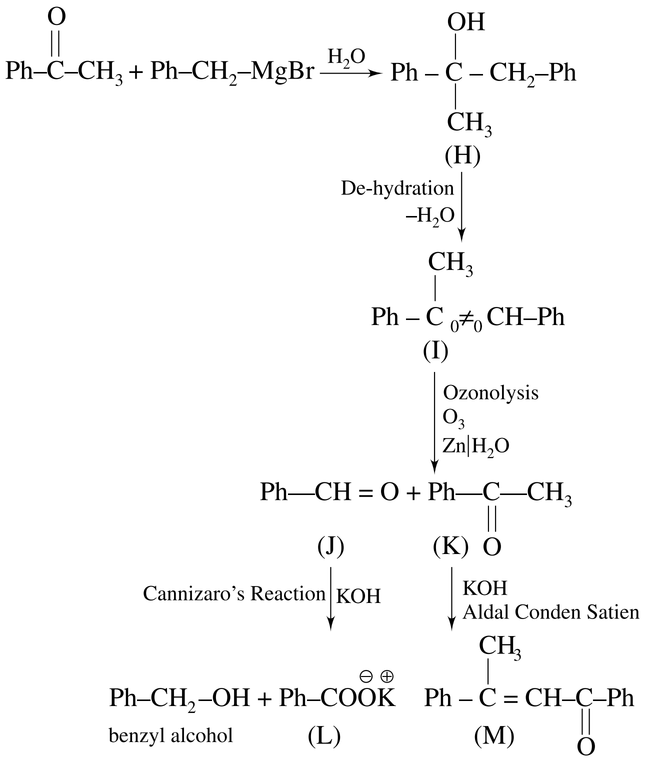
21. [4]

22. [1]

23. [3]



24. [2]

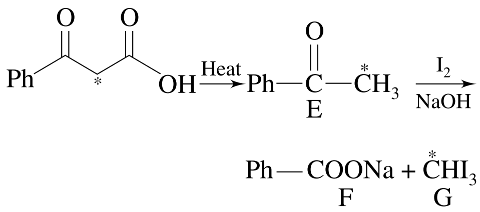


Since H is tertiary alcohol and gives de-hydration hence H is formed by treatment of grignard reagent having with ketone as shown above.

25. [4]

As per above reaction.

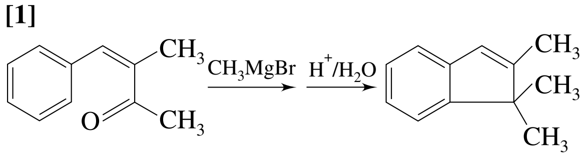
26. [4]



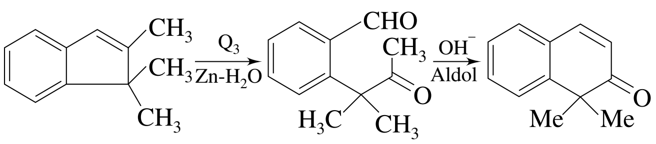
27. [2]

28. [2]

29. [1]

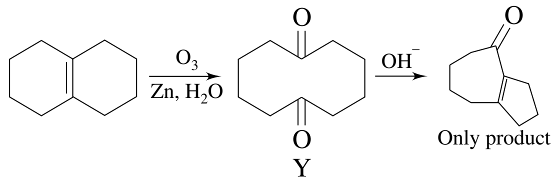


P (Gives positive iodoform test) Q



Q R S

30. [1]



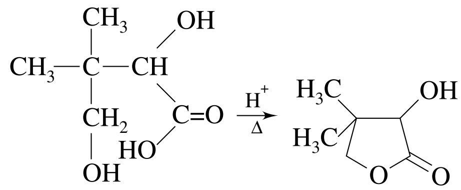
31. [1]

32. [2]

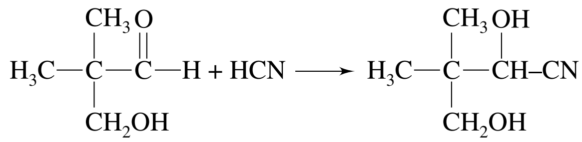
33. [1]

34. [4]

The given product is an ester, obtained by condensation of a hydroxy acid obtained through hydrolysis of a cyanohydrin.

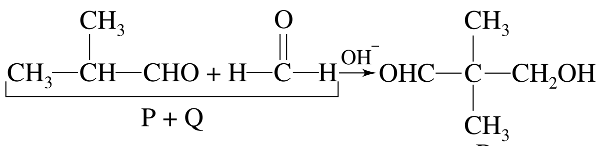


Acid above is obtained by acid hydrolysis of cyanohydrin S as



R S

R is obtained by treatment of P and Q with aqueous K_2CO_3 through aldol condensation reaction as



R

35. [3]

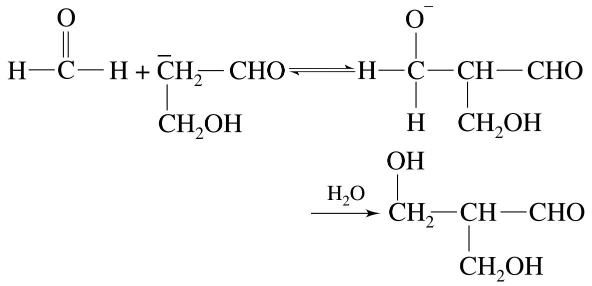
The given reaction is an example of repeated aldol condensation followed by Cannizzaro reaction.

Step I $CH_3CHO + OH^- \longrightarrow \bar{C}H_2\text{—}CHO + H_2O$

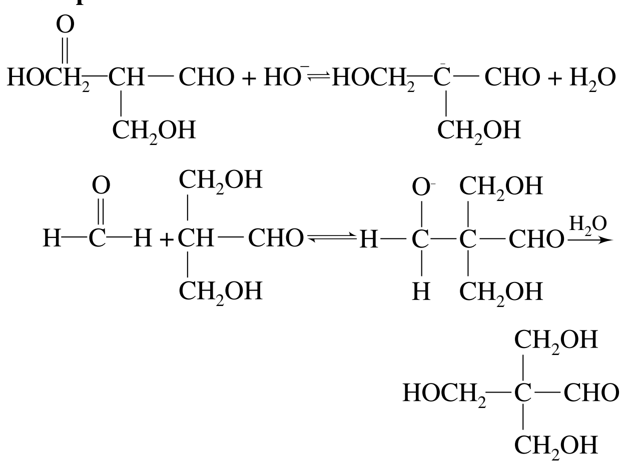
$$H\text{—}\overset{\overset{O}{\|}}{C}\text{—}H + \bar{C}H_2\text{—}CHO \rightleftharpoons H\text{—}\underset{\underset{H}{|}}{\overset{\overset{O^-}{|}}{C}}\text{—}CH_2\text{—}CHO$$

$$\xrightarrow{H_2O} \overset{\overset{OH}{|}}{C}H_2\text{—}CH_2\text{—}CHO$$

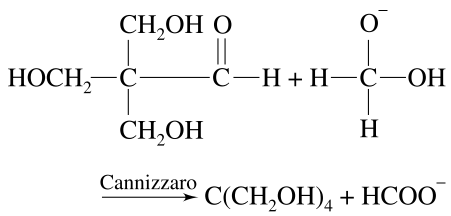
Step II $HOCH_2\text{—}CH_2\text{—}CHO + HO^- \rightleftharpoons HO\text{—}CH_2\text{—}\bar{C}H\text{—}CHO + H_2O$



Step III



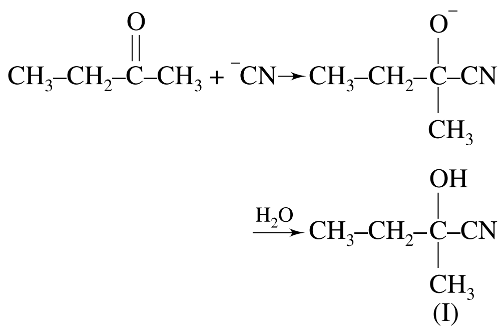
Step IV



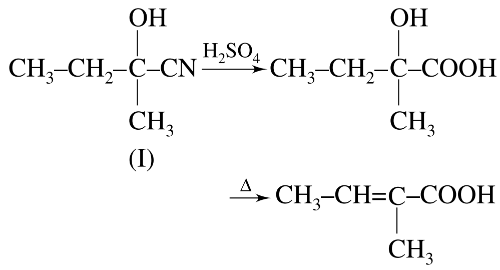
In the last step, formaldehyde is oxidised and the other aldehyde is reduced giving the desired products.

36. **[1]**

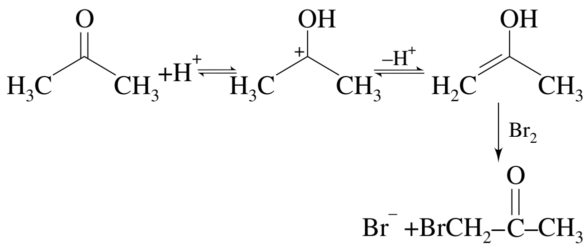
The first step is cyanohydrin reaction.



In the second step, the —CN of intermediate (I) is first hydrolysed and then dehydrated on heating in the presence of conc. H_2SO_4.



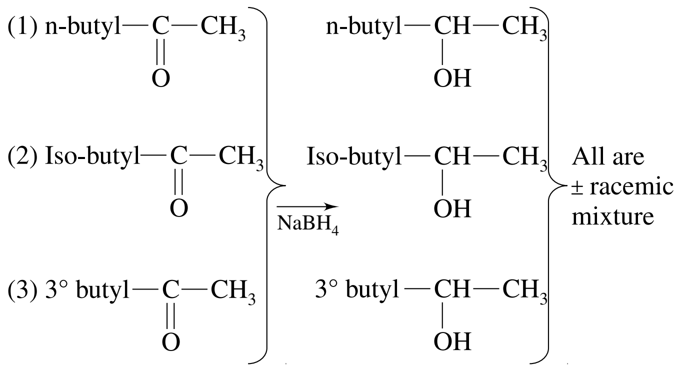
37. **[3]**

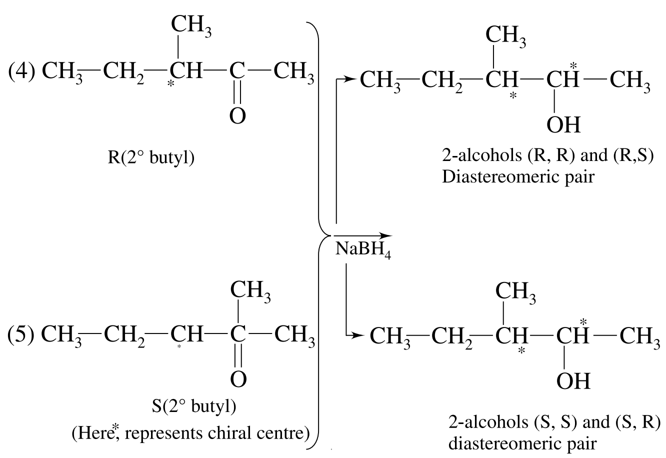


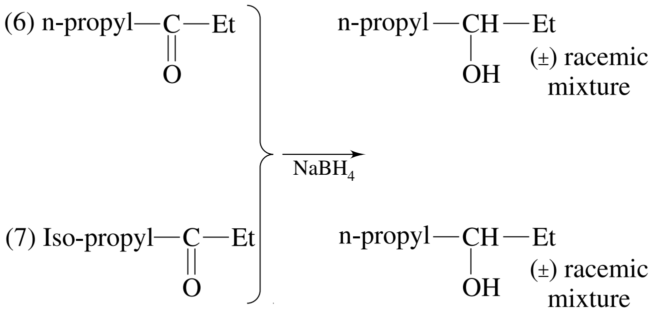
38. **[5]**

Molecular weight of the ketone is 100.

So, molecular formula = $C_6H_{12}O$





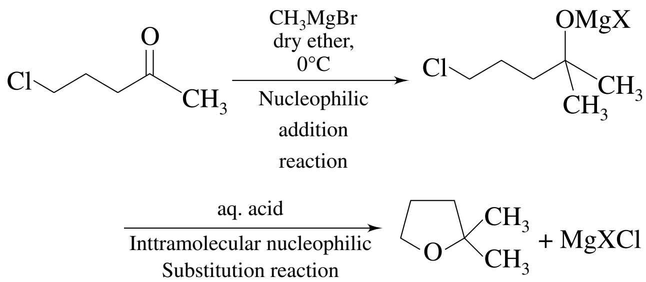


While in case of (4) and (5), they do not produce enantiomer due to the presence of stereogenic centre on ketone.

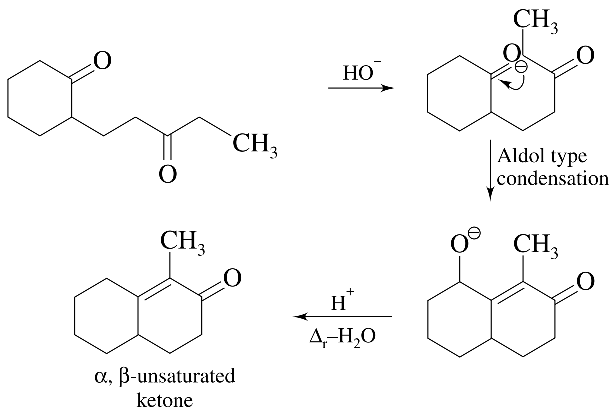
39. [4]

This problem includes concept of nucleophilic addition reaction to carbonyl compound (ketone here) and intramolecular nucleophilic substitution reaction.

Complete reaction sequence is as shown below



40. [1]

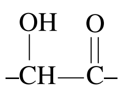


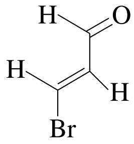
41. [1, 2, 3]

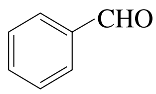
$$RCHO + Ag_2O \xrightarrow{OH^-} RCOOH + 2Ag$$

(Tollen's reagent) (Silver mirror)

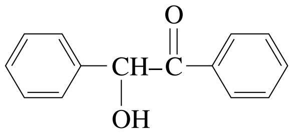
Tollens' test is given by all aldehydes and all reducing sugars as glucose, fructose and α-hydroxy ketones



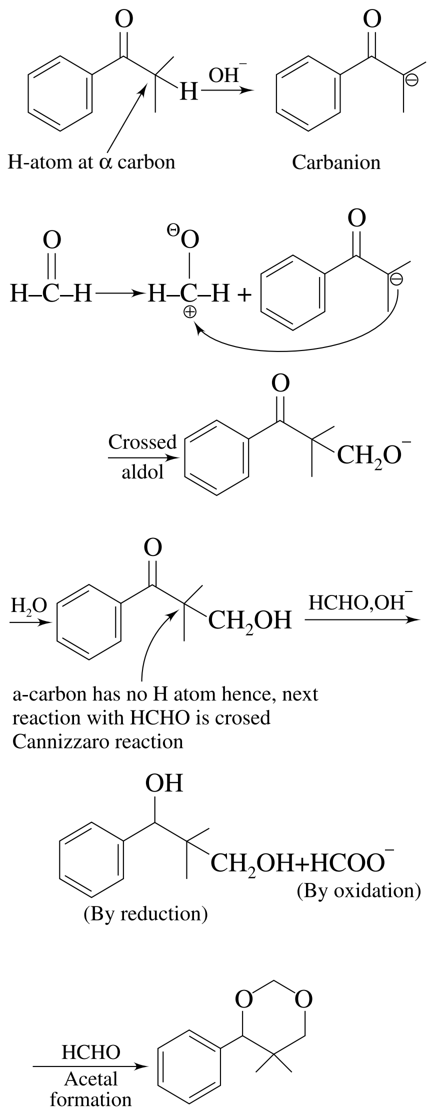
(1)  having an aldehyde group gives Tollens' test

(2) 

Aldehyde

(3) 

42. [1]



Comment: Please check, α-carbon should be α-carbon

Chapter 4

Carboxylic Acids and its Derivatives

Introduction

Carboxylic Acids

- Saturated monocarboxylic acids have general formula, $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$.
- The carboxylic carbon and the two oxygen atoms in carboxylic acid are sp^2 hybridised.
- The C–O (single bond) of carboxylic group is shorter (1.36 Å) than normal C–O single bond (1.43 Å) in alcohols and ethers, due to resonance.
- The C=O double bond in carboxylic group is slightly longer (1.23 Å) than the normal C=O double bond (1.20 Å) in ketones and aldehyde.
- Carboxylic acid exhibits isomerism as illustrated below:

(a) Chain isomerism:

$$\underset{\text{pentanoic acid}}{CH_3CH_2CH_2CH_2–COOH} \quad \& \quad \underset{\text{2-Methyl butanoic acid}}{CH_3–CH_2–\overset{\overset{CH_3}{|}}{C}H–COOH}$$

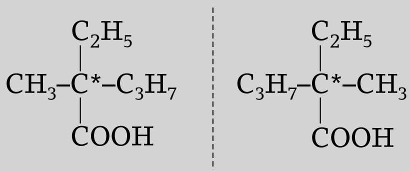
(b) Position isomerism:

$$\underset{\text{3-Methyl butanoic acid}}{CH_3–\overset{\overset{CH_3}{|}}{C}H–CH_2–COOH} \text{ and } \underset{\text{2-Methyl butanoic acid}}{CH_3–CH_2–\overset{\overset{CH_3}{|}}{C}H–COOH}$$

(c) Functional isomerism:

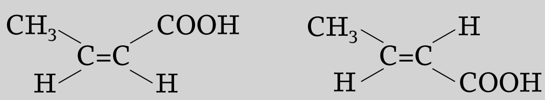
$$\underset{\text{propionic acid}}{CH_3–CH_2–COOH} \quad \& \quad \underset{\text{Methyl acetate}}{CH_3–\overset{\overset{O}{\|}}{C}–OCH_3} \quad \& \quad \underset{\text{Ethyl formate}}{H–\overset{\overset{O}{\|}}{C}–OC_2H_5}$$

(d) Optical isomerism:



2-Ethyl-2-methyl pentanoic acid

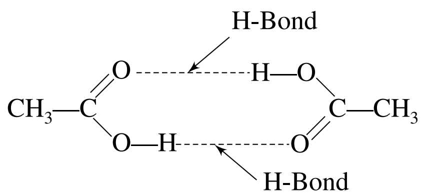
(e) Geometrical isomerism:



cis-But-2-enoic acid *tras*-But-2-enoic acid

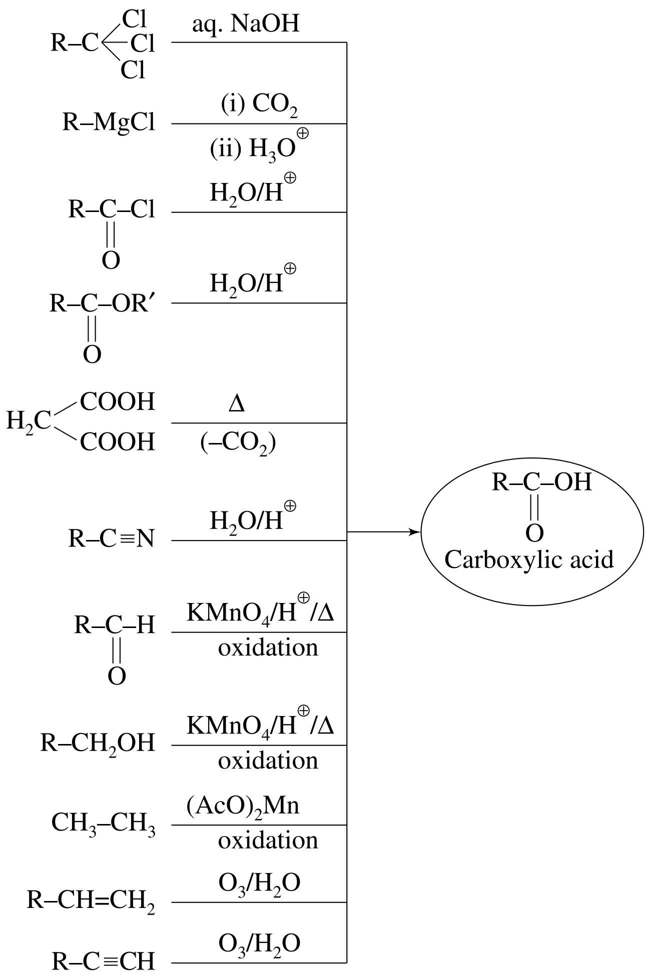
PHYSICAL PROPERTIES

- Fatty acids upto C_{10} are colourless liquid. The higher ones are colourless waxy solids.
- The first three members have a sharp pungent odour but the middle ones C_4–C_9 have the smell of rancid butter, whereas higher members are odourless.
- Lower members are completely miscible with water because of the formation of the hydrogen bonds. However, solubility decreases with increasing molecular weight because of increased effect of non-polar long carbon chain which results in weak H-bonding or no H-bonding.
- Boiling point of carboxylic acids increases regularly with increase in molecular weight. B.P. of R–COOH > R–OH due to hydrogen bonding and they exist as dimer.

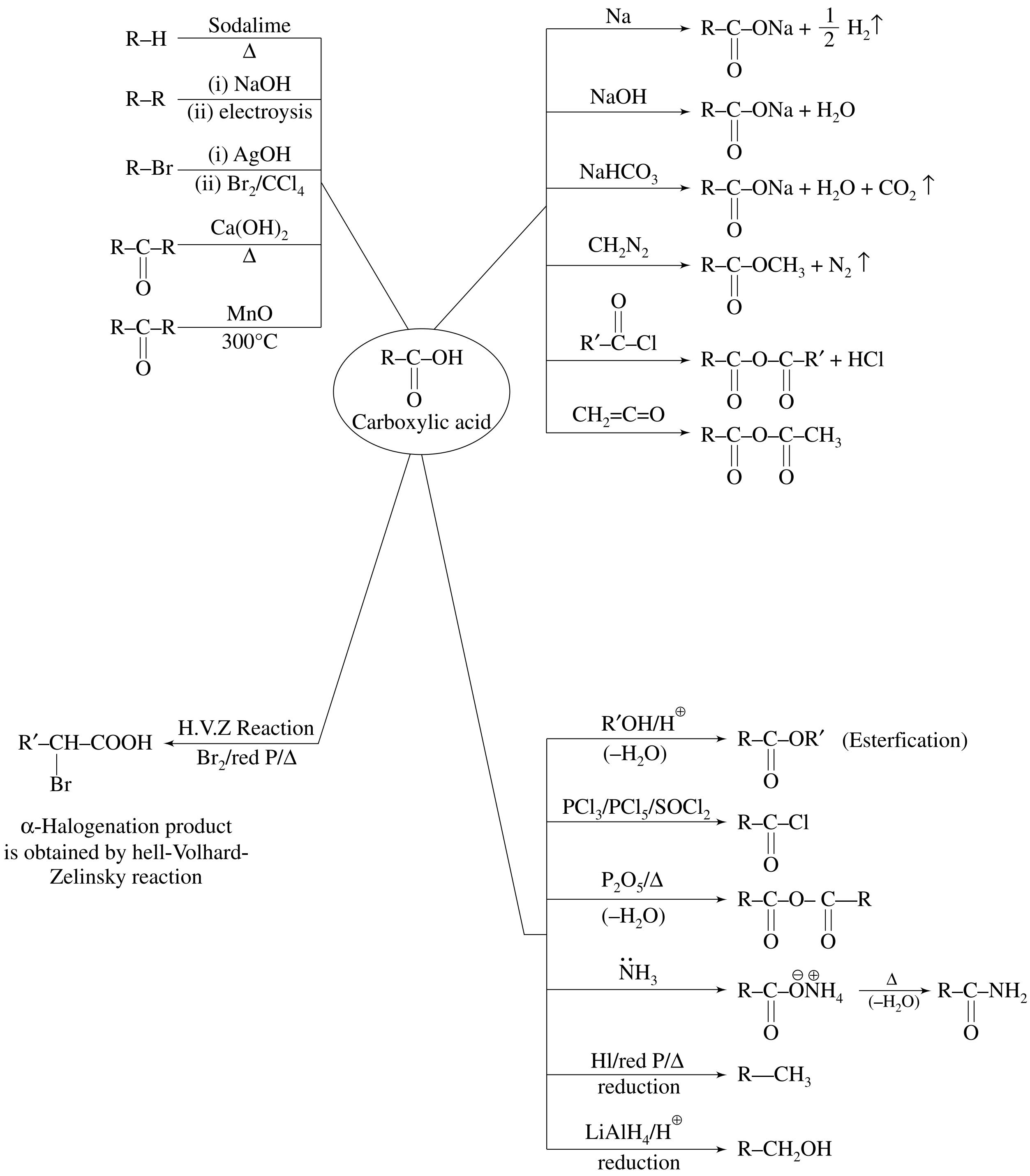


A dimer of a carboxylic acid

METHODS OF PREPARATION OF CARBOXYLIC ACIDS



CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

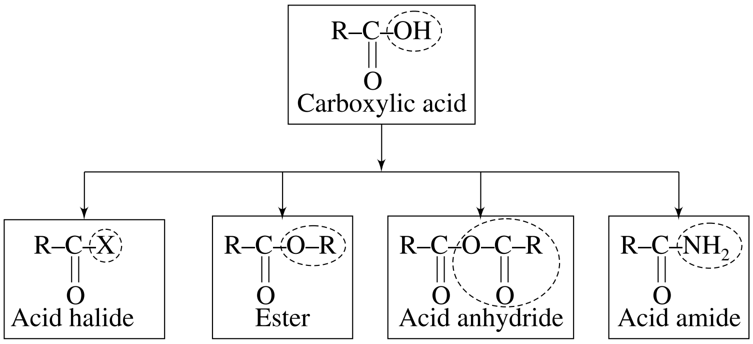


COMPARISON OF FORMIC ACID AND ACETIC ACID

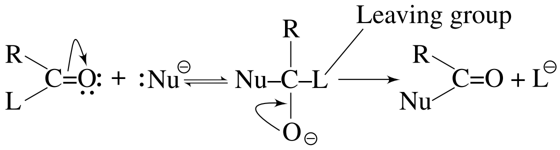
	Property	Formic acid	Acetic acid
1.	**Acidic nature**		
(i)	Reaction with electro positive metals	$HCOOH + Na \rightarrow HCOONa + 1/2\ H_2 \uparrow$	$CH_3COOH + Na \rightarrow CH_3COONa + 1/2\ H_2 \uparrow$
(ii)	Reaction with bases	$HCOOH + NaOH \rightarrow HCOONa + H_2O$	$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii)	Reaction with carbonates and bicarbonates	$HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2 \uparrow$	$CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2 \uparrow$
2.	Esterification	$HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	$CH_3COOH + C_2H_5OH$ $\xrightarrow[\text{Conc.}]{H_2SO_4} CH_3COOC_2H_5 + H_2O$
3.	Reaction with PCL_5	$HCOOH + PCl_5 \rightarrow HCOCl + POCl + HCl$ $\downarrow$ $CO + HCl$	$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
4.	Heating Ammonium salts	$HCOONH_4 \rightarrow HCONH_2 + H_2O$	$CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5.	Heating alone	$HCOOH \rightarrow CO_2 \uparrow + H_2 \uparrow$	Unaffected
6.	Reaction with conc. H_2SO_4	$HCOOH \xrightarrow[\text{Conc.}]{H_2SO_4} CO \uparrow + H_2O$	Unaffected
7.	Reaction with Cl_2/red P	Unaffected	Form $ClCH_2COOH$; $Cl_2CHCOOH$, Cl_3CCOOH
8.	Action of heat on salts		
(i)	Calcium salt	$(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	$(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii)	Sodium salt	$2HCOONa \xrightarrow{360°C} \begin{matrix} COONa \\ \vert \\ COONa \end{matrix} + H_2 \uparrow$	Unaffected
(iii)	Sodium salt (NaOH + CaO)	$HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2 \uparrow$	$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
9.	Electrolysis of Na or K salt	$H_2 \uparrow$	$CH_3–CH_3$ formed
10.	On heating with P_2O_5	Unaffected	$2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11.	Reducing nature		
(i)	Tollens' reagent	$HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	Unaffected
(ii)	Fehling's solution	$HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	Unaffected
(iii)	Mercuric chloride	$HCOOH + HgCl_2 \rightarrow Hg_2Cl_2 + CO_2 + 2HCl$ $HCOOH + Hg_2Cl_2 \rightarrow 2Hg + CO_2 + 2HCl$	Unaffected
12.	Acid (neutral solution) + $NaHSO_3$ + sodium Nitroprusside	Greenish blue colour	Unaffected
13.	Acid (neutral solution) + neutral ferric chloride	Red colour which changes to brown ppt. on heating.	Wine red colour
14.	Uses	(i) For preparation of CO_2 in laboratory. (ii) In the preservation of fruits. (iii) In the preparation of nickel formate, which is used as catalyst the hydrogenation of oil. (iv) As a reducing agent (v) In the manufacture of oxalic acid (vi) As an antiseptic and in the treatment of gout. (vii) As coagulating agent for rubber latex (viii) In lather tanning.	(i) As solvent and a laboratory reagent. (ii) For making various organic compound such as CH_3COCH_3; $(CH_3CO)_2O$; CH_3COCl, CH_3CONH_2 and CH_3COOR. (iii) For making various useful acetate, of Cu, Al, Fe, Cr, Pb. (a) $(CH_3COO)_2Cu$; Making green paints. (b) Al, Fe and Cr acetate; mordant in dying. (c) $(CH_3\ COO)_4$ Pb: oxidising agent. (iv) **Basic $(CH_3COO)_2$Pb:** manufacture of white lead. (v) Aluminium acetate; water proof fabrics. (vi) **Alkali acetate:** Diuretics (vii) **Cellulose acetate:** Artificial silk and Celluloid

CARBOXYLIC ACIDS DERIVATIVES

General Introduction



- Derivatives are characterised by **Nucleophilic Substitution Reaction** which take place at the acyl carbon (carbonyl group).



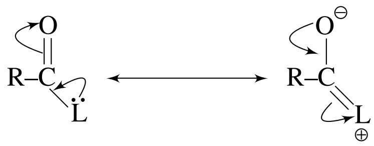
(L : Cl, OCOR', NH_2 or OR' or even –OH in acid)

- **Relative reactivity of acyl compounds:**

$$\boxed{R-\overset{\displaystyle O}{\overset{\|}{C}}-Cl > R-\overset{\displaystyle O}{\overset{\|}{C}}-O-\overset{\displaystyle O}{\overset{\|}{C}}-R' > R-\overset{\displaystyle O}{\overset{\|}{C}}-OR' > R-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2}$$

This overall order of reactivity can be accounted for in terms of the following three factors-

1. **Effects of the basicity on leaving group**
   - Weaker bases are good leaving group.
   - Hence acid derivative with weaker bases as leaving group are more reactive.
   - Chloride ion being the weakest base, acyl chloride is the most reactive of the acid derivatives.
   - Amines are the strongest bases (as compared to $Cl^{\ominus}$, $^{\ominus}OOCR$, $^{\ominus}OR$) hence are least reactive.
2. **Resonance effect**
   - The leaving group in each case has an atom with a lone pair of electron adjacent to carbonyl group.
   - The compound exists, therefore, as resonance hybrid



   - The greater the stabilisation, the lower is the reactivity of the acyl compound.
   - Acyl chlorides are the least affected by resonance due to the ineffective overlapping (i.e., 2p-orbital of carbon with 3p-orbital of Cl)
   - Stabilisation is achieved by acid anhydride, ester and amide (due to effective overlapping of 2p-orbital of carbon–oxygen and carbon–nitrogen.)
   - The stabilisation on particular carbon in acid anhydride is less than that of ester since the resonance effect is shared between two carbonyl groups.

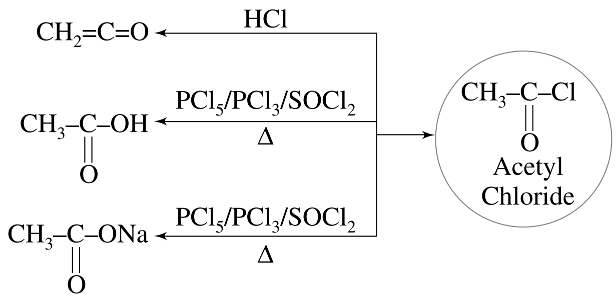
3. Inductive effect

- The inductive effect of oxygen in ester is greater than that of nitrogen in amide. Hence ester is more reactive than an amide.

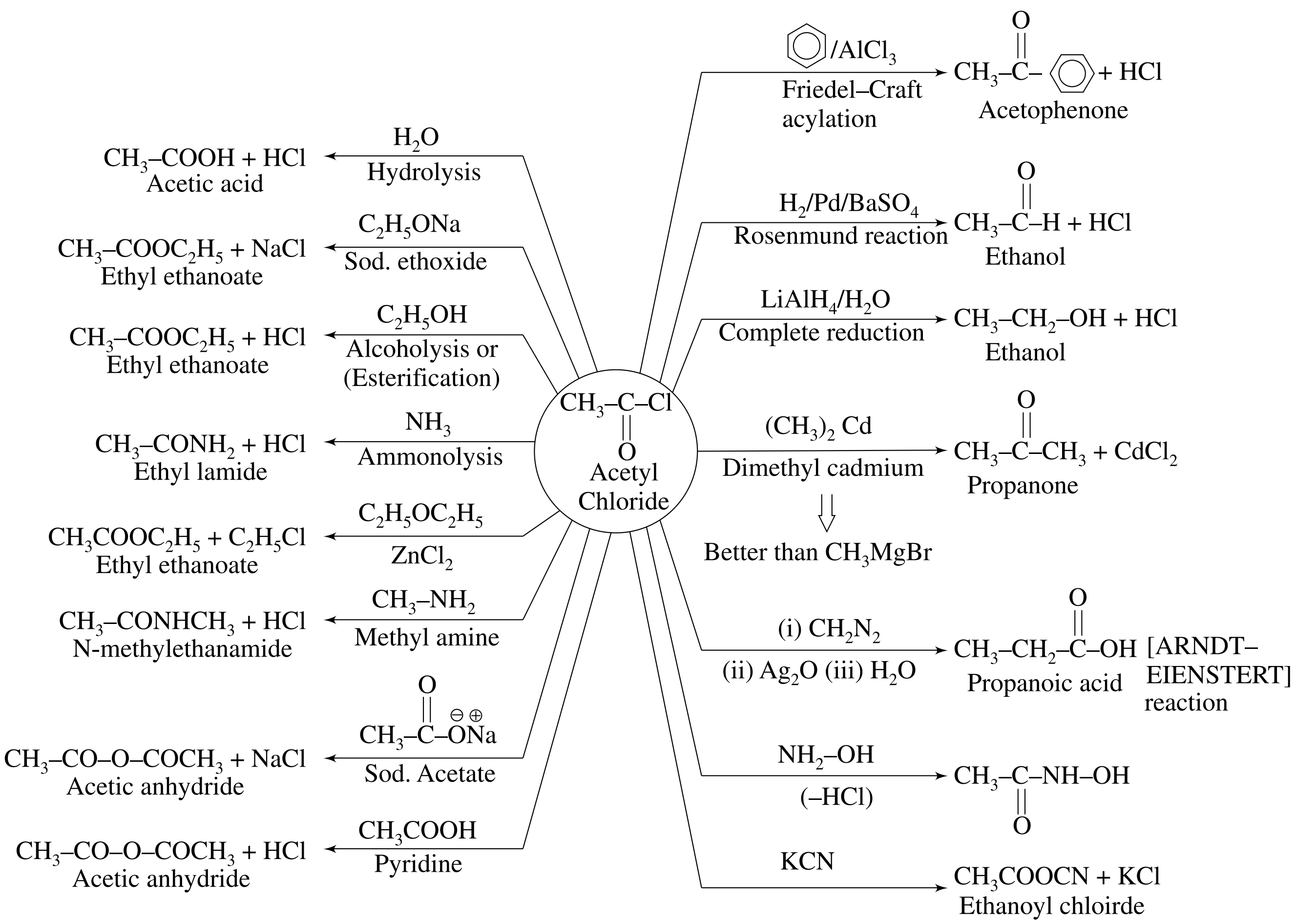
Special Points

- Methyl acetate and ethyl acetate are Fruity smelling liquids.
- Acetamide is a white crystalline solid having pungent smell of dead mouse.
  Therefore, acid derivatatives have higher boiling points than corresponding hydrocarbons but lower boiling points than corresponding carboxylic acids.
- Primary amides have quite high boiling point and melting points because they form strong intermolecular H-bonding.

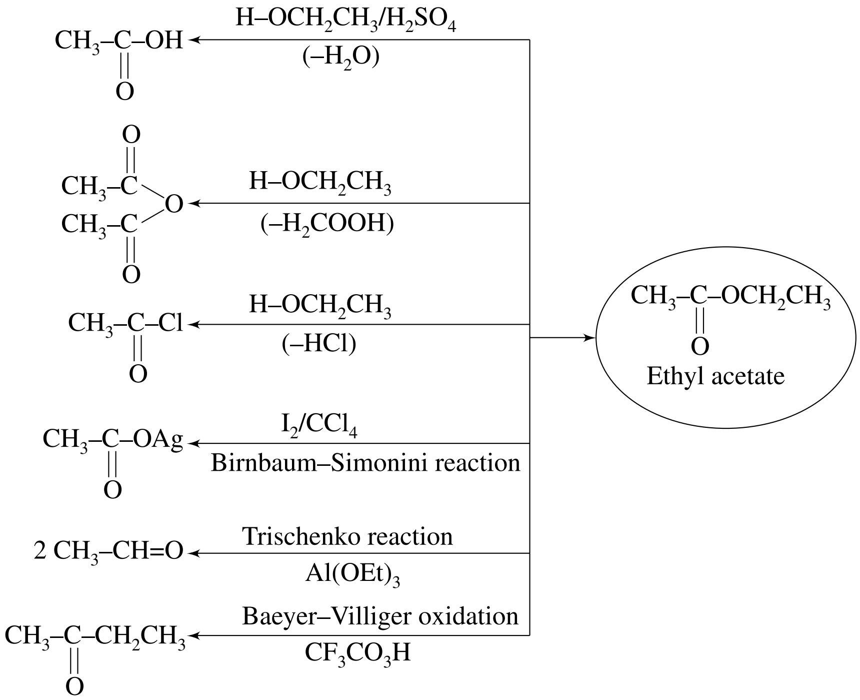
METHODS OF PREPARATION OF ACID CHLORIDE



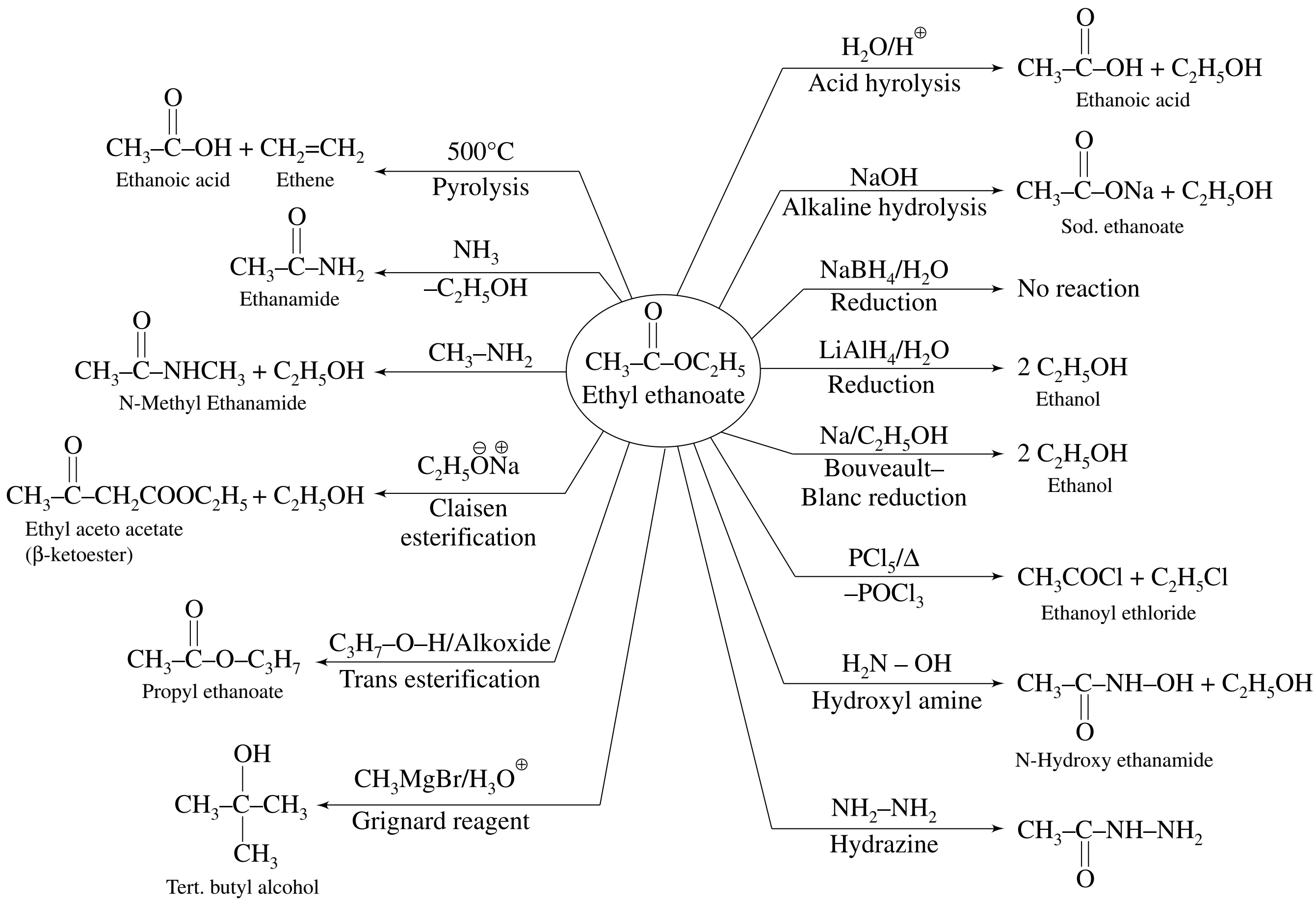
CHEMICAL PROPERTIES OF ACID CHILORIDE



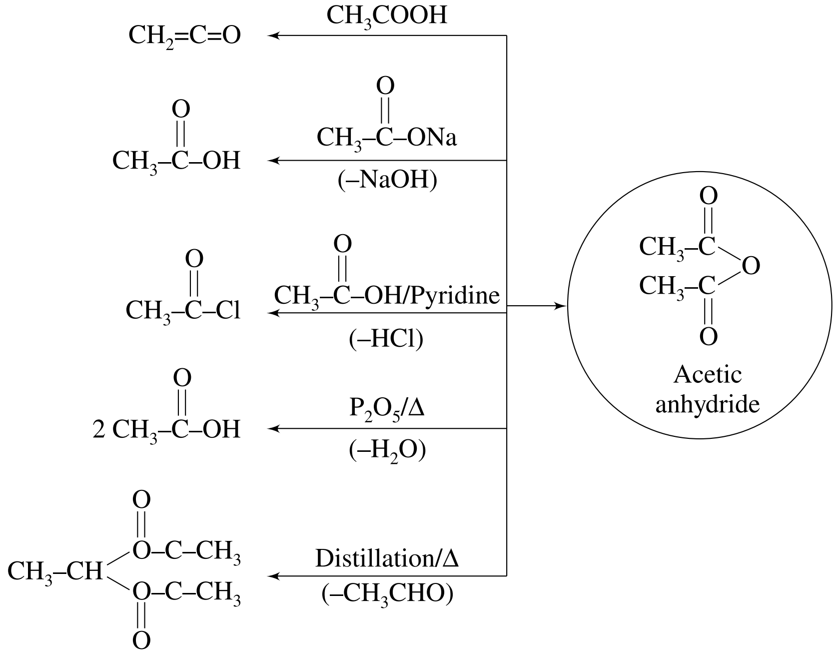
METHODS OF PREPARATION OF ESTER



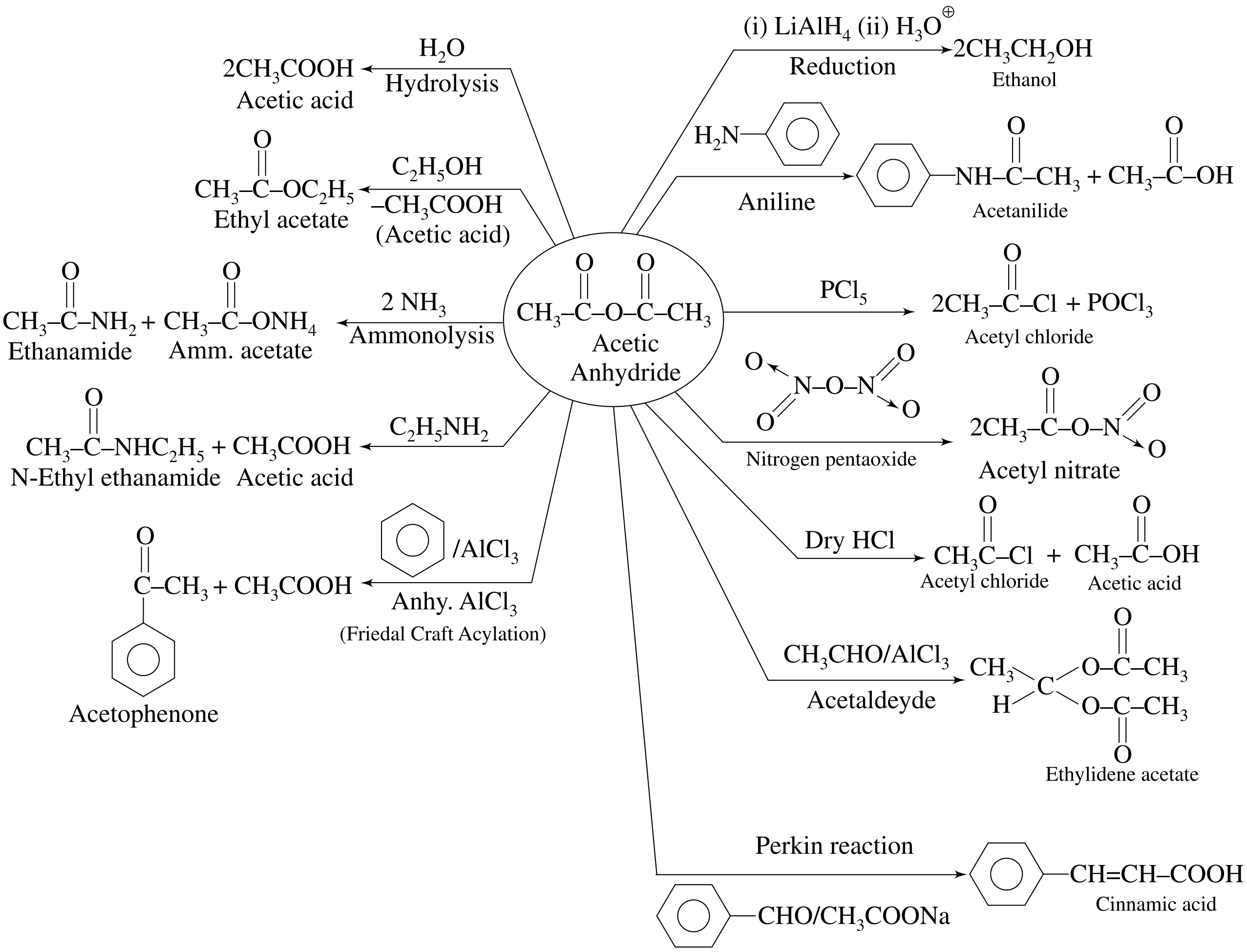
CHEMICAL PROPERTIES OF ESTER



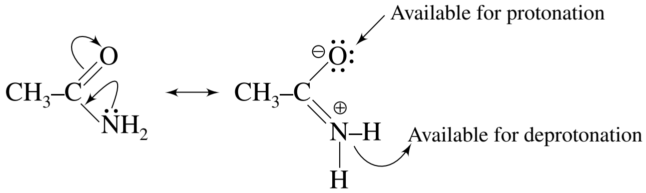
METHODS OF PREPARATION OF ACID ANHYDRIDE

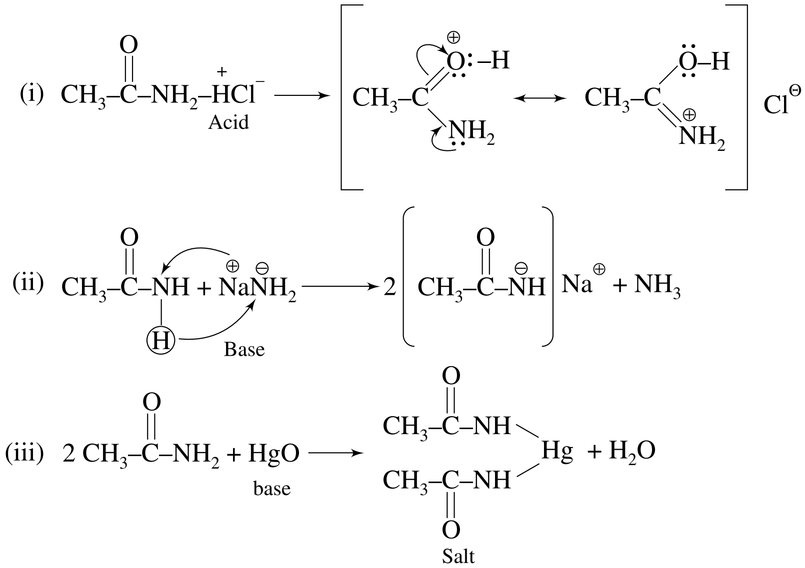


CHEMICAL PROPERTIES OF ACID ANHYDRIDE

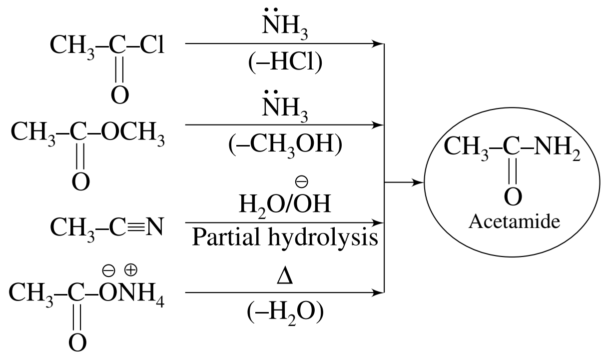


AMPHOTERIC CHARACTER OF ACETAMIDE:

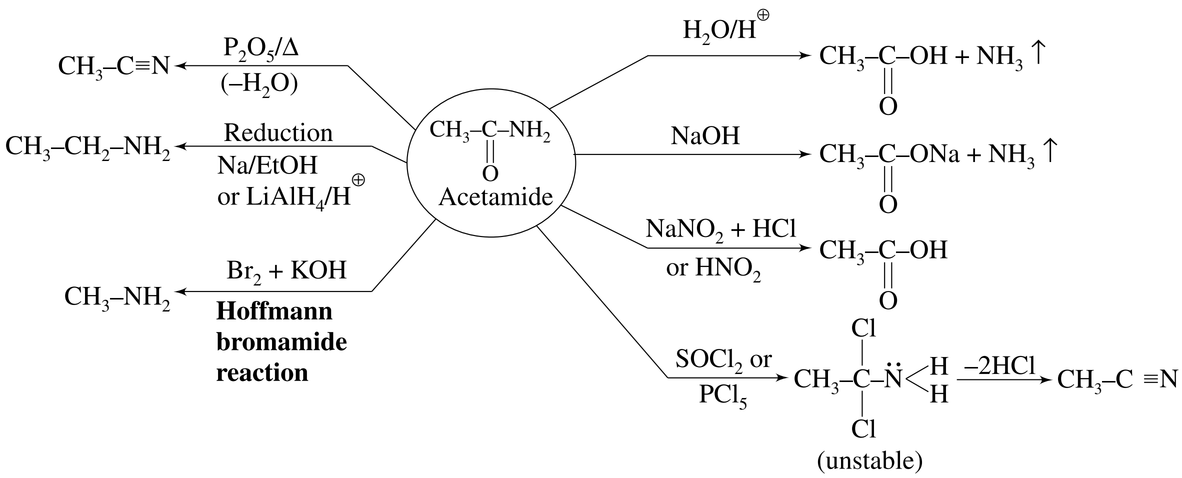




METHODS OF PREPARATION OF ACID AMIDE



CHEMICAL PROPERTIES OF ACID AMIDE



SOLVED EXAMPLE

1. Pyruvic acid is obtained by
(1) Acidic hydrolysis of acetone cyanohydrin
(2) Acidic hydrolysis of acetaldehyde cyanohydrin followed by acidification with $KMnO_4$
(3) Acidic hydrolysis of formaldehyde cyanohydrin
(4) Reaction of HCN with CH_3CHO followed by treatment with $NaOH/I_2$

Sol. **[2]**

$$CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{HCN} CH_3-\underset{\underset{OH}{|}}{CH}-CN \xrightarrow{H_2O/H^+} CH_3-\underset{\underset{OH}{|}}{CH}-COOH \xrightarrow{KMnO_4\ [O]} CH_3-\underset{\underset{O}{\|}}{C}-COOH$$

2. Formic acid and acetic acid are distinguished by
(1) $NaHCO_3$ (2) $FeCl_3$
(3) Victor Meyer's test (4) Tollens' reagent

Sol. **[4]**

$$H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\text{reagent}]{\text{Tollens'}} \text{Silver mirror}$$

Formic acid (Aldehyde group)

$$CH_3COOH \xrightarrow[\text{reagent}]{\text{Tollens'}} \text{Negative test}$$

Absence of aldehyde group

3. An organic liquid of the composition $C_4H_8O_2$ yields a sodium salt of an acid $C_3H_6O_2$ and methanol on boiling with NaOH solution. The given liquid is
(1) $CH_3CH_2COOCH_3$ (2) $CH_3COOC_2H_5$
(3) $HCOOC_3H_7$ (4) $CH_3CH_2CH_2COOH$

Sol. **[1]**

$$CH_3-CH_2-CO|O-CH_3 \xrightarrow{NaOH} CH_3-CH_2-COONa + |CH_3OH$$

4. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from:
(1) methyl group
(2) carboxylic acid group
(3) methylene group
(4) bicarbonate group

Sol. **[4]**

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{NaHCO_3} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-ONa + \underbrace{CO_2 + H_2O}_{\text{From bicarbonate group}}$$

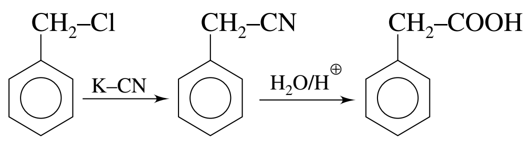
5. Ph–CH_2–CH_2OH can be converted into $PhCH_2CH_2COOH$. The correct sequence of reagents is
(1) PBr_3, KCN, H^+ (2) PBr_3, KCN, H_2
(3) KCN, H^+, PBr_3 (4) PBr_3, HCN, H^+

Sol. **[1]**

$$Ph-CH_2-CH_2-OH \xrightarrow{PBr_3} Ph-CH_2-CH_2-Br \xrightarrow{KCN} Ph-CH_2-CH_2-CN \xrightarrow{H^\oplus} Ph-CH_2-CH_2-COOH$$

6. When benzyl chloride is treated with ethanolic KCN, followed by acidification, the major product formed is:
(1) benzoic acid
(2) benzyl alcohol
(3) benzyl cyanide
(4) phenyl acetic acid

Sol. **[4]**



Phenyl acetic acid

7. Guess the product $CH_2CH_2CONH_2 \xrightarrow[\Delta]{PCI_5}$?
(1) CH_3CH_2–CN (2) CH_3CH_2COCI
(3) $CH_3CCl_2CONH_2$ (4) $CH_3CH_2CCl_2$–NH_2

Sol. **[1]**

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{PCl_5} CH_3-CH_2-CN$$

De-hydration

8. Which of the following reagents can distinguish 4-oxopentanoic acid from 2-oxopentanoic acid?
(1) $NaHCO_3$
(2) 2,4-Dinitrophenylhydrazine
(3) $AgNO_3$, aq. NH_3
(4) I_2,NaOH

Sol. **[4]**

$$C-\underset{\underset{O}{\|}}{C}-C-C-COOH \qquad C-C-C-\underset{\underset{O}{\|}}{C}-COOH$$

$NaHCO_3$	+Ve	+Ve
DNP	+Ve	+Ve
$AgNO_3$/aq NH_3	–Ve	–Ve
I_2/NaOH	+Ve	–Ve

9. A compound (X), $C_4H_8O_3$, liberates CO_2 on reaction with $NaHCO_3$. When (X) is treated with pyridinium chlorochromate, it is converted into a new compound (Y), $C_4H_6O_3$, which on heating expels CO_2 to form acetone. The compound (X) is:

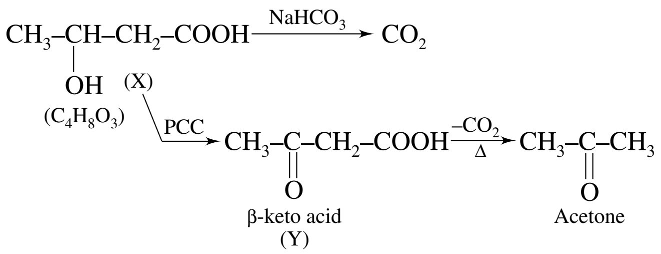
(1) $HOCH_2CH(CH_3)CO_2H$

(2) $CH_3C(CH_3)(OH)CO_2H$

(3) $CH_3CHOHCH_2CO_2H$

(4) $CH_3CH_2CH(OH)CO_2H$

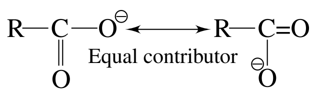
Sol. **[3]**



10. Carboxylic acids, RCOOH, furnish H^+ ions to water forming H_3O^+ and carboxylate ions, $RCOO^-$. The major reason for this acidic behaviour is that

(1) The carboxylate ion is stabilised by salvation with H_2O
(2) The carboxylic acid is stabilised by resonance
(3) The carboxylate ion is stabilised by resonance
(4) The carboxylate ion is more resonance stabilised than the unionised carboxylic acid is

Sol. **[4]**



11. Formic acid on being heated with concentrated H_2SO_4 is converted into:

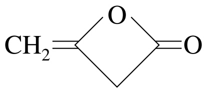
(1) CH_3COOH (2) CO
(3) CO_2 (4) HOOCCOOH

Sol. **[2]**

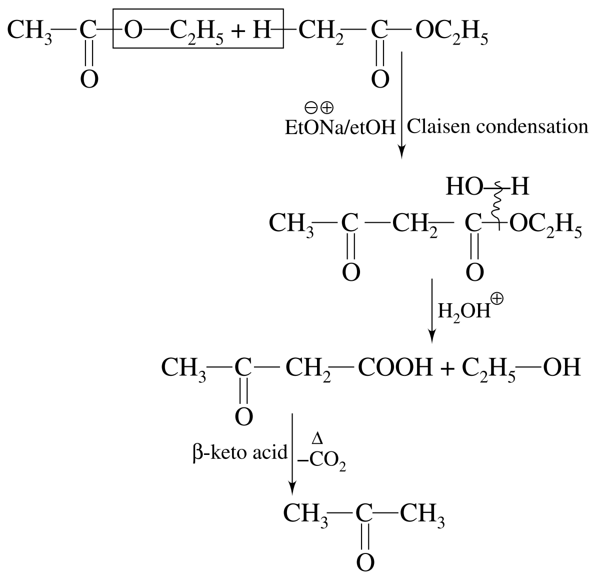
$$H{-}\overset{\overset{\large O}{\|}}{C}{-}OH \xrightarrow[\text{De-hydration}]{\text{Conc. } H_2SO_4} CO + H_2O$$

12. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B compound B is-

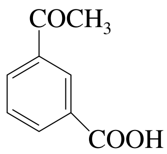
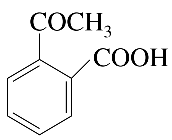
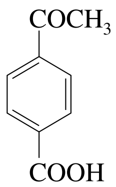
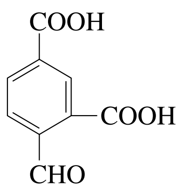
(1) CH_3COCH_2COOH (2) CH_3COCH_3

(3)  (4) $CH_2{=}C(OC_2H_5)_2$

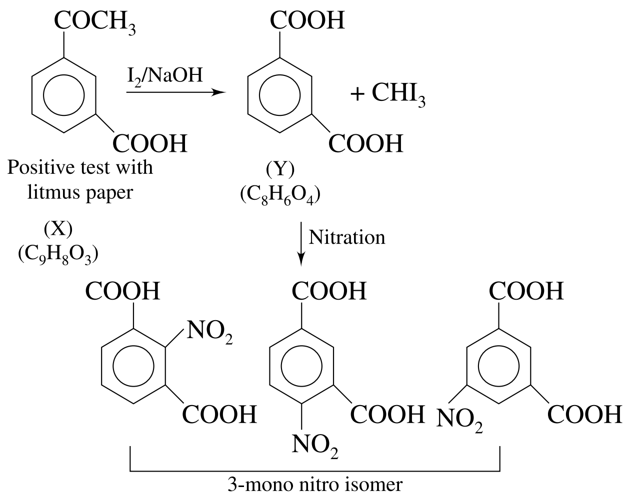
Sol. **[2]**



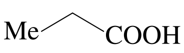
13. An aromatic compound 'X' ($C_9H_8O_3$) turns blue litmus to red. It gives yellow precipitate with I_2/NaOH and forms Y($C_8H_6O_4$). Y forms three mononitro isomeric products. Identify X.

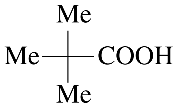
(1) 
(2) 
(3) 
(4) 

Sol. **[1]**



14. The following acids can be differentiated by

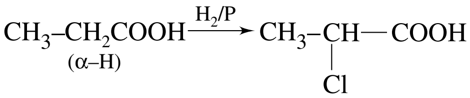
(I) 

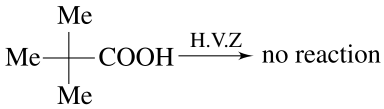
(II) 

(1) $NaHCO_3$ (2) $AgNO_3$
(3) H. V. Z. reaction (4) Hunsdiecker reaction

Sol. **[3]**

(I) Only α–H containing carboxylic acid forms-halo acid with X_2/P_4 is known as H. V. Z reaction

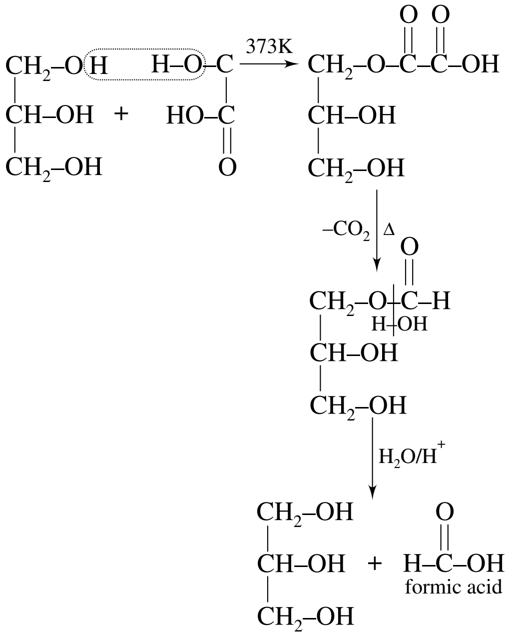


(II) 

15. Formic acid is obtained when:

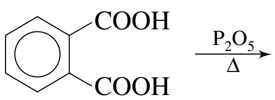
(1) Calcium acetate is heated with conc. H_2SO_4
(2) Calcium formate is heated with calcium acetate
(3) Glycerol is heated with oxalic acid at 373 K
(4) Acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4

Sol. **[3]**



EXERCISE 1

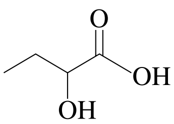
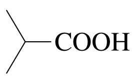
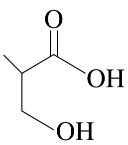
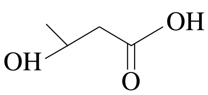
1. Which reactions give acid anhydride as product?

(i) $C_6H_5COOH + CH_3COCl \xrightarrow{\text{Pyridine}}$
(ii) $C_6H_5COO^{\ominus}Na^{\oplus} + C_6H_5COCl \longrightarrow$
(iii) $C_6H_5CONH_2 + CH_3COO^{\ominus}\ Na^{\oplus} \longrightarrow$
(iv) 

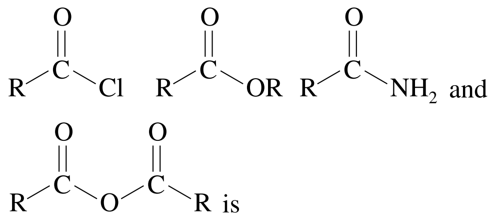
(v) 

(1) i, ii, iii, iv only (2) i, ii, iv, v only
(3) i, ii, iii only (4) iv & v only

2. An optically active compound 'X' has molecular formula $C_4H_8O_3$. It evolves CO_2 with $NaHCO_3$. 'X' on reaction with $LiAlH_4$ give achiral compound. 'X' is–

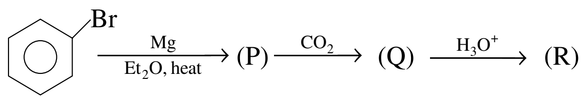
(1) 
(2) 
(3) 
(4) 

3. The order of decreasing ease of hydrolysis of the compound

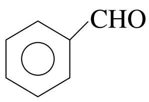


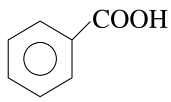
(1) I > IV > II > III (2) I > II > III > IV
(3) I > III > II > IV (4) IV > III > II > I

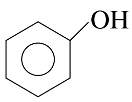
4. Consider the following sequence of reaction.

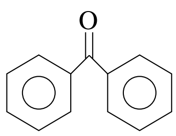


The final product (R) is

(1) 

(2) 

(3) 

(4) 

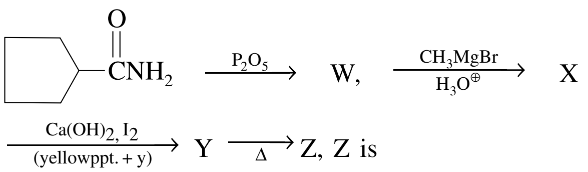
5. $Ph\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}O\text{–}H + CH_3\text{–}\overset{18}{O}H \rightleftharpoons (X) + H_2O$

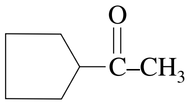
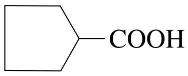
(1) $X = Ph\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3$ (Trans esterificarion)

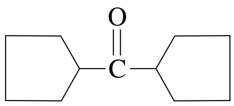
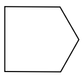
(2) $X = Ph\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3$ (Esterification reaction)

(3) $X = Ph\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}\overset{18}{O}\text{–}CH_3$ (Saponification)

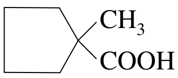
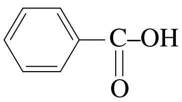
(4) $X = Ph\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}O\text{–}CH_3$ (Hydrolysis)

6. 

(1)  (2) 

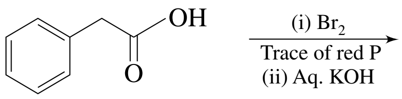
(3)  (4) 

7. Which of the following give HVZ reaction?

(1)  (2) 

(3) $H\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}OH$ (4) $CH_3\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}OH$

8. Give the major product of the following reaction sequence:



(1) $C_6H_5\overset{\overset{\displaystyle OH}{|}}{C}HCOOH$

(2) $C_6H_5CH_2COBr$

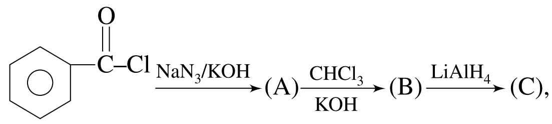
(3) *p*-Br-$C_6H_4CH_2COOH$

(4) *m*-Br-$C_6H_4CH_2COOH$

9. $Ph\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}O\text{–}H \xrightarrow{+\ Na\overset{14}{H}CO_3}$ the gas evolved is:

(1) CO_2 (2) $\overset{14}{C}O_2$

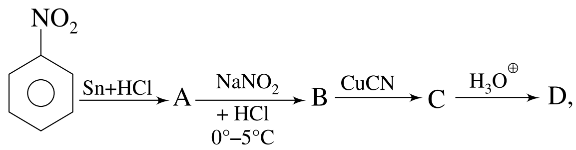
(3) H_2 (4) NH_3

10. 

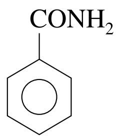
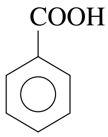
Identify C

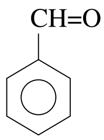
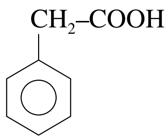
(1) $Ph\text{–}CH_2\text{–}NH_2$ (2) $Ph\text{–}NH_2$

(3) $Ph\text{–}CO_2H$ (4) $Ph\text{–}NH\text{–}CH_3$

11. 

'D' is:

(1)  (2) 

(3)  (4) 

12. The conversion $CH_3OH \rightarrow CH_3COOH$ can be effected by allowing CH_3OH to react with

(1) carbon monoxide in the presence of Monsanto catalyst, a complex compound of rhodium, $[Rh(CO)_2I_2]^-$

(2) formic acid in the presence of concentrated H_2SO_4

(3) ethylene in the presence of $PdCl_2$

(4) formaldehyde in the presence of dry HCl gas

13. In a nucleophilic acyl substitution, the hybridisation of carbon atom at the substrate centre changes in the order (substrate → intermediate → product)

(1) $sp^2 \rightarrow sp^2 \rightarrow sp^2$ (2) $sp^3 \rightarrow sp^3 \rightarrow sp^2$

(3) $sp^2 \rightarrow sp^3 \rightarrow sp^2$ (4) $sp^2 \rightarrow sp^2 \rightarrow sp^3$

14. $CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}Cl + Nu^- \longrightarrow CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}Nu + Cl^-$

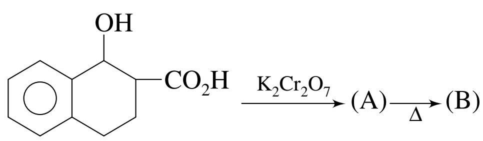
The reactivity order of different nucleophiles (NH_2^-, CH_3COO^-, HO^-) is in order

(1) $NH_2^- < CH_3COO^- < OH^-$

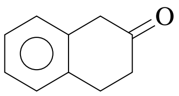
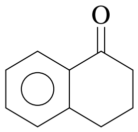
(2) $CH_3COO^- < OH^- < NH_2^-$

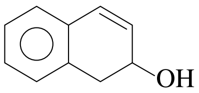
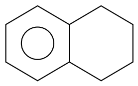
(3) $NH_2^- < OH^- < CH_3COO^-$

(4) $CH_3COO^- < NH_2^- < OH^-$

15.  Product

(B) is:

(1)    (2) 

(3)    (4) 

16. The conversion of acetophenone into benzoic acid can be achieved by reaction with:

(1) sodium hydroxide followed by acidification
(2) iodine and sodium hydroxide, followed by acidification
(3) hydroxylamine followed by reaction with H_2SO_4
(4) *m*-chloroperoxobenzoic acid

17. The nucleophilic acyl substitution

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-L + Nu\overset{-}{:} \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Nu + L\overset{-}{:}$$

will occur smoothly if:

(1) $Nu:^-$ is a stronger base than $L:^-$
(2) $Nu:^-$ is a weaker base than $L:^-$
(3) $Nu:^-$ and $L:^-$ have equal basicity
(4) $R:^-$, $Nu:^-$ and $L:^-$ all have equal basicity

18. Consider the following sequence of reactions,

$PCl_5 + SO_2 \rightarrow A + B$

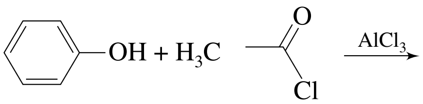
$CH_3COOH + A \rightarrow C + SO_2 + HCl$

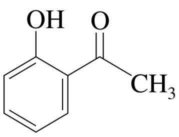
$2C + (CH_3)_2Cd \rightarrow 2D + CdCl_2$

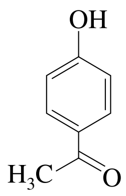
The end product (D) is:

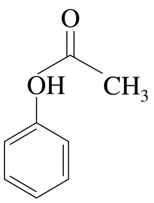
(1) CH_3COCl (2) CH_3COOCH_3
(3) CH_3COCH_3 (4) $(CH_3)_2CHCOCl$

19. Predict the product of the reaction below:



(1) 

(2) 

(3) 

(4) Both (1) and (2)

20. Which of the following does not give benzoic acid on hydrolysis?

(1) phenyl cyanide   (2) benzoyl chloride
(3) benzyl chloride   (4) methyl benzoate

21. $CH_3CH_2ONa \xrightarrow[\text{Pressure (ii) } H^+]{\text{(i) CO, } \Delta} A$

$CH_2 = CH_2 + CO + H_2O \xrightarrow[670°C]{H_3PO_4} B$

A and B are:

(1) CH_3CH_2COOH in both cases
(2) CH_3CH_2CHO in both cases
(3) CH_3CH_2COOH, CH_3CHO
(4) CH_3CHO, CH_3COOH

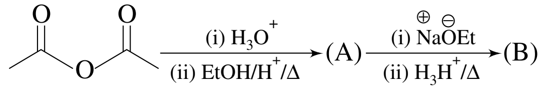
22. Which of the following sets of reagents X and Y will convert propanoic acid into alanine (an amino acid)?

$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{X} CH_3-\overset{\overset{\displaystyle Br}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[PH=4.3]{Y} CH_3-\overset{\overset{\displaystyle \overset{\oplus}{N}H_3}{|}}{CH}-COOH$$

	X	Y
(1)	Br_2	$NaNH_2$
(2)	Br_2/P	NaOH
(3)	Br_2/P	NH_3
(4)	Br_2/HBr	$NaNH_2$

23. Which of the following compounds will develop a blue colour on successive treatment with aqueous KI containing KIO_3 and starch solution?

(1) Benzoic acid   (2) Phenol
(3) Ethanol   (4) Ethyl acetate

24. 

Select correct option

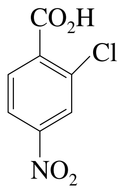
(1) Compound (B) is acetone
(2) Compound (B) is acetic acid
(3) Compound (B) is ethyl acetate
(4) Compound (A) evolve H_2 (g) on reacting with Na-metal

25. Ethyl acetate is hydrolysed by heating with an aqueous NaOH solution. Which one of the following is the correct mechanism of the reaction?

(1) Acyl-oxygen bond cleavage; unimolecular
(2) Acyl-oxygen bond cleavage; bimolecular
(3) Alkyl-oxygen bond cleavage; unimolecular
(4) Alkyl-oxygen bond cleavage; bimolecular

EXERCISE 2

1. Which one of the following is the best synthesis of 2-chloro-4-nitrobenzoic acid?



2-chloro-4-nitrobenzoic

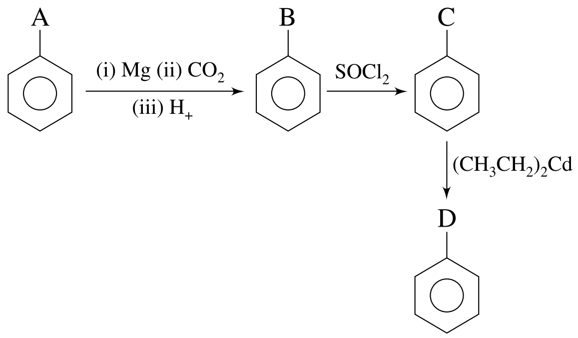
(1) 1. Heat benzoic acid with HNO_3, H_2SO_4
2. Cl_2, $FeCl_3$, heat

(2) 1. Treat toluene with HNO_3, H_2SO_4
2. $K_2Cr_2O_7$, H_2O, H_2SO_4, heat
3. Cl_2, $FeCl_3$, heat

(3) 1. Treat toluene with HNO_3, H_2SO_4
2. Cl_2, $FeCl_3$, heat
3. $K_2Cr_2O_7$, H_2O, H_2SO_4, heat

(4) 1. Treat nitrobenzene with Cl_2, $FeCl_3$, and heat
2. CH_3Cl, $AlCl_3$
3. $K_2Cr_2O_7$, H_2O, H_2SO_4, heat

2. Consider the following sequence of reactions:



Identify A, B, C and D

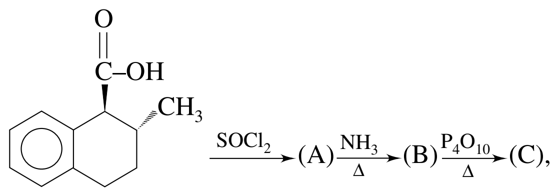
	A	B	C	D
(1)	–F,	$-COCH_3$,	$-COC_3H_7$	–CHO
(2)	–CHO,	–COOH,	–COCl,	$-COC_2H_5$
(3)	–Br,	–COOH,	–COCl,	$-COC_2H_5$
(4)	–Br,	–COOH,	–COCl,	–CHO

3. The products A, B, C and D in the reaction

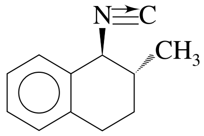
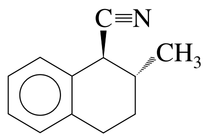
$$A + B \xleftarrow[H_2SO_4]{\text{Heat}} H\text{–}COOH \xrightarrow[H_2SO_4]{\text{Conc.}} C + D$$

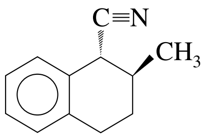
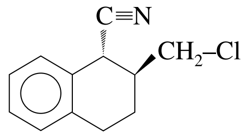
are given by the set:

(1) CO, H_2O, CO_2, H_2 (2) CH_2, H_2O, CO, H_2
(3) CO_2, H_2, CO, H_2O (4) CO, H_2, CO_2, H_2O

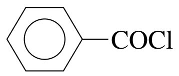
4. 

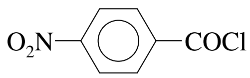
structure of (C) is–

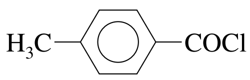
(1)  (2) 

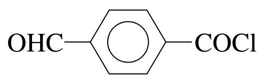
(3)  (4) 

5. Consider the following compounds.


I


II

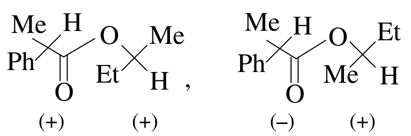

III

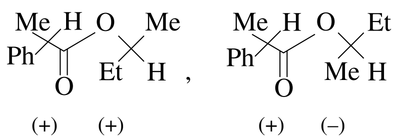

IV

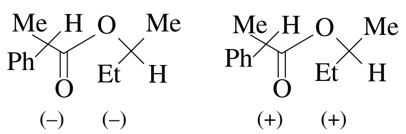
The correct order of decreasing reactivity of the above compounds towards hydrolysis is

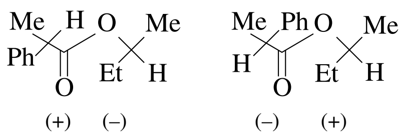
(1) II > IV > III > I (2) II > IV > I > III
(3) I > II > III > IV (4) IV > II > I >III

6. A racemic mixture of (±) 2-phenyl propanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of two esters formed.

(1) 

(2) 

(3) 

(4) 

7. Consider the following sequence of reactions:

$BaCO_3 + H_2SO_4 \rightarrow X(gas)$

$CH_2 = CHBr \xrightarrow[\substack{2.\ X \\ 3.\ H_3O^+}]{1.\ Mg,\ THF,\ heat}$

The product (Y) is:

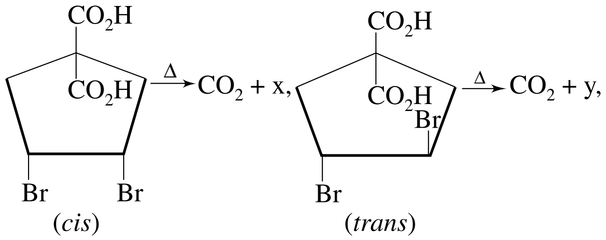
(1) $CH_2 = CHCHO$

(2) $CH_2{=}CHCOOH$

(3) $CH_2{=}CHCOBr$

(4) $CH_3CH{=}CHCH_2CH_2NH_2$

8. Products obtained in the given reaction are shown below:

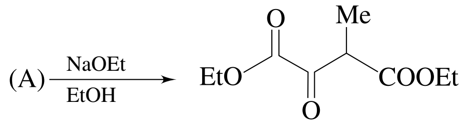


The number of possible products for x and y is:

(1) 1, 1 (2) 1, 2

(3) 2, 1 (4) 2, 2

9. The reactant (A) is the reaction is:



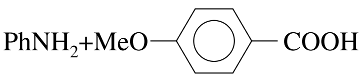
(1) MeCOOEt and $EtO-\underset{\displaystyle O}{\underset{||}{C}}-\underset{\displaystyle O}{\underset{||}{C}}-Et$

(2) EtCOOEt + EtOOC – COOEt

(3) $EtOOC-\underset{\displaystyle Me}{\underset{|}{CH}}-COOEt + HCOOEt$

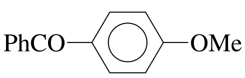
(4) EtCOOEt + HCOOEt

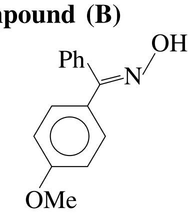
10. Ketone (A) $\xrightarrow{NH_2OH\,.\,HCl}$ (B) $\xrightarrow{H^{\oplus}}$

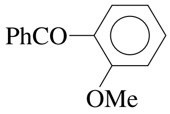


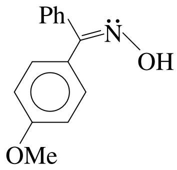
The ketone (A) and compound (B), respectively, are:

Ketone (A) **Compound (B)**

(I) 

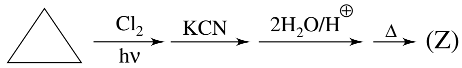
(III) 

(II) 

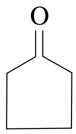
(IV) 

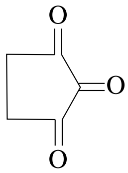
(1) (I), (III) (2) (I), (IV)

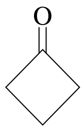
(3) (II), (III) (4) (II), (IV)

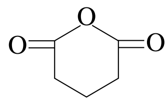
11. 

Final product (Z) will be:

(1) 

(2) 

(3) 

(4) 

12. Which of the following statements is wrong?

(1) Formic acid is a stronger acid than acetic acid

(2) o-Bromobenzoic acid is a weaker acid than o-chlorobenzoic acid.

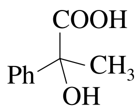
(3) Lactic acid does not respond positively to silver mirror test with Tollens reagent

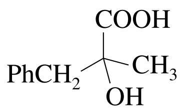
(4) Benzaldehyde does not reduce Fehling's solution

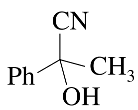
13. In a set of reactions, acetic acid yielded a product (D).

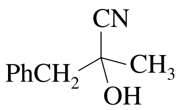
$CH_3COOH \xrightarrow{SOCl_2} (A) \xrightarrow[anhyd.\,AlCl_3]{benzene} (B) \xrightarrow{HCN} (C) \xrightarrow[heat]{H_3O^+} (D)$

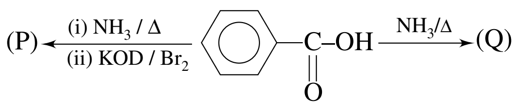
The structure of (D) would be

(1) 

(2) 

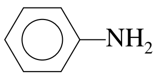
(3) 

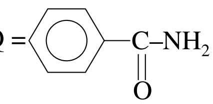
(4) 

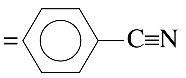
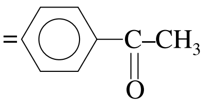
14. 

$\xrightarrow{P_2O_5} (R) \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ CH_3MgBr} (S) \xrightarrow[(ii)\ H^+/\Delta]{(i)\ H_2NOH} T + U$

Which of following are correct?

(I) P = 

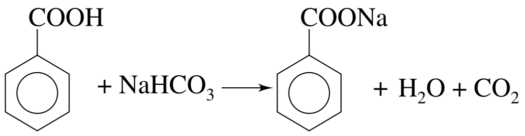
(II) Q = 

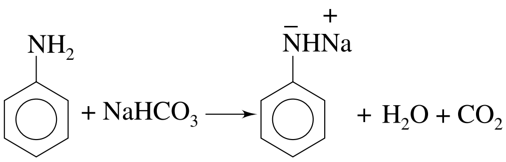
(III) R =  (IV) S = 

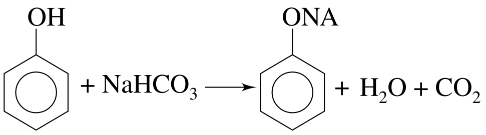
(V) $T = Ph–\underset{\underset{O}{||}}{C}–NH–CH_3$ (VI) $U = CH_3–\underset{\underset{O}{||}}{C}–NH–Ph$

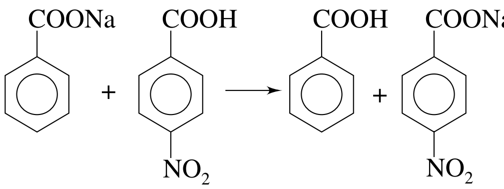
(1) I, II, III, IV only (2) II, III, IV, V, VI
(3) I, III, IV, V (4) All are correct

15. Which of the following reactions are feasible (practically possible)?

(I) 

(II) 

(III) 

(IV) 

(1) I, II (2) II, III
(3) III, IV (4) I, IV

16. Carboxylic acid, although unreactive to alcohols, reacts in the presence of small amount of conc. H_2SO_4 or with 2-3% of HCl?

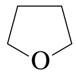
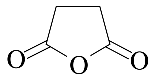
(I) This reaction is called Fischer esterification reaction.
(II) The equilibrium is shifted to R.H.S. if H_2O is removed by azeotropic distillation with benzene.
(III) The reaction of RCOCl and R′OH to give ester (RCOOR′) is irreversible and more feasible than Esterification of RCOOH.
(IV) If the above esterification of RCOOH is carried out in excess of R′OH, the equilibrium is shifted to R.H.S.

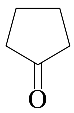
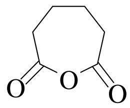
(1) (I), (II) (2) (I), (II), (III)
(3) (I), (II), (IV) (4) (I), (II), (III), (IV)

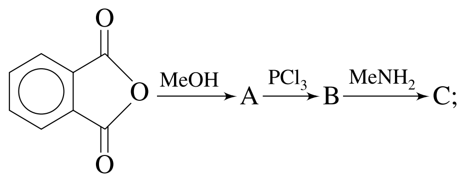
17. An ester (A) with molecular formula $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give a olefin (B). Ozonolysis of (B) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The Structure of (A) is

(1) $C_6H_5COOC_2H_5$
(2) $CH_3COCH_2COC_6H_5$
(3) p–$CH_3O–C_6H_4–COCH_3$
(4) $C_6H_5COOC_6H_5$

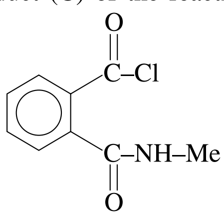
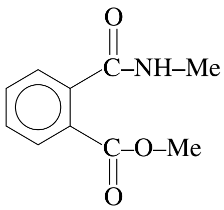
18. Which of the following products is formed when adipic acid is heated?

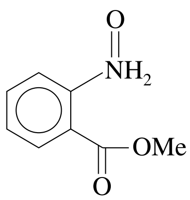
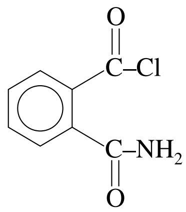
(1)  (2) 

(3)  (4) 

19. 

Product (C) of the reaction is:

(1)  (2) 

(3)  (4) 

20. $H–O–\overset{\overset{O}{||}}{C}–(CH_2)_n–\overset{\overset{O}{||}}{C}–O–H \xrightarrow[\Delta]{}$ Product, At what value of (n) given compound will not evolve CO_2 gas:

(1) n = 5 (2) n = 4
(3) n = 2 (4) n = 1

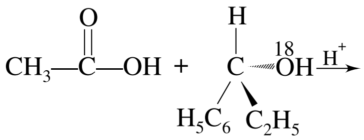
EXERCISE 3

One and More Than One Option Correct Type Question

1. Which reagent(s) given below can be used to separate a mixture of butanol and butanoic acid from its ethereal solution?

(1) $NaNH_2$ (aq) (2) NH_3 (aq)
(3) NaOH (4) $NaHCO_3$

2. Consider the following Fischer esterification reaction



A pure enantiomer

The correct statement is/are

(1) O^{18} will be a part of ester

(2) Alcohol will retain its configuration

(3) O^{18} will be sp^2-hybridised in ester

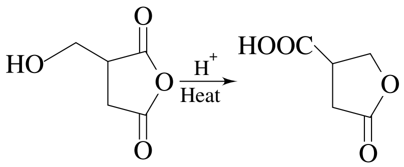
(4) Sign of specific rotation of ester is same as that of alcohol

3. Which is/are not a suitable nucleophilic substitution reaction?

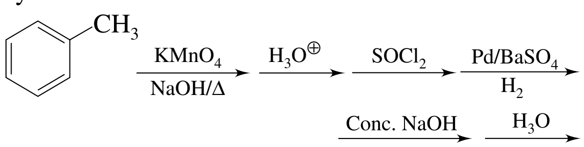
(1) $CH_3COCl + CH_3MgBr/$ (excess) $\xrightarrow{Et_2O} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(2) $CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3NH_2 \longrightarrow CH_3-CONHCH_3+CH_3COOH$

(3) $CH_3CONH_2 + CH_3MgBr \xrightarrow{Et_2O} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(4) 

4. Consider the reaction sequence in the following synthesis

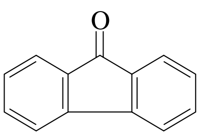


The end product (s) is/are

(1) $C_6H_5-\overset{\overset{O}{\|}}{C}-OCH_2C_6H_5$

(2) C_6H_5COOH

(3) $C_6H_5CH_2OH$

(4) 

5. The correct statement regarding the following transformation is/are

$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_3 + CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 + CH_3CH_2CH_2OH$$

(1) Presence of excess of ethanol favours the reaction

(2) Both acid and base can act as catalyst

(3) Smaller alcohols always displace the larger alcohols from ester

(4) The reaction is second order in both acid and base catalysed condition

6. In the reaction given below, the intermediates formed is/are

$$CH_3CH_2CONH_2 + NaOH + Br_2 \longrightarrow CH_3CH_2NH_2$$

(1) $CH_3CH_2CONHBr$ (2) $CH_3CH_2-\overset{\overset{O}{\|}}{C}-\ddot{N}:$

(3) $CH_3CH_2CONHOH$ (4) CH_3CH_2NCO

Statement Type Question

(1) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(2) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(3) Statement-1 is True, Statement-2 is False.

(4) Statement-1 is False, Statement-2 is True.

7. **Statement-1:** α, α'-dichloro acetic acid does not undergo haloform reaction

Statement-2: α, α'-dichloro acetic acid has alpha-hydrogen.

8. **Statement I:** CH_3COOH when treated with $C_2H_5\overset{18}{O}H/H^+$, $CH_3CO\overset{18}{O}C_2H_5$ is formed.

Statement II: In Fischer esterification, protonated acid undergoes nucleophilic attack by alcohol in the slow, rate determining step.

9. **Statement I:** In the following reaction,

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow[\text{(ii) } H_2SO_4/\Delta]{\text{(i) } NaBH_4} P \xrightarrow[H_2SO_4/\Delta]{CH_3COOH}$$

Racemic mixture of esters

Statement II: Alcohol (P) undergoes nucleophilic addition on protonated acetic acid.

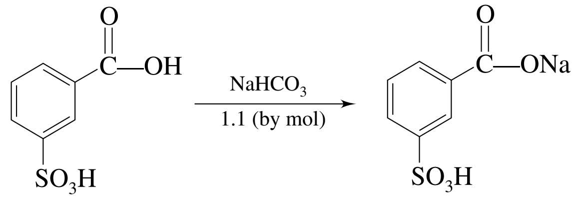
10. **Statement I:** Ester formation from acid and alcohol occur in acidic medium but not in alkaline medium. However, hydrolysis of esters proceeds in both acidic and alkaline medium.

Statement II: In alkaline medium carboxylic acid in neutralised into salt which do not undergo nucleophilic attack by alcohols.

11. **Statement I:** *p*-nitrobenzoic acid is more reactive than benzoic acid in acid catalysed esterification reaction.

Statement II: Rate determining step in Fischer's esterification reaction of carboxylic acid in nucleophilic attack by alcohols on protonated acid.

12. **Statement I:** Consider the following neutralisation reaction,

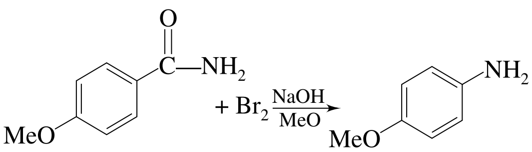


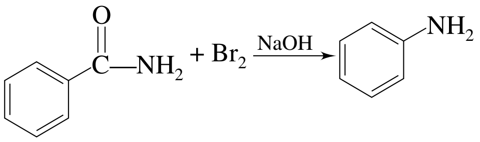
Statement II: —SO_3H is an electron withdrawing group, increased the acidity of —COOH.

13. **Statement I:** Acetyl chloride (CH_3COCl) undergoes faster nucleophilic substitution reaction (S_N2) than chloroethane.

Statement II: In acetyl chloride, the leaving group (—Cl) is in resonance with the carbonyl ($>C=O$) group.

14. **Statement I:** Consider the following two amides undergoing Hofmann's bromamide reaction.

I. 

II. 

Reaction (I) occurs more easily than (II).

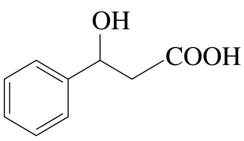
Statement II: the rate determining step in Hofmann's bromamide reaction is unimolecular elimination of bromide (Br^-) forming isocyanate.

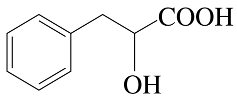
Comprehension Type Question

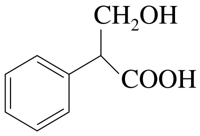
Passage based questions (Q. 15–17)

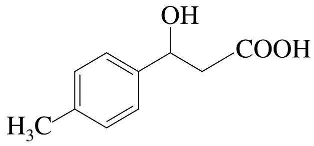
An organic compound A ($C_9H_{10}O_3$) is optically active. A changes orange colour of CrO_3–H_2SO_4 solution to blue–green. A on vigorous oxidation with hot, concentrated, alkaline $KMnO_4$ gives benzoic acid. Also A on treatment with HBr gives B ($C_9H_9O_2Br$) with same configuration as that of A.

15. What is the structure of A?

(1) 

(2) 

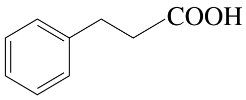
(3) 

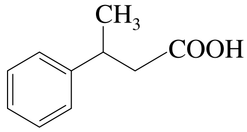
(4) 

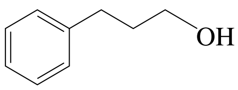
16. Consider the following reaction,

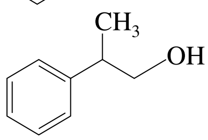
$$B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) NaOH}} \xrightarrow[\text{Heat}^+]{H_3PO_4} \xrightarrow[H_2]{[(C_6H_5)_3P]_3\,RhCl} C$$

The structure of C is

(1) 

(2) 

(3) 

(4) 

17. Which of the following sequence of reaction gives C as the major product?

(1) $Ph—CH_2CH_2Cl \xrightarrow[Et_2O]{Mg} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2}$

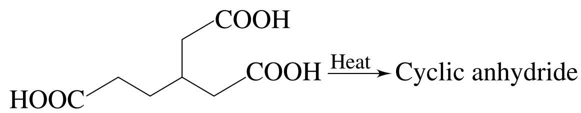
(2) $Ph—\underset{\underset{Cl}{|}}{CH}—CH_3 \xrightarrow[\text{(ii) } CO_2]{\text{(i) Mg/Et}_2O} \xrightarrow{H_3O^+}$

(3) $Ph—CH_2CH_2—CH{=}CH_2 \xrightarrow[H_2O_2]{O_3}$

(4) $Ph—\underset{\underset{CH_3}{|}}{CH}—CH{=}CH_2 \xrightarrow[\text{NaOH/Heat}]{\text{Conc. } KMnO_4}$

Single Digit Integer Type Question

18. Consider the following reaction



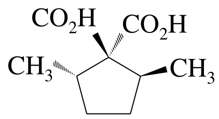
How many carbon atoms are present in the ring of cyclic anhydride?

19. How many different isomers exist for $C_3H_6O_2$ which reduces Tollens' reagent as well as forms $C_5H_8O_3$ upon treatment with acetic anhydride?

20. How many amide isomer sexist for C_4H_9ON that do not form amine on treatment with Br_2-NaOH?

21. How many different isomers of $C_4H_{11}N$ on heating with CS_2 followed by the addition of $HgCl_2$ gives alkyl isothiocyanide (RNCS)?

22. If a mixture containing ethyl acetate and ethyl propanoate is refluxed with C_2H_5ONa/C_2H_5OH, ester condensation takes place. How many different condensation would be formed?

23. 

How many product will be formed when above compound undergo de-carboxylation?

EXERCISE 4

1. End product of the following reaction is **(AIEEE 2002)**

$$CH_3CH_2COOH \xrightarrow[\text{Red P}]{Cl_2} \xrightarrow{\text{Alcoholic KOH}}$$

(1) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCOOH$ (2) $\underset{\displaystyle OH}{\underset{|}{C}}H_2CH_2COOH$

(3) $CH_2{=}CHCOOH$ (4) $\underset{\displaystyle Cl}{\underset{|}{C}}H_2\underset{\displaystyle OH}{\underset{|}{C}}HCOOH$

2. In the anion $HCOO^-$ the two carbon–oxygen bonds are found to be of equal length. What is the reason for it? **[AIEEE-2003]**

(1) The anion $HCOO^-$ has two resonating structures

(2) The anion is obtained by removal of a proton from the acid molecule

(3) Electronic orbitals of carbon atom are hybridised

(4) The C=O bonds is weaker than the C—O bond

3. Ethyl isocyanide on hydrolysis in acidic medium generates **(AIEEE 2003)**

(1) ethylamine salt and methanoic acid

(2) propanoic acid and ammonium salt

(3) ethanoic acid and ammonium salt

(4) methylamine salt and ethanoic acid

$$C_2H_5NC + H_2O \xrightarrow{H^+} \underset{\text{Fromic acid}}{HOOCH} + C_2H_5NH_2$$

$$C_2H_5NH_2 + H^+ \longrightarrow \underset{\text{Salt}}{C_2H_5NH_3^+}$$

4. When $CH_2{=}CH{—}COOH$ is reduced with $LiAlH_4$, the compound obtained will be **(AIEEE 2003)**

(1) $CH_3{—}CH_2{—}COOH$ (2) $CH_2{=}CH{—}CH_2OH$

(3) $CH_3{—}CH_2{—}CH_2OH$ (4) $CH_3{—}CH_2{—}CHO$

5. The general formula $C_nH_{2n}O_2$ could be for open chain **(AIEEE 2003)**

(1) Diketones (2) Carboxylic acids

(3) Diols (4) Dialdehydes

6. Which one of the following does not have sp^2 hybridised carbon? **[AIEEE-2004]**

(1) Acetone (2) Acetic acid

(3) Acetonitrile (4) Acetamide

7. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **(AIEEE 2005)**

(1) CH_3OH (2) HCHO

(3) CH_3COCH_3 (4) CH_3COOH

8. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[AIEEE-2007]**

(1) Benzophenone (2) Acetophenone

(3) Benzoic acid (4) Benzyl alcohol

9. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is **(AIEEE 2011)**

(1) diethyl ether (2) 2-butanone

(3) ethyl chloride (4) ethyl ethanoate

10. The strongest acid amongst the following compounds is **(AIEEE 2011)**

(1) CH_3COOH

(2) HCOOH

(3) $CH_3CH_2CH(Cl)CO_2H$

(4) $ClCH_2CH_2CH_2COOH$

11. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in the presence of KOH reacts with Br_2 give $CH_3CH_2NH_2$. A is **(JEE Main 2013)**

(1) CH_3COOH (2) $CH_3CH_2CH_2COOH$

(3) $CH_3{—}\underset{\displaystyle CH_3}{\underset{|}{C}}H{—}COOH$ (4) CH_3CH_2COOH

12. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is

(JEE Main 2013)

(1) 2 (2) 5
(3) 4 (4) 6

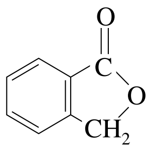
13. In the reaction,

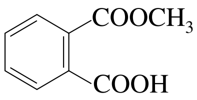
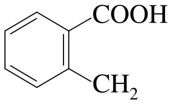
$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{alc.\ KOH} C$$

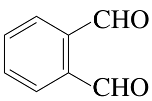
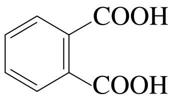
the product C is **(JEE Main 2014)**

(1) Acetaldehyde (2) Acetylene
(3) Ethylene (4) Acetyl chloride

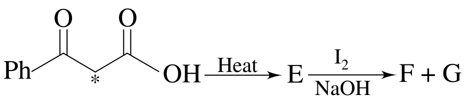
14. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the: **[IIT-2006]**



(1)  (2) 

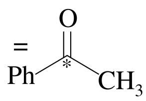
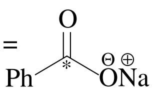
(3)  (4) 

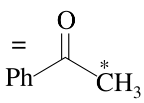
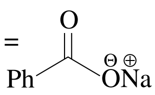
15. In the following reaction sequence, the correct structures of E, F and G are

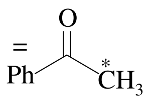
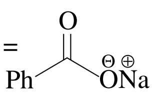


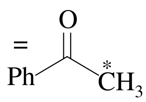
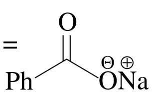
(* implies ^{13}C labelled carbon)

(2008, Only One Options Correct Type)

(1) E =  F =  $G = CHI_3$

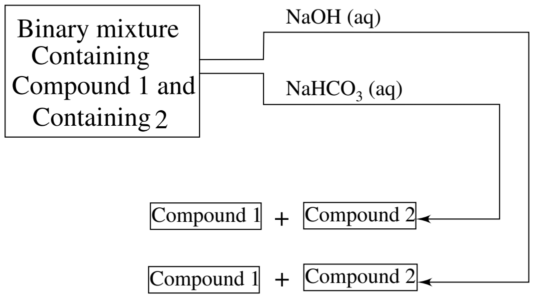
(2) E =  F =  $G = CHI_3$

(3) E =  F =  $G = \overset{*}{C}HI_3$

(4) E =  F =  $G = \overset{*}{C}HI_3$

16. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme.

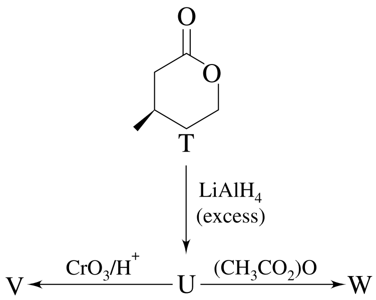
(2012, One or More than One Options Correct Type)



(1) C_6H_5OH and C_6H_5COOH
(2) C_6H_5COOH and $C_6H_5CH_2OH$
(3) $C_6H_5CH_2OH$ and C_6H_5OH
(4) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

17. With reference to the scheme given, which of the given statement(s) about T, U, and W is(are) correct?

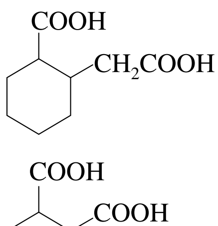
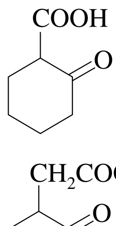
(2012, One or More than One Options Correct Type)

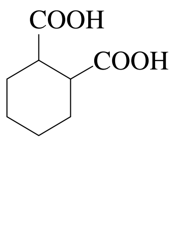
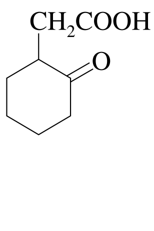


(1) T is soluble in hot aqueous NaOH
(2) U is optically active
(3) Molecular formula of W is $C_{10}H_{18}O_4$
(4) V gives effervescence on treatment with aqueous $NaHCO_3$

18. The compound that undergoes decarboxylation most readily under mild condition is

(2012, Only One Option Correct Type)

(1)  (2) 

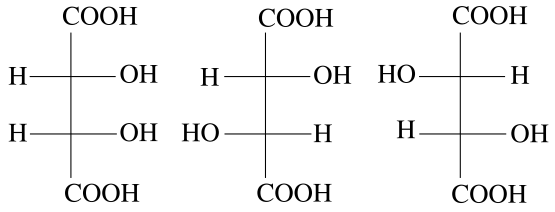
(3)  (4) 

Passage Based Questions: (Q. 19 and 20)

P and Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolourise Br_2/H_2O. On heating. P form the cyclic anhydride.

Upon treatment with dilute alkaline $KMnO_4$. P as well as Q could produce one or more than one forms S, T and U

(2013 Adv., Comprehension Type)



5 T U

19. Compounds formed from P and Q, respectively, are:

(1) Optically active S and optically active pair (T, U)

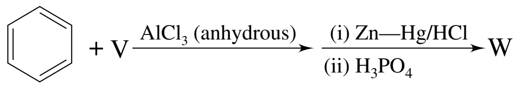
(2) Optically inactive S and optically inactive pair (T, U)

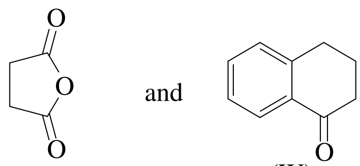
(3) Optically active pair (T, U) and optically active S

(4) Optically inactive pair (T, U) and optically inactive S

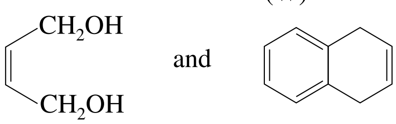
20. In the following reaction sequences V and W, respectively, are

$$Q \xrightarrow[\Delta]{H_2/Ni} V$$

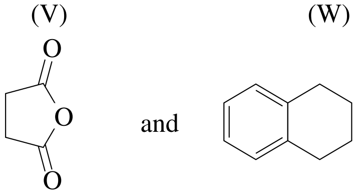


(1) 

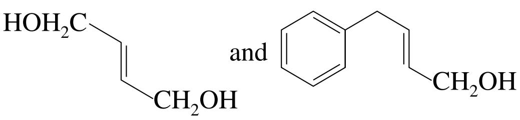
(W)

(2) 

(V) (W)

(3) 

(V) (W)

(4) 

(V) (W)

21. The compound that does not liberate CO_2, on treatment with aqueous sodium, is

(2013 Adv., Only One Option Correct Type)

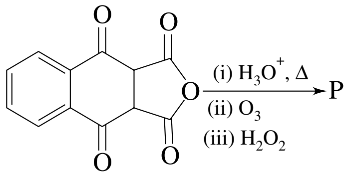
(1) Benzoic acid

(2) Benzenesulphonic acid

(3) Salicylic acid

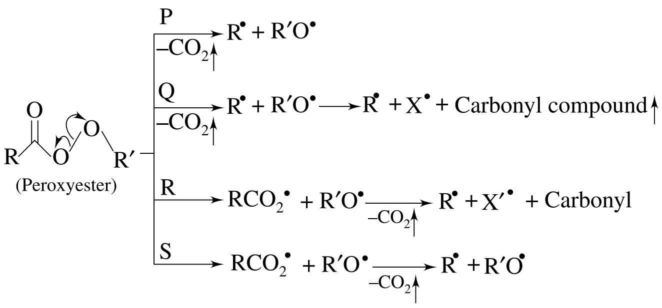
(4) Carbolic acid (Phenol)

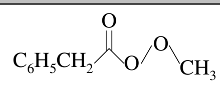
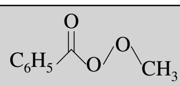
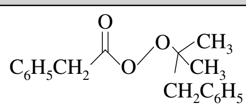
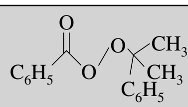
22. The total number of carboxylic acid group in the product P is **(2013 Adv., Integer Type)**



23. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from Column I with an appropriate structure in Column II and select the correct answer using the code given below the lists.

(2014 Adv., Matching Type)



	Column I		Column II
I.	Pathway P	p.	
II.	Pathway Q	q.	
III.	Pathway R	r.	
IV.	Pathway S	s.	

Codes

	I	II	III	IV
(1)	p	r	s	q
(2)	q	s	r	p
(3)	s	p	q	r
(4)	r	q	p	s

ANSWER KEY

EXERCISE # 1

1. (2)	2. (3)	3. (1)	4. (2)	5. (2)
6. (3)	7. (4)	8. (1)	9. (2)	10. (4)
11. (2)	12. (1)	13. (3)	14. (2)	15. (2)
16. (2)	17. (1)	18. (3)	19. (4)	20. (3)
21. (1)	22. (3)	23. (1)	24. (1)	25. (2)

EXERCISE # 2

1. (3)	2. (3)	3. (3)	4. (3)	5. (2)
6. (1)	7. (2)	8. (3)	9. (2)	10. (2)
11. (4)	12. (2)	13. (1)	14. (2)	15. (4)
16. (4)	17. (1)	18. (3)	19. (2)	20. (3)

EXERCISE # 3

1. (3,4)	2. (1,2)	3. (1,3)	4. (2,3)	
5. (1,2,4)	6. (1,4)	7. (2)	8. (1)	9. (2)
10. (1)	11. (1)	12. (4)	13. (2)	14. (2)
15. (3)	16. (2)	17. (2)	18. (5)	19. (4)
20. (6)	21. (5)	22. (6)	23. (1)	

EXERCISE # 4

1. (3)	2. (1)	3. (1)	4. (2)	5. (2)
6. (3)	7. (4)	8. (3)	9. (4)	10. (3)
11. (4)	12. (2)	13. (3)	14. (3)	15. (3)
16. (2,4)	17. (1.3.4)	18. (2)	19. (2)	20. (1)
21. (4)	22. (2)	23. (1)		

HINT AND SOLUTION

EXERCISE # 1

1. [2]

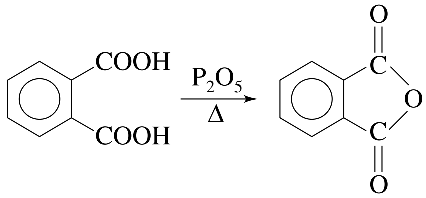
(i) $C_6H_5COOH + CH_3COCl$

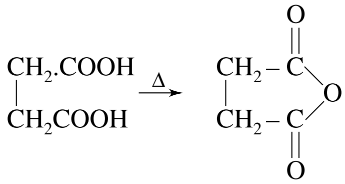
$$\xrightarrow{\text{Pyridine}} C_6H_5-\underset{\underset{O}{||}}{C}-O-\underset{\underset{O}{||}}{C}-CH_3$$

(ii) $C_6H_5COO^{\ominus}Na^{\oplus} + C_6H_5COCl$

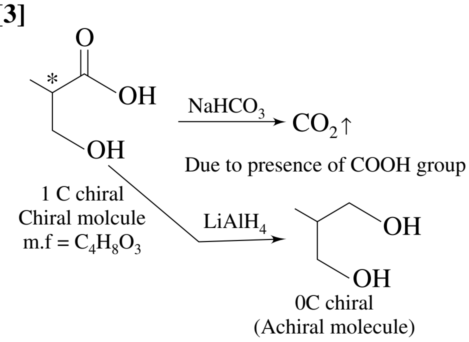
$$\longrightarrow C_6H_5-\underset{\underset{O}{||}}{C}-O-\underset{\underset{O}{||}}{C}-C_6H_5$$

(iii) $C_6H_5ONH_2 + CH_3COO^{\ominus}\ Na^{\oplus} \longrightarrow$ no anhydride $-NH_2$ is poor leaving group, so SN reaction does not take place.

(iv) 

(v) 

2. [3]



3. [1]

Rate of hydrolysis ∝ power of leaving tendency ∝ $\dfrac{1}{\text{Base strength}}$ (for acid derivative via SN_2 reaction)

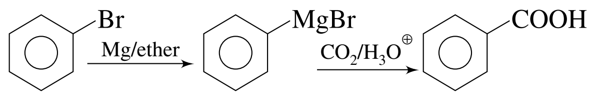
$Cl^{\ominus}$	$\overset{\ominus}{O}-R$	$\overset{\ominus}{N}H_2$	$\overset{\ominus}{O}-\overset{\overset{O}{||}}{C}-R$
	EN factor		Resonance
size↑	EN↑	EN↓	B.S↓
B.S↓	B.S↓	B.S↑	L.g↑
L.g↑	L.g↑	L.g↓	

Order of factor

Size, resonance, EN

(I) > (IV) > (II) > (III)

4. [2]

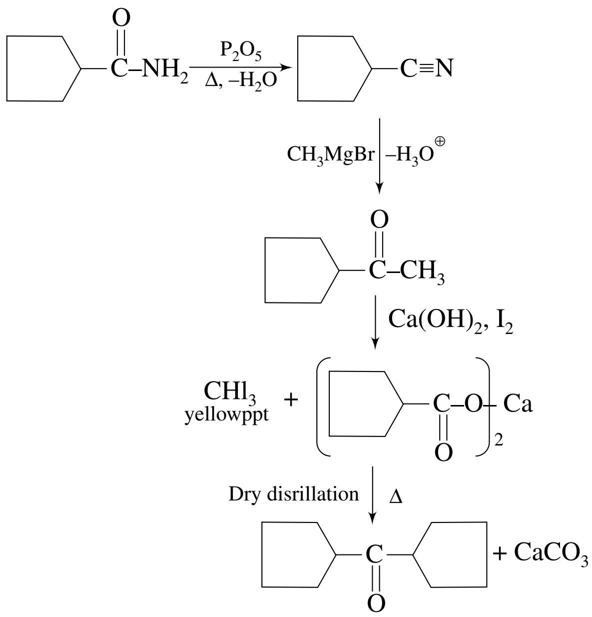


5. [2]

$$Ph-\overset{\overset{O}{||}}{C}-O-H + H-\overset{18}{O}-CH_3 \longrightarrow Ph-\overset{\overset{O}{||}}{C}-\overset{18}{O}-CH_3 + H_2O$$

Estrification

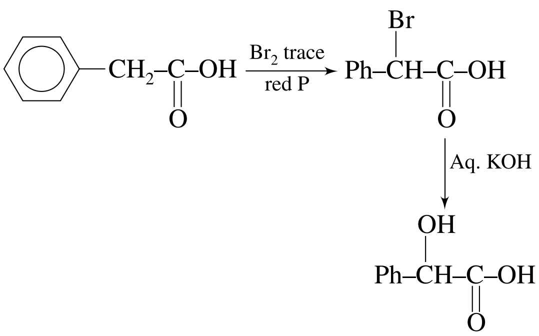
6. [3]



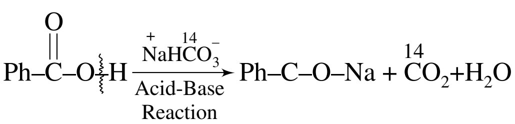
7. [4]

Carboxylic acid having at least one α-H, will give HVZ reaction.

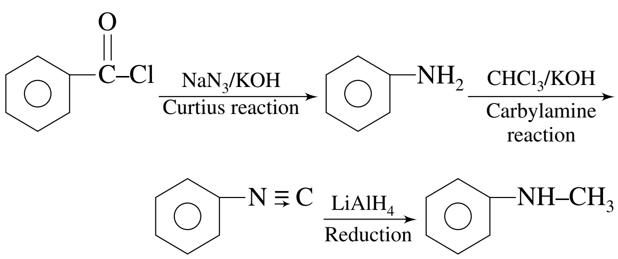
8. [1]



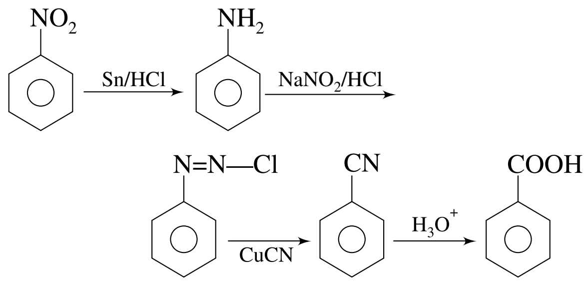
9. [2]



10. [4]



11. [2]

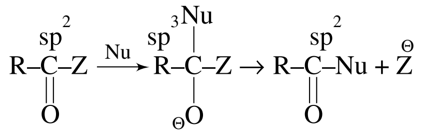


12. [1]

$$R–OH \xrightarrow[{[Rh(CO)_2I_2]^-}]{CO} R–COOH$$

Gurbet reaction

13. [3]



14. [2]

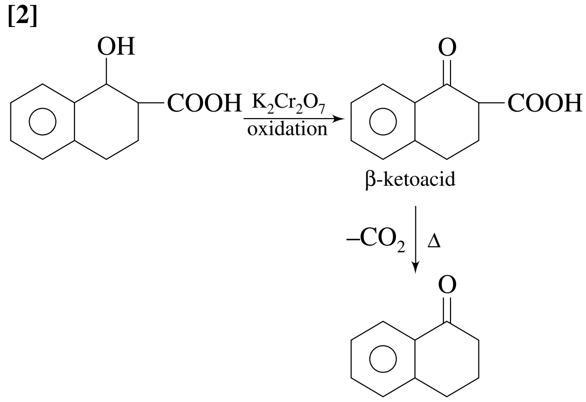
When nucleophilic site belongs to same period than Nucleophilic strength ∝ base strength

$CH_3–\overset{\overset{\displaystyle O}{\|}}{C}–O^{\ominus}$	$\overset{\ominus}{O}H$	$\overset{\ominus}{N}H_2$
–ve charge delocalised	E.N ↑	E.N ↓
Less basic	B.S ↓	B.S ↑
Less N.S.	N.S ↓	N.S ↑

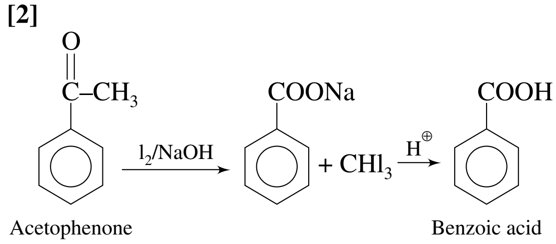
thus correct order is

$CH_3–COO^- < \overset{\ominus}{O}H < \overset{\ominus}{N}H2$

15. [2]



16. [2]



17. [1]

For acyl substitution base strength of Nu:$^-$ greater than LG.

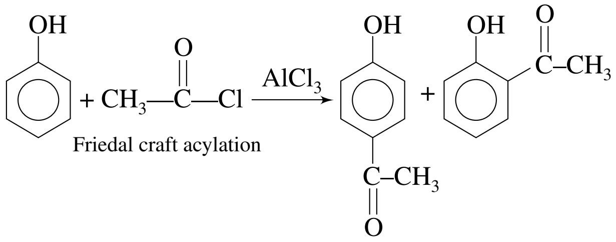
18. [3]

$PCl_5 + SO_2 \rightarrow \underset{(A)}{SO\text{–}Cl_2} + \underset{(B)}{PCl_3}$

$CH_3\text{–}\underset{\underset{O}{||}}{C}\text{–}OH + \underset{(A)}{SOCl_2} \rightarrow CH_3\text{–}\underset{\underset{O\ (C)}{||}}{C}\text{–}Cl$

$2CH_3\text{–}\underset{\underset{O\ (C)}{||}}{C}\text{–}Cl + (CH_3)_2Cd \xrightarrow[SN_2]{} CH_3\text{–}\underset{\underset{O\ (D)}{||}}{C}\text{–}CH_3$

19. [4]



20. [3]

$Ph\text{–}CN \xrightarrow{H_3O^+} Ph\text{–}COOH$

$Ph\text{–}\underset{\underset{O}{||}}{C}\text{–}Cl \xrightarrow{H_3O^+} Ph\text{–}COOH$

$Ph\text{–}CH_2\text{–}Cl \xrightarrow{H_3O^+} Ph\text{–}CH_2\text{–}OH$

$Ph\text{–}COO\text{–}CH_3 \xrightarrow{H_3O^+} Ph\text{–}COOH$

21. [1]

$CH_3CH_2ONa \xrightarrow[\text{Pressure (ii)}H^+]{\text{(i) CO, }\Delta} CH_3\text{–}CH_2\text{–}COONa$

$\xrightarrow{H^+} CH_3\text{–}CH_2\text{–}COOH$

$CH_2 = CH_2 + CO + H_2O \xrightarrow[670°C]{H_3P0_4}$

Carboxylation

$CH_3\text{–}CH_2\text{–}COOH$

22. [3]

$CH_3\text{–}CH_2\text{–}COOH \xrightarrow[\text{(X)}]{Br_2/P} CH_3\text{–}\underset{\underset{Br}{|}}{CH}\text{–}COOH$

H.V.Z

$\downarrow NH_3\ (y)$

$CH_3\text{–}\underset{\underset{NH_2}{|}}{CH}\text{–}COOH$ ← basic site

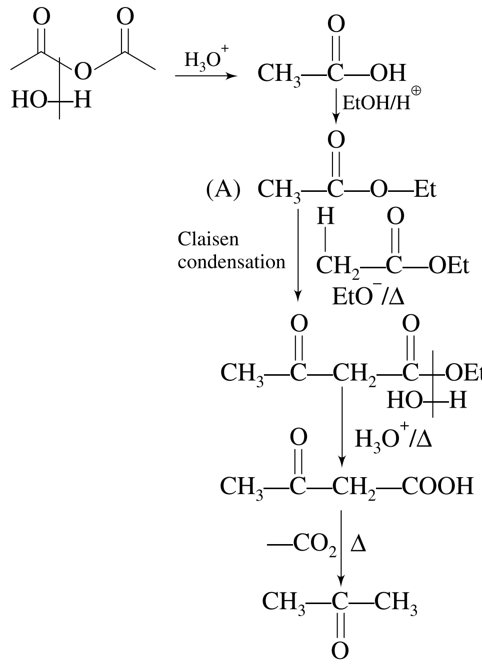
$\downarrow$ pH=4.3 $H^\oplus$

$CH_3\text{–}\underset{\underset{\overset{\oplus}{N}H_3}{|}}{CH}\text{–}COOH$

23. [1]

Theory based

24. [1]



(Acetone)
(B)

25. [2]

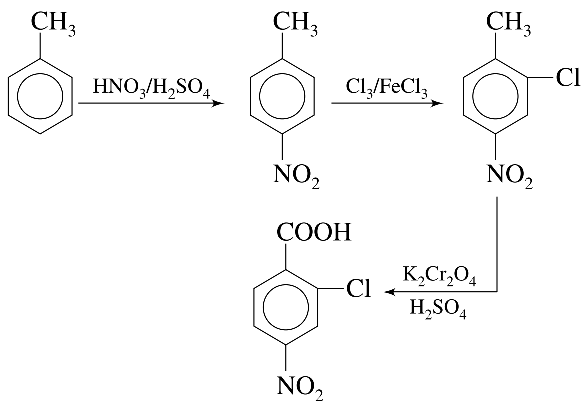
$CH_3\text{–}\overset{\overset{O}{||}}{C}\text{–}O\text{–}C_2H_5 \xrightarrow[\overset{\ominus}{O}H\ SN_2]{NaOH} CH_3\text{–}\overset{\overset{O}{||}}{C}\text{–}OH + C_2H_5O^\ominus$

acyl | oxygen

(2^{nd} order reaction)

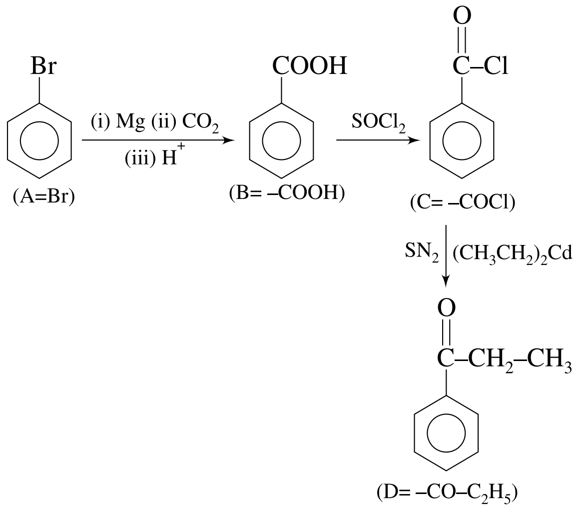
EXERCISE # 2

1. [3]



2–chloro-4-nitro benzoicacid

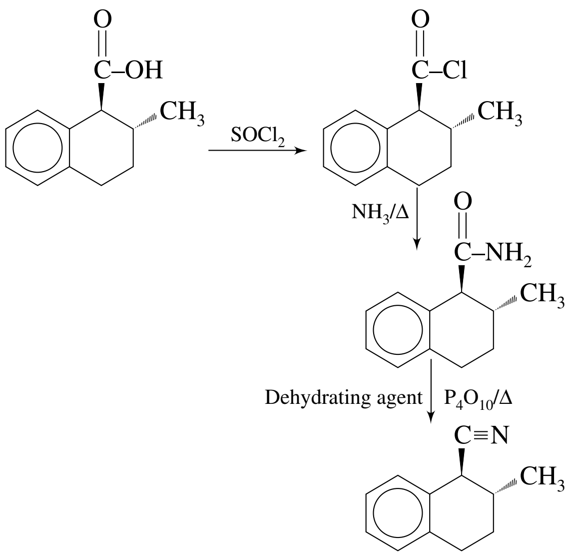
2. [3]



3. [3]

$$CO_2 + H_2 \xrightarrow[\Delta]{H_2SO_4} H\text{–}COOH \xrightarrow[H_2SO_4]{\text{Conc.}} CO + H_2O$$

4. [2]



5. [2]

Rate of hydrolysis for same gr. (SN_2 reaction) $\propto$ EWG $\propto \dfrac{1}{\text{ERG}}$

Thus (II) > (IV) > (I) > (III)

6. [1]

Acid + alcohol $\longrightarrow$ ester

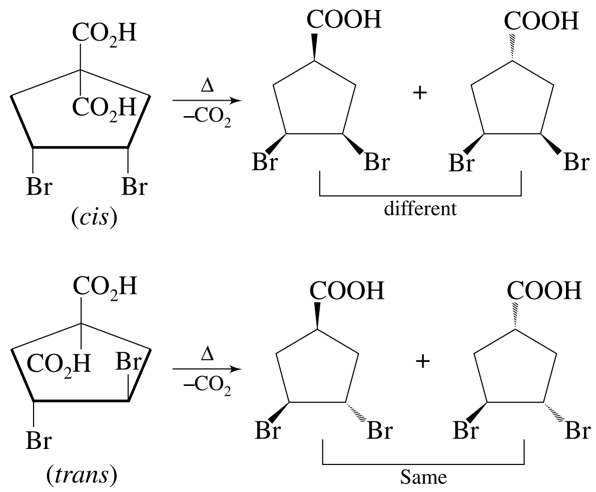
(±) (+) (+ +) & (– +)

7. [2]

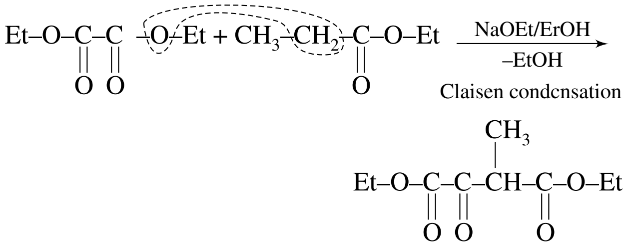
$$BaCO_3 + H_2SO_4 \longrightarrow CO_2\,(x)$$

$$CH_2{=}CH\text{–}Br \xrightarrow{\text{Mg/THF}} CH_2{=}CH\text{–}MgBr \xrightarrow[H_3O^+]{CO_2(X)} CH_2{=}CH\text{–}COOH$$

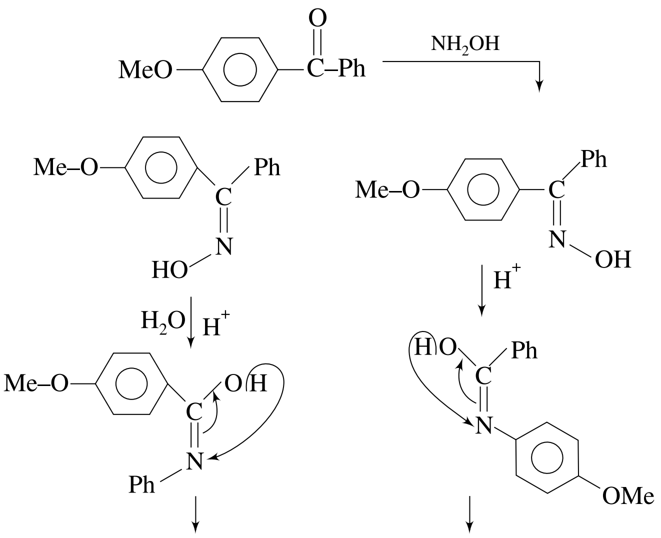
8. [3]

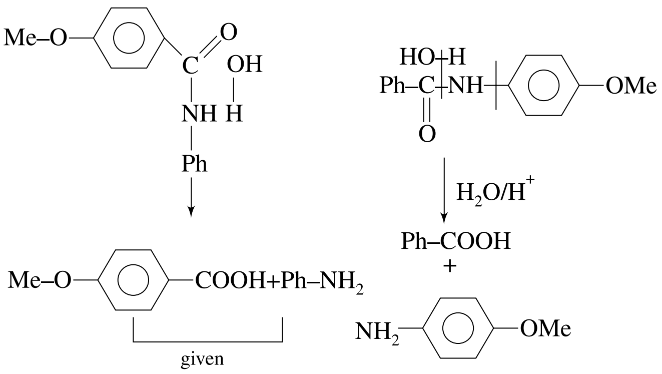


9. [2]

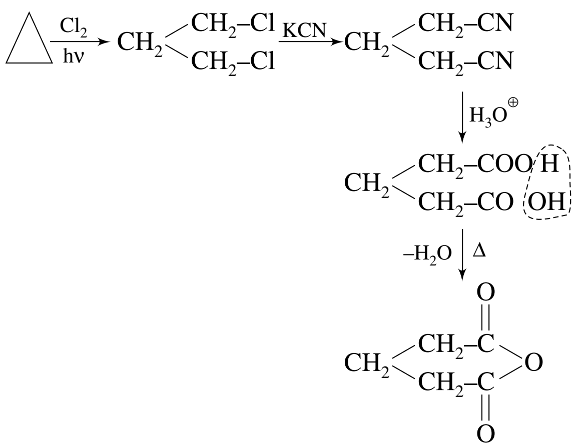


10. [2]





11. [4]

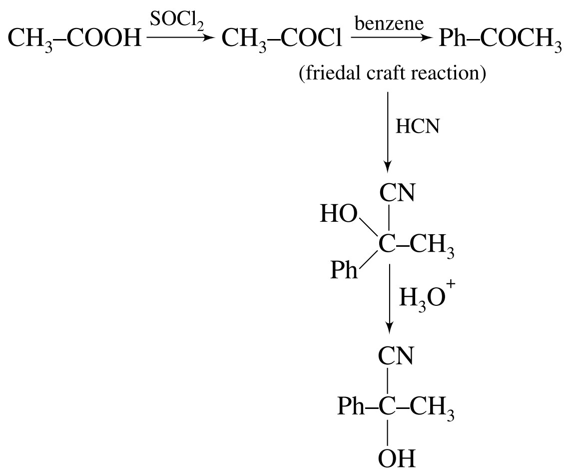


12. [2]

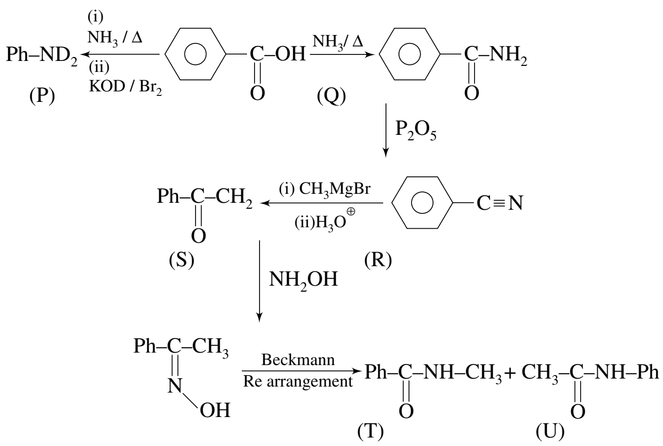
(1) HCOOH is more acidic than acidic acid due to presence of ERG (CH_3) in acetic acid.

(2) o-bromobenzoic acid is more acidic than o-chloro benzoic acid due to ortho effect so it is wrong given (3) & (4) are also correct (refer key concept).

13. [1]



14. [2]

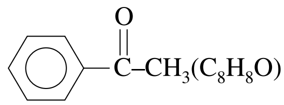


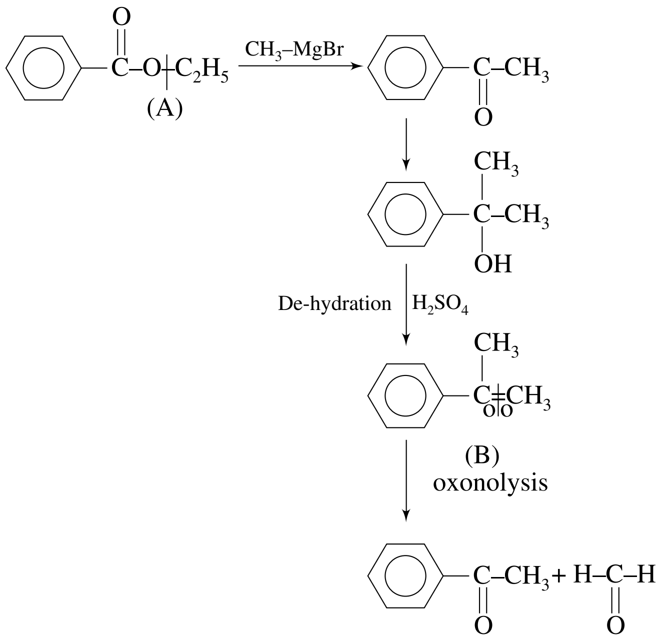
15. [4]

16. [4]

17. [1]

$$\underset{\text{Ester}}{C_9H_{10}O_2\ (A)} \xrightarrow[H_2SO_4]{CH_3\text{–}MgBr} \underset{\text{olefin}}{(B)} \xrightarrow{\text{ozonolysis}} \underset{\substack{\text{Ketone}\\ \text{+ve iodoform test}}}{C_8H_8O}$$

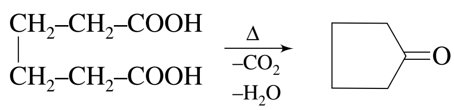
Thus, Ketone should be 



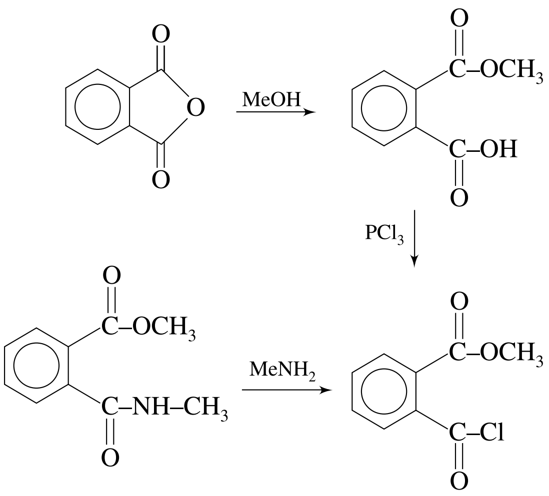
Gives +ve iodoform test

18. [3]

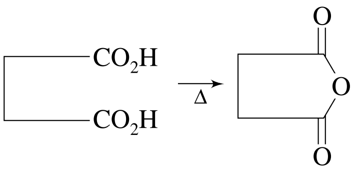
Removal of both CO_2 and H_2O takes place



19. [2]



20. [3]



Succinic acid on heating form anhydride.

EXERCISE # 3

One and more than one option correct type question

1. [3,4]

Both NaOH and $NaHCO_3$ form salt with butanoic acid but not with butanol.

2. [1,2]

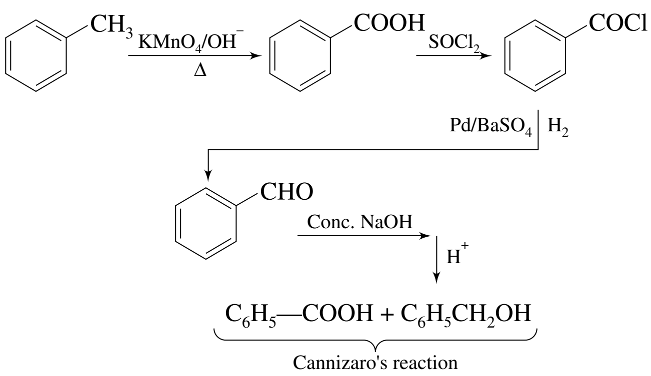
During esterification (Fischer), nucleophilic attack occur from sp^3 oxygen of alcohol, hence configuration of α-carbon of alcohol is retained.

3. [1,3]

(1) Grignard reagent attack further on ketone.

(3) Grignard reagent takes $H^{\oplus}$ from amide.

4. [2,3]



5. [1,2,4]

(1) Excess of ethanol drive the equilibrium in forward direction (Le Chatelier's principle).

(2) Transesterification proceeds well in both acidic and basic medium.

(3) It is wrong, condition can be made suitable so that even larger alcohol can replace the smaller one.

(4) In the presence of acid or base catalyst, reaction is always bimolecular second order.

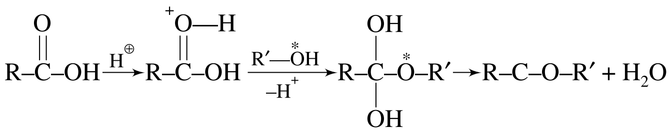
6. [1, 4]

In Hofmann's bromamide degradation, N-bromamide is formed in the first step and isocyanate is formed in the slow rate determining step. Nitrine and hydroxamic acids are not formed.

Statement Type Question

7. [2]

8. [1]



9. [2]

Both are independently correct but formation of racemic mixture of esters is due to the formation of racemic mixture of alcohols (P) by hydride ion attack on planar carbonyl carbon of butanone.

10. [1]

RCOOH is neutralised to RCOONa which itself is a nucleophile and it does not undergo nucleophilic attack by poor nucleophile ROH.

11. [1]

Electron withdrawing nitro group increases electrophilic character of —COOH, hence increases reactivity in Fischer's esterification.

12. [4]

—SO_3H is more acidic than —COOH, hence sulphonic acid group would be neutralised first.

13. [2]

Both are correct but greater reactivity of acid chloride is due to sp^2-hybridised carboxyl carbon and greater electrophilic character of the same.

14. [2]

Electron releasing methoxy group from para position increases the reactivity in Hofmann's reaction

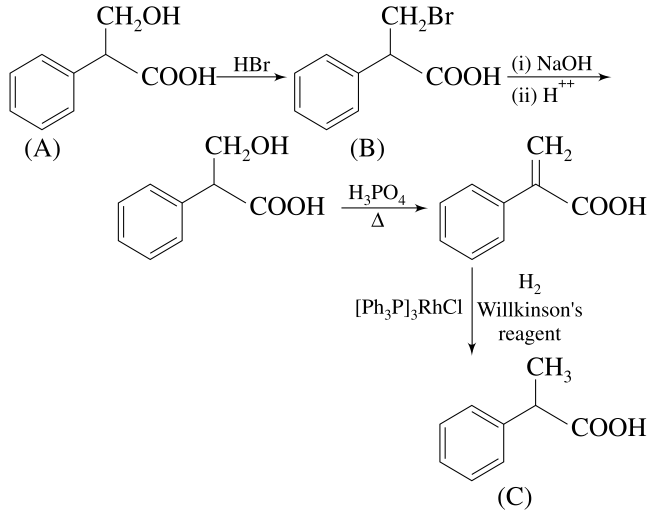
Comprehension type question

Passage Based Questions (17 to 19)

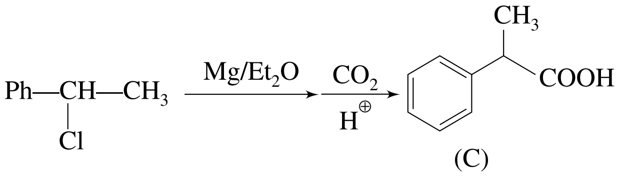
15. [3]

From the above discussion, structure of A satisfying all the criteria of option 3.

16. [2]

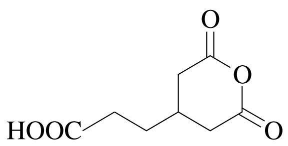


17. [2]



Single Digit Integer Type Question

18. [5]



19. [4]

$CH_3-\overset{*}{C}H(OH)-CHO$ (d & *l*), $CH_2(OH)-CH_2-CHO$, $CH_3-C(=O)-CH_2-OH$

α-hydroxy ketones also reduces Tollens' reagent.

20. [6]

2° and 3° amine isomers do not form amine on treatment with Br_2 + NaOH.

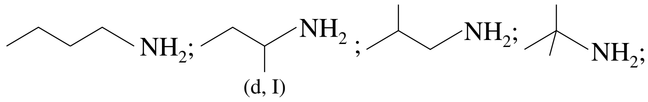
$C_2H_5-C(=O)-NHCH_3$, (I) $CH_3-C(=O)-NHC_2H_5$, (II)

$H-C(=O)-NHCH_2CH_2CH_3$, (III) $H-C(=O)-NH-CH(CH_3)_2$ (IV)

$CH_3-C(=O)-N(CH_3)_2$, (V) $H-C(=O)-N(CH_3)-C_2H_5$ (VI)

21. [5]

It is mustard oil reaction which is given by primary amines only.

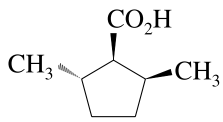


22. [6]

$CH_3-C(=O)-CH_2-C(=O)-OC_2H_5$, $CH_3H_2C-C(=O)-CH(CH_3)-C(=O)-OC_2H_5$ (d + I)

$H_3C-C(=O)-CH(CH_3)-C(=O)-OC_2H_5$ (d + I), $CH_3H_2C-C(=O)-CH_2-C(=O)-OC_2H_5$

23. [1]

 Only one product will obtained.

EXERCISE # 4

1. [3]

$$CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} CH_3CH(Cl)COOH \xrightarrow[\text{(elimination)}]{\text{Alcoholic KOH}} CH_2{=}CHCOOH$$

(HVZ reaction) acrylic acid

2. [1]

$$H-C(=O)-O^{\ominus} \longleftrightarrow H-C(-O^{\ominus})=O$$

equal contributed canonical form

3. [1]

$$C_2H_5NC + H_2O \xrightarrow{H^+} \underset{\text{Formic acid}}{HOOCH} + C_2H_5NH_2$$

$$C_2H_5NH_2 + H^+ \longrightarrow \underset{\text{Salt}}{C_2H_5NH_3^+}$$

4. [2]

$LiAlH_4$ reduces —COOH to —CH_2OH without affecting C=C bond.

5. [2]

$C_nH_{2n}O_2$ is general formula for open chain carboxylic acids and esters.

e.g., n = 3 $C_3H_6O_2$

Acid $CH_3CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—O—H$

Ester $CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—O—CH_3$

6. [3]

$\underset{sp^3}{CH_3}—\underset{sp}{C}\equiv N$

7. [4]

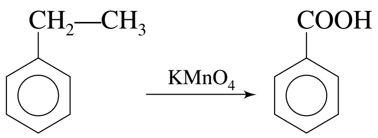
A liquid + $C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4}$ Compound (Fruity smell)

Fruity smell is the characteristic property of ester, thus the above reaction leads to the formation of ester.

$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\substack{\text{(Ethyl acetate)} \\ \text{(Fruty smell)}}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}—OC_2H_5} + H_2O$$

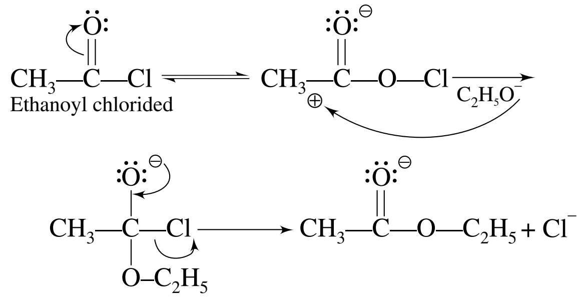
This reaction is called esterification.

8. [3]



9. [4]

$$C_2H_5O^-Na^+ \rightleftharpoons C_2H_5O^- + Na^+$$



$$Na^+ + Cl^- \longrightarrow NaCl$$

This is by S_N reaction Cl^- is a better leaving group than $C_2H_5O^-$ and then ethyl ethanoate is formed.

10. [3]

–I effect exerting (electron withdrawing) groups increase the acidic strength of an acid by withdrawing electron density towards itself, thereby weakening O—H bond and thus, the release of H^+ ion by an acid becomes easier.

Whereas +I effect excreting (e^- releasing) groups decreases the acidic strength by donating electron density to O-atom.

Further, –I effect decreases with distance. Thus, the acidic strength off the given acids would be:

$$CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{CH} \leftarrow \overset{\overset{\displaystyle O}{\|}}{C} \leftarrow OH > Cl—CH_2—CH_2—CH_2 \twoheadrightarrow \overset{\overset{\displaystyle O}{\|}}{C}—OH >$$

$$CH_3 \twoheadrightarrow \overset{\overset{\displaystyle O}{\|}}{C}—OH > H—\overset{\overset{\displaystyle O}{\|}}{C}—OH$$

Hence, $CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{CH}—\overset{\overset{\displaystyle O}{\|}}{C}—OH$ is most acidic and strongest acid than other given compounds.

11. [4]

$$\underset{A}{CH_3CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—OH} \xrightarrow{NH_3} \underset{B}{CH_3CH_2COONH_4} \xrightarrow{\Delta}$$

$$\underset{C}{CH_3—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2} \xrightarrow[\text{Hofmann bromamide reaction}]{Br_2,\ KOH} CH_3—CH_2—NH_2$$

12. [2]

$$R—NH_2 + CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—Cl \xrightarrow[(-HCl)]{} R—NH—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$

Since, each —$COCH_3$ group displace one H-atom in the reaction of one mole $CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—Cl$ with one —NH_2 group, the molecular mass increases with 42 unit, Since, the mass increases by (390–180) = 210, hence the number of —NH_2 group is $\dfrac{210}{42}$ = 5.

13. [3]

The complete series of reaction can be represented as

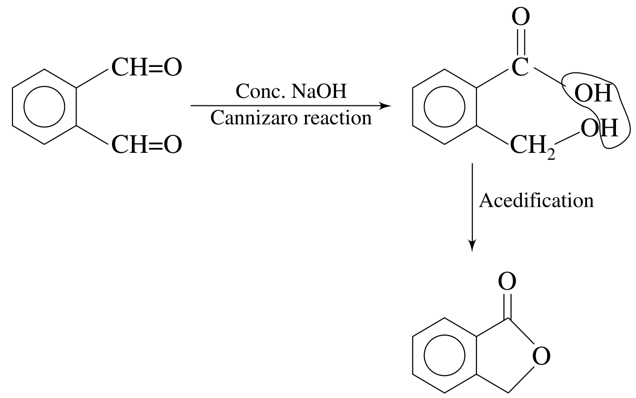
$$CH_3COOH \xrightarrow{LiAlH_4} \underset{A}{CH_3CH_2OH} \xrightarrow{PCl_5}$$

$$CH_3CH_2Cl + POCl_3 + HCl$$

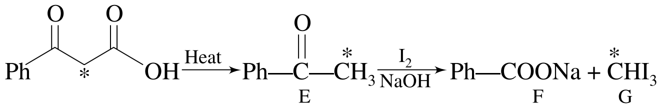
$$\text{(Elimination reaction)} \Big\downarrow \text{Alc. KOH}$$

$$\underset{C}{CH_2{=}CH_2}$$

14. [3]



15. [3]



16. [2,4]

For separation be differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.

(1) Both phenol and benzoic acid form salt with NaOH, hence this mixture cannot be separated.

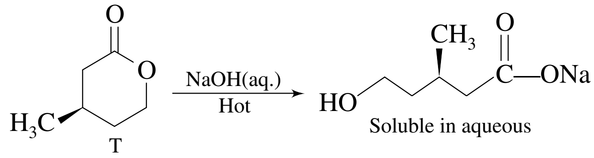
(2) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also benzoic acid forms salt with $NaHCO_3$ but benzyl alcohol does not, hence $NaHCO_3$ can be used for separation.

(3) Neither benzyl alcohol nor phenol forms salt with $NaHCO_2$, mixture cannot be separated using $NaHCO_3$

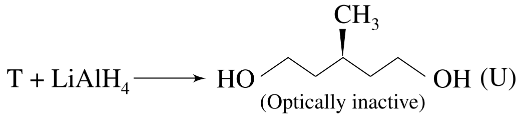
(4) $C_6H_5CH_2COOH$ forms salt with NaOH; $C_6H_5CH_2OH$ does not. Hence mixture can be separated using NaOH.·$C_6H_5CH_2COOH$ forms salt with $NaHCO_3$. but $C_6H_5CH_2OH$ does not; hence mixture can be separated using $NaHCO_3$.

17. [1,3,4]

(1) Undergoes an ester hydrolysis in hot aqueous alkali as

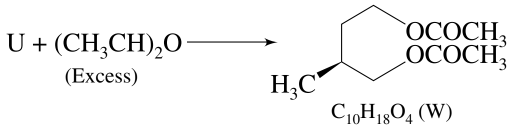


(2) $LiAlH_4$ reduces ester to alcohol as

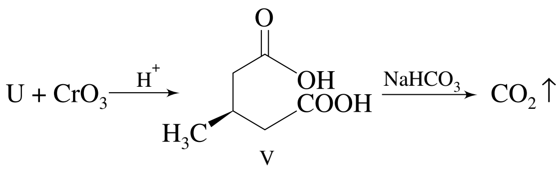


"U" No chiral carbon optically inactive.

(3) U on treatment with excess of acetic anhydride forms a disaster as

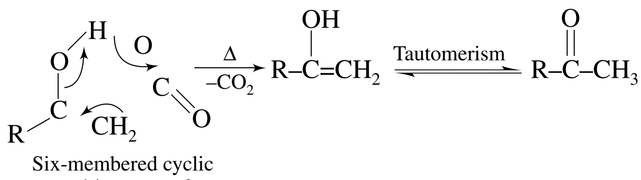


(4) U on treatment with CrO_3H^+ undergoes oxidation to diacid which gives effervescence with $NaHCO_3$.



18. [2]

It is a β-keto acid which undergo decarboxylation in very mild condition, i.e., on simple heating. This occurs through a six-membered cyclic transition state as:



Six-membered cyclic transition state of a β-keto acid

Note (t) (i) Ordinary carboxylic acid require soda time catalyst for decorboxylation

(ii) Final step of decarboxylation in the above shown mechanism involve tatutomerism, therefore, for decarboxylation of β-keto acid by above mechanism, the acid must contain an α-H

Passage Based Questions: (20-21)

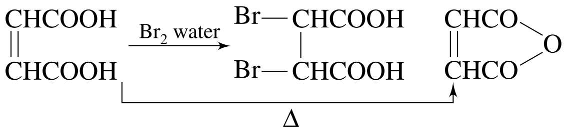
19. [2]

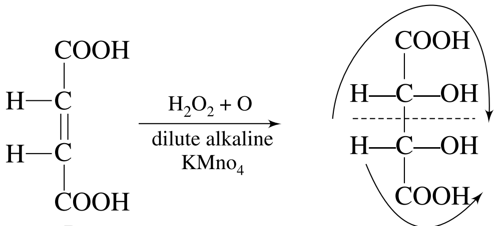
$$P, Q \xrightarrow{Br_2\ water} \text{Decolourised}$$

P and Q have (C = C) bond

P $\xrightarrow{\Delta}$ Anhydride

Thus, P is *cis*-isomer

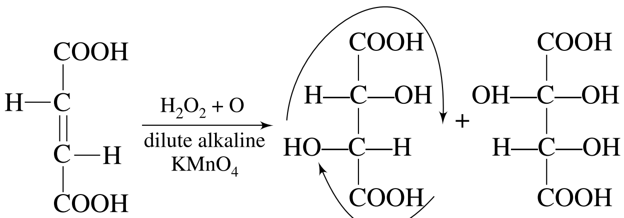




P
(Maleric acid)

S

Optically inactive due to internal compensation of rotation (meso-somer)



Q
Fumaric acid

T, d (+)

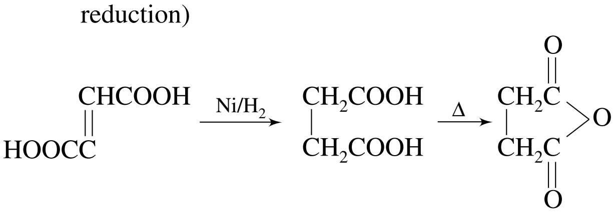
U, l (–)

T and U (in 1 : 1 molar ratio) form optically inactive (racemic mixture) due to external compensation

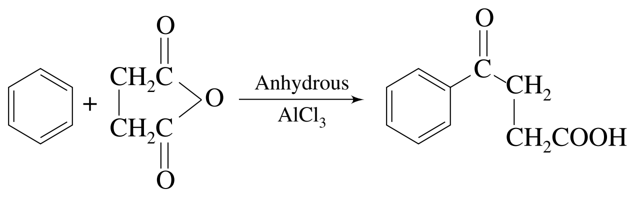
20. [1]

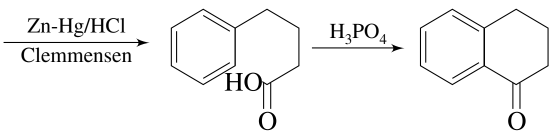
Plan Ni/H_2 reduces (C = C) bond

Benzene undergoes Friedel–Crafts reaction Zn–Hg/HCl reduces carbonyl group (Clemmensen reduction)



Succinic anhydride (v)





W

21. [4]

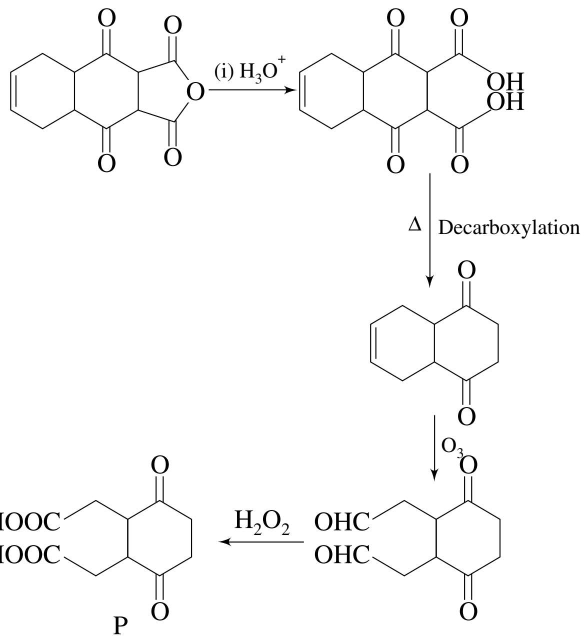
$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$ HCO_3^- is decomposed by acid releasing CO_2

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$

If acid is stronger than HCO_3^- then CO_2 is released. Phenol is less acidic and thus, does not liberate CO_2 with $NsaHCO_3$.

22. [2]

Plan Reactant is cyclic anhydride and changes to dicarboxylic acid on hydrolysis. Also there is decarboxylation on heating if there is keto group w.r.t —COOH group. Ozonolysis cleaves (C=C) bond and H_2O_2 oxidises —CHO to —COOH group.



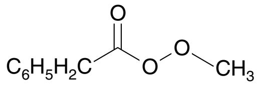
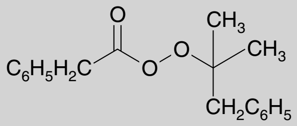
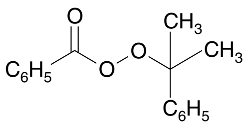
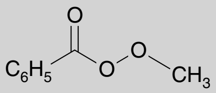
P

Thus, number of —COOH groups in P = 2.

23. [1]

The problem can be solved by using the stability of radical obtained after fragmentation of peroxyester. Allylic radical are more stable than alkyl radical, so when there is a possibility of formation of allyl radical, it will undergo fragmentation through formation of allyl radical, i.e., fragmentation produces stable radical.

One the basis of stability of radical, fragmentation can be done as:

	Column I	Column II	Explanation
i.	p.		$C_6H_5-\dot{C}H_2 + CO_2 + CH_3\dot{O}$
ii.	r.		$C_6H_5-\dot{C}H_2 + CO_2 + Ph-CH_2-\overset{O^{\bullet}}{\underset{CH_3}{C}}-CH_3 \rightarrow Ph-\dot{C}H_2 + CH_3-CO-CH_3$
iii.	s.		$C_6H_5-\dot{C}O_2+CH_3-\overset{O^{\bullet}}{\underset{C_6H_5}{C}}-CH_3 \xrightarrow[-CO_2]{} \dot{Ph}+CH_3-CO-Ph+\dot{C}H_3$
iv.	t.		$C_6H_5-\dot{C}O_2 + \dot{C}H_3O$; $C_6H_5-\dot{C}O_2 \rightarrow C_6H_5^{\bullet} + CO_2$

CHAPTER 5

Nitrogen Containing Compounds

INTRODUCTION

ALIPHATIC AMINES

- General formula $\Rightarrow C_nH_{2n+3}N$
- Classification
  - $\rightarrow R-\ddot{N}H_2$ (1°/p-amine)
  - $\rightarrow R-\ddot{N}H-R$ (2°/s-amine)
  - $\rightarrow R-\ddot{N}(R)-R$ (3°/s-amine)
- Shape: Pyramidal
- Hybridisation of nitrogen sp^3

PHYSICAL PROPERTIES

- Aliphatic amines are colourless volatile compounds having ammonia like smell. Higher amines have fishy smell.
- CH_3NH_2 is gas but $CH_3CH_2NH_2$ and higher members are liquids.
- **BOILING POINT:**

  boiling point $\propto \dfrac{\text{Molecular weigh}}{\text{Number of Branches}}$
- **SOLUBILITY IN WATER:**

  Lower amines are highly soluble in H_2O due to intermolecular H-bonding; solubility decreases as no. of carbon atoms increases. All amines (even 3°) can act as proton acceptors in H-bonding to water molecules.

  Solubility $\propto \dfrac{\text{Number of Branches}}{\text{Molecular weigh}}$
- **COMPARISION OF BASIC STRENGTH OF 1°/2°/3° AMINES AND NH_3:**

  (I) In gaseous state:

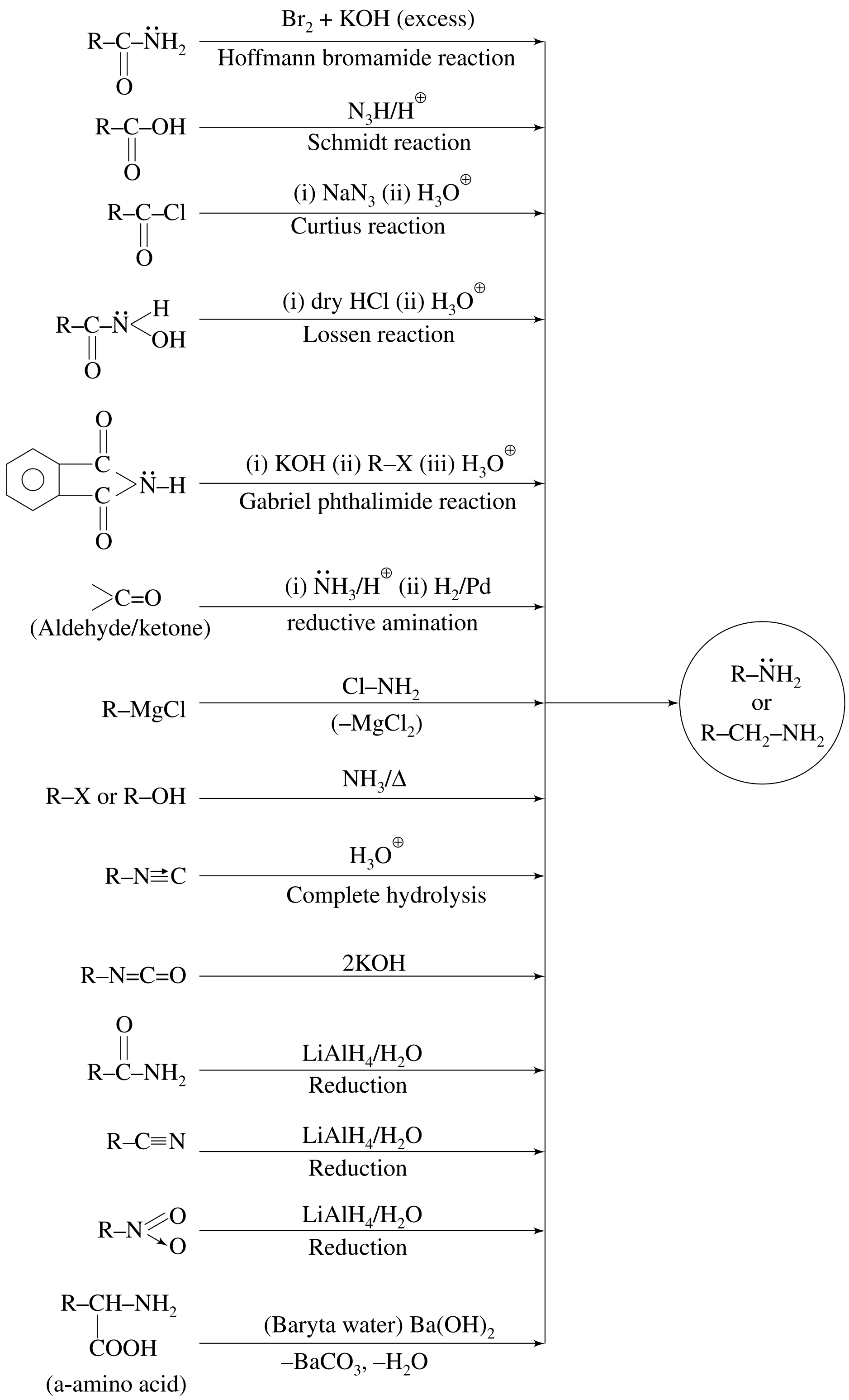
  $\boxed{\text{Basic strengh} \propto +\text{I effect}}$

  (II) In aqueous state:

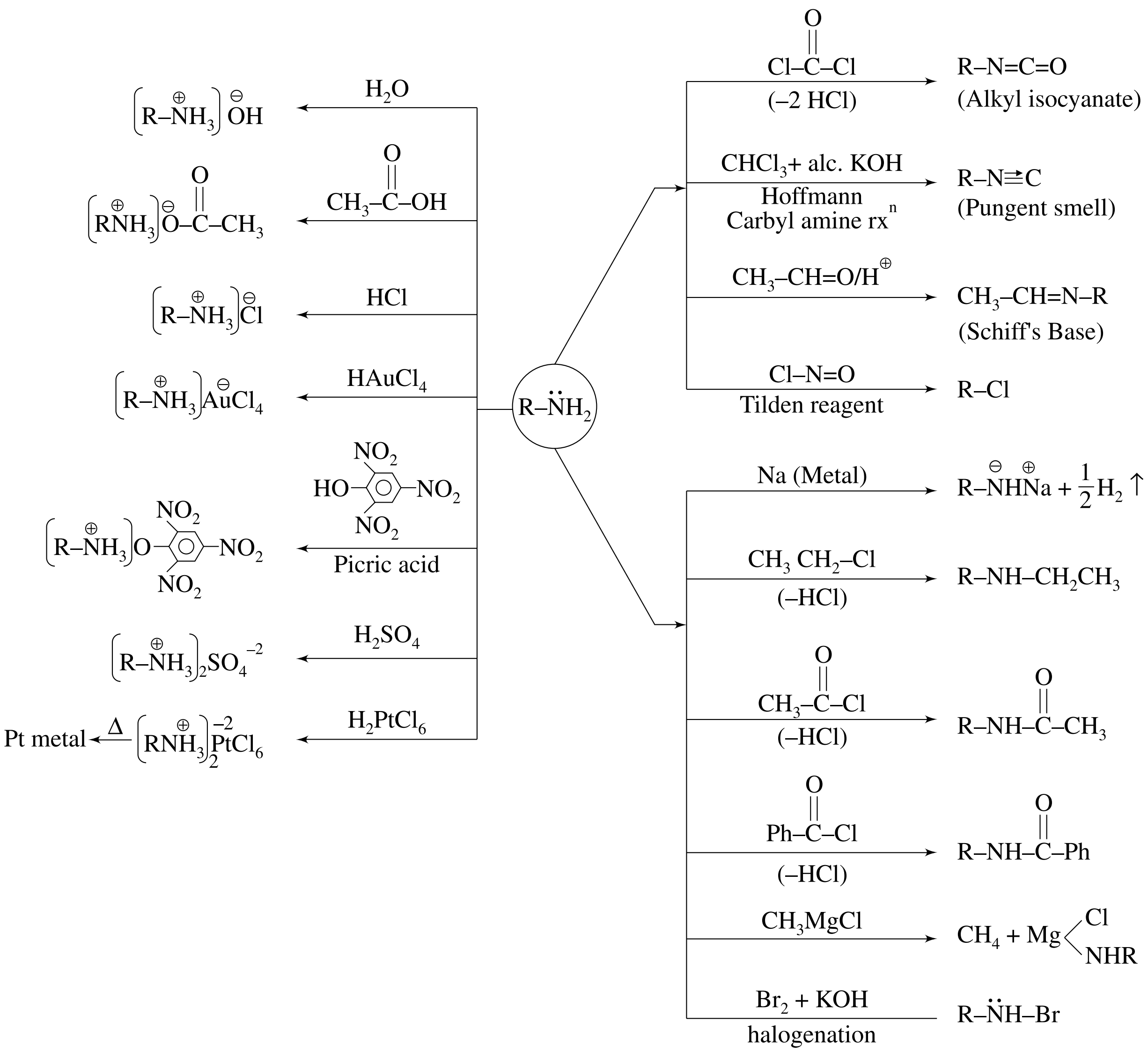
  Basic strength $\propto$ +I effect/Steric hinderance

Value of R	Basic strength order
1. Methyl	2°> 1°> 3°> NH_3
2. Ethyl	2°> 3°> 1°> NH_3
3. Isopropyl	1°> NH_3 > 2°> 3°
4. t-Butyl	NH_3 > 1º > 2º > 3º

METHODS OF PREPARATION OF AMINE

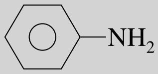


CHEMICAL PROPERTIES OF AMINE



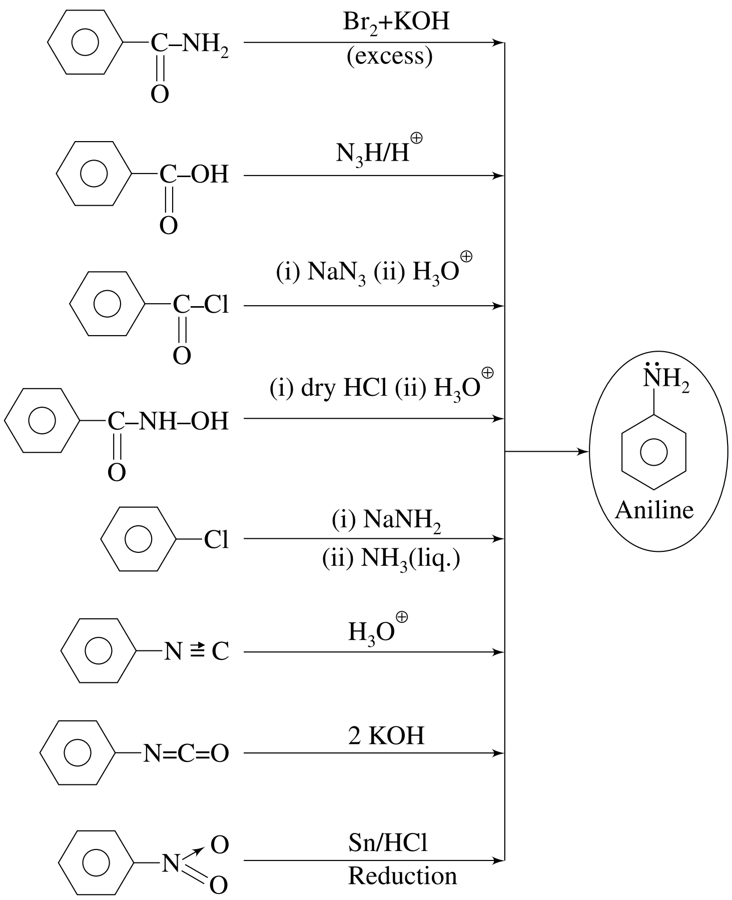
INTRODUCTION

ANILINE

- Structure of aniline is represented by 

- All six carbon atoms in this compound and nitrogen atom are sp^2 hybridised.
- Lone pair on nitrogen atom is delocalised throughout the ring.
- Due to delocalisation basic character is less than aliphatic amine.
- N–H bond of aniline exhibits acidic character.
- Electrophilic substitution usually takes place at ortho and para position.
- It is purified by steam distillation method (B.P. = 184°C)
- It is a colourless oily liquid.
- It has a faint characteristic odour.
- It is partial soluble in water but complete soluble in organic solvents.

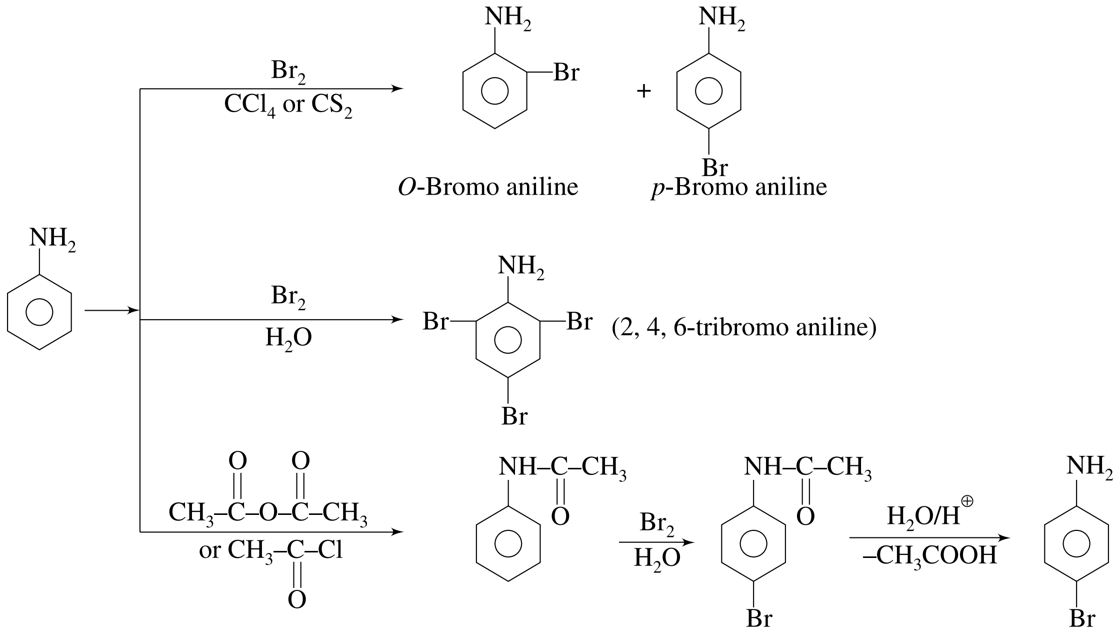
METHODS OF PREPARATION OF ANILINE



CHEMICAL PROPERTIES OF ANILINE

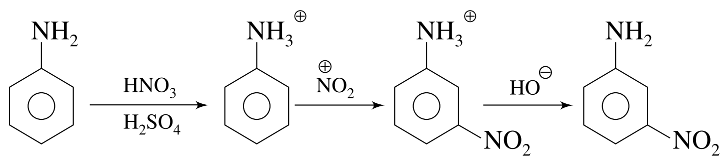
[A] Reactions due to benzene ring (Electrophilic Substitution Reaction or E.S.R.):

(1) Bromination:



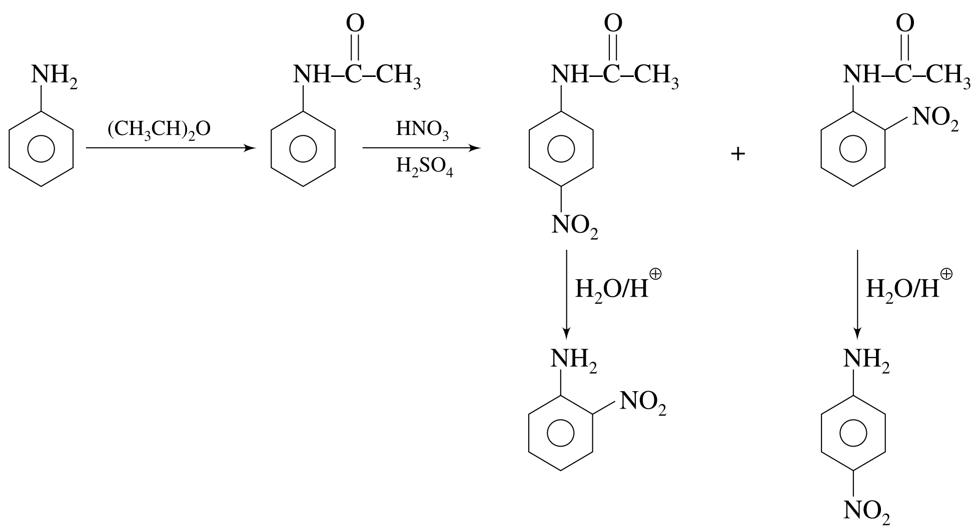
(2) Nitration:

(a) Direct nitration gives meta product.



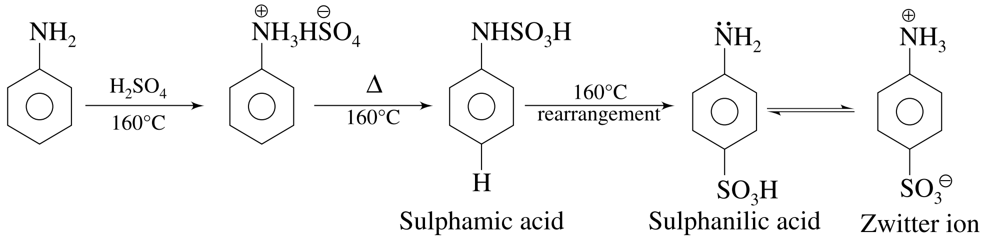
(Major product)

(b) If-NH_2 group is protected via acetylation then ortho/para product is obtained.

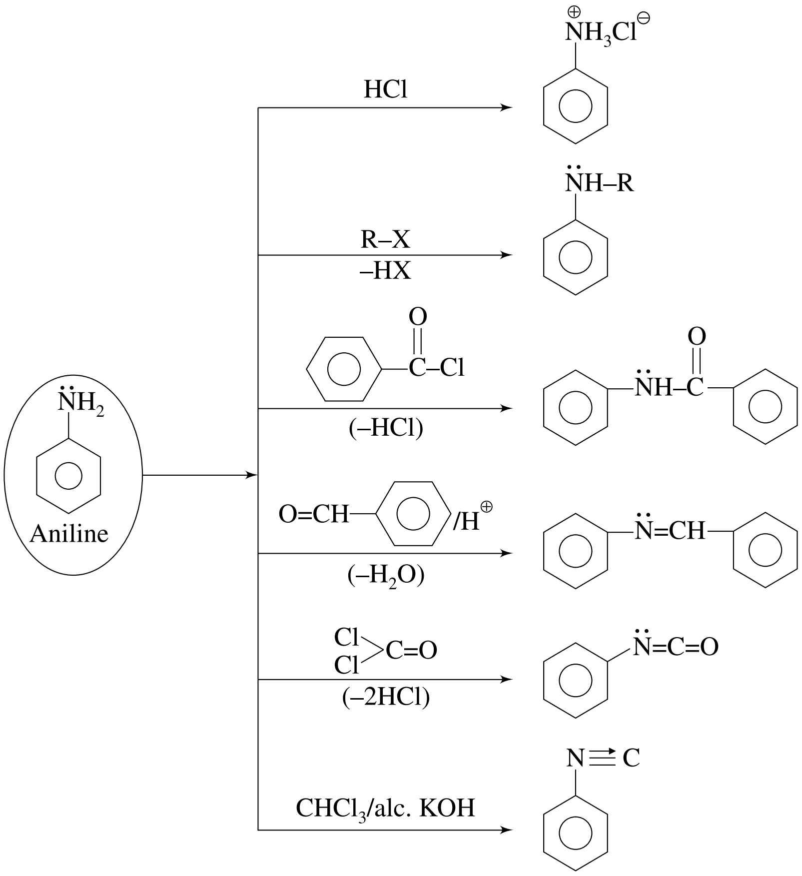


O-Nitro aniline *p*-Nitro aniline

(3) Sulphonation:



[B] Reactions due to NH_2 group:



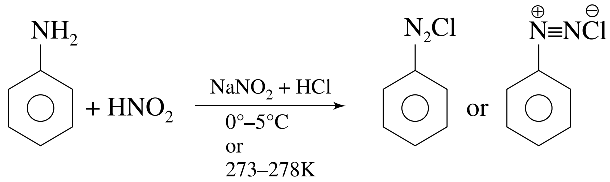
[C] Other reactions:

(1) Oxidation of aniline:

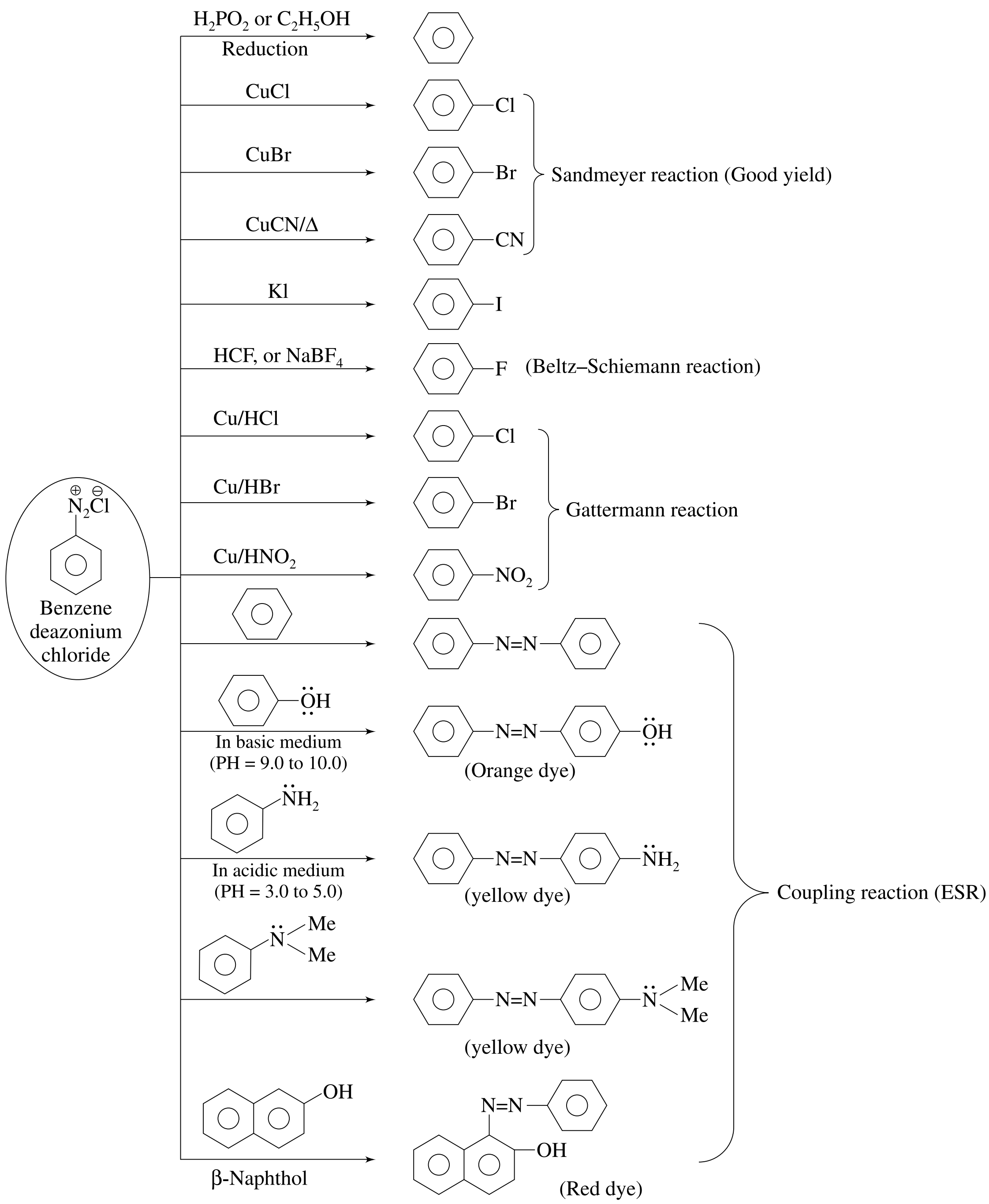
Oxidants	Products
Air and light	p-Benzo quinone
CF_3CO_3H (per acid)	Nitrobenzene
$KMnO_4/H^{\oplus}$	Aniline Black
$KMnO_4/\overset{\ominus}{O}H$	Azo benzene
$KMnO_4$	Azo benzene + Nitrobenzene
H_2SO_5 (Caro's acid)	Nitrosobenzene + Nitrobenzene
NaOCl	p-amino phenol

(2) Formation of diazonium salt:

- When aniline is treated with HNO_2 ($NaNO_2$ + HCl) in cold condition, benzene diazonium chloride (salt) is obtained.

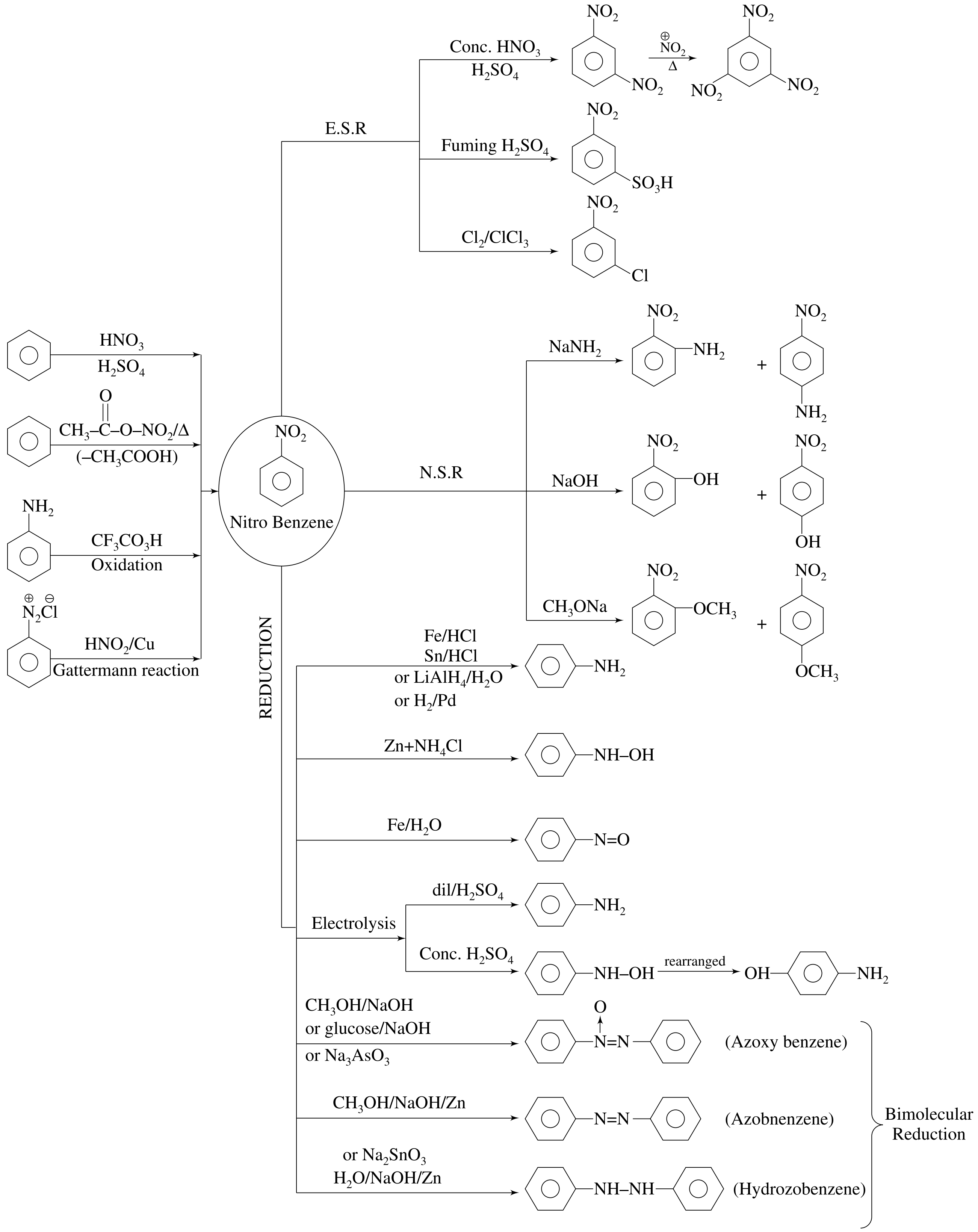


- If room temperature or high temperature is used than phenol is the major product.
- **Benzene diazonium chloride is used in synthesis of following aromatic compounds:**



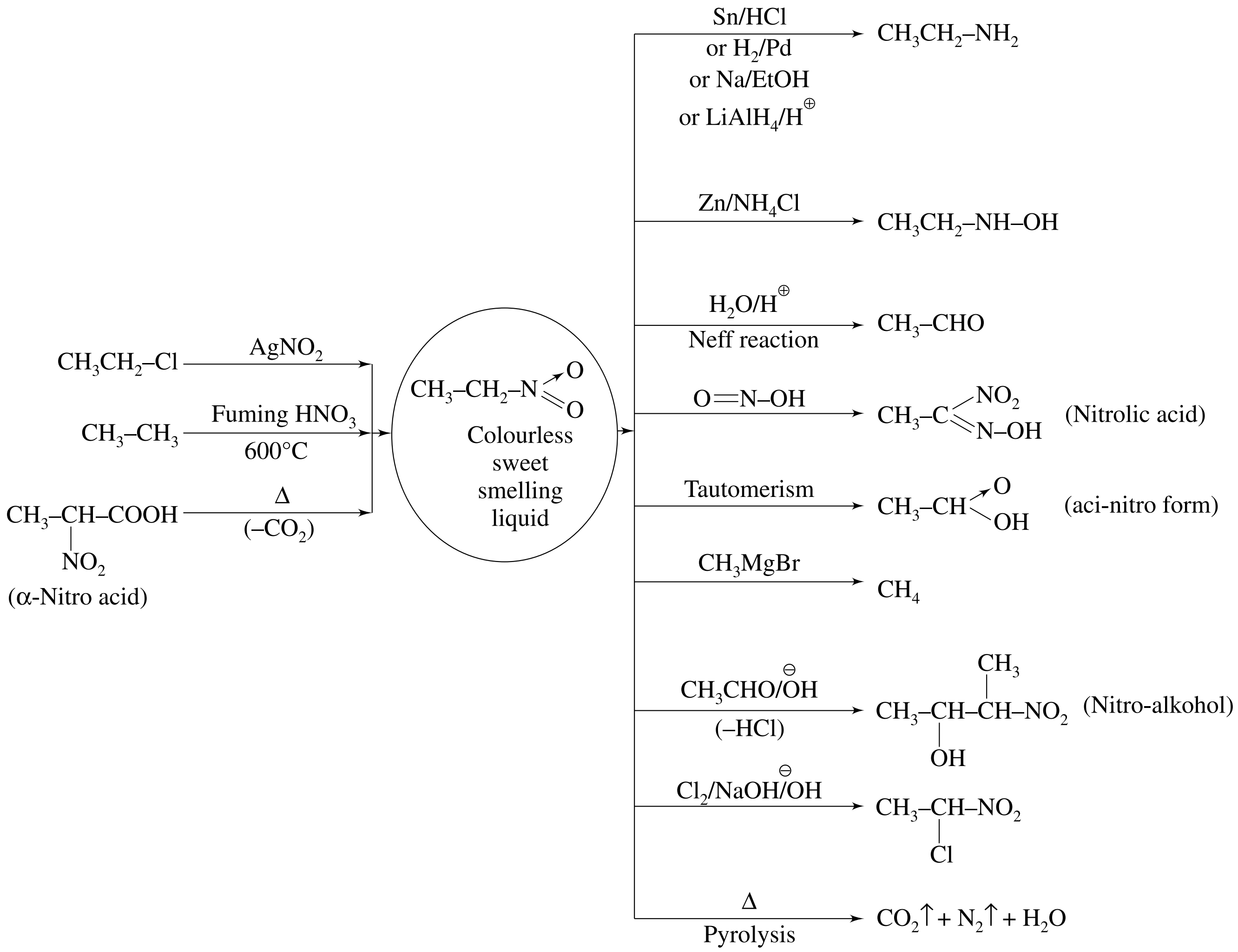
NITROBENZENE (OIL OF MIRBANE)

Methods of Preparation and Chemical Properties of Nitrobenzene



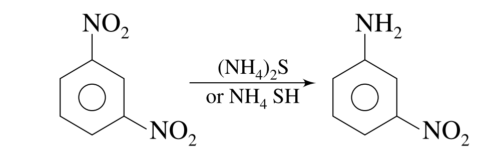
NITROALKANE

Methods of Preparation and Chemical Properties of Nitroalkane



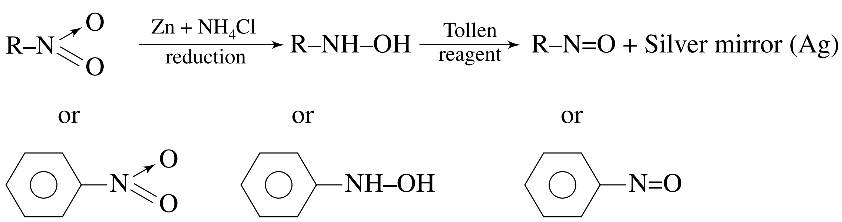
Special Points

1. **Selective reduction:**



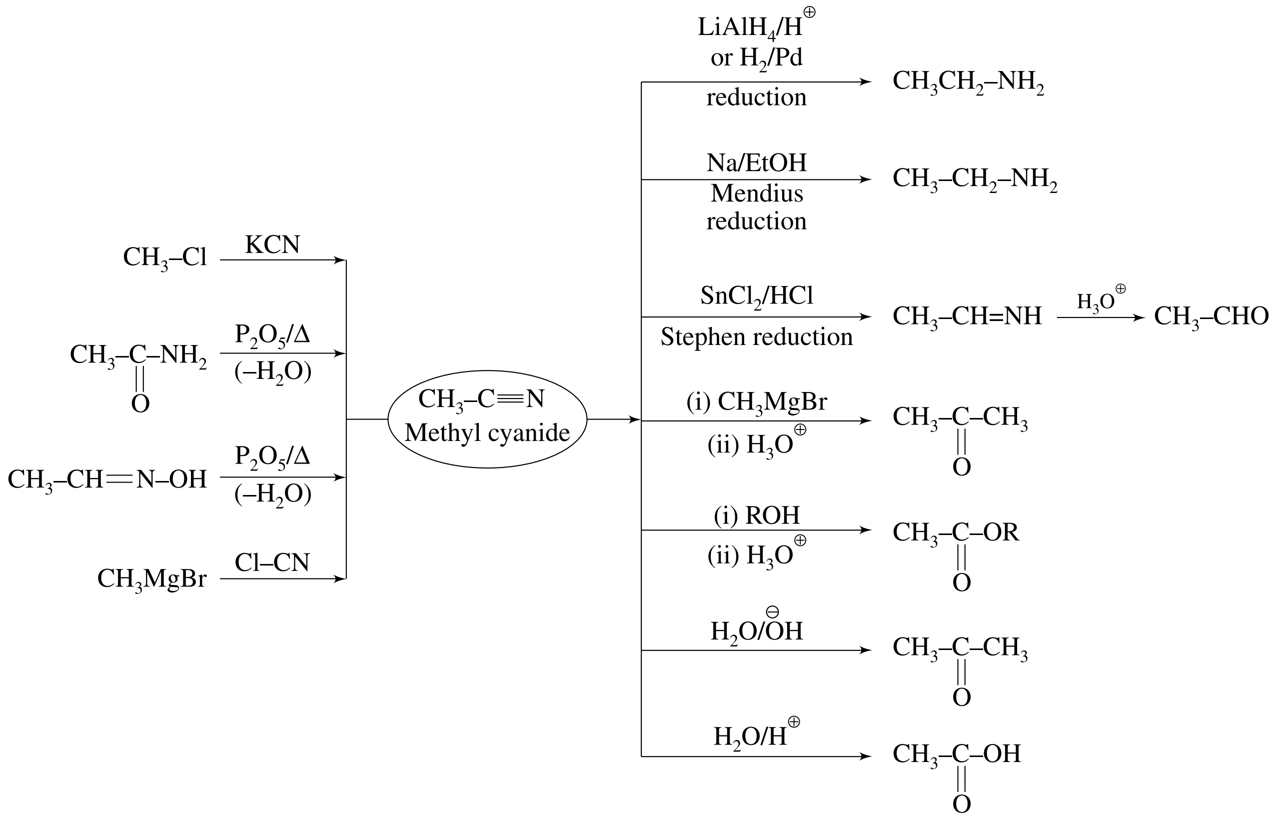
(only *m*-dinitro benzene) (*m*-dinitro benzene)

2. **Muliken–Barker Test:**

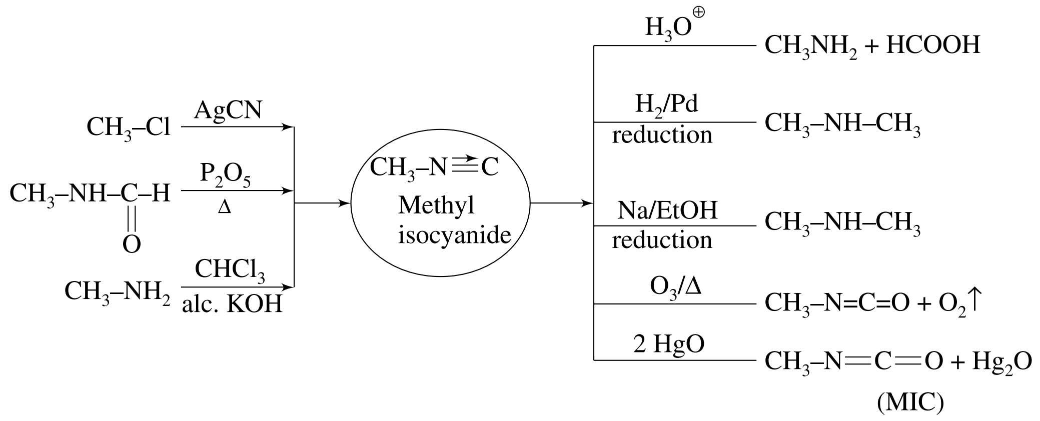


CYANIDE AND ISOCYANIDE

Methods of Preparation and Chemical Properties of Alkyl Cyanide



Methods of Preparation and Chemical Properties Alkyl Isocyanide

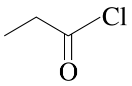
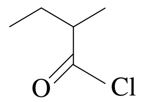


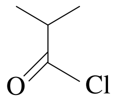
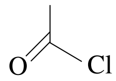
Special Points

- In December 1984 (Bhopal tragedy) **Methyl isocyanate (MIC)** gas was responsible.
- Lower RCN and RNC are colourless liquid but higher members are crystalline solid.
- RCN have sweet smell but RNC have offensive smell.
- Lower RCN compounds are soluble in H_2O but RNC compounds are insoluble.

SOLVED EXAMPLE

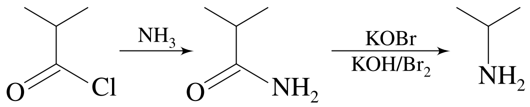
1. (A) $\xrightarrow{NH_3}$ (B) $\xrightarrow[KOH/Br_2]{KOBr}$ $CH_3-\underset{|}{\overset{CH_3}{}}CH-NH_2$; structure of (A) is–

(1)  (2) 

(3)  (4) 

Sol. **[3]**

In Hoffman degradation one carbon decreases



2. Consider the following sequence of reaction

$$Ph-NO_2 \xrightarrow{Sn/HCl} (X) \xrightarrow[0°C]{NaNO2/HCl} (P) \xrightarrow{CuBr/HBr} (Q)$$

The final product (Q) is

(1) chlorobenzene (2) bromobenzene
(3) benzyl bromide (4) benzyl chloride

Sol. **[2]**

$$Ph-NO_2 \xrightarrow{Sn/HCl} Ph-NH_2 \xrightarrow{NaNO_2/HCl}$$

$$Ph-N=N-Cl \xrightarrow[\text{Sandmayer reaction}]{CuBr / HBr} Ph-Br$$

3. Which one of the following compounds on reduction with $LiAlH_4$ yields a secondary amine?

(1) Methyl cyanide (2) Nitroethane
(3) Methyl isocyanide (4) Acetamide

Sol. **[3]**

$$\underset{\text{Methyl isocyanide}}{CH_3-N \equiv C} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{2°\text{amine}}{CH_3-NH-CH_3}$$

4. Which is the most volatile?

(1) $CH_3CH_2CH_2NH_2$ (2) $(CH_3)_3N$
(3) $\begin{matrix}CH_3CH_2 \\ CH_3\end{matrix}\!\!>HN$ (4) CH_3-CH_2-OH

Sol. **[2]**

Volatile nature $\propto \dfrac{1}{\text{Boiling point}}$

$(CH_3)_3N \rightarrow$ No H-bond (less boiling point)
Hence it is most volatile in nature

5. Which of the following gives positive Libermann nitroso test?

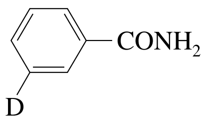
(1) 2-butanamine
(2) N-ethyl-2-pentanamine
(3) N-methylpiperidine
(4) N, N-dimethylcyclohexylamine

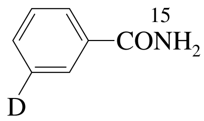
Sol. **[2]**

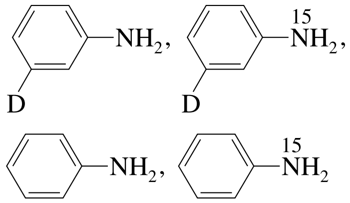
2° amine will give positive nitrosamine test.

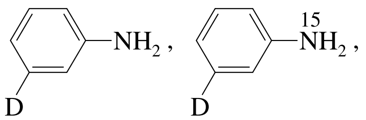
$$\underset{\substack{\text{N-ethyl-2-pentamine} \\ (2°\text{ amine})}}{CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-NH-Et}$$

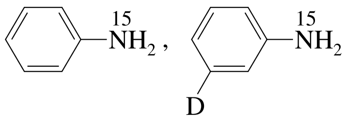
6. What are the constituent amines formed when the mixture of (a) and (b) undergoes Hofmann bromamide degradation?

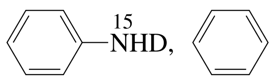

(a)


(b)

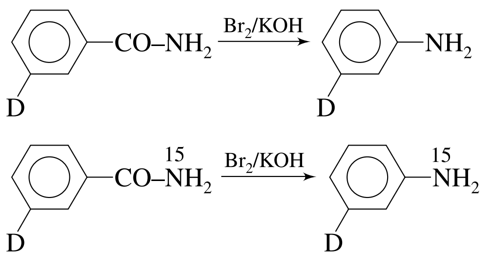
(1) 

(2) 

(3) 

(4) 

Sol. **[2]**



7. Arrange the following compounds in order of their increasing dipole moment:

(I) $CH_3CH_2CH_3$

(II) CH_3CH_2OH

(III) $CH_3CH_2NH_2$

(1) I < II < III (2) II < I < III

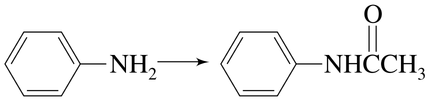
(3) I < III < II (4) III < I < II

Sol. **[3]**

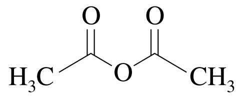
Dipole moment ∝ polarity

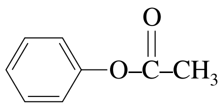
∝ H-bond

8. All but one of the following compounds reacts with aniline to give acetanilide. Which one does not?

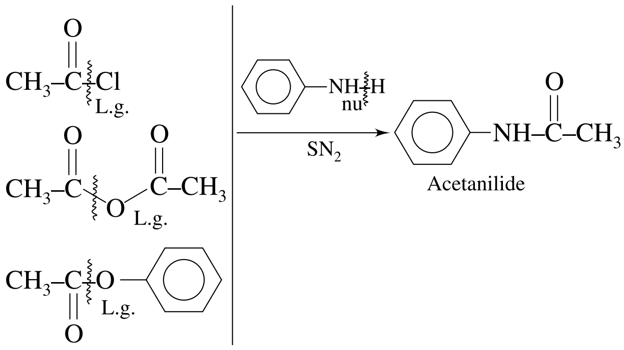


Aniline Acetanilide

(1) $CH_3\overset{O}{\overset{\|}{C}}-Cl$ (2) 

(3) $CH_3\overset{O}{\overset{\|}{C}}-H$ (4) 

Sol. **[3]**



Hence $CH_3-CH=O$ do not give acetanilide with aniline.

9. Which of the following is an intermediate and product formed in the reaction shown below?

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl+NH_3 \longrightarrow \text{Intermediate} \longrightarrow \text{Product}$$

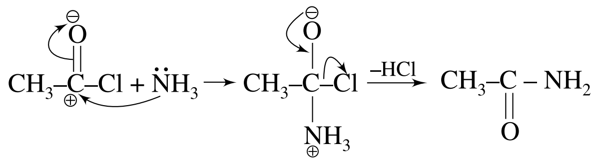
(1) $CH_3-\overset{\oplus}{N}H_3$ & $CH_3-C\equiv N$

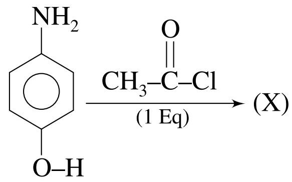
(2) $CH_3-\overset{O}{\overset{\|}{C}}\oplus$ & $CH_3-C\equiv N$

(3) $Cl-\overset{OH}{\overset{|}{\underset{\oplus NH_3}{\underset{|}{C}}}}-Cl$ & $CH_3-\underset{O}{\underset{\|}{C}}-NH_2$

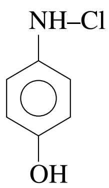
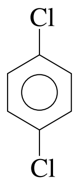
(4) $CH_3-\overset{O^-}{\overset{|}{\underset{\oplus NH_3}{\underset{|}{C}}}}-Cl$ & $CH_3-\underset{O}{\underset{\|}{C}}-NH_2$

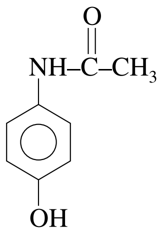
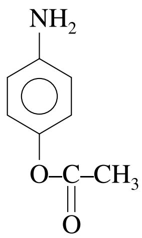
Sol. **[4]**



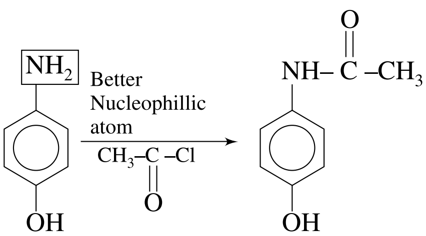
10. 

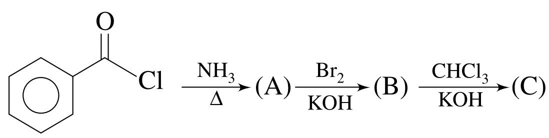
X is–

(1)  (2) 

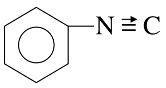
(3)  (4) 

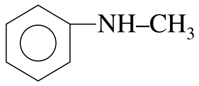
Sol. **[3]**

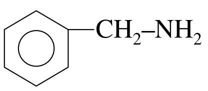


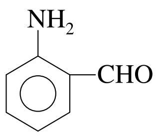
11. 

Product (C) is–

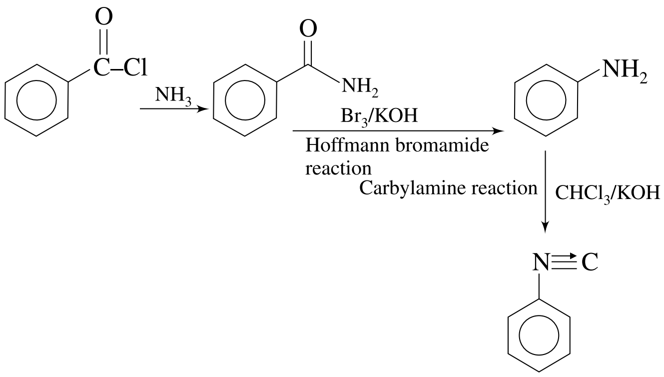
(1) 

(2) 

(3) 

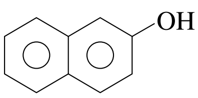
(4) 

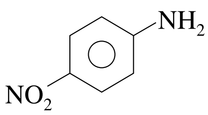
Sol. **[1]**

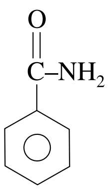


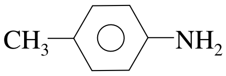
(C)

12. Compound X reacts with $NaNO_2$ and H_2SO_4, and then reacts with ortho cresol to form sharp colour compound. Compound X may be:

(a) 

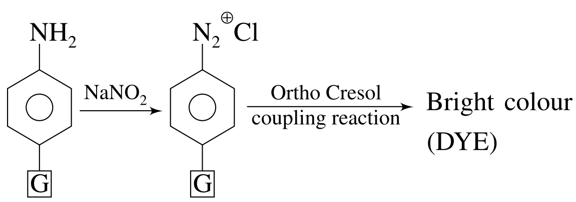
(b) 

(c) 

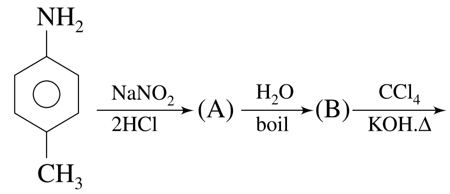
(d) 

(1) a and b (2) a, b and c
(3) c only (4) b and d

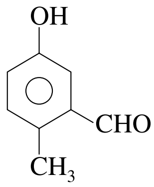
Sol. **[4]**

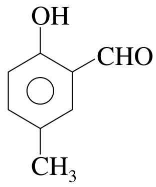


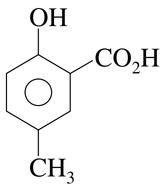
For coupling reaction
G must be electron releasing group like CH_3
Hence option (4) is correct.

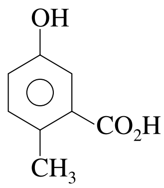
13. 

Major product (C) is:

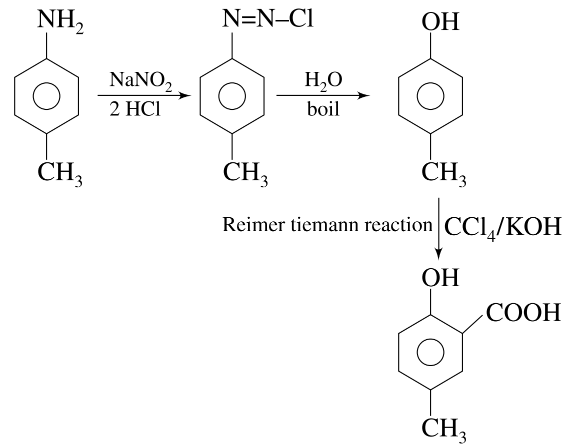
(1) 

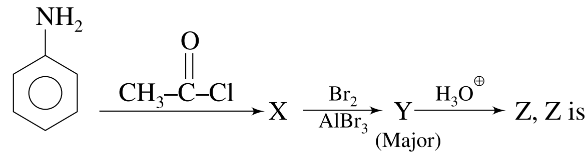
(2) 

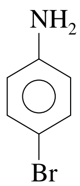
(3) 

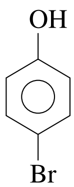
(4) 

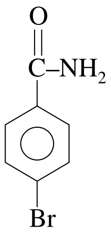
Sol. **[3]**

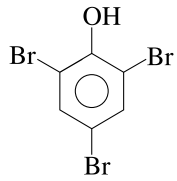


14. 

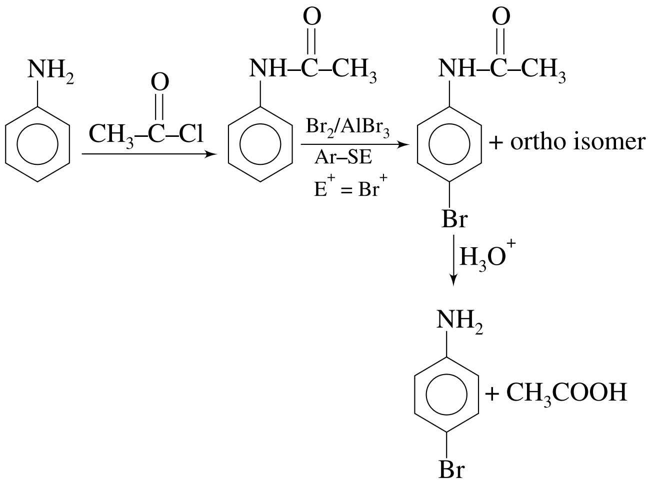
(1) 

(2) 

(3) 

(4) 

Sol. **[1]**



15. Suitable explanation for the order of basic character $(CH_3)_3N < (CH_3)_2NH$ is:

(1) Steric hindrance by bulky methyl group

(2) Higher volatility of 3° amine

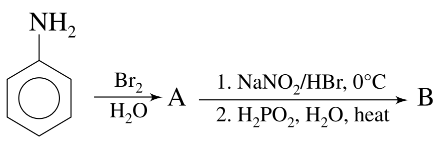
(3) Decreased capacity for H-bond formation with H_2O

(4) Decreased electron-density at N atom

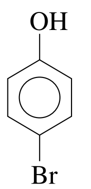
Sol. **[1]**

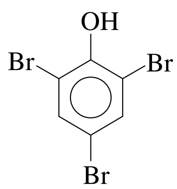
Due to steric hindrance by methyl group removal of ℓp from N-atom becomes difficult

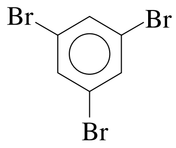
16. Consider the following sequence of reaction.

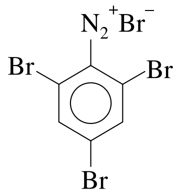


The end product (B) is:

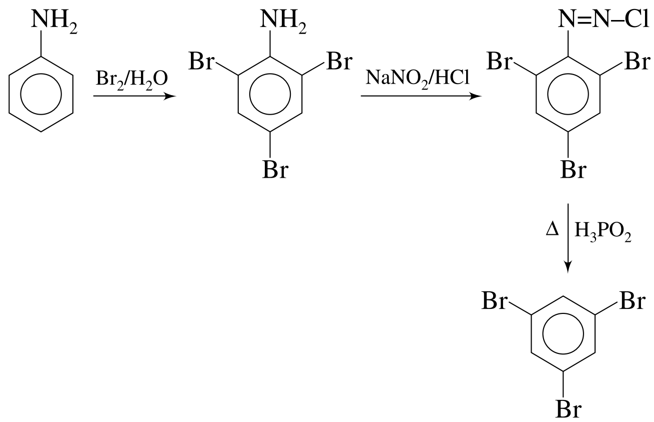
(1) 

(2) 

(3) 

(4) 

Sol. **[3]**



17. A positive carbylamine test is given by:

(1) N, N-dimethylaniline

(2) Acetanilide

(3) N-methyl-o-methylaniline

(4) p-methylbenzylamine

Sol. **[4]**

Only 1° amine will give positive carbylamines test.

18. Which of the following does not give aliphatic primary amine as product?

(1) $CH_3\text{–}\overset{\overset{\large O}{||}}{C}\text{–}OH \xrightarrow[\Delta]{N_3H,\ H_2SO_4}$

(2) $CH_3\text{–}CH = N\text{–}OH \xrightarrow[\Delta]{H^{\oplus}}$

(3) $CH_3\text{–}\overset{\overset{\large O}{||}}{C}\text{–}NH_2 \xrightarrow[\Delta]{Br_2/\overline{O}H}$

(4) $CH_3\text{–}NC \xrightarrow[\Delta]{H_3O^{\oplus}}$

Sol. **[2]**

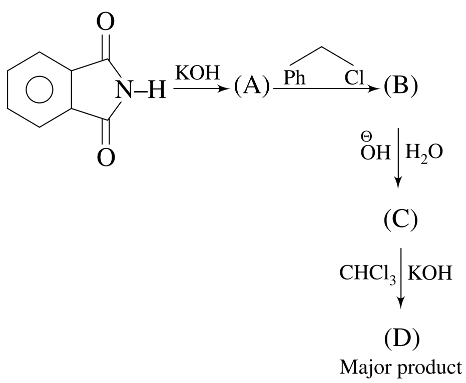
(1) $CH_3\text{–}\overset{\overset{\large O}{||}}{C}\text{–}OH \xrightarrow[\Delta]{N_3H,\ H_2SO_4} CH_3\text{–}NH_2$

(2) $CH_3–CH = N–OH \xrightarrow[\Delta]{H^{\oplus}} CH_3–CH{=}O$

(3) $CH_3–\overset{O}{\overset{\|}{C}}–NH_2 \xrightarrow[\Delta]{Br_2/\overline{O}H} CH_3–NH_2$

(4) $CH_3–NC \xrightarrow[\Delta]{H_3O^{\oplus}} CH_3–NH_2 + H–COOH$

19.

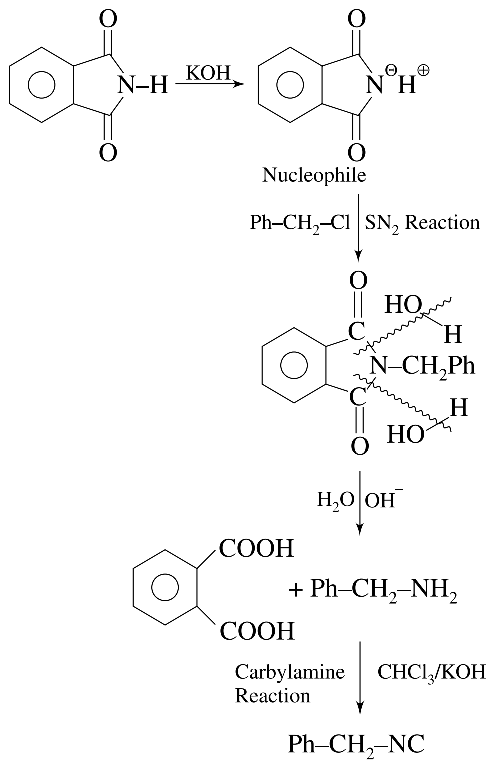


Structure of (D) is:

(1) $Ph–CH_2NH_2$ (2) $Ph–NC$

(3) $PhCH_2NC$ (4) $PhCH_2CN$

Sol. **[3]**



20. Which of the following alkene cannot be prepared by de-amination of n-Bu–NH_2 with $NaNO_2$/HCl?

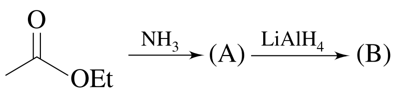
(1) 1-butene (2) *cis*-2-butene

(3) *trans*-2-butene (4) Iso-butene

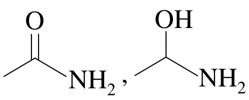
Sol. **[4]**

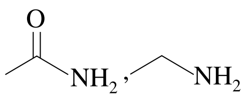
Formation of isobutene (branched alkene) does not take place by using n-BuNH_2 (structure chain).

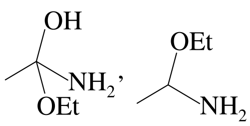
EXERCISE 1

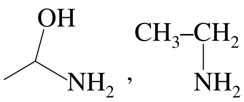
1. 

Products A and B, respectively, are:

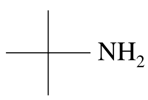
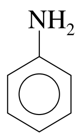
(1) 

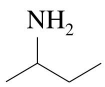
(2) 

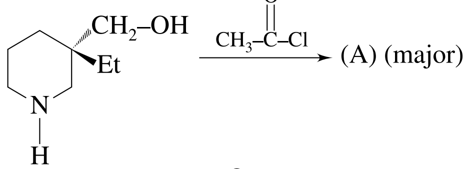
(3) 

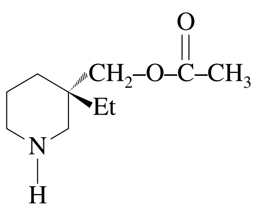
(4) 

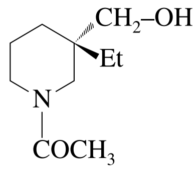
2. Which of the following compounds does not give isocyanide test?

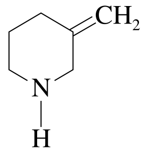
(1)  (2) 

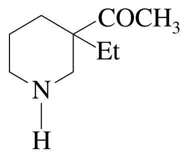
(3) $CH_3–NH–CH_2–CH_3$ (4) 

3. 

(1) 

(2) 

(3) 

(4) 

4. In which of the following reactions does the amine behaves as an acid?

(1) $(C_2H_5)_2NH + H_2PtCl_6$

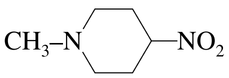
(2) $CH_3NH_2 + H_2O$

(3) $(Me_2CH)_2NH + n\text{–}C_4H_9Li$

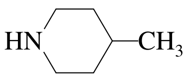
(4) $(C_2H_5)_3\ddot{N} + BF_3$

5. Select correct statement (s)

(1) N-methyl piperidine (A) has higher boiling point than 4-methylpiperidine (B)



(A)



(B)

(2) (B) has higher boiling point than A

(3) (A) and (B) have same boiling point being isomeric amines

(4) None of these

6. Melting points are normally the highest for:

(1) Tertiary amides (2) Secondary amides

(3) Primary amides (4) Amines

7. Arrange the following compounds in an increasing order of their solubility in water:

(I) $C_6H_5NH_2$

(II) $(C_2H_5)_2NH$

(III) $C_2H_5NH_2$

(1) I < II < III (2) II < III < I

(3) III < II < I (4) I = II = III

8. Order of basicity for

(p) Et_2NH

(q) Et_3N

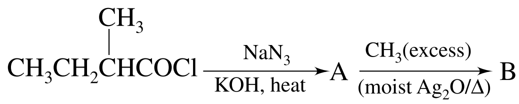
(r) $EtNH_2$

in aqueous medium is

(1) q > p > r (2) p > r > q

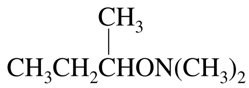
(3) p > q > r (4) r > q > p

9. Consider the following sequence of reactions

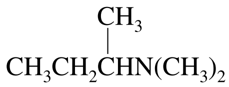


The major product (B) is

(1) $CH_3CH_2CH{=}CH_2$

(2) 

(3) $CH_3CH{=}CHCH_3$

(4) 

10. A compound undergoes the following sequence of reactions:

$$C_3H_5N \xrightarrow{\text{Hydrolysis}} C_3H_6O_2 \xrightarrow{Cl_2/P} C_3H_5O_2Cl \xrightarrow{NH_3} C_3H_7NO_2$$

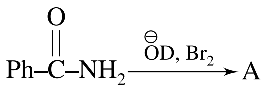
The compound C is:

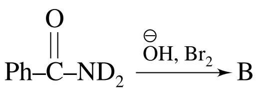
(1) 1-Nitropropane

(2) 2-Nitropropane

(3) 2-Aminopropanoic acid

(4) 2-Hydroxypropanamide

11. **Reaction-I** 

Reaction-II 

Products A and B are:

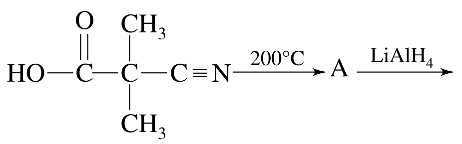
(1) $Ph\text{–}NH_2$ and $Ph\text{–}ND_2$

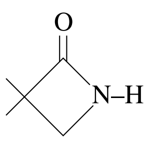
(2) $Ph\text{–}ND_2$ and $Ph\text{–}NH_2$

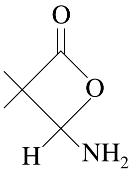
(3) Both $PH\text{–}NH_2$

(4) Both $Ph\text{–}ND_2$

12. Consider the following sequence of reactions:

 ; (B) is:

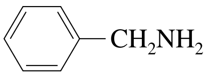
(1) 

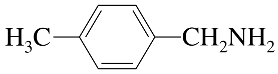
(2) 

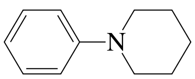
(3) $HO{-}H_2C{-}C(CH_3)_2{-}CH_2{-}NH_2$

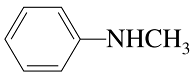
(4) $(H_3C)_2CH{-}CH_2{-}NH_2$

13. Which amine yields N-Nitroso amine after treatment with nitrous acid ($NaNO_2$, HCl)?

(1) 

(2) 

(3) 

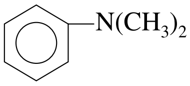
(4) 

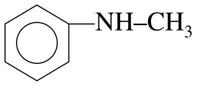
14. **Set-I:** is a list of pair for distinction and
Set-II: is a list of suitable reagent

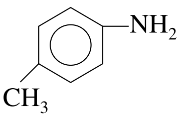
Set-I	Set-II
(A) ethane, ethyne	(P) $CuSO_4$ solution
(B) formic acid, acetic acid	(Q) ammoniacal Cu_2Cl_2
(C) glycine, biuret	(R) neutral $FeCl_3$
(D) benzyl amine, *o*-toluidine	(S) $NaNO_2/HCl$, phenol

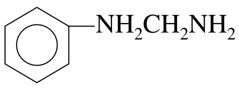
	A	B	C	D
(1)	P	R	Q	S
(2)	R	P	Q	S
(3)	Q	R	P	S
(4)	Q	R	S	P

15. Amongst the compound given, the one that would form a brilliant coloured dye with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is:

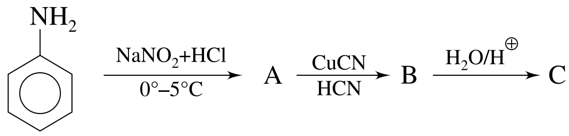
(1) 

(2) 

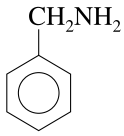
(3) 

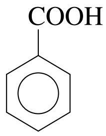
(4) 

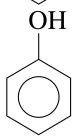
16. In the reaction

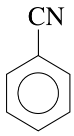


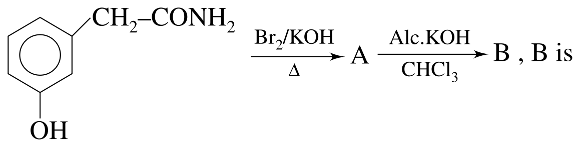
the end product (C) is:

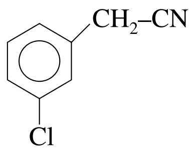
(1) 

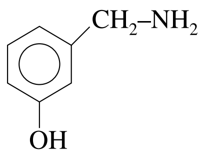
(2) 

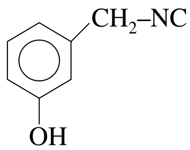
(3) 

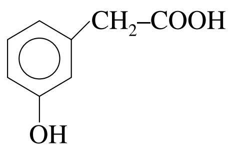
(4) 

17. 

(1) 

(2) 

(3) 

(4) 

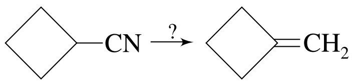
18. Consider the following sequence of reactions.

$$C_6H_5NH_2 \xrightarrow[H_2O]{Br_2} A \xrightarrow[2.\ HBF_4]{1.\ NaNO_2/HCl} B \xrightarrow[\text{anhydrous condition}]{\text{Heat}} C$$

The final product (C) is:

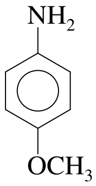
(1) 1-bromo-4-fluorobenzene
(2) 4-bromoaniline
(3) 1, 3, 5-tribromo-2-fluorobenzene
(4) 1, 3, 5-tribromobenzene

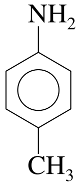
19. What sequence of reaction would best accomplish the following reaction?

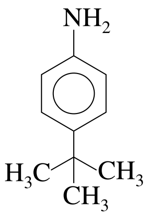


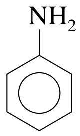
(1) (i) $LiAlH_4$ in ether; (ii) $3CH_3I$ followed by heating with AgOH
(2) (i) $LiAlH_4$ in ether; (ii) P_2O_5 and heat
(3) (i) 20% H_2SO_4 and heat; (ii) P_2O_5
(4) H_2 and Lindlar catalyst

20. What will be reactivity order for isocyanide test for following amines?

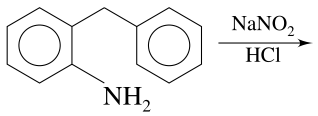
(I) 

(II) 

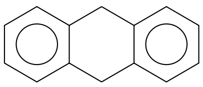
(III) 

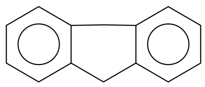
(IV) 

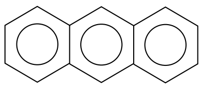
(1) I > III > II > IV
(2) I > IV> II > III
(3) I > II > III > IV
(4) II > III > IV > I

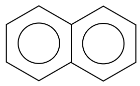
21. 

Product of this reaction is:

(1) 

(2) 

(3) 

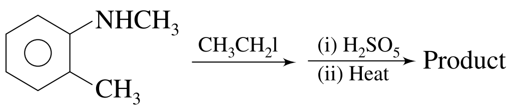
(4) 

22. Among the following compounds, which will react with acetone to give a product containing >C=N?

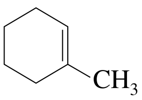
(1) $C_6H_5NH_2$
(2) $(CH_3)_3N$
(3) $C_6H_5NHC_6H_5$
(4) $C_6H_5NHNH_2$

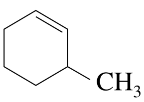
23. N-Ethyl pthalimide on hydrolysis gives:

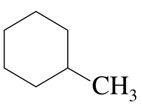
(1) Methyl alcohol
(2) Ethyl amine
(3) Dimethyl amine
(4) Diethyl amine

24. 

The main product is

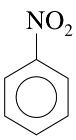
(1) 

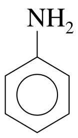
(2) 

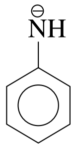
(3) 

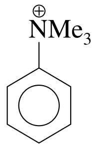
(4) $CH_2{=}CH_2$

25. In which case the reaction with an electrophile, the product is 1,3-disubstituted one?

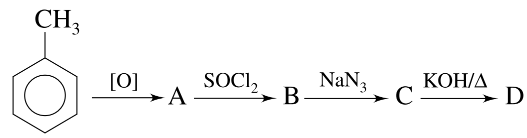
(I) 

(II) 

(III) 

(IV) 

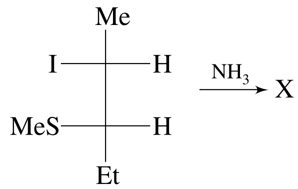
(1) I & II
(2) II & III
(3) III & IV
(4) I & IV

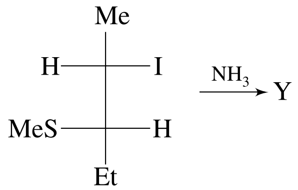
26. 

What is D in above sequence?

(1) An amide
(2) Primary amine
(3) Phenyl isocyanate
(4) None of these

27.



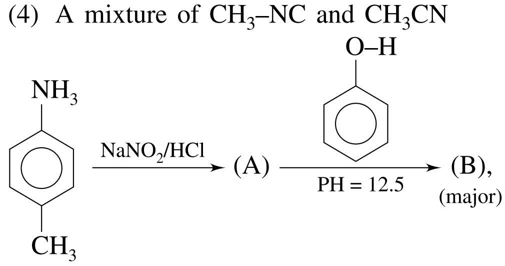


Select true statement for above reactions:

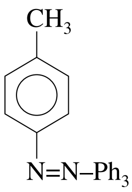
(1) X & Y are same compound and are formed by same mechanism
(2) X & Y are same compound and are formed by different mechanism
(3) X & Y are different compounds and are formed by same mechanism
(4) X & Y are different compounds and are formed by different mechanism

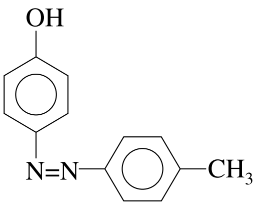
28. An aliphatic organic compound Containing C, H and N reacts with dilute HCl to produce formic acid. It is reduced to dimethylamine by Pt or Ni. The compound can be

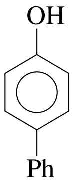
(1) CH_3NC
(2) CH_3CN
(3) CH_3NH_2
(4) A mixture of CH_3–NC and CH_3CN

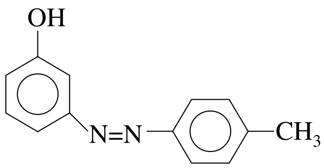
29. 

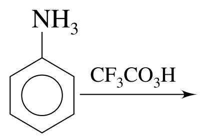
Product (B) of this reaction is:

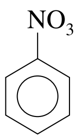
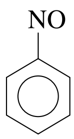
(1) 

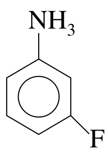
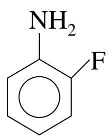
(2) 

(3) 

(4) 

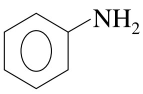
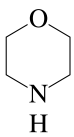
30.  A; A is:

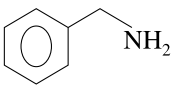
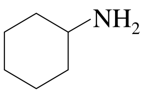
(1)  (2) 

(3)  (4) 

EXERCISE 2

1. Which of the following compounds will not form a Schiff base on reaction with *p*-nitrobenzaldehyde?

(1)  (2) 

(3)  (4) 

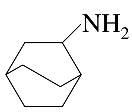
2. Which of the following compounds on treatment with benzene sulphonyl chloride forms and alkali-soluble precipitate?

(1) $(C_2H_5)_2NH$ (2) $C_6H_5NHCOCH_2CH_3$

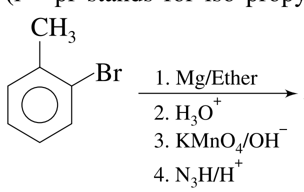
(3) $C_6H_5CH_2NH_2$ (4) CH_3CONH_2

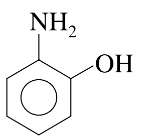
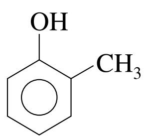
3. The amine which cannot be prepared by Gabriel phthalimide synthesis method is:

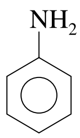
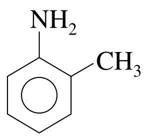
(1) Ph – NH_2 (2) Me – NH_2

(3) i – pr – NH_2 (4) 

(i – pr stands for iso propyl)

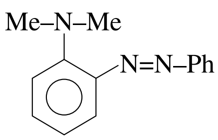
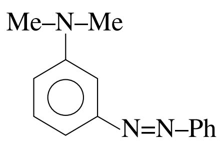
4.  A, Product A is:

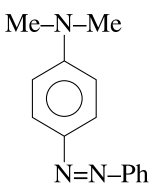
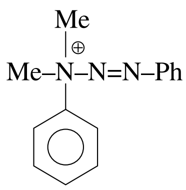
(1)  (2) 

(3)  (4) 

5. $Ph-NH_2 \xrightarrow{CH_3-Cl\ (2\ mole)} (A) \xrightarrow{Ph-\overset{\oplus}{N_2}\overset{-}{Cl}} (B)$ (major)
Butteryellow

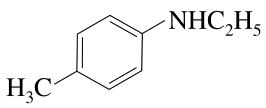
Product of the above reaction is:

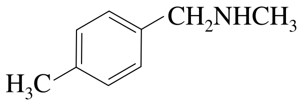
(1)  (2) 

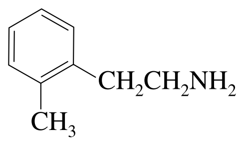
(3)  (4) 

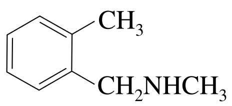
6. Compound A has the formula $C_9H_{13}N$ and forms terephthalic acid with $KMnO_4/OH^-$. It forms a compound (in liquid state) with $(COOC_2H_5)_2$ which gets

decomposed by KOH. The possible structure of compound A is

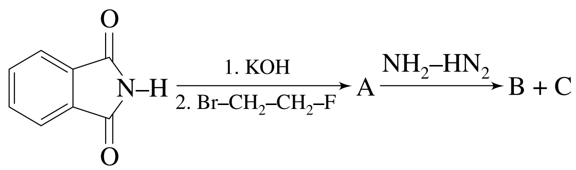
(1) 

(2) 

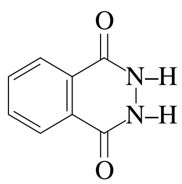
(3) 

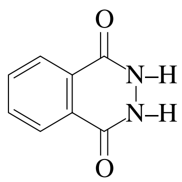
(4) 

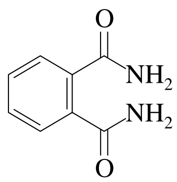
7. Consider the following sequence of reactions:

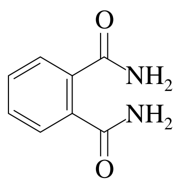


The products (B) and (C) are:

(1)  $+ NH_2–CH_2–CH_2–Br$

(2)  $+ NH_2–CH_2–CH_2–F$

(3)  $+ NH_2–CH_2–CH_2–F$

(4)  $+ NH_2–CH_2–CH_2–Br$

8. $CH_3—\overset{O}{\overset{||}{C}}—NH_2 \xrightarrow{KOBr} A$

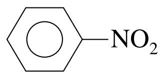
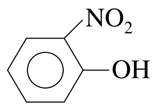
$CH_3—\overset{O}{\overset{||}{C}}—NH_2 \xrightarrow{LiH} B$

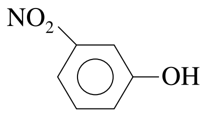
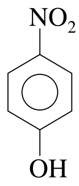
Relation between A and B is

(1) Chain isomer (2) Homologues

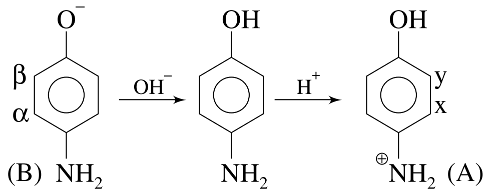
(3) Functional isomer (4) Identical

9. Which one of the following compounds will have the highest dipole moment?

(1)  (2) 

(3)  (4) 

10. Consider *p*-amino phenol

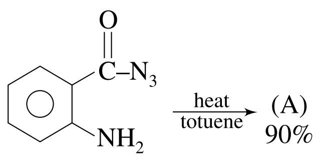


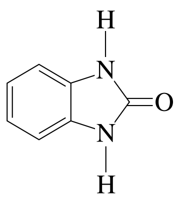
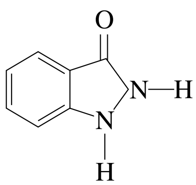
Which positions are activated in acidic and basic media for coupling?

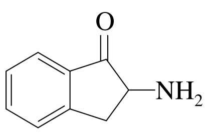
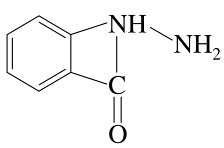
(1) x in A and β in B (2) x in A and α in B

(3) y in A and α in B (4) y in A and β in B

11. Heating the acyl azide in dry toluene under reflux for 3-hours give a 90% yield for a heterocyclic product. Identify the product (A).

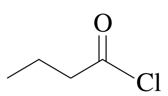
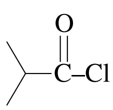


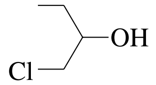
(1)  (2) 

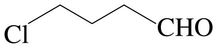
(3)  (4) 

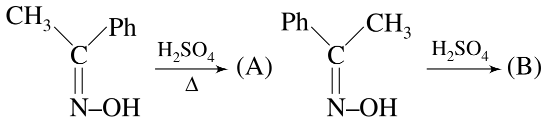
12. (x) $C_4H_7OCl \xrightarrow{NH_3} C_4H_9ON \xrightarrow[KOH]{Br_3} CH_4–CH_2–CH_2–NH_2$

Compound x is

(1)  (2) 

(3) 

(4) 

13. 

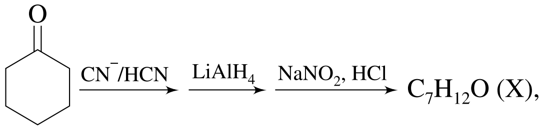
Products (A) and (B), respectively, in the above reaction are:

(1) $Ph{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$, $Ph{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$

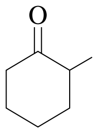
(2) $CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}Ph$, $CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}Ph$

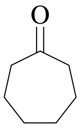
(3) $Ph{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$, $CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}Ph$

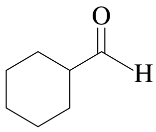
(4) $CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}Ph$, $Ph{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$

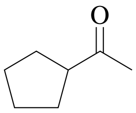
14. 

(X) is:

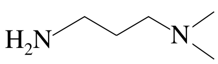
(1) 

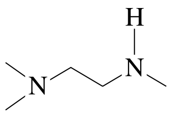
(2) 

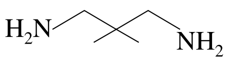
(3) 

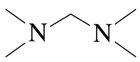
(4) 

15. The Hinsberg test of a $C_5H_{14}N_2$ compound produces a solid that is insoluble in 10% aq. NaOH. This solid derivative dissolves in 10% aq. H_2SO_4. Which of the following would best fit these facts?

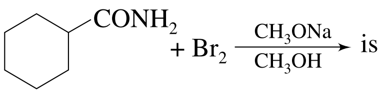
(1) 

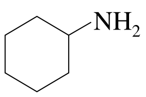
(2) 

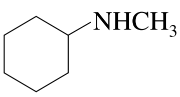
(3) 

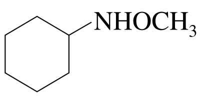
(4) 

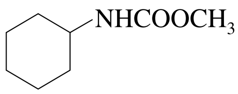
16. The product formed in the reaction



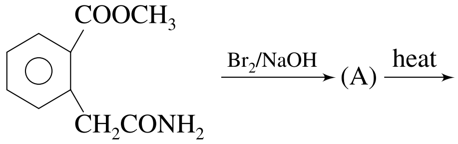
(1) 

(2) 

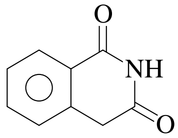
(3) 

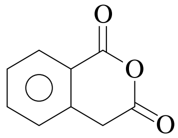
(4) 

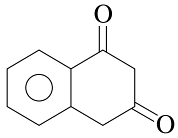
17. The following reactions are carried out.

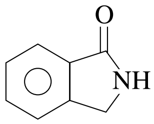


The product (B) is

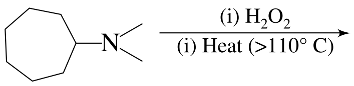
(1) 

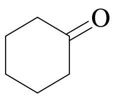
(2) 

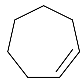
(3) 

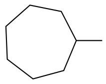
(4) 

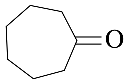
18. What is the likely product from the following reaction?

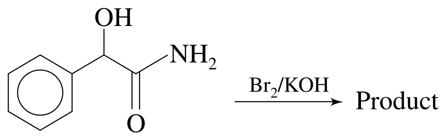


(1) 

(2) 

(3) 

(4) 

19. 

(α-hydroxy amide)

Product of this Hofmann bromamide reaction is

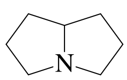
(1) $Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

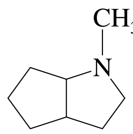
(2) Ph—CHO

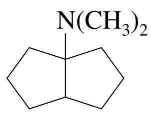
(3) $Ph{-}CH\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown NH_2}$

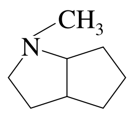
(4) $Ph{-}CH_2{-}NH_2$

20. The nitrogen atom in each of the following tertiary amines may be removed as trimethyl amine by repeated Hofmann eliminations (exhaustive methylation followed by heating with AgOH). Which of the amines requires the greater number of Hofmann sequences to accomplish this?

(1) 

(2) 

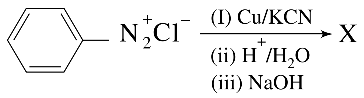
(3) 

(4) 

EXERCISE 3

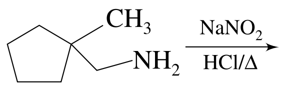
One and More Than One Option Correct Type Question

1. The following reaction sequence involves the formation of

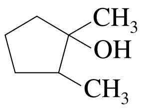
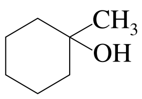


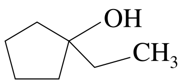
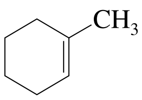
(1) a cyanide (2) a carboxylic acid
(3) an amide (4) an arene

2. In the following reaction,

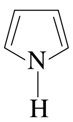


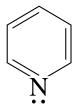
the expected product(s) is/are

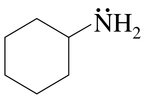
(1)  (2) 

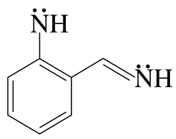
(3)  (4) 

3. Which of the following statements is/are correct?


(I)


(II)


(III)


(IV)

(1) I and II are aromatic and have equal basic strength
(2) I is aromatic and II is anti-aromatic but II is stronger base than I
(3) The order of basicity of the above of the above compounds is IV > III > II > I
(4) The conjugate acid of IV is more stabilised the conjugate acid of II

4. $\underset{X}{C_4H_{11}N} + HNO_2 \longrightarrow C_4H_{10}O$ (3° alcohol). Hence, X will give
(1) Carbylamine reaction
(2) Hofmann mustard oil reaction
(3) Diazonium salt (as the intermediate) with HNO_3
(4) Hofmann bromamide reaction

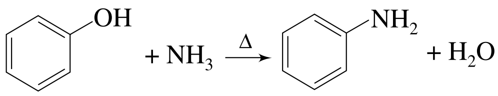
5. An amine A ($C_6H_{15}N$) on treatment with MeI and the KOH gives B ($C_8H_{20}N^+OH^-$). This on heating produces C, an alkene 'isobutene' and D an amine. The possible structure of amine A is/are
(1) $(CH_3)CHCH_2NHCH_2CH_3$
(2) $(CH_3)_3CNHCH_2CH_3$
(3) $CH_3CH_2CH_2CH_2NHCH_2CH_3$
(4) $CH_3(CH_2)_5NH_2$

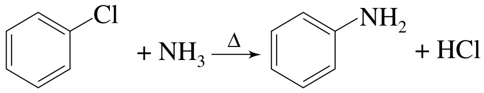
6. Dichlorocarbene is involved as an intermediate in the reaction of
(1) phenol + $CHCl_3$ + 4KOH
(2) ethylamine + $CHCl_3$ + KOH
(3) phenol + CCl_4
(4) $CHCl_3$ + KOH

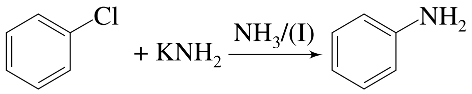
7. $A \xleftarrow[\text{Heat}]{H_3O^+} CH_3\underset{\underset{CH_3}{|}}{C}HNC \xleftarrow[\text{Heat}]{N_2,Ni} B$

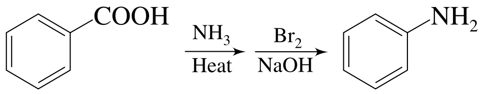
Product A and B can be distinguished by
(1) The treatment of $CHCl_3$, ^-OH
(2) The action of HNO_2; A liberates N_2 gas while B does not
(3) The action of $CS_2/HgCl_2$ B gives odour of mustard oil while A does not
(4) The treatment of p-toluene sulphonyl chloride; A gives alkali soluble product

8. Which of the following reactions can be used for preparation of aniline?

(1) 

(2) 

(3) 

(4) 

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

9. Statement I: Diazotisation of aniline can be used for its identification reaction.

Statement II: Diazonium salts of aniline forms various coloured azo dyes via coupling with suitable reagents.

10. Statement I: N, N-diethylaniline is a stronger base than aniline.

Statement II: Ethyl group is electron releasing by +I effect

11. Statement 1: Aniline does not undergo Friedel–Crafts reaction (Alkylation and acetylation).

Statement 2: Aniline forms salt with $AlCl_3$, due to which nitrogen of aniline of acquires positive charge hence acting as strong deactivator for any further reaction.

12. Statement-I: $(CH_3)_3CNH_2$ cannot be prepared by the Gabriel phthalimide reaction.

Statement-II: A tertiary alkyl halide is required in first step of S_N2 reactions.

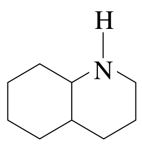
13. Statement-I: $NaBH_3CN$ can be used to reduce imine to 1° amine.

Statement-II: Protonated imine undergoes reduction in reductive amination reactions.

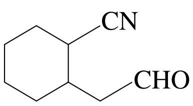
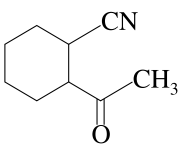
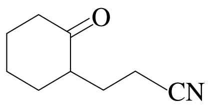
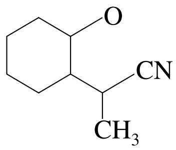
Comprehension Type Question

Passage Based Questions: (Q. 14–16)

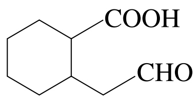
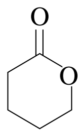
An organic compound A has molecular formula $C_6H_{13}NO$ and it can be resolved into enantiomers. A does not decolourise Br_2–H_2O solution. A on hydrolysis with dil. H_2SO_4 gives B ($C_9H_{14}O_3$) which gives effervescence with $NaHCO_3$. B on treatment with $NaBH_4$ followed by heating with concentrated H_2SO_4 yielded a sweet smelling liquid C ($C_9H_{14}O_3$). Also, A on reduction with $LiAlH_4$ yields $C_9H_{19}ON$ which on further heating with concentrated H_2SO_4 produces the following compound.

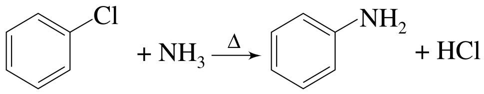


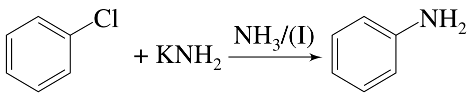
14. What is the structure of A?

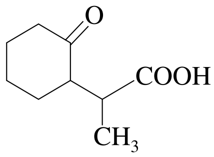
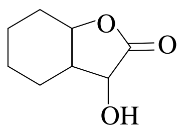
(1) 
(2) 
(3) 
(4) 

15. B and C, respectively, are

(1)  and 

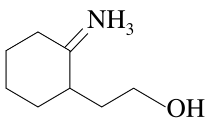
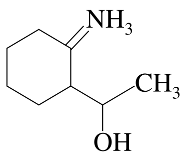
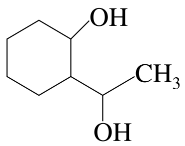
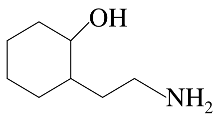
(2) 

(3) 

(4)  and 

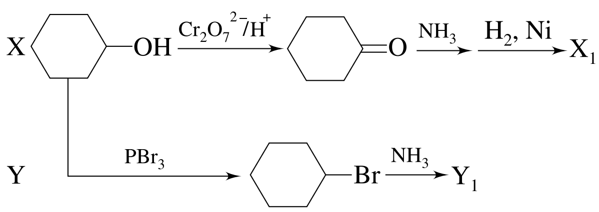
16. What is formed at the end of following reaction

$C \xrightarrow[\Delta]{NH_3} \xrightarrow[Br_2]{NaOH} ?$

(1) 
(2) 
(3) 
(4) 

Passage Based Questions: (Q. 17 and 18)

Two synthetic routes were planned to synthesise cyclohexylamine



Taking all the aspects of 2° alcohols and 2° alkyl halide, answer the following questions.

17. Select the correct statements (s)

(1) Plan Y is preferred to plan X since, it involves lesser number of steps
(2) Plan X is preferred to plan Y since, plan Y also involves the elimination of HBr from 2° alkyl halide

(3) Plan X involves reductive amination which gives better yield

(4) Plan Y involves S_N reaction and being faster gives better yield

18. Cyclohexyl bromide can also be converted into cyclohexylamine in good yield using

(1) NaN_3 followed by reduction with $LiAlH_4$ since, N_3^- is a good nucleophile

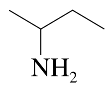
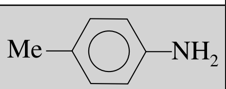
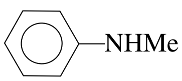
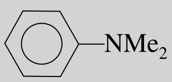
(2) NaCN followed by reduction using Pt/H_2 since, CN^- is a strong nucleophile

(3) Both (1) and (2)

(4) None of the above

Column Matching Type Question

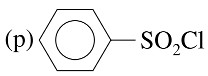
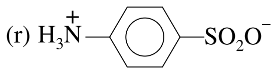
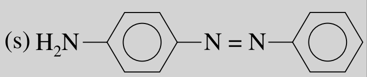
19. Match the column I with Column II and mark the correct option from the codes given below.

	Column I (Compound)		Column II (Test)
i.		**p.**	Liebermann's nitroso reaction
ii.		**q.**	Evolution of N_2 with HNO_2
iii.		**r.**	Dye test
iv.		**s.**	Green colour with HNO_2
		t.	Carbylamine test

Codes

	i	ii	iii	iv
(1)	q, t	r, t	p	s
(2)	q	q, s	q	r, s
(3)	q	s	r, t	p
(4)	p, s	r	r, t	q, s

20. Match the reagents given in Column-I to the structures given in Column-II

Column-I	Column-II
(a) Zwitter ion structure	
(b) Schiff's base	(q) $C_6H_5N(CH_3)NO$
(c) Hinsberg's Reagent	
(d) Nitrosamine	
(e) Azo dye	(t) R–CH=NR

(1) a→r; b→t; c→p; d→q; e→s

(2) a→r; b→t; c→q; d→s; e→p

(3) a→q; b→s; c→p; d→r; e→t

(4) a→t; b→p; c→s; d→q; e→r

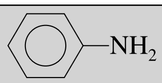
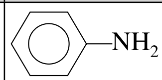
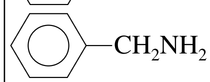
21. Match the column I with Column II and mark the correct option from the codes given below.

	Column I		Column II
i.	CH_3 Ph—C—NH_2 CH_3	**p.**	Treatment of CS_2, $HgCl_2$ gives out alkyl isothiocyanate
ii.	$CH_3CH_2NH_2$	**q.**	Treatment of *p*-toluene sulphonyl produces the compound insoluble in alkali
iii.	$CH_3CH_2NCH_3$ CH_3	**r.**	Treatment of H_2O_2; heat gives out alkene
iv.	$CH_3CH_2NHCH_3$	**s.**	Treatment of carbon disulphide produces dithiocarbamic acid

Codes

	i	ii	iii	iv
(1)	p, s	r, s	q	p, q
(2)	p, s	q	r	r, s
(3)	p, s	p, s	r	q
(4)	p	p, s	q	r, s

22. Match the column I with Column II and mark the correct option from the codes given below.

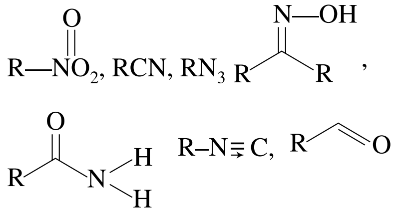
	Column I (Pair of distinction)		Column II (Reagent/test)
i.	$CH_3CH_2NH_2$, $(CH_3)_2NH$	**p.**	HNO_2 + β-naphthol
ii.	CH_3NH_2, 	**q.**	$NaNO_2$ + HCl
iii.	 	**r.**	Hofmann mustard oil reaction
iv.	$(CH_3)_3N$, $CH_3CH_2CH_2CH_2NH_2$	**s.**	Carbylamine

Codes

	i	ii	iii	iv
(1)	q, r, s	p	p	q, r, s
(2)	r	p, q	s	p, q
(3)	p, s	r	p, q	q, s
(4)	p, s	q	r, s	p, q

Single Digit Integer Type Question

23. How many of the following is reduced by lithium aluminium hydride to give 1° amine?



24. Consider the following reaction.

$CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} A$ (mixture)

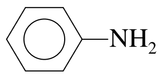
The mixture contains how many constituents?

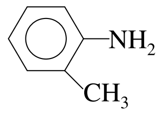
EXERCISE 4

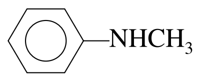
1. On heating benzyl amine with chloroform and ethanolic KOH, product obtained is **(AIEEE 2002)**

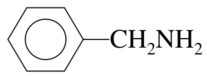
(1) benzyl alcohol (2) benzaldehyde
(3) benzonitrile (4) benzyl isocyanide

2. Which of the following is the strongest base? **(AIEEE 2004)**

(1) 

(2) 

(3) 

(4) 

3. Amongst the following the most basic compound is **(AIEEE 2005)**

(1) *p*-nitroaniline (2) acetanilide
(3) aniline (4) benzylamine

4. Which one of the following methods is neither meant for the synthesis nor for separation of amines? **(AIEEE 2005)**

(1) Curtius reaction (2) Wurtz reaction
(3) Hofmann method (4) Hinsberg method

5. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound. Water during the reaction is continuously removed. The compound formed is generally known as **(AIEEE 2005)**

(1) an amine (2) an imine
(3) an enamine (4) a Schiff's base

6. Fluorobenzene (C_6H_5F) can be synthesised in the laboratory **(AIEEE 2006)**

(1) By heating phenol with HF and KF
(2) From aniline by diazotisation followed by heating the diazonium salt with HBF_4
(3) By direct fluorination of benzene with F_2 gas
(4) By reacting bromobenzene with NaF solution

7. In the chemical reaction,

$CH_3—CH_2NH_2 + CHCl_3 + 3\ KOH \rightarrow A + B + 3H_2O.$
the compounds A and B are, respectively, **(AIEEE 2007)**

(1) C_2H_5CN and 3KCl
(2) $CH_3CH_2CONH_2$ and 3KCl
(3) C_2H_5 NC and 3KCl
(4) CH_3NC and 3KCl

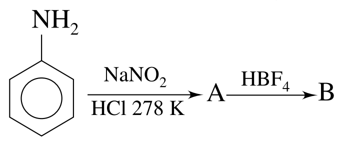
8. Which one of the following is the strongest base in aqueous solution? **(AIEEE 2007)**

(1) Trimethalmine (2) Aniline
(3) Dimethhylamine (4) Methylamine

9. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains **(AIEEE 2008)**

(1) mixture of *o*-and *p*-bromotoluenes
(2) mixture of *o*-and *p*-dibromobenzens
(3) mixture of *o*-and *p*-bromoanilines
(4) mixture of *o*-and *m*-bromotoluenes

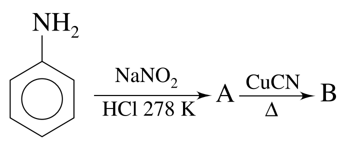
10. In the chemical reaction, **(AIEEE 2010)**



the compound A and B, respectively, are

(1) nitrobenzene and fluorobenzene
(2) phenol and benzene
(3) benzene diazonium chloride and fluorobenzene
(4) nitrobenzene and chlorobenzene

11. In the chemical reaction, **(AIEEE 2011)**



compounds A and B, respectively, are

(1) fluorobenzene and phenol
(2) benzene diazonium chloride and benzonitrile
(3) nitrobenzene and chlorobernzene
(4) phenol and bromobenzene

12. A compound with molecular mass 180 amu is acylated with CH_3COCl, to get a compound with molecular mass 390 amu. The number of amino groups present per molecule of the former compound is

(JEE Main 2013)

(1) 6 (2) 2
(3) 5 (4) 4

13. An organic compound A on reacting with NH_3 gives B. On heating B gives C. C in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is

(JEE Main 2013)

(1) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}H}—COOH$
(2) $CH_3CH_2CH_2CH_2COOH$
(3) CH_3CH_2COOH
(4) CH_3COOH

14. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?

(JEE Main 2013)

(1) $(CH_3)_2NH$ (2) CH_3NH_2
(3) $(CH_3)_3N$ (4) $C_6H_5NH_2$

15. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is **(JEE Main 2014)**

(1) an alkanol (2) an alkanediol
(3) an alkyl cyanide (4) an alkyl isocyanide

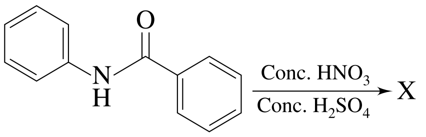
16. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + KCl + H_2O.
Nitrogen containing compound is

(2006, Only One Option Correct Type)

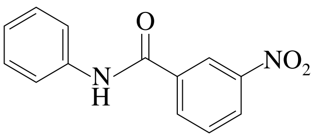
(1) CH_3CN (2) CH_3NHCH_3
(3) $CH_3—\overset{-}{N}\equiv\overset{+}{C}$ (4) $CH_3—\overset{+}{N}\equiv\overset{-}{C}$

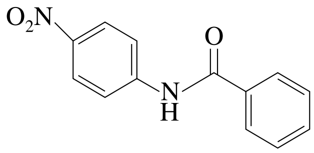
17. In the following reaction,

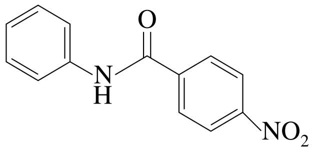
(2007, only one option correct type)

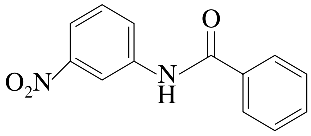


The structure of the major product X is

(1) 

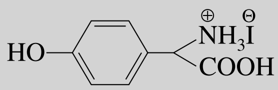
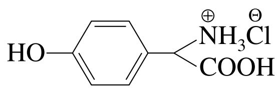
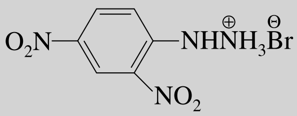
(2) 

(3) 

(4) 

18. Match the column I with Column II and mark the correct option from the codes given below.

(2008, Matching type)

	Column I		Column II
i.	$H_2N—NH_3Cl$	p.	Sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
ii.		q.	Gives positive $FeCl_3$ test
iii.		r.	Gives white precipitate with $AgNO_3$
iv.		s.	Reacts with aldehydes to form the corresponding hydrazone derivative

Codes

	i	ii	iii	iv
(1)	r	p, q	p	q, s
(2)	r, s	p, q	p, q, r	p
(3)	q, r	r, s	p	p
(4)	q, s	q, r, s	p, q	p, q

19. (1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I
(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

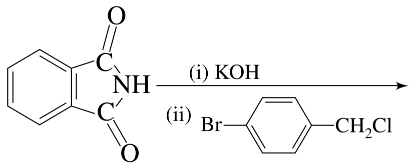
Statement I: Aniline on reaction with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

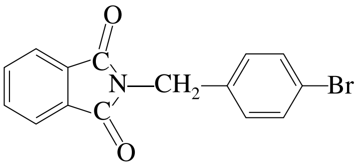
(2008, Statement type)

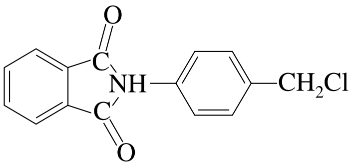
Statement II: The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with βnaphthol is due to the extended conjugation.

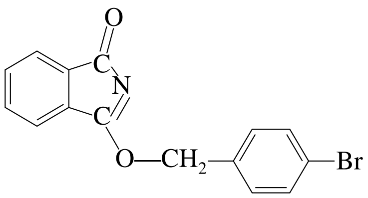
20. The major product of the following reaction is

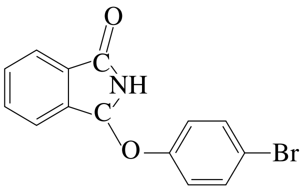
(2011, Only one options correct type)



(1) 

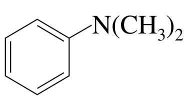
(2) 

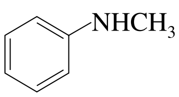
(3) 

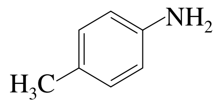
(4) 

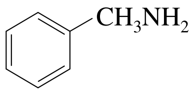
21. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

(2011, Only one options correct type)

(1) 

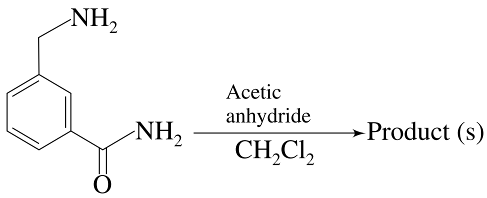
(2) 

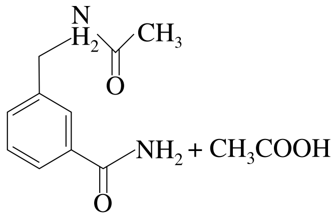
(3) 

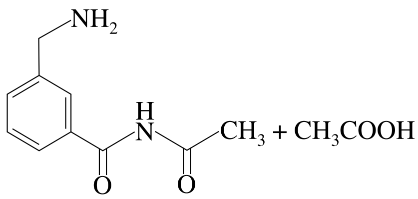
(4) 

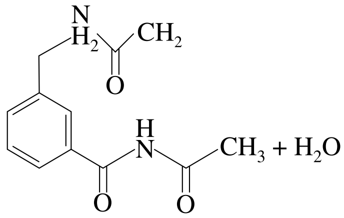
22. In the reaction shown below, the major product(s) formed is/are

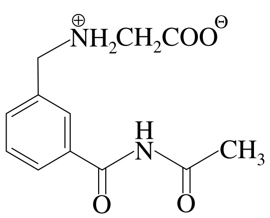
(2014 Adv., One or more than one options correct type)



(1) 

(2) 

(3) 

(4) 

23. Match the column I with Column II and mark the correct option from the codes given below.

(2007, Only one option correct type)

	Column I		Column II
i.	$CH_3CH_2CH_2CN$	p.	Reduction with Pd – C/ H_2
ii.	$CH_3CH_2OCOCH_3$	q.	Reduction with $SnCl_2$/ HCl
iii.	$CH_3CH{=}CHCH_2OH$	r.	Development of foul smell on treatment with chloroform and alcoholic KOH.
iv.	$CH_3CH_2CH_2CH_2NH_2$	s.	Reduction with di-isobutyl aluminium hydride (DIBAL-H)
		t.	Alkaline hydrolysis

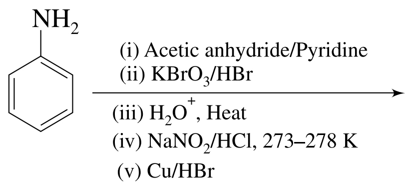
Codes

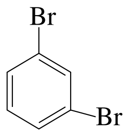
	i	ii	iii	iv
(1)	p, q, s, t	p, s, t	p	r
(2)	q, s	p, r	p, q, s	s, t
(3)	r	q, s	p, q	r, s, t
(4)	p, q	p, q	q, s	s, t

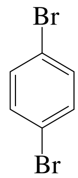
24. In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are **[JEE Adv. 2016]**

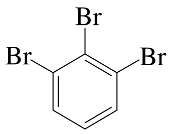
(1) four moles of NaOH and two moles of Br_2
(2) two moles of NaOH and two moles of Br_2
(3) four moles of NaOH and one mole of Br_2
(4) one moles of NaOH and one mole of Br_2

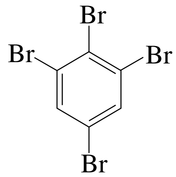
25. The product(s) of the following reaction sequence is (are) **[JEE Adv. 2016]**



(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

1. (4) 2. (3) 3. (1) 4. (3) 5. (1)
6. (2) 7. (4) 8. (3) 9. (4) 10. (2)
11. (3) 12. (1) 13. (1) 14. (3) 15. (3)
16. (4) 17. (1) 18. (1) 19. (2) 20. (1)
21. (2) 22. (2) 23. (2) 24. (4) 25. (2)
26. (2) 27. (3) 28. (3) 29. (2) 30. (1)

EXERCISE # 2

1. (2) 2. (4) 3. (2) 4. (2) 5. (1)
6. (3) 7. (1) 8. (4) 9. (2) 10. (2)
11. (1) 12. (2) 13. (2) 14. (1) 15. (2)
16. (3) 17. (2) 18. (1) 19. (3) 20. (4)

EXERCISE # 3

1. (1,2,4) 2. (1,2,3,4) 3. (1,2,4) 4. (1,3,4) 5. (1,4)
6. (1,3,4) 7. (1,2,3) 8. (1,3) 9. (1) 10. (2)
11. (1) 12. (1) 13. (2) 14. (3) 15. (3)
16. (4) 17. (2,3) 18. (1) 19. (1) 20. (1)
21. (3) 22. (1) 23. (4) 24. (6)

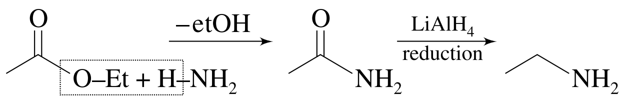
EXERCISE # 4

1. (1) 2. (2) 3. (3) 4. (2) 5. (1)
6. (3) 7. (2) 8. (2) 9. (4) 10. (2)
11. (3) 12. (4) 13. (3) 14. (3) 15. (2)
16. (3) 17. (2) 18. (4) 19. (1) 20. (2)
21. (2) 22. (2) 23. (3) 24. (3) 25. (1)

HINT AND SOLUTION

EXERCISE # 1

1. [2]

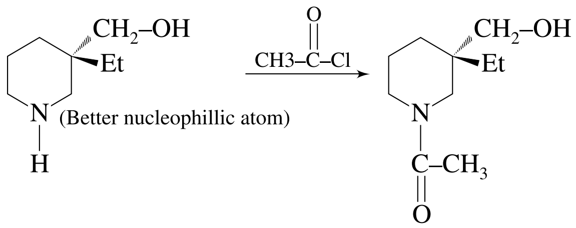


2. [3]

Only 1° amine will give positive isocyanides test

3. [2]

Removal of more acidic H takes place during acetylation



4. [3]

n–C_4H_9Li (organometallic substance) behaves as bronsted base so that amine behaves as an acid.

5. [2]

Due to H-bond, B has higher boiling point than A.

6. [3]

Due to H-bond and relatively greater mol. wt. from amines, 2° amide have higher m.pt.

7. [1]

(i) Solubility $\propto \dfrac{1}{\text{molecular weight}}$

(ii) $\dfrac{1^\circ\text{amine} > 2^\circ\text{ amine} > 3^\circ\text{ amine}}{\text{H-bond tendency}\downarrow}$

Solubility$\downarrow$

8. [3]

As per NCERT value

If R = Et then

2° > 3° > 1°

9. [1]

$$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-COCl \xrightarrow[KOH,\ \Delta]{NaN_3} CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-NH_2$$

Curtius reaction

$$\downarrow CH_3-I(\text{excess})$$

$$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{\oplus}{N}(CH_3)_3I^-$$

$$\downarrow AgOH$$

$$CH_3-CH_2-CH=CH_2 \xleftarrow[E_{ICB}]{\Delta} CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{O}H$$

1-butene (major) Hoffmann elimination

10. [3]

$$CH_3-CH_2-C\equiv N \xrightarrow{H_3O^+} CH_3-CH_2-\underset{O}{\underset{\|}{C}}-OH$$

$$\downarrow \text{H.V.Z}\ Cl_2/P$$

$$CH_3-\underset{Cl}{\underset{|}{CH}}-COOH$$

$$\downarrow NH_3$$

$$CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH$$

$(C_3H_5NO_2)$

2-Amino propanoic acid

11. [2]

$$Ph-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{\bar{O}D/Br_2} Ph-ND_2$$

$$Ph-\overset{O}{\overset{\|}{C}}-ND_2 \xrightarrow{\bar{O}D/Br} Ph-NH_2$$

Hoffmann bromamide reaction (for detail see mechanism)

12. [4]

$$HO-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-C\equiv N \xrightarrow[\substack{\text{De-carboxylation}\\ -CO_2}]{200^\circ C} CH_3-\overset{CH_3}{\overset{|}{CH}}-C\equiv N$$

$$\downarrow \text{reducation}\ LiAlH_4$$

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-NH_2$$

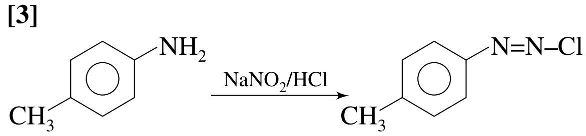
13. [4]

Only 2° amine will give positive nitrosoamine test

14. [3]

Theory based.

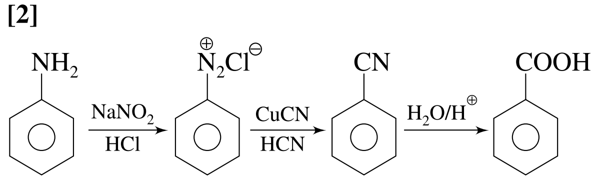
15. [3]



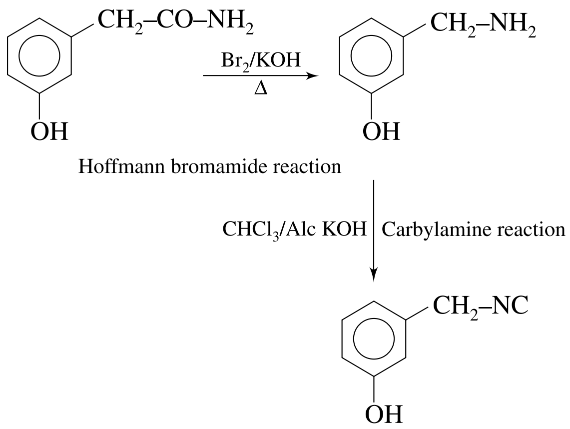
(Azonium salt)

$\xrightarrow{\beta\text{-Napthol}}$ Dye formation

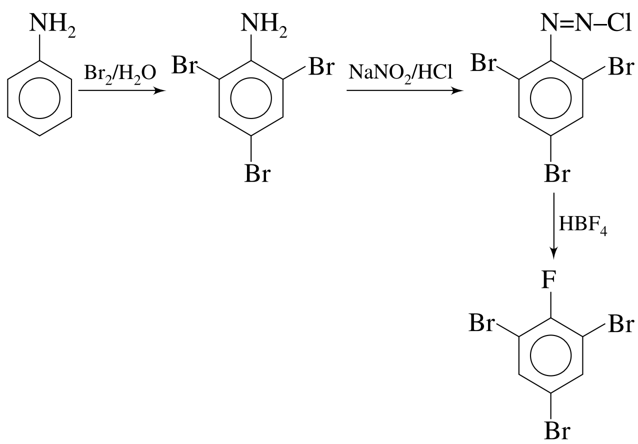
16. [2]



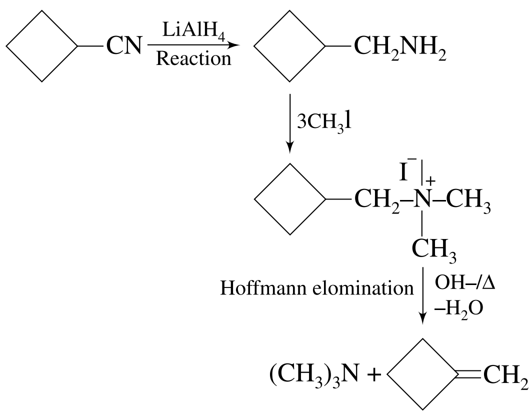
17. [3]



18. [3]



19. [2]

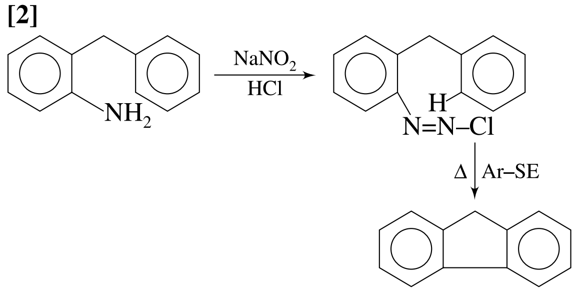


20. [3]

Reactivity of isocyanide test ∝ Electron releasing power

ERG ($-OCH_3 > -\underbrace{CH_3 > -C(CH_3)_3}_{\text{Due to H-effect}}$)

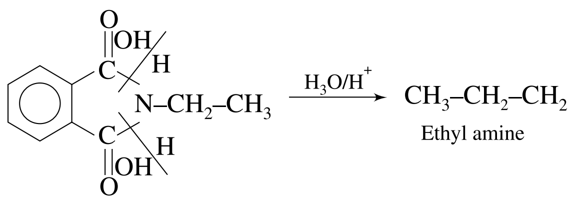
21. [2]



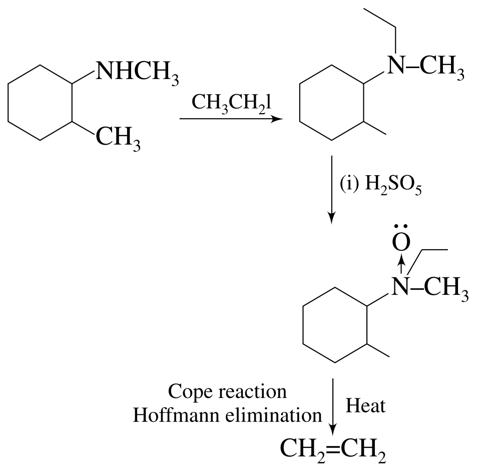
22. [4]

$-NH_2$ group (lp not in conjugation) containing amine will give $>C=N$ with acetone

23. [2]



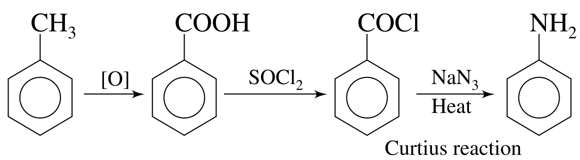
24. [4]



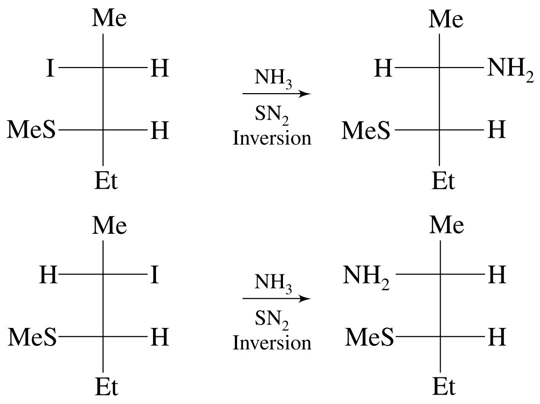
25. [4]

Meta directing group $-NO_2$ and $-\overset{+}{N}(CH_3)_3$ will give 1, 3 disubstituted product.

26. [3]



27. [3]

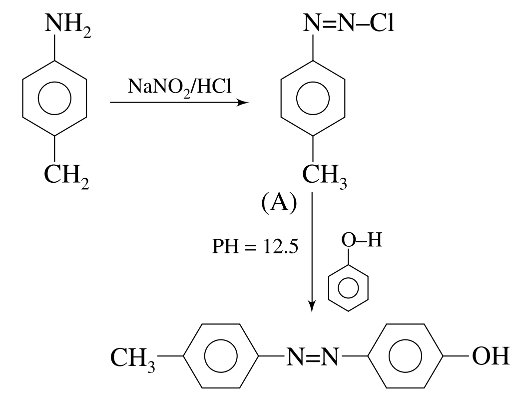


28. [1]

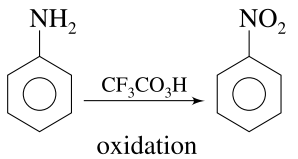
$$CH_3\text{–}N\equiv C \xrightarrow{\text{Dil HCl}} CH_3NH_2 + HCOOH$$

$$CH_3\text{–}N\equiv C \xrightarrow[\text{Reduction}]{\text{Pr or Ni}} \underset{\text{Di-methyl amine}}{CH_3\text{–}NH\text{–}CH_3}$$

29. [2]



30. [1]



EXERCISE # 2

1. [2]

$$\underset{1^\circ\text{ amino}}{R\text{–}NH_2} + O = C\begin{matrix}H \\ R'\end{matrix} \longrightarrow \underset{\text{Schiff}}{R\text{–}N = C\begin{matrix}H \\ R'\end{matrix}}$$

Only 1° amine will form Schiff base with carbonyl substance

2. [3]

$$\underset{1^\circ\text{ amine}}{C_6H_5\text{–}CH_2\text{–}NH_2} + \underset{\substack{\text{Hinsberg reagent} \\ \text{(benzene sulphonyl} \\ \text{chloride)}}}{Cl\text{–}SO_2\text{–}Ph} \longrightarrow C_6H_5\text{–}CH_2\text{–}NH\text{–}SO_2\text{–}Ph$$

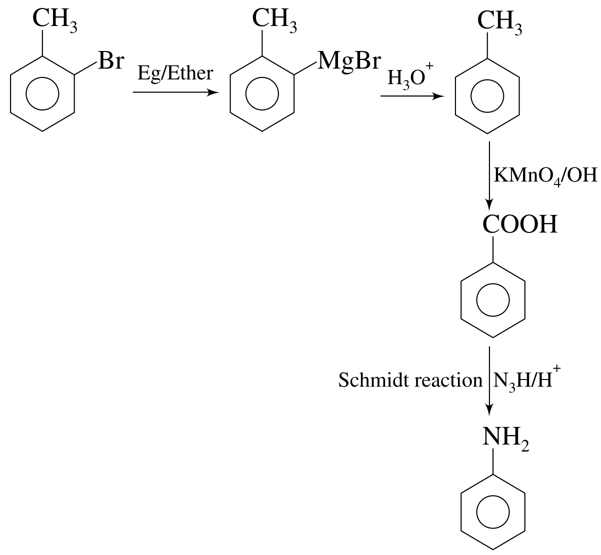
$$\xrightarrow{\text{Alkali (NaOH)}} \underset{\text{Water soluble}}{C_6H_5\text{–}CH_2\text{–}\overset{\ominus}{N}\text{–}SO_2\text{–}Ph \; Na^{\oplus}}$$

3. [1]

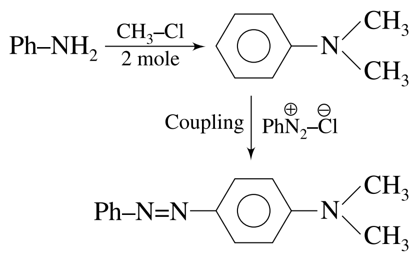
Aryl halide does not given SN reaction in ordinarily condition.

so that Ph–NH_2 can't be prepared.

4. [3]

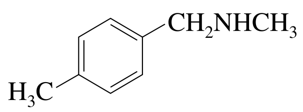


5. [3]

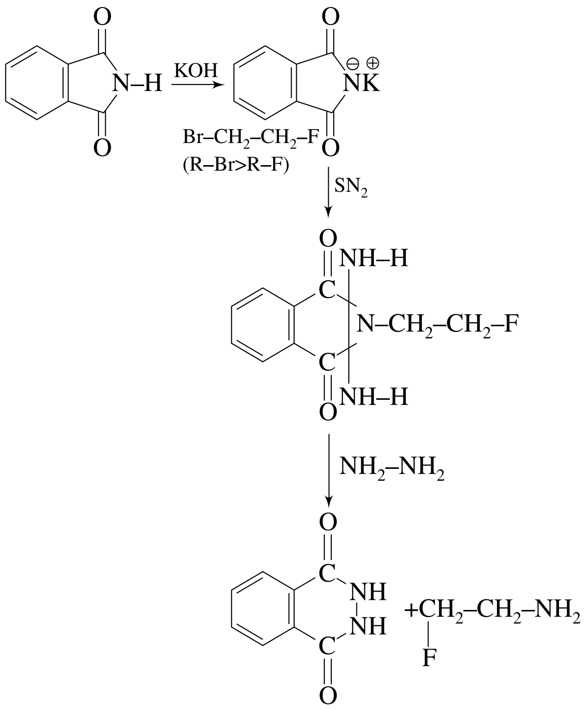


6. [2]

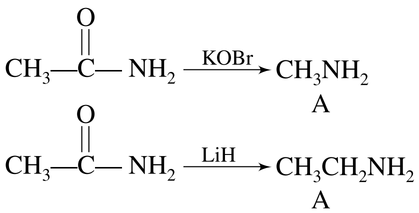
Formation of terephthalic acid on oxidation with $KMnO_4/^{-}OH$ suggests the presence of two carbon chains at the benzene nucleus at 1, 4 positions. Further formation of a liquid with oxamic ester that gets decomposed by KOH shows that, it is a secondary (2° amine). Hence, its possible structure is



7. [2]



8. [2]

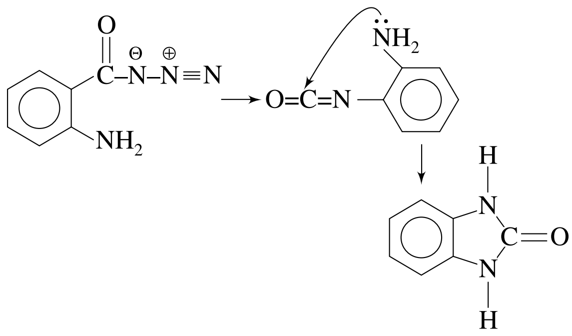


A and B belong to same homologous series, so they are homologues.

9. [2]

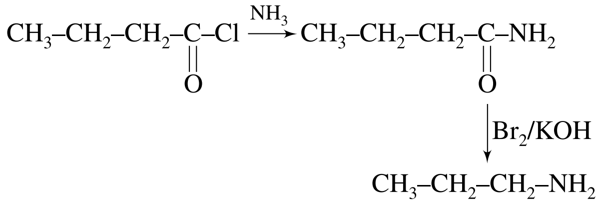
10. [1]

11. [1]



12. [1]

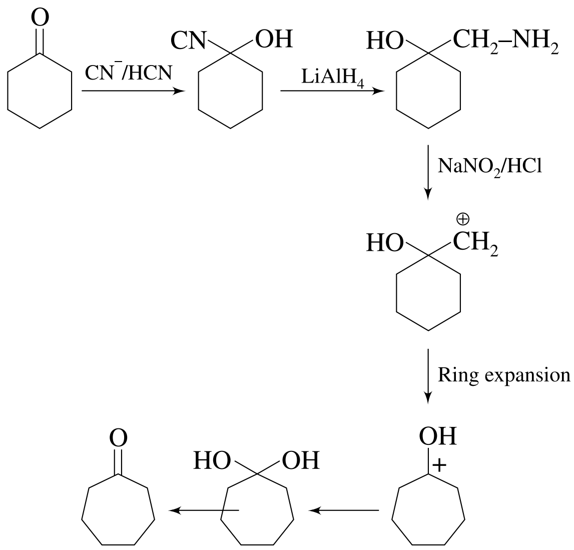
Since the 1° amine has no branching thus acid chloride must be



13. [3]

Re-arrangement takes place via anti elimination followed by tautomerisation to get stabilised.

14. [2]

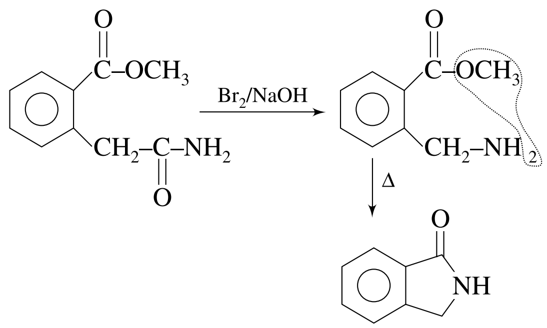


15. [2]

By Hinsberg reagent insoluble solid formation indicating that amine must be secondary amine.

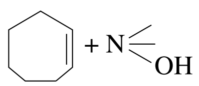
16 [4]

17. [4]



18. [2]

This is an example of Cope elimination. Thus, the product is



19. [2]

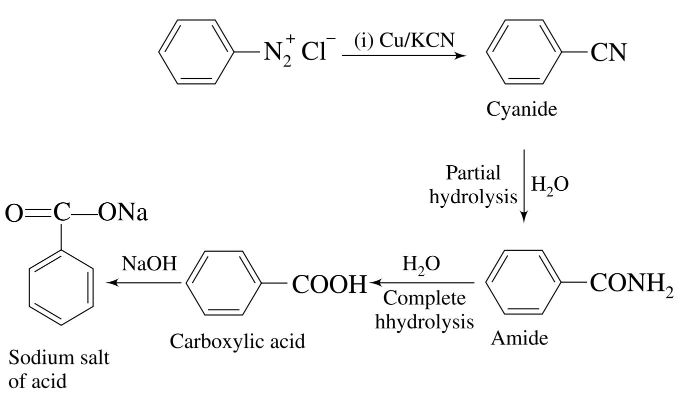
$$\underset{\text{}}{Ph-\overset{\overset{OH}{|}}{C}H-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[KOH]{Br_2} \underset{\text{Unstable}}{Ph-\overset{\overset{OH}{|}}{C}H-NH_2} \xrightarrow{-NH_3} \underset{\text{Benzaldehyde}}{Ph-\overset{\overset{O}{\|}}{C}-H}$$

20. [1]

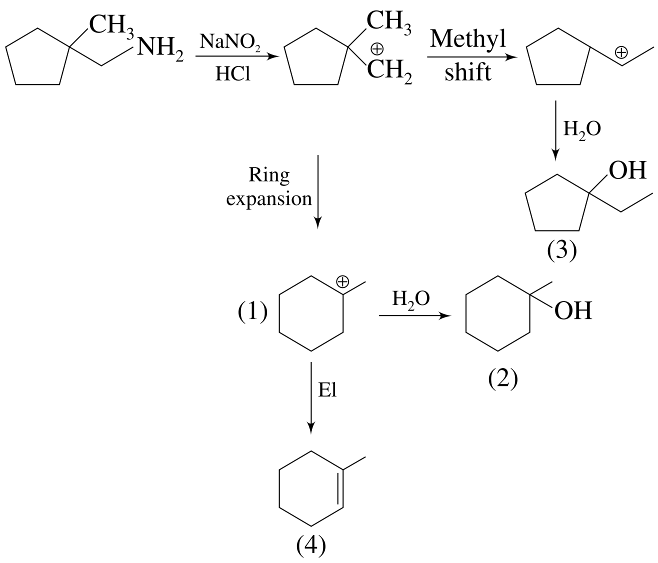
It would require Hofmann's elimination to be repeated to three times (which is the highest).

EXERCISE # 3

1. [1, 2, 3]



2. [2, 3, 4]



3. [3, 4]

IV is more basic as lone pair of electron is not a part of delocalisation. In III and II no delocalisation of lone pair of electrons $\ddot{N}H_2$ on $\ddot{N}$ takes place. In I, delocalisation of lone pair of e^- takes place. The order of basic character is IV > III > II > I.

4. [1, 2, 3]

The possible structure of 3° alcohol is $(CH_3)_3C-OH$, so structure of amine is $(CH_3)_3CNH_2$.

Being 1° amine, it will give all the reactions except Hofmann bromamide reaction, which is given by 1° amides

5. [1, 2]

$$\underset{\text{(2° amine as 2 mol of Mel are added)}}{C_6H_{15}N} + Mel \longrightarrow C_6H_{14}N-Me \xrightarrow{Mel} C_6H_{20}\overset{+}{N}(Me)_2\, I^- \xrightarrow{KOH} C_6H_{20}\overset{+}{N}(Me)_2\,OH^- \text{ or } C_6H_{20}\overset{+}{N}OH^-$$

$$\xrightarrow{\Delta} CH_2{=}\overset{\overset{CH_3}{|}}{C}-CH_3 + (CH_3)_2\,NEt + H_2O$$

Thus, possible structure of A is

$$CH_3-\overset{\overset{CH_3}{|}}{C}HCH_2NHCH_2CH_3 \text{ or } CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH-CH_2CH_3$$

6. [1, 2, 4]

$$CHCl_3 + {}^-OH \xrightarrow[-H_2O]{} \underset{\text{unstable}}{:\overset{\ominus}{C}Cl_3} \xrightarrow[-Cl^-]{} \underset{\text{Dichlorocarbene (Stable)}}{:CCl_2} + Cl^{\ominus}$$

7. [1, 2, 4]

$$\underset{A}{CH_3\underset{\underset{CH_3}{|}}{C}HNH_2} + HCOOH \xrightarrow[\Delta]{H_3O^+} CH_3\underset{\underset{CH_3}{|}}{C}HNC \xrightarrow[\Delta]{H_2,\,Ni} \underset{B}{CH_3\underset{\underset{CH_3}{|}}{C}HNHCH_3}$$

A is a primary (1°) amine; so it gives carbylamine reaction (with $CHCl_3/O^-H$), forms soluble sulphonamide with p-toluene sulphonyl chloride, liberates N_2 to give alcohol with HNO_2, A also gives smell of mustard oil when treated with $CS_2/HgCl_2$.

B is a secondary amine, so it does not give carbylamine or Hofmann mustard oil reaction.

Further, it forms oily nitrosamine with HNO_2 and alkali insoluble sulphonamide with p-toluene sulphonyl chloride.

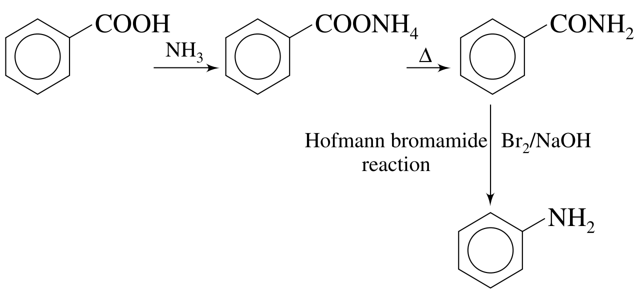
8. [2, 3, 4]

(1) —OH group of phenol does not undergo nucleophilic substitution reaction, so reaction given in option (1) is not feasible.

(2) At high temperature, chlorobenzene reacts with ammonia to give aniline via nucleophilic substitution reaction.

(3) It occurs by benzyne mechanism.

(4)



9. [1]

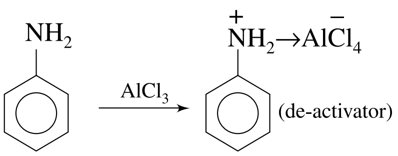
Diazonium salts undergo coupling reaction with β-naphthol to give coloured dye, hence can be used for identification of aniline.

10. [2]

Both are the correct statements.

N, N-diethyl aniline is more basic as compared to aniline. This is because of the presence of bulky ethyl groups on nitrogen which destroy planarity and hence, resonance of nitrogen lone pair with aromatic ring. Consequently basic strength increases.

11. [1]



12. [1]

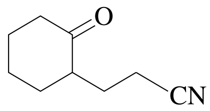
$(CH_3)_3CNH_2$ although is a 1° amine, but it cannot be prepared by the Gabriel phthalimide reaction because it would require an S_N2 reaction on a tertiary alkyl halide in the first step. In such a condition elimination takes place instead of substitution and alkene is the main product.

13. [2]

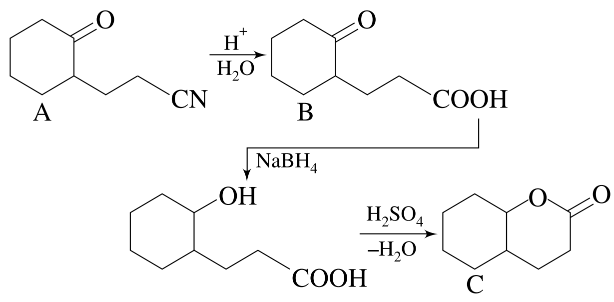
Both the statements are true, $NaBH_3CN$ being a good reducing agent reduces imine into 1° amine.

14. [3]

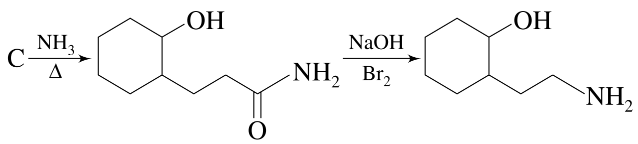
A satisfying the above criterion is



15. [3]



16. [4]

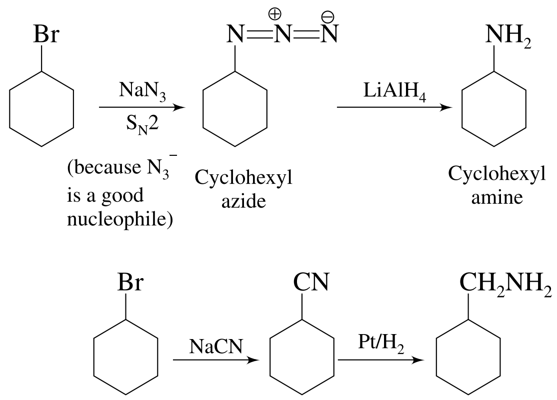


17. [2, 3]

Plane X is better because of the involvement of reductive amination.

Further, plane Y involves the elimination of HBr from 2° alkyl halide, so yield is lesser.

18. [1]



19. [1]

1° aliphatic amines give alcohols and N_2 gas with nitrous acid. These also give carbylamine reaction.

So, **(i)** → **(q, t)**

Aniline is also a 1° amine but it is aromatic, so it forms a dye with HNO_2 and naphthalene (or any other such compound), i.e., gives dye test. Being 1° it also gives carbylamine reaction

So, **(ii)** → **(r, t)**

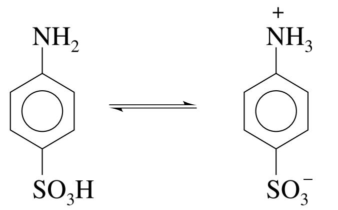
2° aromatic amines give N-nitroso compound when treated with HNO_2, which gives Liebermann's nitroso reaction.

So, **(iii)** → **(p)**

3° aromatic amines form p-nitroso compound with HNO_2. The colour of this compound is green.

So, **(iv)** → **(s)**

20. [1]

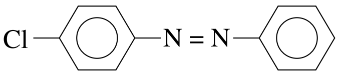
(a) 

(zwitter ion)

(b) Shiff base → >C=N–R

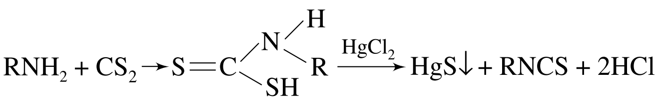
(c) Hinsberg reagent → Ph–SO_2–Cl

(d) Nitrosamine → C_6H_5–N (CH_3) NO yellow only liquid formed by 2° amine with HNO_2

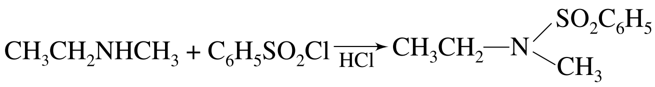
(e) Azo dye →  type

21. [3]

Primary (1°) amines (compound having —NH_2 group) give Hofmann mustard oil reaction, i.e., they first produce dithiocarbamic acid with CS_2 which is decomposed by $HgCl_2$ into alkyl isothiocyanate, with smell of mustard oil.

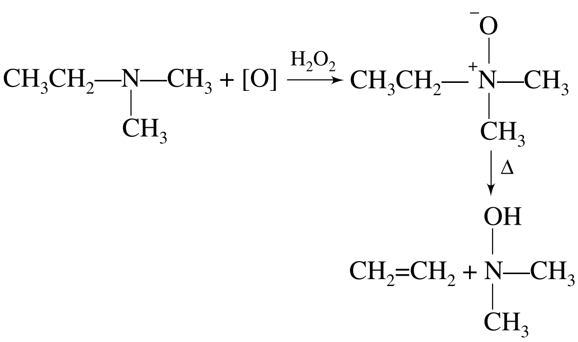


2° (secondary amines) produce alkali insoluble sulphonamide with p-toluene sulphonyl chloride.



Insoluble in alkene

3° amines produce alkene, i.e., they undergo Cope elimination with H_2O_2.



22. [1]

(i) $CH_3CH_2NH_2$ is a 1° amine and $(CH_3)_2NH$ is a 2° amine. 1° amines react with $NaNO_2$ + HCl to release N_2 gas, CS_2 + $HgCl_2$ (Hofmann mustard oil reaction) to give isothiocyanate (which has odour of mustard oil) and $CHCl_3$/KOH (carbylamine reaction) to give bas smelling isocyanides.

Whereas 2° amines give no reaction with $CHCl_3$/KOH and CS_2/$HgCl_2$ and $NaNO_2$ + HCl, it forms oily nitrosamine.

So, (i) → (q, r, s)

(ii) Both are primary amines but CH_3NH_2 being aliphatic forms unstable compound with HNO_2 so gives no reaction with β-naphthol whereas $C_6H_5NH_2$ being aromatic forms stable diazo compound and gives dye with b-naphthol.

So, (ii) → (p)

(iii) Similar is true in this case as former is aromatic but latter is aliphatic.

So, (iii) → (p)

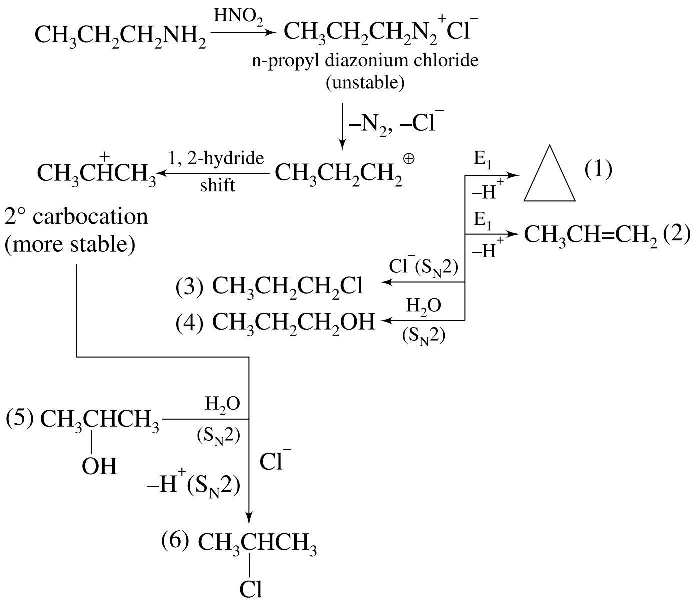
(iv) 3° and 1° amines are also separated by the methods as discussed in A.

So, (iv) → (q, r, s)

23. [4]

Only RNO_2, RCN and R–C(=NOH)–R, and R–C(=O)–NH_2 get reduced by LAH to 1° amine, but others given do not undergo the reaction.

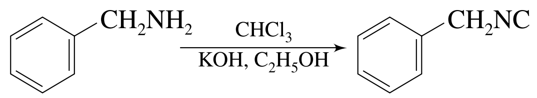
24. [6]



EXERCISE # 4

1. [4]

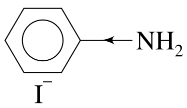
It is carbylamine reaction

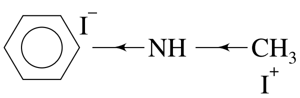


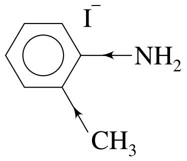
Benzyl amino   Benzyl isocyanide

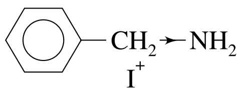
2. [4]

CH_3 — [an electron releasing (+I) group] increases electron density at N-atom, hence basic nature is increased.

(1) 

(2) 

(3) 

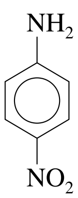
(4) 

C_6H_5 decrease electron density on N-atom due to delocalisation of e^- of NH_2 with πe^- of benzene. Thus, basic nature is decreased.

Hence, (4) is the strongest base.

3. [4]

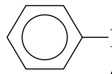
Basic nature of the compound is related to their tendency to donate their lone pair of electrons more readily. –I effect exerting [e^- withdrawing] group decreases the basic strength while + I effect exerting [e^- donating] group increases the basic strength of the compound.

(1) 

—NO2 group
(electron withdraqing
decreases basic nature of aniline)

(2) $CH_3\overset{\overset{O}{||}}{C}NH_2$

$CH_3\overset{\overset{O}{||}}{C}$—group is also electron withdrawing

(3)  $-\ddot{N}H_2$ phenyl group is Also electron withdrawing

(4) Benzylamine ($C_6H_5CH_2NH_2$) contains alkyl group linked to amine, —NH_2 group. The alkyl group is + I effect exerting [e^- donating] group which increases the basicity of benzylamine.

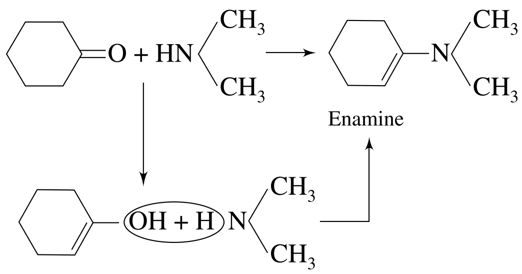
Thus, most basic compound is benzylamine.

4. [2]

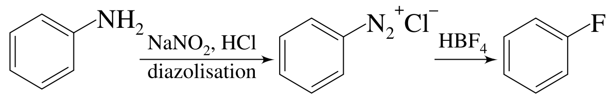
Wurtz reaction is used to prepare alkanes from alkyl halides.

$$2R{-}X + 2Na \xrightarrow{\text{Dry ether}} R{-}R + 2NaX$$

5. [3]



6. [2]



7. [3]

$$CH_3CH_2CH_2 + CHCl_3 + 3KOH \ \text{(alc)}$$

$$\downarrow$$

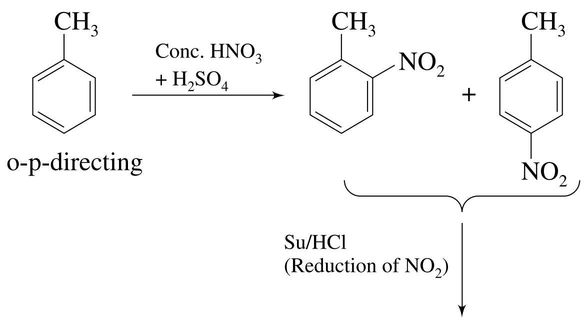
$$\underset{A}{CH_3\,CH_2 - N \equiv C} + \underset{B}{3KCl} + 3H_2O$$

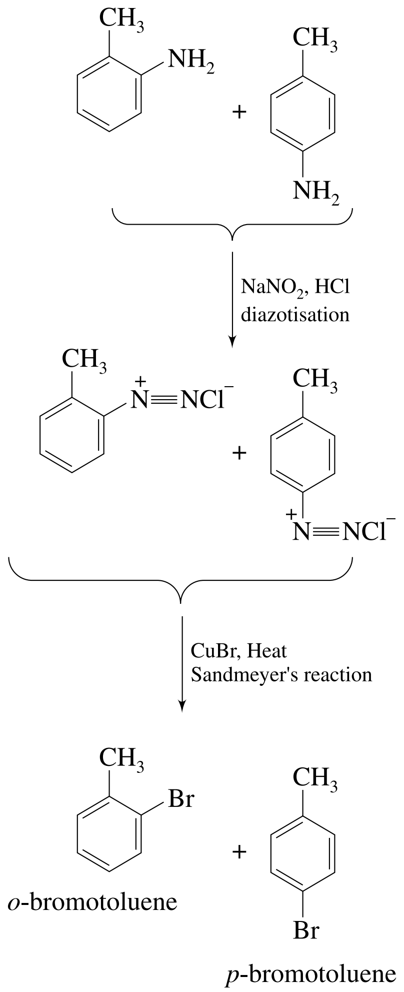
The above reaction is called carbylamine reaction in which isocyanides or carbylamines are produced.

8. [3]

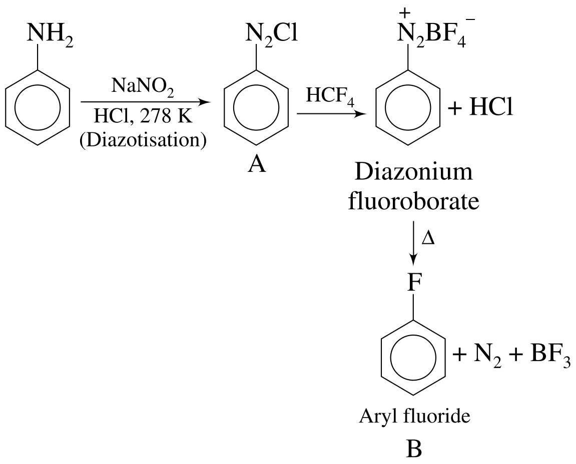
In aqueous solution, basicity order is dimethylamine > methylamine > trimethylamine > aniline. This order depends upon the inductive effect and steric hindrances of alkyl groups.

9. [1]





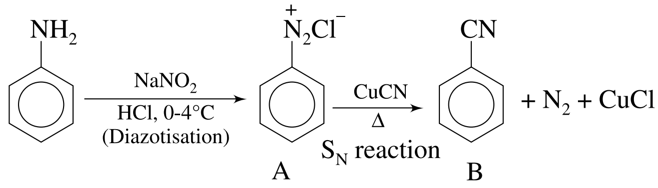
10. [3]



The reaction of diazonium chloride with fluoroboric acid (HBF_4) is called Baiz–Schiemann reaction.

11. [2]

Formation of A is by diazotisation and formation of B from A is by S_N reaction. Thus, the complete series of reaction is given by



12. [3]

During acetylation, one H-atom with atomic mass 1 amu of —NH_2 group is replaced by an acetyl group CH_3CO [molecular mass = 43 u]. Thus,

$$—NH_3 + CH_3COCl \longrightarrow —NHCOCH_3 + HCl$$

The above equation suggests that, the acylation of each —NH_2 group increases the mass by 42 u [43 – 1]. If the molecular mass of the organic compound is 180 u while that of the acylated product is 390 u, then the increase in the mass due to acylation is given by

$$390 - 180 = 210 \text{ u}$$

Hence, the number of —NH_2 groups $= \dfrac{210\,\text{u}}{42\,\text{u}} = 5$

13. [3]

$$A \xrightarrow{NH_3} B \xrightarrow{\Delta} C \xrightarrow{KOH/Br_2} CH_3\,CH_2\,NH_2$$

The reaction of C with KOH/Br_2 to give amine is called Hofmann bromamide reaction. This reaction is given by acid amides only, in which $R—CH_3—\overset{O}{\overset{\|}{C}}—NH_2$ group undergoes rearrangement along with the loss of CO_2 molecules. Thus, the compound C must be acid amide with three carbon atoms.

Hence, the compound C is $CH_3—CH_2—\overset{O}{\overset{\|}{C}}—NH_2$.

All the options show that A is an acid and it forms acid amide on reaction with NH_3. Thus, acid must contain three carbon atoms. Hence, the compound A is CH_3CH_2COOH. The complete series of reaction can be represented as

$$\underset{(A)}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2CO\bar{O}\,NH_4^+} \xrightarrow{\Delta} CH_3CH_2—\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow[\text{Hofmann bromamide reaction}]{KOH/Br_2} CH_3CH_2NH_2$$

14. [1]

It is known that, $pK_b = -\log K_b$. Thus, larger the value of K_b, smaller is the value of pK_b and hence, stronger is the base.

The order of basic strength of given amines is as follows

$(CH_3)_2\ \ddot{N}H > CH_3\ \ddot{N}H_2 > (CH_3)_3\ N > C_6H_5\ \ddot{N}H_2$

The basic strength of amines depends on the inductive effect as well as steric hindrance of alkyl groups. Hence, $(CH_3)_2\ \ddot{N}H$ [secondary amine] possesses the smallest value of pK_b.

15. [4]

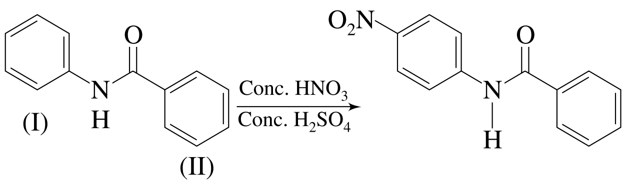
Reaction of aliphatic primary amine with chloroform and ethanolic potassium hydroxide, leads to the formation of isocyanides/carbylamines. Thus, this reaction is called carbylamine reaction.

$$R{-}NH_2 + CHCl_3 + KOH \xrightarrow{\Delta} \underset{\substack{\text{Alkylic}\\ \text{isocyanide}}}{R{-}NC} + 3KCl + 3H_2O$$

16. [4]

$$CH_3NH_2 + CHCl_3 + KOH \longrightarrow \underset{\text{Isocyanide}}{CH_3{-}\overset{+}{N} \equiv \overset{-}{C}} + KCl + H_2O$$

17. [2]



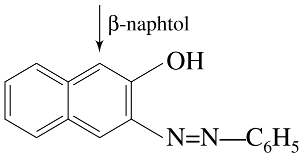
Ring-I is activated while ring-II is deactivated towards electrophilic aromatic substitution reaction.

18. [2]

Sodium fusion extract gives Prussian blue colouration, when nitrogen and carbon both are present in the compound. Phenolic group and salt of carboxylic acid gives $FeCl_3$ test. Chloride salt gives white precipitate of AgCl on treatment with $AgNO_3$.

19. [4]

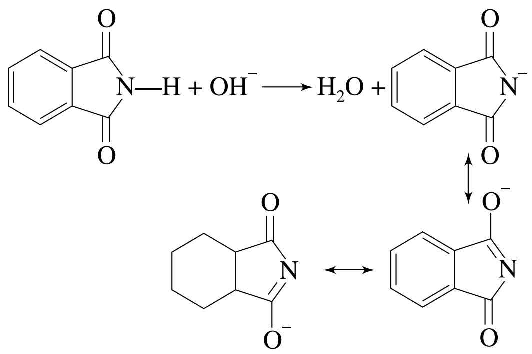
$$C_6H_5NH_2 + NaNO_2/HCl \xrightarrow{0°C} C_6H_5N_2^+Cl^-$$



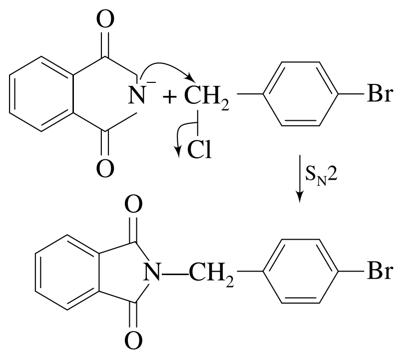
Coloured dye (orange or red)

20. [1]

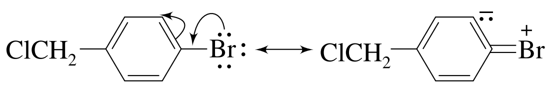
It is the first step of Gabriel's phthalimide synthesis. The hydrogen bonded to nitrogen is sufficiently acidic due to two α-carbonyl groups.



The conjugate base formed above acts as nucleophile in the subsequent step of reaction. As shown above, the nucleophile exists in three resonating forms, one may think of oxygen being the donor atom in the nucleophilic attack. However, nitrogen acts as donor as it is better donor than oxygen.



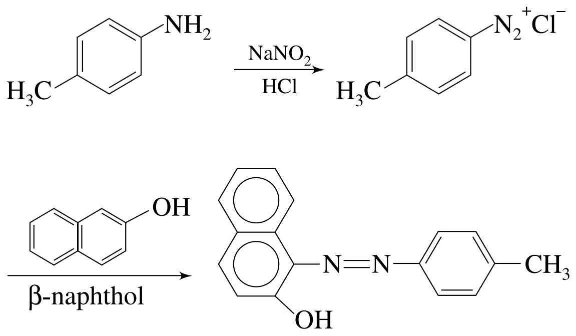
Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C—Br bond, hence difficult to break.



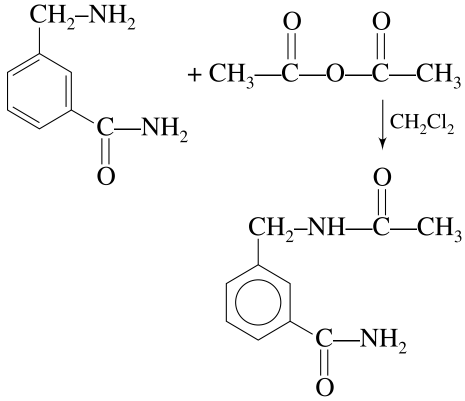
21. [3]

As we know, benzene diazonium salt forms brilliant coloured dye with β-naphthol, the compound under consideration must be *p*-toluidine (c) as it is a primary aromatic amine.

Primary aromatic amine, on treatment with $NaNO_2$ in dil. HCl forms the corresponding diazonium chloride salt.



22. [1]



$-CH_2-NH_2$ is more nucleophilic than $-CONH_2$

23. [1]

(i) $\rightarrow$ **p, q, s, t;**

(ii) $\rightarrow$ **p, s, t;**

(iii) $\rightarrow$ **p;**

(iv) $\rightarrow$ **r**

i.	$CH_3CH_2CH_2CN$:	Gives amine with Pd-C/H_2 Gives aldehyde with $SnCl_2/Cl_2$ Gives amide with di-isobutyl-aluminium hydride. Gives carboxylic acid on alkaline hydrolysis
ii.	$CH_3CH_2OCOCH_3$: Ester	Reduced to alcohol with Pd-C/H_2 Reduced with di-isobutyl aluminium hydride into aldehyde. Undergoes alkaline hydrolysis.
iii.	$CH_3CH{=}CHCH_2OH$:	Reduced to butanol when treated with Pd-C/H_2 Not reduced with $SnCl_2$, di-isobutyl aluminium hydride.
iv.	$CH_3CH_2CH_2CH_2NH_2$:	A primary amine, gives carbylamine test.

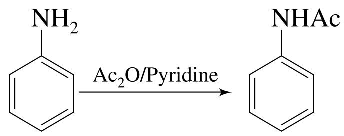
24. [3]

Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \rightarrow \underset{(1^\circ\ \text{amine})}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

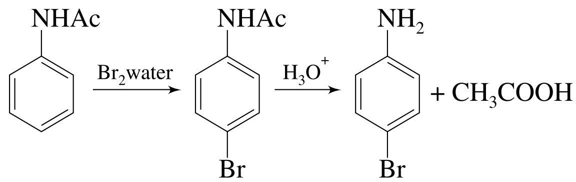
Hence, four moles of NaOH and one mole of Br_2 is used.

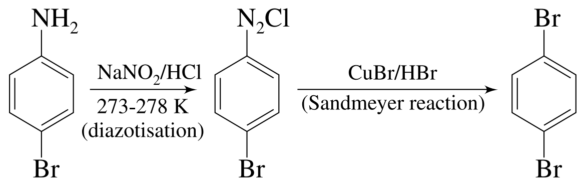
25. [2]



$$KBrO_3 + HBr \longrightarrow Br_2$$

Ac is CH_3CO (acetyl), it protects $-NH_2$ group from being oxidised.





CHAPTER 6

Biomolecules

Macromolecules which are found in living organisms (animals and plants) and essential for our vital activities are known as **Biomolecules**.

The most important biomolecules are

(1) Carbohydrate

(2) Protein

(3) Nucleic acid

(4) Vitamins

(1) CARBOHYDRATES

Carbohydrates are defined as the optically active polyhydroxy aldehydes or ketones.

These are also called **hydrates of carbon.**

Classification of Carbohydrates

- Carbohydrates
  - Sugar (sweet in taste, crystalline, Soluble in H_2O)
    - Monosaccharide (simple sugar) Further not hydrolysis
      - Aldose (having aldehyde group glucose)
      - Ketose (having ketone group Fructose)
    - Oligosaccharide
      - Di ⇒ sucrose, maltose, lactose
      - Tri ⇒ Rebinose
      - Tetra
      - Penta
  - Non Sugar (starch, cellulose) (tasteless, non crystalline, amorphous, In soluble in H_2O)

Monosaccharides

(a) These are the simplest sugar.

(b) In these compounds C:H:O = 1:2:1

(c) General formula is: $C_n(H_2O)_n$ or $C_x(H_2O)_y$ (where n = 3 to 7)

(d) They cannot be hydrolysed to give still simpler carbohydrates.

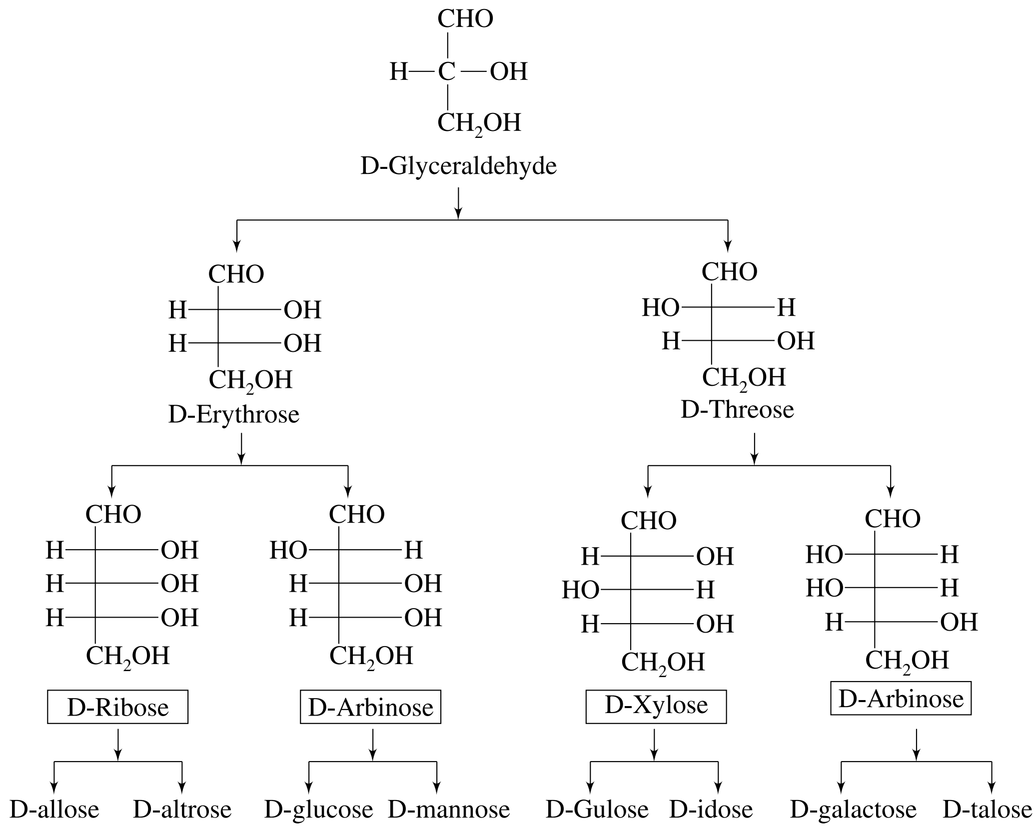
(e) They can be further classified into different categories depending upon the number of carbon atoms. There naming is of following type:

Carbon Atoms (n)	Molecular Formula	General Term	Aldose	Ketose
n = 3	$C_3H_6O_3$	Triose	Glyceraldehyde	Dihydroxy acetone.
n= 4	$C_4H_8O_4$	Tetrose	Erythrose	Erythrulose
n = 5	$C_5H_{10}O_5$	Pentose	Ribose	Ribulose
n = 6	$C_6H_{12}O_6$	Hexose	Glucose	Fructose

(f) In aldose aldehyde group is present and all central molecules are asymmetrical (chiral)

(g) In ketose, ketone group is present and except 2nd carbon all molecules are asymmetrical.

D-Family Aldoeses



GLUCOSE ($C_6H_{12}O_6$)

- Glucose is an aldohexose.
- It is the monomer of many of the larger carbohydrates such as starch, cellulose.
- It is also known as blood sugar/grape sugar.
- It naturally occurs in D- form, so also named as 'dextrose'.

Preparation of Glucose

1. By hydrolysis of cane-sugar

In laboratory glucose can be prepared by hydrolysis of cane-sugar in the presence of alcohol using dilute hydrochloric acid. Glucose and fructose and formed in equal amounts. Glucose, begin less soluble in ethyl alcohol than fructose, crystallises out.

$$\underset{\text{Sucrose (Can sugar)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Table sugar (Kitchen sugar) (α-D-glucose) (β-D-fructose)

2. **By hydrolysis of starch**

   Glucose is obtained, **on commercial scale,** by hydrolysis of starch by boiling it with dilute sulphuric acid at 393 K under a pressure of 2–3 bar.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)n} + nH_2O \xrightarrow[393K,\ 2\text{–}3bar]{H^+} \underset{\text{Glocose}}{nC_6H_{12}O_6}$$

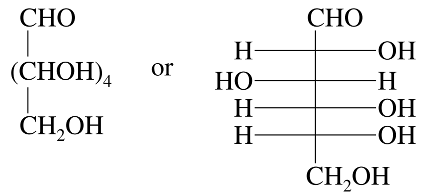
3. **Photosynthesis Reaction**

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyl}]{\text{Sunlight}} C_6H_{12}O_6 + 6CO_2 + 6H_2O$$

Chlorophyll		Haemoglobin	
(1)	It is green pigment	(1)	It is red pigment
(2)	It is found in green plants	(2)	It is found in animal blood
(3)	Coordinate compound	(3)	Coordinate compound
(4)	Central metal ‘Mg^{2+}’	(4)	Central Metal ‘Fe^{2+}’
(5)	Function: Photosynthesis reaction in plants.	(5)	Function: Circulation of oxygen in all body parts

Structure of Glucose

The reactions of glucose indicate that its molecule contains one primary ($-CH_2OH$) and four secondary (>CHOH) hydroxyl groups.



Evidences that support the linear structure of glucose

1. **Reduction**

$$\underset{\text{Glucose}}{HOH_2C \cdot (CHOH)_4 \cdot CHO} + H_2 \xrightarrow{Ni} \underset{\text{Sorbitol}}{HOH_2C \cdot (CHOH)_4 \cdot CH_2OH}$$

2. **Reaction with hydrogen iodide**

$$\underset{\text{Glucose}}{HOCH_2\text{–}(CHOH)_4\text{–}CHO} \xrightarrow{HI} \underset{\text{n-Hexane}}{H_3C\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2}$$

3. **Oxidation**

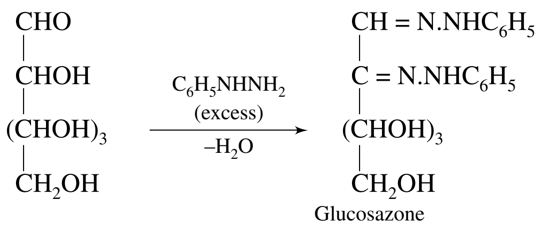
   (i) $$\underset{\text{Glucose}}{HOH_2C \cdot (CHOH)_4 \cdot CHO} + [O] \xrightarrow{Br_2/H_2O} \underset{\text{Gluconic acid}}{HOCH_2 \cdot (CHOH)_4 \cdot COOH}$$

   (ii) $$\underset{\text{Glucose}}{HOH_2C \cdot (CHOH)_4 \cdot CHO} + [O] \xrightarrow{\text{Conc. } HNO_3} \underset{\text{Glucoric acid (Saccharic acid)}}{HOOC \cdot (CHOH)_4 \cdot COOH}$$

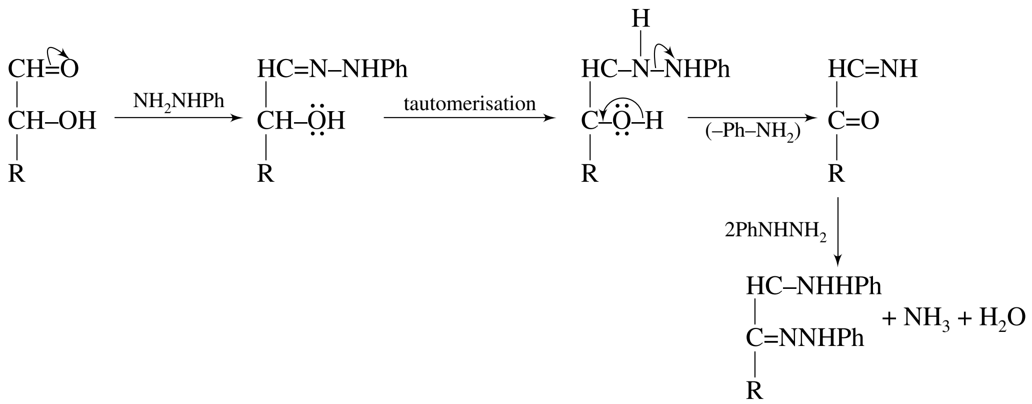
4. **Acetylation**

$$\underset{\text{Glucose}}{OHC \cdot (CHOH)_4 \cdot CH_2OH} + \underset{\text{Acetic anhydride}}{5Ac_2O} \longrightarrow \underset{\text{Pentaacetyl glucose}}{OHC \cdot (CHOAC)_4 \cdot CH_2OAc}$$

5. **Formation of osazone**



Mechanism:

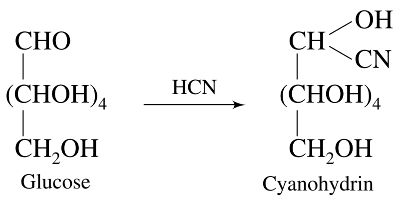


Osazone formation results in a loss of the stereocentre at C-2, but it does not affect other stereocentres; D-glucose and D-mannose, for example, yield the same phenyl osazone.

6. Reaction with Hydroxylamine

$HOCH_2 - (CHOH)_4 - CHO + NH_2OH \longrightarrow HOCH_2–(CHOH)_4–CH=N–OH + H_2O$

7. Formation of Cyanohydrin



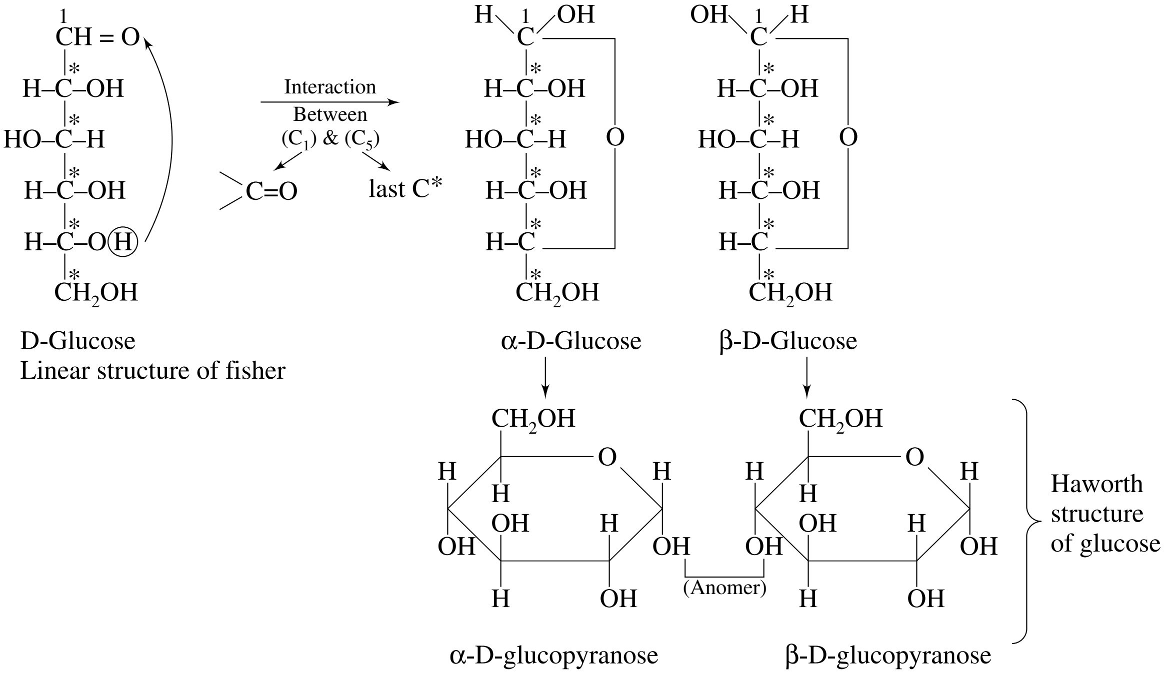
Objection to Linear Structure

1. In spite of the presence of an aldehydic group, glucose does not restore the pink colour of Schiff's reagent, does not give 2, 4-DNP test and does not form addition products with sodium hydrogen sulphite and ammonia.
2. Glucose pentaacetate does not react with hydroxyl amine.

   The above facts indicating the absence of free –CHO group in glucose.

Cyclic Structure of Glucose

The above facts about glucose can be explained in terms of cyclic structure of glucose. The cyclic Structure of glucose is formed through intramolecular hemiacetal formation which leads to cyclisation.



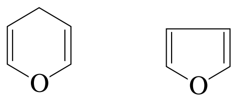
Anomeric carbon: Carbon of carbonyl group involves in internal hemiacetal formation is known as anomeric carbon.

Anomers: Such distereomers which are mirror image with respect to anomeric carbon is known as anomers.

Notation of α, β- If –OH at RHS of anomeric carbon → α

If –OH at LHS of anomeric carbon → β

Haworth Structure:



Pyrane   Furane

(1) Pyranose structure- Structure like pyrene, i.e., 6-member atom ring

(2) Furanose structure- Structure like furan, i.e., 5-member atom ring

Mutarotation: When pure α-D glucose is dissolved in water its specific rotation is found to be + 112° with time however the specific rotation of solution decrease ultimately reaches stable value of +52.5°.

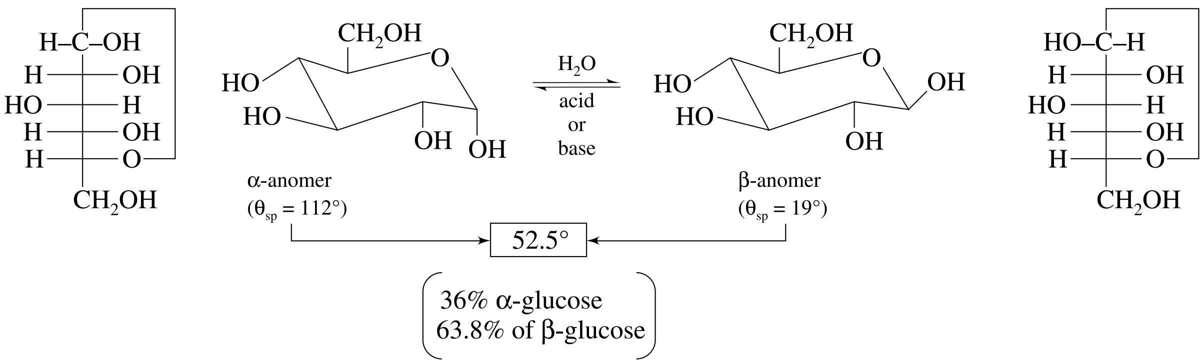
When β-D-Glucose is dissolved in water, it has specific rotation of 19°, the specific rotation of this solution increase with time also to +52.5°.

(a) This change of optical rotation with time is called mutarotation.

(b) It causes by the conversion of α and β gluco pyranose anomers in to an equilibrium mixture of both.

(c) Mutarotation is catalysed by both acid and base but also occur in pure H_2O.

(d) Mutarotation is characteristics of cyclic hemiacetal form of glucose.

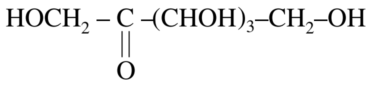


Fructose (Laevulose), $C_6H_{12}O_6$

Fructose is a ketohexose. It is obtained along with glucose by the hydrolysis of sucrose.

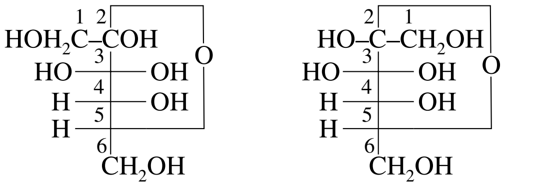
Structure of Fructose

Fructose has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at C-2 and six carbon atoms in straight chain as in case of glucose. It belongs to D-series and is a laevorotary compound. Therefore, fructose is correctly named as D(–)-fructose. Its open chain structure may be written as:



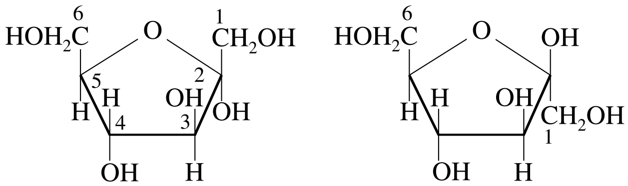
D(–) Fructose

Fructose also exists in two cyclic forms which are obtained by the interaction of –OH at C–5 to the ($\rangle$C = O) group. The ring thus formed is a five-membered ring and is named as furanose with analogy to the compound furan.



α-D(-)-Fructofuranose β-D(-)-Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given



α-D(-)-Fructofuranose β-D(-)-Fructofuranose

Isomerism

Carbohydrates which differ in configuration at the glycosidic carbon or anomeric carbon (i.e., C_1 in aldoses and C_2 in ketoses) are called **anomers**.

For example, α-D-glucose and β-D-glucose are anomers since they differ in configuration at C_1 (glycosidic carbon).

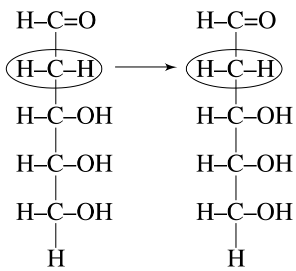
Carbohydrates which differ in configuration at any carbon other than glycosidic carbon are called **epimers**.

For example, glucose and mannose are called **epimers** since they differ in configuration at C_4 (other than the glycosidic carbon).

Derivatives of Monosaccharides

Following are derivatives of monosaccharides.

(a) Deoxysugar: If one hydrogen occupies the position of one –OH, then deoxysugar is formed.



Deoxyribose Ribose

(b) **Amino sugar-**When –OH group of aldose is replaced by $-NH_2$ group, then it is called as amino sugar. Example D-glucosamine, D-galactosamine

Oligosaccharides

It is formed by combination of 2 to 10 monosaccharide units.

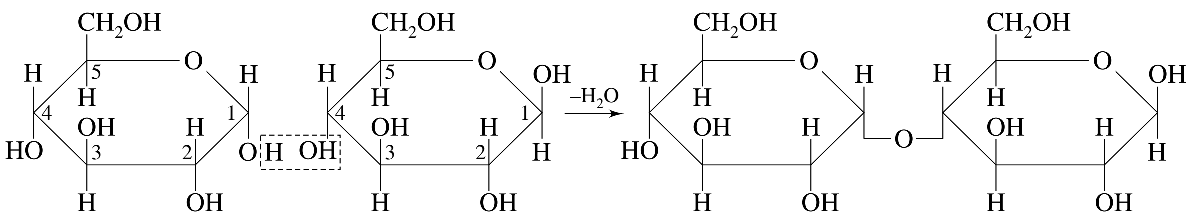
Disaccharides

(a) Disaccharides are sugars composed of two molecules of the same or two different monosaccharides.
(b) Generally one molecule of water is reduced in forming disaccharides reaction is called as dehydration.
(c) General formula is $C_n(H_2O)_{n-1}$.
(d) Bond present in between them is called as **glycosidic bond.** [Acetals of carbohydrate are called glycoside.]
(e) All non-reducing sugar do not show mutarotation because there is no free –C=O group; so it is non reducing sugar.

Some Important Disaccharides

(i) **Maltose (reducing sugar, malt sugar)**

α-D-glucose + α-D-glucose $\xrightarrow{-H_2O}$ Maltose α, 1:4 glycosidic bond

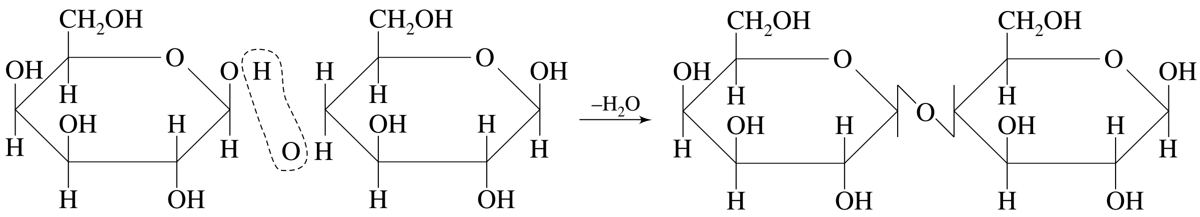


α-1,4,-glycosidic bond

- Maltose gives negative test with Schiff reagent.
- Maltose shows mutarotation.
- Maltose gives positive Tollens' test.
- Maltose does not form adduct with $NaHSO_3$ and NH_3.
- Maltose gives positive Fehling's test.

(ii) **Lactose (Reducing sugar, Milk sugar)**

α-D-galactose + β-D-glucose $\xrightarrow{-H_2O}$ Lactose (β-1,4,-glycosidic bond)

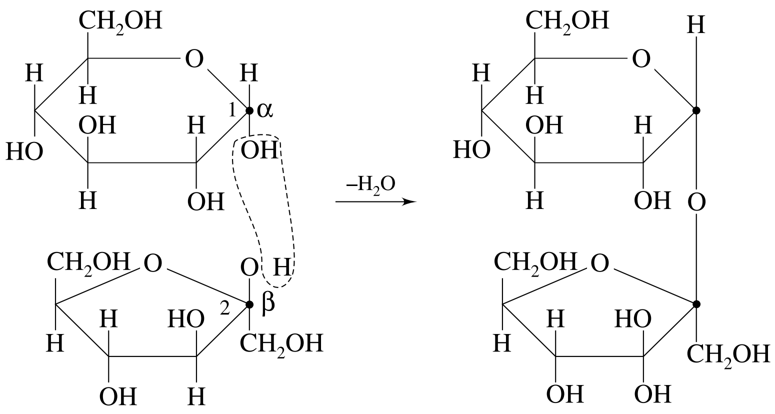


b-1,4,- glycoidic bond

- Lactose gives negative test with Schiff reagent.
- Lactose shows mutarotation.
- Lactose gives positive Tollens' test.
- Lactose does not form adduct with $NaHSO_3$ and NH_3.
- Lactose gives positive Fehling's test.

(iii) Sucrose

α-D-glucose + β-D-fructose $\xrightarrow{-H_2O}$ Sucrose (α, β-1, 2,-glycosidic bond)



α, β-1,2,-glycosidic bond

Invert Sugar: Hydrolysis of sucrose brings about a change in sign of rotation from dextro to leavo and this change in rotation is known as inversion of cane sugar and forming mixture of glucose and fructose is known as invert sugar.

- Sucrose is non-reducing sugar.
- Sucrose is soluble in water and sweet in taste
- Sucrose do not form osazone
- Sucrose do not show muta rotation
- Sucrose is a commercial or kitchen sugar.

Polysaccharides:

(a) Polysaccharides yield more than 6 molecules of monosaccharides on hydrolysis.

(b) General formula is $(C_6H_{10}O_5)_n$.

(c) These are linear polymers and also highly branched

(d) These are not called as sugar because are not sweet in taste.
Exception- Inulin is sweet.

(i) Starch [Monomer of α-D-Glucose]

- It is stored food of plant
- It is insoluble in water.
- It gives blue colour with iodine.
- It is formed of two types of polymer of α-D glucose

Amylose	Amylopectin
It has 250–300 monomers.	Branch of 24–30 glucose monomers.
It is unbranched helical structure.	Many branches are present
These are combined with a 1, 4-linkage	In straight chain, it is attached by a 1, 4 glycosidic bond while in branched chain it is linked by a-1, 6 linkage
They give blue colour with I_2.	They give red colour with I_2.
It is 15–20% in starch.	It is 80–85% in starch

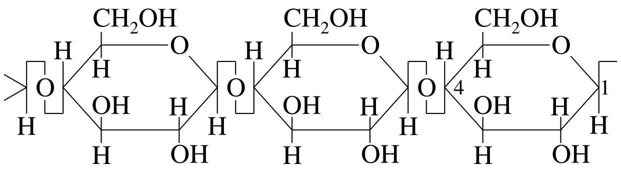
(ii) Glycogen (animal starch): [Monomer of D-glucose]

- It is found in form of reserve food in animals.
- It is found in more amount in Liver and muscles.

- It is formed by only amylopectin polymer of α-D glucose.
- Give red colour with I_2.

(iii) Cellulose [Monomer of D-glucose]

- It is main constituent of cell wall.



Structure of Cellulose

- It does not give colour with I_2.
- β-1, 4 glycosidic bond is present.
- It is insoluble in water.
- Water hydrolysis is done by cellulose enzyme.

Biological Importance of Carbohydrate:

(i) It is main source of energy
(ii) It is called fuel of the body.
(iii) Cell wall of plant cell in made up of cellulose.
(iv) Exoskeleton of insect is formed of chitin.
(v) Sugar is structural component of DNA and RNA.
(vi) 1 g carbohydrate gives 4.1 kcal of energy.

Test of Carbohydrates

(a) Carbohydrate with Tollens' reagent (ammoniacal silver nitrate) gives silver mirror test.
(b) Carbohydrate with Fehling's solution (alkaline $CuSO_4$) gives a red ppt.
Molisch's test: Carbohydrates when treated with Molisch's reagent (1% alcoholic solution of α-naphthol) in presence of conc. H_2SO_4 from violet ring.
(c) When heated in dry test tube, it melts, turns brown and finally black giving a smell of burning sugar.

(2) Proteins:

(a) Proteins are polymers of amino acids.
(b) Protein is 3/4 part of dry weight of tissues.
(c) Protein forms structure of body.
(d) C, H, O, N are necessarily present in proteins.
(e) In some proteins P, S, Fe, Cu, I, also may be present. They are called trace elements.
(f) 70 types of amino acids are known. But in proteins about 20 types of amino acids are used. Other amino acids are called non-proteinous amino acid; e.g., citruline, ornithine

Chemical Structure:

(a) Amino acids can be given by the general formula.

$$H_2N-\underset{\displaystyle H}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle O}{\underset{\|}{C}}-OH \quad \text{Or} \quad H_2N-\underset{\displaystyle H}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-COOH$$

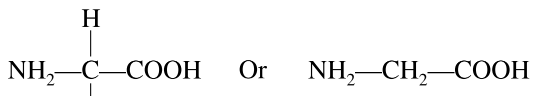
R = Alkyl group

(b) If 'R' changes amino acid also changes.
For example, if R = H $\rightarrow$ Glycine (Simplest Amino acid)

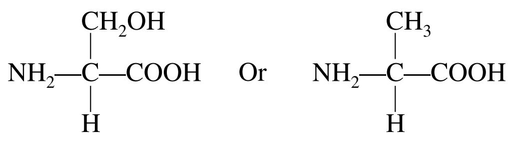
If R = CH_3 → Alanine

If R = CH_2OH → Serine.

'R' group attach with the carbon than that carbon is called α-carbon.



Glycine



Serine Glycine

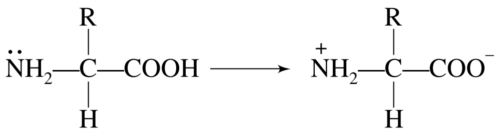
(c) Except glycine all amino acids are optically active.

(d) In glycine chiral carbon atom is absent. It is optically inactive.

(e) L-form of amino acids are synthesised protein.

Zwitter ion (Amphoteric ion or dipolar ion)

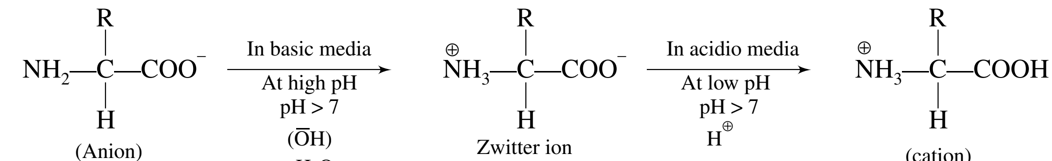
The amino acids ($RCHNH_2COOH$) contain both an acidic group (–COOH) and a basic group ($–NH_2$). So, they are amphoteric. They undergo **intramolecular acid–base reaction** to from an **internal** salt having a dipolar structure as shown below. Such a dipolar ion is called a **zwitter ion**. In the dry solid state, amino acids exist as zwitter ions.



α-Amino acid Zwitterion of α-amino acid

Acid–base Properties

In a strongly acidic medium, an amino acid zwitter ion behaves as a base. It picks up a proton from the medium at the carboxylate ion to form a cationic species, $H_3N^+CH(R)\ COOH$. In a strongly basic medium, the zwitter ion loses a proton to the base from the ammonium ion portion ($–N^+H_3$) to yield an anionic species $H_2NCH(R)COO^-$.



(Anion) (Migrate towards anode) Zwitter ion (cation) (Migrate towards cathode)

Isoelectric Point (pI)

At some characteristic pH, the amino acid will not migrate towards any electrode. This particular pH is called the isoelectric point, pI, of the amino acid. At this pH value, the concentration of zwitterions is at its maximum and the concentrations of the anionic and cationic species are equal. At isoelectric point an amino acid has the least solubility in water and this property is exploited in the separation of different amino acids obtained from the hydrolysis of a protein.

(i) For a neutral amino acid, such as alanine the isoelectric point (pI) is the average of pk_{a_1} and pk_{a_2}.

$$pI = \frac{1}{2}(pk_{a_1} + pk_{a_2})$$

(ii) For a basic amino acid, the pI is the average of the pk_a values of the two positively charged amine groups in its acidic form.

(iii) For an acidic amino acid, the pI is the average of the pk_a value of the two –COOH groups (uncharged) in its acidic form.

Classification of Amino Acids

(I) On the basis of number of $–NH_2$ and –COOH groups

(i) Neutral amino acid → these amino acids contain one $–NH_2$ group and one –COOH group (see table)

(ii) Acidic amino acid → These amino acids contain two –COOH groups but one $–HN_2$ group (see table).

(iii) Basic amino acid → These amino acids contain two or more $–HN_2$ groups but one –COOH group (see table).

(II) On the Basis of Synthesis

20 type **Amino acids are** used in protein synthesis, which divide in three categories

(i) Essential amino acids:

- These are not synthesised in the body.
- These are taken with food.
- These are as follows

(1) Leucine **(2)** Isoleucine **(3)** Lysine **(4)** Methionine
(5) Phyenylalanine **(6)** Threonine **(7)** Tryptophan **(8)** Valine

(ii) Non-essential amino acid:

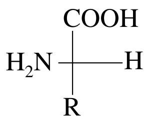
- These are synthesised in body.
- These are not required in food.
- These are as follows

(1) Alanine **(2)** Aspargine **(3)** Aspartic acid **(4)** Cysteine
(5) Glutamic acid **(6)** Glutamine **(7)** Glycine **(8)** Proline
(9) Serine **(10)** Tyrosine

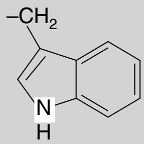
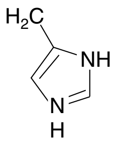
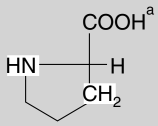
(iii) Semi essential amino acids:

They are 50% synthesised in body +50% taken by food.

(1) Arginine **(2)** Histidine

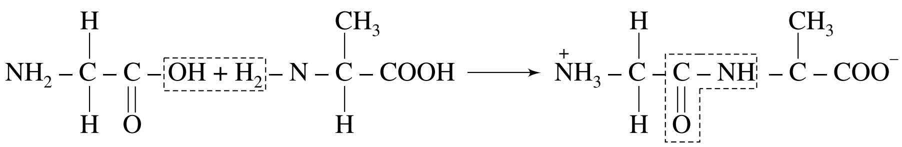
Natural amino acids 

S. N.	Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1.	Glycine	H	Gly	G
2.	Alanine	$–CH_3$	Ala	A
3.	Valine*	$(H_3C)_2CH–$	Val	V
4.	Leucine*	$(H_3C)_2CH–CH_2–$	Leu	L
5.	Isoleucine*	$H_3C–CH_2–CH_2–$ CH_3	Ile	I
6.	Arginine*	$HN=C–NH–(CH_2)_3–$ NH_2	Arg	R
7.	Lysine*	$H_2N–(CH_2)_4–$	Lys	K
8.	Glutamic acid	$HOOC–CH_2–CH_2–$	Glu	E

S. N.	Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
9.	Aspartic acid	$HOOC–CH_2–$	Asp	D
10.	Glutamine	$H_2N–C(=O)–CH_2–CH_2–$	Gln	Q
11.	Asparagine	$H_2N–C(=O)–CH_2–$	Asn	N
12.	Threonine*	$H_3C–CHOH–$	Thr	T
13.	Serine	$HO–CH_2–$	Ser	S
14.	Cysteine	$HS–CH_2–$	Cys	C
15.	Methionine*	$H_3C–S–CH_2–CH_2–$	Met	M
16.	Phenylalanine*	$C_6H_5–CH_2–$	Phe	F
17.	Tyrosine	(p) $HO–C_6H_4–CH_2–$	Tyr	Y
18.	Tryptophan*		Trp	W
19.	Histidine*		His	H
20.	Proline		Pro	P

*Essential amino acid

Peptide Bond: You have already read that proteins are the polymers of α-amino acids and they are connected to each other by **peptide bond** or **peptide linkage**. Chemically, peptide linkage is an amide formed between –COOH group and $–NH_2$ group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of peptide bond –CO–NH–.



(Glycine) Gly — (Alanine) Ala — (Gly – Ala bond) Peptide bond

- It is planar and stabilised by resonance
- According to number of amino acid, peptide bond must be two, three, resulting into dipeptide, tripeptide, etc., respectively.
- Number of peptide bond = (number of amino acid) – 1

Configuration of Proteins

(a) Biological nature or function of protein was confirmed by its conformation.

(b) This conformation is of four types

Primary Secondary Tertiary Quatemany

Primary Structure

- This type of structure was given by **Friedrich Sanger** in 1953 in Insulin (of one chain)
- Primary structure is conformed by a single polypeptide chain in a linear manner.
- All amino acid are attached in a straight chain by peptide bond.
- No biological importance and soon changed to other forms.

Secondary Structure

- In it structure of straight chain from irregular changes to form coils.
- H-bond + peptide bond present in secondary structure.
- This H bond is present between hydrogen of Amino group and oxygen atom carboxylic acid group.
- This structure is of two types

(i) α-helix Structure

- Chain is spiral
- 3 to 7 atoms in one coiling
- Right handed circular.

Example: Myosin, Keratin, etc.

(ii) β-pleated Sheet

- Structure of protein is not arranged in a sequence.
- Polypeptide chain are parallel to each other
- H- bond form by near chains

Example: Silk fibres.

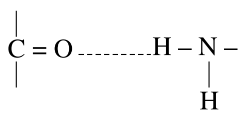
Tertiary Structure

- In this structure of protein atoms are highly coiled and form a spherical form.

E.g. Albumin

- This structure is formed by 4 regular hydrogen bonds which makes a regularity in it

(i) Hydrogen Bond



Hydrogen bond

- They are formed between oxygen of acidic amino acid and H of basic amino acid.

(ii) Hydrophobic Bond

- Non-polar side chains of neutral amino acid tend to be closely associated with one another in proteins.
- Present in between the amino Acid.
- These are not true bonds.

(iii) Ionic bond:

$-COO^- \ldots H_3^+N-$

Ionic bond

- These are salt bonds formed between oppositely charged groups in side chains of Amino acids

Example: Aspartic acid

Glutamic acid

(iv) Disulphide bonds:

|------S – S-----|

- Relatively stable bond and thus is not broken readily under usual conditions of denaturation.
- Formed between the –SH group of Amino acid. Example:amples are Cysteine and Methionine.

Quaternary Structure

- When two or more polypeptide chains united by forces other than covalent bonds (i.e., not peptide and disulphide bonds) are called quaternary structure.
- It is the most stable structure.

  Example: Haemoglobin

Classification of Proteins

Classification of proteins is based upon three general properties- shape, solubility and chemical composition.

Proteins

Simple   Conjugated   Derived

Simple Proteins

It is formed of only Amino Acids

Fibrous Protein	Globular Protein
1. It is thread like protein (elongated shape)	1. It is globe like Protein (spherical shape)
2. It is water insoluble	2. It is water soluble
3. It consists of two type of bonds (a) disulphide bond (b) H–bond	3. It consists of four type of bonds. (a) disulphide bond (b) H–bond (c) ionic bond (d) hydrophobic bond
4. Examples (i) Keratin in hair, nails wool, etc. (ii) Myosin in muscles (iii) Casein in bones	4. Examples (i) Albumin in egg. (ii) Haemoglobin in blood

Conjugated Proteins

These are complex proteins in which protein molecule is combined with characteristic non-amino acid substance.

Non-amino acid or non-protein part is called as prosthetic group

Example: Nucleoproteins (Protein + $(PO_3)^{2-}$)

Example: Casein of milk, Vitelline of egg yolk

Derived Proteins:

(a) These are obtained as a result of partial hydrolysis of natural proteins.

Example: Proteose, Metaproteins, Peptones

(b) Denaturation of proteins

When a protein in its native form, is subjected to a physical change like change in temperature, or a chemical change like change in pH, the native conformation of the molecule is disrupted and proteins so formed are called denaturated proteins.

The denaturation may be reversible or irreversible.

The coagulation of egg on boiling is an example of irreversible protein denaturation.

However, it has been shown now that in some cases, the process is actually reversible. The reverse process is called **renaturation.**

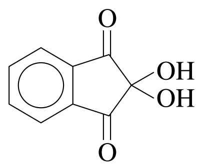
Test of Protein

(a) With conc. HNO_3 on heating give yellow precipitate, which on more heating gives solution. On adding NH_4OH red colour appears. It is **Xanthoprotic test**.

(b) (NH_4OH) + dil. $CuSO_4$ protein give blue violet colour. It is a **biuret test**.

(c) **Millon's reaction.** Proteins on adding Millon's reagent (a solution of mercuric [$Hg(NO_3)_2$] and mercurous nitrates ($HgNO_3$) in nitric acid containing a little nitrous acid) followed by heating the solution give red precipitate or colour.

(d) **Ninhydrin reaction.** Proteins, peptides and α-amino acids give a characteristic blue colour on treatment with ninhydrin.



[$C_6H_6O_4$]

Ninhydrin

Biological Importance of Protein

(a) Component of plasma membrane

(b) All enzymes are protein

(c) Many hormones are protein

(d) Antigen and antibody are protein

(e) Action and myosin protein are important in muscle contraction

(f) Proteins are important in growth, regeneration and repairing

(g) Calorific value 4.0 kcal

(3) Nucleic Acid

(a) These are special type of acids that are present in nucleus and cytoplasm.

(b) These are control the metabolic activities of cell

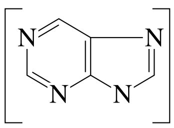
(c) These are also found in Mitochondria, centriole and chloroplast

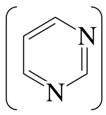
(d) **Fischer** discovered Nitrogen bases in 1888

Nitrogen Base

↓ type

Purine | Pyrimidine





(e) **Levan** found sugar

Sugar

↓ 2 type

Ribose (RNA) | Decoxyribose (DNA)

Types of nucleic acid → These are of two types

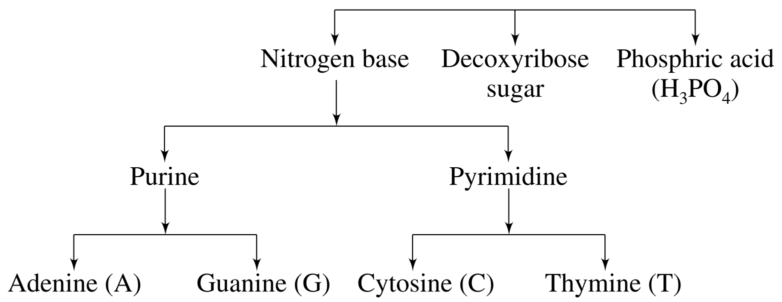
(I) DNA (Deoxyribonucleic acid)

(II) RNA (Ribonucleic acid)

(I) Deoxyribonuclic Acid (D.N.A.):

(a) It is found in nucleus.

(b) DNA made up of 3 units



(d) Nucleoside [Nitrogen base + deoxyribose sugar]

When nitrogen base combined with deoxyribose sugar it constitutes a nucleoside.

Deoxyribonucleoside

1. Adenine + Deoxyribose → Deoxyadenosine
2. Guanine + Deoxyribose → Deoxyguanosine
3. Cytosine + Deoxyribose → Deoxycytidine
4. Thymine + Deoxyribose → Deoxythymidine

Nucleotide

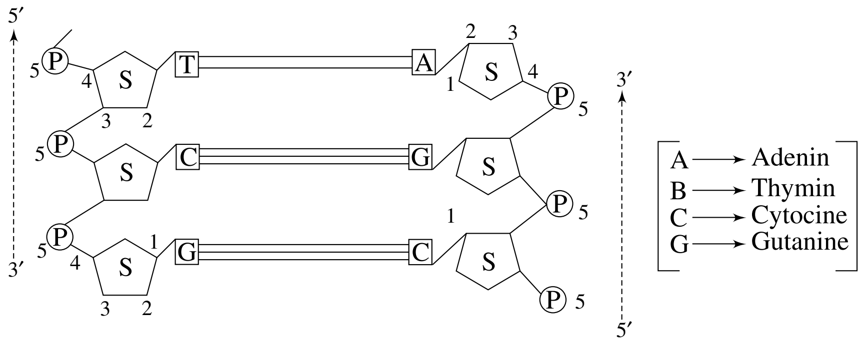
(a) Nitrogen bas + Sugar + Phosphate → Nucleotide

(b) Nucleotide is a unit of DNA.

(c) All nucleotides combined and form a chain called polynucleotides by which RNA and DNA formed.

Structure of DNA

(a) Double helical model of DNA was proposed by biochemist **J. D. Watson** and British chemist **F. H. C. Crick** in 1953.



(b) DNA in double stranded structure is made up of two chains of polynucleotides.

(c) DNA is a polymer of nucleotide.

(d) Nucleotides are joined by 3′ → 5′ phosphodiester bonds.

(e) Sugar and phosphorous are alternately arranged.

(f) In both chains, in between A and T, 2 Hydrogen bonds are present while in C and G 3H bonds are present. (A = T) (C ≡ G).

(g) A always attaches with T while C always attaches with G.

(h) Purine and pyrimidine are found in ratio 1 : 1.

Function of DNA

(i) Self-replication or self-duplication

DNA has the property of self-replication. It is therefore a reproducing molecule. This unique property of DNA is at the root of all reproduction. Through its replication, **DNA acts as the key to heredity**. In the replication of DNA, the two strands of a double helix unwind and separate as a template for the formation of a new complementary strand.

(ii) Protein Synthesis

The specific sequence of base pair in DNA represents coded information for the manufacture of specific proteins. These code instructions first are transcribed into the matching nitrogen-base sequences within mRNA and the instructions in such RNA subsequently are translated into particular sequence of amino acid units within the polypeptide chains and proteins.

The major steps in the utilisation of the genetic information can be represented as:

$$\text{DNA} \xrightarrow{\text{Replication}} \text{DNA} \xrightarrow{\text{Transcription}} \text{RNA} \xrightarrow{\text{Transcription}} \text{Protein}$$

(II) Ribonucleic Acid (RNA):

It is found in cytoplasm as well as in nucleus.

Chemical nature

- Ribonucleic acid is a polymer of purine and pyrimidine ribonucleotides
- It is linked by $3' \rightarrow 5'$ phosphodiester bridges.
- The number of nucleotides in RNA ranges from as **few as 75 to many thousands.**

Difference between DNA and RNA

- As indicated by its name, sugar in RNA to which the phosphate and nitrogen-bases are attached is ribose rather than the deoxyribose of DNA.
- Although RNA contains the ribonucleotides of adenine, guanine, and cytosine, it does not possess thymine. Instead of thymine, RNA contains the ribonucleotides of uracil. Thus, the pyrimidine components of RNA differ from those of DNA.
- RNA exists basically **as a single-stranded molecule** rather than as a double-stranded helical molecule, as does DNA. However, the single strand of RNA is capable of folding back on itself like a hairpin and thus acquiring double-stranded characteristics. In these regions. A pairs with U and G pairs with C. Thus, a given segment of a long RNA molecule might, for example, be represented as follows.

$$\begin{array}{cccccccccc} P- & R- & P- & R- & P- & R- & P- & R- & P- & R \\ & | & & | & & | & & | & & | \\ & A & & U & & G & & G & & C \end{array}$$

- where R stands for ribose; A, U, G, and C for a Adenine, Uracil, Guanine and Cytosine respectively.

Types of RNA and their functions

There are three main types of RNA molecules

(i) Messenger RNA (mRNA)
(ii) Transfer RNA (tRNA)
(iii) Ribosomal RNA (rRNA)

(i) Messenger RNA (mRNA)

- This type of RNA consists of **single strand** of variable length and serves as a template for protein synthesis. Codon in the chromosomes.
- mRNA forms complimentary copy of DNA as it carries **chemical messages in the form of nitrogen-base sequence from the nucleus to the ribosomes,** i.e., from **DNA to cytoplasm where proteins are synthesised.** Therefore, it is called messenger RNA or mRNA.
- mRNA is synthesised from DNA in the nucleus.
- It is called **transcription**.

(ii) Ribosomal RNA

- A ribosome is a cytoplasmic nucleoprotein structure which serves as the organellar machinery for protein synthesis from mRNA templates.
- On the ribosome, the mRNA and tRNA molecules interact to translate into a specific protein molecule the information transcribed from the DNA.
- rRNA constitutes the largest part of total RNA (highest)- 80%

(iii) Transfer RNA (RNA)

- These are also called **soluble RNA**.
- Single stranded
- 10–15% of the total RNA.
- **Size- Smallest** $\rightarrow$ 75–80 nucleotides only.
- **Synthesis-** Within **nucleus** from **DNA**.
- **Function –** It transport amino acid from cytoplasm to the site of protein synthesis.

(4) Vitamin

The organic compounds other than carbohydrates, proteins and fats that are necessary to maintain normal health, growth and nutrition are called vitamins.

These compounds required in small quantity, taken by food. Because their deficiency causes some specific disease.

Classification of vitamins

These are classified into two types

(1) Fat soluble $\rightarrow$ A, D, E, K

Fat soluble vitamins are stored in liver and adipose tissues.

(2) Water soluble $\rightarrow$ B(B_1, B_2, B_6, B_{12}), C

Water soluble vitamins are stored in the cells in much lesser amounts.

Vitamins and their important sources

Vitamin	Chemical name	Source	Deficiency disease
A	Retinol	Green vegetable, carrot, papaya, cod liver oil	Night blindness
D	Calciferol	Sunlight, cod liver oil	Rickets (Paralysis)
E	Tocopherrol	Sunflower oil	Weakness in muscles and loss of sexual power of reproduction
K	Phylloquinone	Green leafy vegetable	Delay in blood clotting
C	Ascorbic acid	Lemon, Amala, Oranges	Scurvy
B_1	Thiamine	Milk, egg	Beriberi, loss of appetite
B_2	Riboflavin	Milk, egg	Cracked lips, sore tongue and skin disorders
B_6	Pyridoxine	Milk, egg	Convulsion
B_{12}	Cyanocobalamine	Meat, fish, egg. Curd	Anaemia (deficiency of haemoglobin in RBC)

SOLVED EXAMPLE

1. Which compound can exist in a dipolar (zwitter ion) structure?

(1) $C_6H_5CH_2CH(N{=}CH_2)COOH$

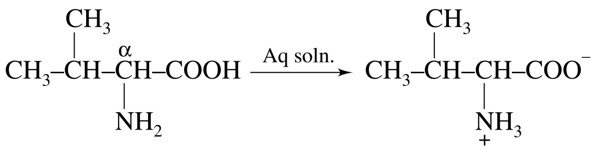
(2) $(CH_3)_2CHCH(NH_2)COOH$

(3) $C_6H_5CONHCH_2COOH$

(4) $HOOCCH_2CH_2COCOOH$

Sol. **[2]**

α-amino acid forms dipolar (zwitter ion) structure

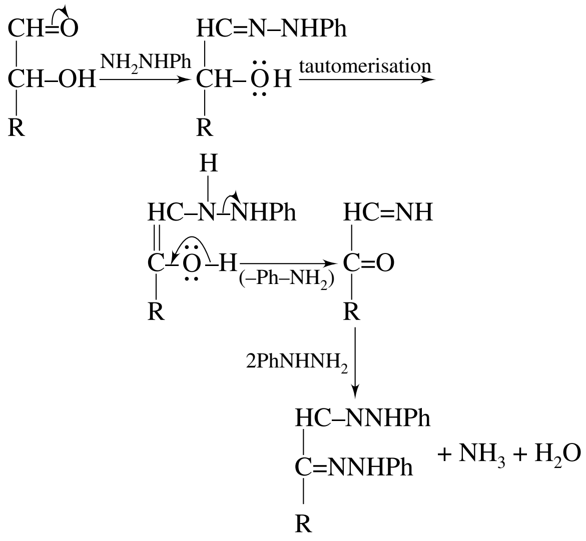


2. A glucose molecule reacts with 'X' number of molecule of phenylhydrazine to yield osazone. The value of x is:

(1) three (2) two

(3) one (4) four

Sol. **[1]**



Mole of Ph–NH–NH_2 used = 3 mole

3. The pair of compounds in which both the compounds give positive test with Tollens' reagent is
(1) starch and cellulose
(2) fructose and sucrose
(3) acetophenone and hexanal
(4) maltose and lactose

Sol. **[4]**
Both maltose and lactose are reducing sugar so they positive test with Tollens' reagent.

4. Chargaff's rule states that in an organism
(1) the amount of adenine (A) is equal to that of thymine (T) and that of guanine (G) is equal to that of cytosine (C)
(2) the amount of adenine (A) is equal to that of guanine (G) and that of thymine (T) is equal to that of cytosine (C)
(3) the amount of adenine (A) is equal to that of cytosine (C) and that of thymine (T) is equal to that of guanine (G)
(4) the amounts of all the bases are equal

Sol. **[1]**
According to Chargaff's rule
- Purine base = pyrimidine base

A + G = C + T

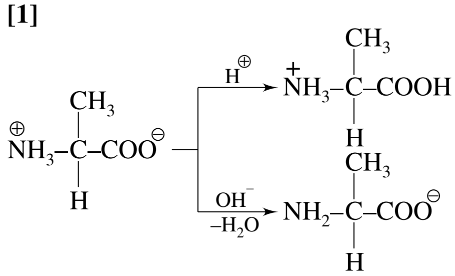
A always combines with T and G always combines with C. Hence the amount of adenine (A) is equal to that of thymine (T) and of the amount of guanine (G) is equal to that of cytosine (C).

5. Which of the following biomolecules is insoluble water?
(1) α-keratin (2) Haemoglobin
(3) Ribonuclease (4) Adenine

Sol. **[1]**
α-keratin is fibrous protein hence it is water insoluble.

6. The structures obtained on acidification (H^+) and basification (OH^-) of alanine yields respectively:
(1) $CH_3–CH(\overset{+}{N}H_3)–COOH$, $CH_3–CH(NH_2)–CHOO^-$
(2) $CH_3–CH(\overset{+}{N}H_4)–COO^-$, $CH_3–CH(NH_2OH)–CHOO^-$
(3) $CH_3–CH_2(\overset{+}{N}H_3)–COO^-$, $CH_3–C(=\overset{+}{N}H)–COO^-$
(4) $CH_3–CH_2(\overset{+}{N}H_3)–COO^+_2$, $HOCH_2–CH(\overset{+}{N}H_3)COO^-$

Sol. **[1]**



7. The vitamin which is water-soluble and is an anti-oxidant is:
(1) vitamin E (2) vitamin B_1
(3) vitamin C (4) vitamin D

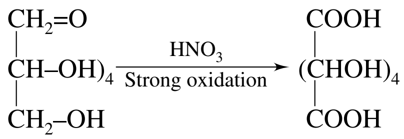
Sol. **[3]**
Vitamin C is water-soluble and is an antioxidant.

8. Vitamin B_1 is also known as:
(1) ascorbic acid (2) riboflavin
(3) pyridoxine (4) thiamine

Sol. **[4]**
Vitamin B_1 is also known as thiamine.

9. Glucose on oxidation with nitric acid gives:
(1) Gluconic acid (2) Saccharic acid
(3) Sorbic acid (4) Aldonic acid

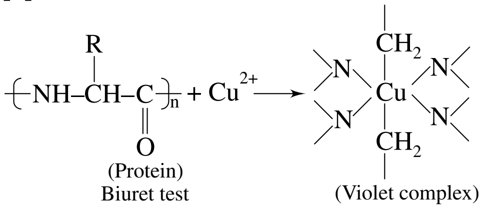
Sol. **[2]**



Sacharic acid

10. The metal ion which forms a violet-coloured complex with a protein in the presence of an alkali is:
(1) Cu^{2+} (2) Zn^{3+}
(3) Co^{3+} (4) Fe^{3+}

Sol. **[1]**



11. The glycosidic linkage involved in the linking of the glucose units in amylase part of starch is

(1) $C_1 - C_4$ β-linkage (2) $C_1 - C_6$ α-linkage
(3) $C_1 - C_4$ α-linkage (4) $C_1 - C_6$ β-linkage

Sol. **[3]**

Amylose part of starch is linear structure formed by $C_1 - C_4$, α linkage between glucose units.

12. In nucleic acids, the three components- base, sugar and phosphate are arranged in the sequence:

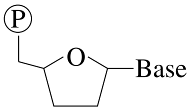
(1) ∿∿∿ base–sugar–O–P(=O)(O⁻)–O ∿∿∿

(2) ∿∿∿ sugar–base–O–P(=O)(O⁻)–O ∿∿∿

(3) ∿∿∿ sugar–O–P(=O)(O⁻)–O base ∿∿∿

(4) ∿∿∿ sugar(–base)–O–P(=O)(O⁻)–O ∿∿∿

Sol. **[4]**



Sequence of nucleotide unit of nucleic acid

13. A nanopeptide contains _____ peptide linkages.

(1) 10 (2) 8
(3) 9 (4) 18

Sol. **[2]**

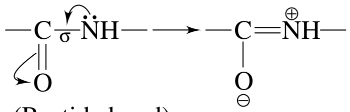
Nanopeptide structure formed by 9 amino acids

Number of peptide bond = number of AA – 1
= 9 – 1
= 8

14. Which statement is incorrect about peptide bond?

(1) C–N bond length in proteins is longer than usual bond length of C–N bond
(2) Spectroscopic analysis shows planar structure of peptide bond
(3) C–N bond length in proteins is smaller than usual bond length of C–N bond
(4) None of these

Sol. **[3]**



(Peptide bond)

Resonance present; so B.L. (C–N) ↓

Bond length of single bond $\propto \dfrac{1}{\text{Resonance}}$

15. The given structure of α-amino acid will exist at which pH?

$R{-}CH(\overset{+}{N}H_3){-}COOH$

(1) 7 (2) 14
(3) 4.3 (4) 12

Sol. **[3]**

$$R{-}CH(NH_2){-}COOH \xrightarrow{\text{In Aq soln.}} R{-}CH(\overset{+}{N}H_3){-}COO^- \xrightarrow[H^+]{pH = 4.3} R{-}CH(\overset{+}{N}H_3){-}COOH$$

16. An α-helix is a structure feature of:

(1) Polypeptides (2) Polyethylene
(3) Cellulose (4) Rubber

Sol. **[1]**

- α-Helix is the 2° structure of protein.
- Protein contain polypeptide linkage.

17. The transfer RNA anticodon for the messenger RNA codon G–C–A is:

(1) G–C–U (2) U–G–C
(3) C–G–U (4) G–U–C

Sol. **[3]**

G replace by C and A replace by U

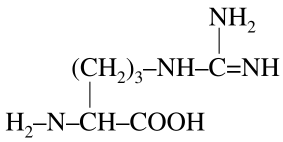
Hence, anticodon of G – C – A is C – G – U

18. Identify the basic amino acid.

(1) Glycine (2) Alanine
(3) Arginine (4) Aspartic acid

Sol. **[3]**

Such amino acid in which number of $-NH_2$ group greater that number of –COOH are basic amino acid



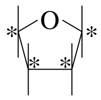
Arginine (arg)

19. RNA and DNA are chiral molecules, their chirality is due to:

(1) D-sugar compound
(2) L-sugar component
(3) chiral bases
(4) Chiral phosphate ester groups

Sol. **[1]**

Sugar unit in RNA/DNA is

 $\longrightarrow$ chiral (pentose sugar)

20. Which of the following statements about proteins is not correct?

(1) Proteins are polymers of amino acids
(2) Eggs are rich in proteins
(3) Pulses are good sources of proteins
(4) Proteins are polymers having the formula $(C_6H_{10}O_5)$n.

Sol. **[4]**

Protein is polymer of amino acid

EXERCISE 1

1. Which of the following statements is correct for glucose?

(1) It gives a positive reaction to Schiff's test for aldehydes
(2) It reacts with sodium bisulphate and ammonia
(3) Glucose penta-acetate does not react with hydroxylamine
(4) It gives a negative reaction to Tollens' test for aldehydes

2. Which of the following statements is true for protein synthesis (translation)?

(1) Amino acids are directly recognised by m-RNA
(2) The third base of the codon is less specific
(3) Only one codon codes for an amino acid
(4) Every *t*-RNA molecule has more than one amino acid attachment

3. Periodic acid splits glucose and fructose into formic acid and formaldehyde. Ratio of formaldehyde and formic acid from glucose and fructose is

(1) 1 : 5 and 1 : 2 (2) 1 : 5 and 2 : 3
(3) 1 : 2 and 1 : 24 (4) 2 : 3 and 1 : 2

4. Which of the following gives reddish brown precipitate with dilute solution of resorcinol in dilute HCl?

(1) Glucose (2) Fructose
(3) Lactose (4) Maltose

5. Which of the following statements most correctly defines the isoelectric point?

(1) The pH at which all molecular species are ionized and that carry the same charge.
(2) The pH at which all molecular species are neutral and uncharge.
(3) The pH at which half of the molecular species are ionized and the other half unionized.
(4) The pH at which negatively and positively charged molecular species are present in equal concentration.

6. Which of the following pair gives same phenyl osazone?

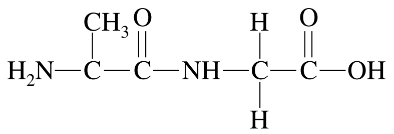
(I) D-Glucose and D-Allose
(II) D-Glucose and D-Fructose
(III) D-Glucose and D-Mannose
(IV) D-Glucose and D-Galactose

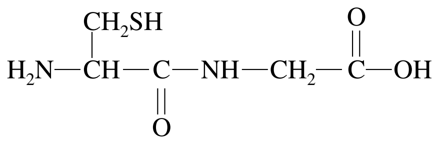
(1) I and II (2) II and III
(3) III and IV (4) II and IV

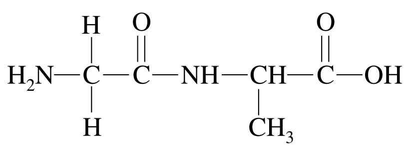
7. Ribose and 2-deoxyribose can be differentiated by

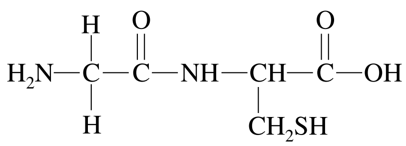
(1) Fehling's reagent (2) Tollen's reagent
(3) Osazone formation (4) Barfoed's reagent

8. The correct structure of the dipeptide gly–ala is

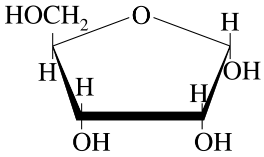
(1) 

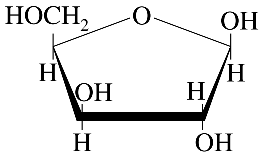
(2) 

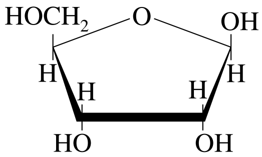
(3) 

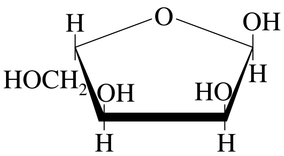
(4) 

9. Which of the following represents the anomer of the compound shown?



(1) 

(2) 

(3) 

(4) None of these

10. Which one of the following is non-reducing sugar?

(1) Glucose (2) Arabinose
(3) Lactose (4) Sucrose

11. Consider the following statements about amino acids.

(a) The amino acids that constitute proteins are all L-amino acids
(b) Among the twenty common amino acids that constitute proteins, glycine is the only one that does not possess a chiral centre.
(c) An important and sensitive test for the detection of L-amino acids is the ninhydrin colour test
(d) Nitrous acid liberates nitrous oxide from amino acids

Which of the following statements is correct?

(1) a, b and d (2) a, c and d
(3) b and d (4) a, b and c

12. In both DNA and RNA, heterocyclic base and phosphate ester linkage are at:

(1) C^1_5 and C^1_2 respectively of the sugar molecule
(2) C^1_2 and C^1_5 respectively of the sugar molecule
(3) C^1_1 and C^1_5 respectively of the sugar molecule
(4) C^1_5 and C^1_1 respectively of the sugar molecule

13. Synthesis of each molecule of glucose in photosynthesis involves

(1) 6 molecules of ATP (2) 18 molecules of ATP
(3) 10 molecules of ATP (4) 8 molecules of ATP

14. The number of atoms in the ring structure of pyranoses are:

	Carbon	**Oxygen**
(1)	5	1
(2)	4	2
(3)	4	1
(4)	3	2

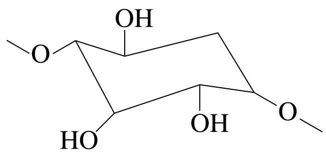
15. Which of the following is reducing sugar?

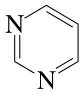
(1) Sucrose (2) Amylose
(3) Lactose (4) Cellulose

16. Which of the following is a fat-soluble vitamin?

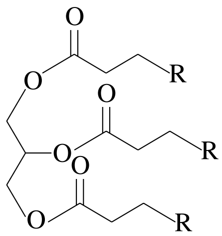
(1) Retinol (2) Pyridoxine
(3) Riboflavin (4) Thiamine

17. Which of the following chemical units is certainly to be found in an enzyme?

(1) 

(2) 

(3) 

(4) 

18. Thymine is:

(1) 5-Methyluracil (2) 4-Methyluracil
(3) 3-Methyluracil (4) 1-Methyluracil

19. Cellulose is a straight-chain polysaccharide composed of only:

(1) D-Glucose units joined by α-glycosidic linkage
(2) D-Glucose units joined by β-glycosidic linkage
(3) D-Galactose units joined by α-glycosidic linkage
(4) Galactose units joined by β-glycosidic linkage

20. During aerobic respiration, one molecule of glucose produces:

(1) 2 ATP molecules (2) 50 ATP molecules
(3) 38 ATP molecules (4) 36 ATP molecules

21. Mark the incorrect statement about ATP
(1) It is a nucleotide
(2) It contains the purine adenine.
(3) The enzyme-catalysed hydrolysis of ATP to ADP and AMP is accompanied by absorption of energy.
(4) Energy is stored in the cell in the form of ATP

22. The secondary structure of a protein refers to:
(1) The order of arrangement of its amino acid residues within the polypeptide chain
(2) The conformation adopted by its polypeptide chain
(3) The way in which the entire molecule folds to produce a specific shape
(4) The description of the arrangement and ways in which the subunits are held together

23. The pH of blood does not change appreciably on addition of a small amount of acid or base because:
(1) haemoglobin present in blood has a significant buffer capacity due to high content of histidine
(2) haemoglobin present in blood contains iron which controls the pH
(3) blood is easily coagulated and neutralises the added acid or base
(4) blood contains hydrogen phosphates-phosphoric acid buffer mixture

24. Transporting oxygen is an important function of blood. Partial pressure of O_2 is highest and lowest, respectively, in:
(1) muscles and heart (2) lungs and muscles
(3) heart and lungs (4) muscles and lungs

25. The successive nucleotides of a nucleic acid are connected to each other by a phosphodiester linkage formed between:
(1) C–5 hydroxy group of the pentose of one nucleotide and C–3 hydroxy group of the pentose of the next nucleotide group
(2) C–5 hydroxy groups of the pentose of the consecutive nucleotides
(3) C–3 hydroxy groups of the pentose of the consecutive nucleotides
(4) C–1 hydroxy groups of the pentoses of the consecutive nucleotides

26. Which of the following statements about RNA is not correct?
(1) The RNA molecule exists as a single strand of polynucleotide chain
(2) Messenger RNA functions as a template for the synthesis of proteins.
(3) Transfer RNA reads the code of messenger RNA and directs a specific amino acid to be placed in the growing protein chain.
(4) The nucleoside present in RNA are cytidine, thymidine, adenosine and guanosine

27. A chemical substance that acts as an immediate source of energy for many biological reactions is:
(1) protein
(2) adenosine triphosphate
(3) glucose
(4) adenosine monophosphate

28. Which of the following statement is not correct about an enzyme?
(1) It acts as a biocatalyst
(2) Its catalytic efficiency is temperature-dependent
(3) It can catalyse any chemical reaction
(4) Its aqueous solution is colloidal

29. Amongst the following statements about enzymes, which one is incorrect?
(1) Enzymes catalyse biological reactions by lowering their activation energies
(2) Enzymes are usually reaction specific, substrate specific, kinetic specific and stereospecific
(3) Enzymes are not enantioselective
(4) Pepsin is a proteolytic enzyme

30. The metal ion which is bound to carboxypeptidase-A is:
(1) Zn^{2+} (2) Cu^{2+}
(3) Fe^{2+} (4) Co^{2+}

EXERCISE 2

1. Hydrolysis of lactose with dilute acid yields:
(1) Equimolar mixture of D-glucose and D-glucose
(2) Equimolar mixture of D-glucose and D-galactose
(3) Equimolar mixture of D-glucose and D-fructose
(4) Equimolar mixture of D-galactose and D-galactose

2. Which one of the following metal ions is essential inside the cell for the metabolism of glucose/synthesis of proteins?
(1) Na^+ (2) K^+
(3) Mg^{2+} (4) Ca^{2+}

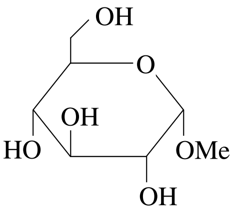
3. A certain compound gives negative test with ninhydrin and positive test with Benedict's solution, the compound is:

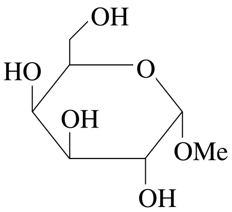
(1) a protein (2) a lipid
(3) a monosaccharide (4) an amino acid

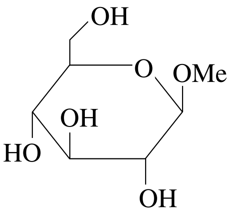
4. Aqueous solution of carbohydrate with 2 drops of alcoholic solution of α-naphthol and H_2SO_4 gives a ring at the junction. The colour of the ring is:

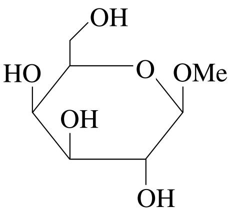
(1) Yellow (2) Green
(3) Violet (4) Red

5. Identify the correct set of stereochemical relationships amongst the following monosaccharides I-IV

(I)


(II)


(III)


(IV)


(1) I and II are anomers; III and IV are epimers
(2) I and III are epimers; II and IV are anomers
(3) I and II are epimers; III and IV are anomers
(4) I and III are anomers; I and II are epimers

6. Which one of the following is not correct?

(1) D(–) Fructose exists in furanose structure
(2) D(+) Glucose exists in pyranose structure
(3) In sucrose the two monosaccharides are held together by peptide linkage
(4) Pentaacetate of glucose does not react with hydroxylamine

7. The number of disulphide linkages present in insulin is

(1) 4 (2) 3
(3) 2 (4) 1

8. (A) $\underset{}{\overset{HO^-}{\rightleftharpoons}}$ D-Glucose $\overset{HO^-}{\rightleftharpoons}$ D-fructose

Product (A) of above reaction is:

(1) D-glucose (2) D-Mannose
(3) D-talose (4) D-idose

9. What would be the net charge on the given amino acid at pH = 14

$H_2N–CH(COOH)–(CH_2)_4–C(=O)–OH$

(1) –1 (2) –2
(3) +1 (4) +2

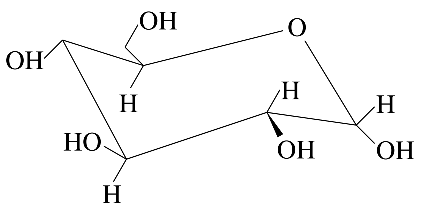
10. Natural glucose is termed D –glucose because:

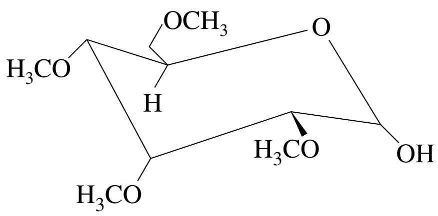
(1) – OH on then fifth carbon is on the right side in Fischer projection
(2) – OH on the second carbon is on the right side in Fischer projection
(3) – OH on the sixth carbon is on the right side in Fischer projection
(4) It is dextrorotatory

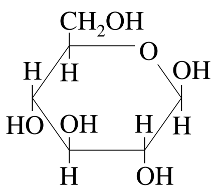
11. Peptide linkage is present in:

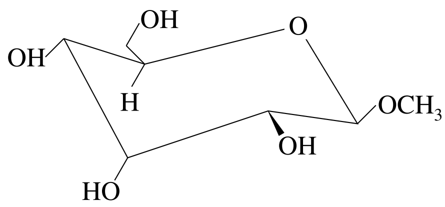
(1) Protein (2) Nylon-6,6
(3) Sucrose (4) Both (1) & (2)

12. Identify the non-reducing sugar

(1)


(2)


(3)


(4) 

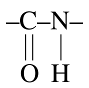
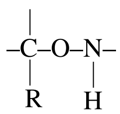
13. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which category?

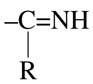
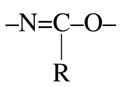
(1) A coenzyme (2) A hormone
(3) An enzyme (4) An antibiotic

14. Which one is not correct?

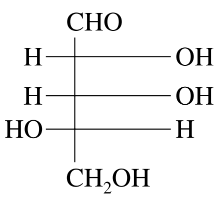
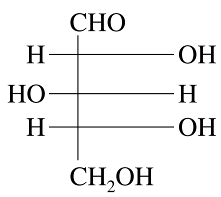
(1) Sucrose → α–D–Glucose + β–D–Fructose
(2) Maltose → α–D–Glucose + β–D–Glucose
(3) Lactose → β–D–Galactose + α–D–Glucose
(4) Cellulose → polymer of α-D-Glucose

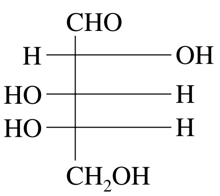
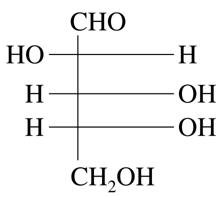
15. Which on among the following is a peptide linkage?

(1)  (2) 

(3)  (4) 

16. Which of the following gives an optically inactive aldaric acid on oxidation with dilute HNO_3 acid?

(1)  (2) 

(3)  (4) 

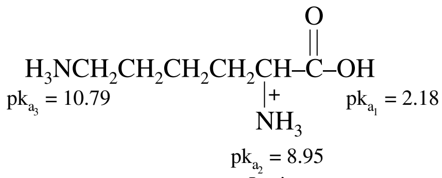
17. The protein which transports oxygen in the blood-stream is:

(1) haemoglobin (2) insulin
(3) albumin (4) collagen

18. The pk_{a_1} and pk_{a_2} value of alanine are 2.3 and 9.7 respectively. The isoelectric point of alanine is

(1) 7.4 (2) 6.0
(3) 5.7 (4) 9.7

19. Lysine has pk_{a_1} = 2.18 and pk_{a_2} = 8.95. the pk_{a_3} for ionisation of the side chain is 10.97



Lysine

What is the isoelectric point of lysine?

(1) 5.56 (2) 6.48
(3) 9.87 (4) 10.83

20. The successive nucleotides of both DNA and RNA are covalently linked to each other through:

(1) an either linkage between their sugar units
(2) a phosphate linkage between their sugar units
(3) a phosphate linkage between their bases
(4) an imino (–NH–) bridge between their bases

21. The number of hydrogen bonds present in the sequence of a stretch of a double helical DNA 5' ATGCCTAAG 3' is:

(1) 24 (2) 19
(3) 22 (4) 20

22. Enzyme trypsin effects the conversion of:

(1) Amino acids into proteins
(2) Glucose into glycogen
(3) Starch into sugar
(4) Proteins into a mixture of smaller peptides

23. The vitamin that regulates metabolism of calcium and phosphate is:

(1) vitamin A (2) vitamin D
(3) vitamin C (4) vitamin B_1

24. The vitamin that contains sugar units is:

(1) vitamin B_1 (2) vitamin B_2
(3) vitamin A (4) vitamin D

25. Which of the following peptide hormones controls blood pressure?

(1) Vasopressin (2) Oxytocin
(3) Bradykinin (4) Insulin

26. The metal atoms present in vitamin B_{12} and chlorophyll are respectively:

(1) Fe and Co (2) Co and Mg
(3) Fe and Mg (4) Fe and Zn

27. Mention true (T) and false (F) out of the following

S_1: Sucrose gives negative tests with benedict's and Tollens' solutions.

S_2: Sucrose does not form osazone

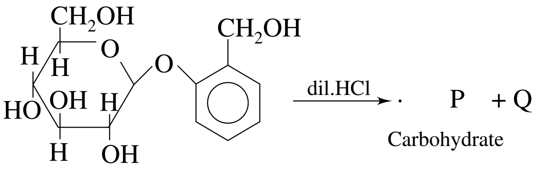
S_3: Sucrose does not undergo mutarotation

S_4: Octamethyl derivative of sucrose, on hydrolysis, gives 2, 3, 4, 6-tetra-O-methyl-D-glucose and 1, 3, 4, 6-tetra-O-methyl D-fructose

S_5: One mole of sucrose on acid hydrolysis yields one mole of D-glucose and one mole of D-fructose

(1) TTTTT (2) FTFTF
(3) FFFTT (4) TFFFT

28. Salicin (structure given below) is a glycoside, found in the bark of willow tree, used in relieving pain. Observe the following reaction of salicin



Salicin

The correct statement is:

(1) P is D-glucose
(2) Q is 2-hydroxybenzylalcohol
(3) Q can be converted to a modern analgesic (pain Killer), aspirin
(4) P & Q reduce Tollens' reagent

29. Which of the following statements correctly describes the migration aptitude of aspartic acid during electrophoresis?

(pK_1 = 2; pK_2 = 3.90; pK_3 = 10.0)

$$HOOC\text{–}\underset{}{\overset{NH_2}{\overset{|}{C}H}}\text{–}CH_2\text{–}COOH$$

(1) at pH = 1; aspartic acid migrate towards (+) electrode
(2) at pH = 2.45; aspartic acid show no net migration towards any electrode
(3) at pH = 7.0; aspartic acid show no net migration toward any electrode
(4) at pH = 9.0; aspartic acid show a net migration towards (–) electrode

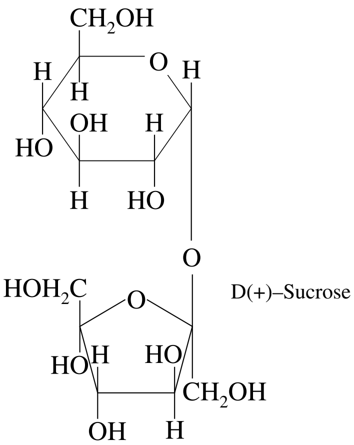
30. Select the correct statement among following:

(1) Number of chiral atom in β-D-glucose is less than D-glucose
(2) D-glucose and D-fructose give same product with HIO_4
(3) D-glucose and D-fructose give same product with H_2NOH
(4) D-glucose and D-fructose form same product with $H_2N\text{–}NH\text{–}Ph$

31. Incorrect statement from the following is:

(1) The non-reducing half in lactose is β-galactose
(2) Cellulose is polymer of β-D-glucose
(3) Starch is polymer of α-D-glucose
(4) In amylose glucose residues are connected by 1,6 glycosidic linkage

32. The number of chiral centres present in the following compound is:



(1) 7 (2) 8
(3) 9 (4) 10

33. During the process of digestion, the proteins present in food materials are hydrolysed to amino acids. The two enzymes involved in the process

$$\text{Proteins} \xrightarrow{\text{Enzyme(A)}} \text{Polypeptides} \xrightarrow{\text{Enzyme(B)}} \text{Amino acid}$$

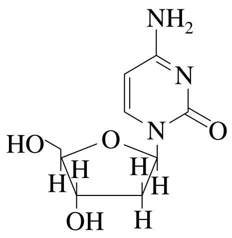
A & B are respectively:

(1) Invertase and Zymase
(2) Amylase and Maltase
(3) Diastase and Lipase
(4) Pepsin and Trypsin

34. Which of the following hormones contains iodine?

(1) testosterone (2) adrenaline
(3) thyroxine (4) insulin

35. Consider the following structure of a nucleoside.



This structure shows

(1) an amino acid joined to sucrose
(2) β-glycosides of D-deoxyribofuranose
(3) β-glycosides of D-ribofuranose
(4) α-glycosides of D-ribofuranose

EXERCISE 3

One and More Than One Option Correct Type Question

1. Which statement is/are correct in following?

(1) Glucose does not give 2,4-DNP test.

(2) Cane sugar give non-equimolar mixture of D-(+)-glucose and D-(–)-fructose.

(3) Cellulose does not give reaction with Tollens' Reagent.

(4) Fructose is reducing sugar

2. Which one of the following statements is/are true regarding (+) lactose?

(1) (+) Lactose, $C_{12}H_{22}O_{11}$, contains eight –OH groups

(2) On hydrolysis (+) lactose gives equal amount of D(+) glucose and D(+) galactose

(3) (+) Lactose in a β,1:4-glycoside formed by the union of a molecule of D(+) glucose and a molecule of D(+) galactose

(4) (+) Lactose is reducing sugar and does not exhibit mutarotation

3. Which statement about ribose is correct?

(1) A polyhydroxy compound

(2) An aldehyde sugar

(3) Sweet in taste

(4) Exhibits optical activity

4. Which of the following statements is/are correct?

(1) All proteins are polymers of α-amino acids.

(2) Glycogen is the food reserve of animals.

(3) Cellulose is a linear polymer of α-glucose.

(4) Amylopectin is a linear polymer of α-glucose.

5. What is/are true regarding the two anomers (α and β-forms) of D-(+)-glucose?

(1) α-D (+) glucose is more stable than its β-anomers

(2) β-D (+) glucose is more stable than its β-anomers

(3) The two anomers are diastereomers.

(4) In β-D (+) glucose, all the bigger groups occupy equatorial position in its most stable chair conformation

6. D-glucose and D-fructose both form the same osazone. Which statement(s) is/are correct about the above reaction?

(1) D-glucose and D-fructose are epimers

(2) D-glucose and D-fructose are anomers

(3) The configurations of the —OH group at C-3 and C-4 in glucose and fructose are same

(4) The configuration of the —OH group at C-4 and C-5 in glucose and fructose are same

7. Which of the following statements is/are true?

(1) Sucrose has a pyranose and a furanose ring hooked together by 1, 1′-glycosidic linkage

(2) Maltose has one glycosidic linkage and a free hemiacetal end

(3) Behaviour of hydrolysis product of maltose and sucrose is similar towards plane polarised light

(4) Sucrose is a dextrorotatory sugar

8. Which of the following statements regarding a peptide linkage in a protein molecule is/are correct?

(1) It is an amide linkage

(2) It has partial double bond character

(3) It is hydrophobic in nature

(4) It connects protein molecules through H-bonds

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

9. **Statement I:** Glucose reacts with phenyl hydrazine and Fehling's solution but not with $NaHSO_3$.

Statement II: $NaHSO_3$ cannot break the ring structure.

10. **Statement I:** Honey mainly contains invert sugar.

Statement II: Bees supply the enzyme invertase.

11. **Statement I:** Vitamin C cannot be stored in our body.

Statement II: Vitamin C is a water-soluble vitamin.

12. **Statement I:** α-D-glucopyranose is the most abundant naturally occurring aldohexose.

Statement II: All the ring substituents in the chair conformation are equatorial.

13. **Statement I:** Glycine, as well as other amino acids, is amphoteric.

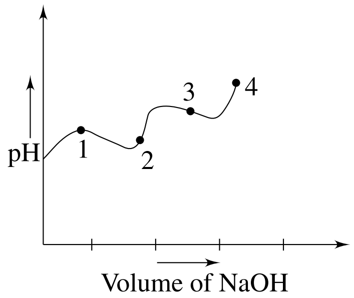
Statement II: The acidic functional group is the ammonium ions ($—\overset{+}{N}H_3$) and the basic functional group is the carboxylate ion ($—CO_2^-$).

Comprehension Type Question

Passage Based Questions (Q. 14–16)

A solution of alanine hydrochloride, $[H_3N—CH(CH_3)—COOH]^+Cl^-$ is titrated with a solution of sodium hydroxide to produce a curve as follows:

K_1 and K_2 of alanine hydrochloride are 4.6×10^{-3} and 2.0×10^{-10} respectively.



14. In the curve, at point 4 which of the molecule is found?

(1) $H_3\overset{+}{N}—CH(CH_3)—COOH$ (2) $H_3\overset{+}{N}—CH(CH_3)—COO^-$

(3) $H_2N—CH(CH_3)—COOH$ (4) $H_2\overset{+}{N}—CH(CH_3)—COO^-$

15. The pH at point 3 is

(1) 2.34 (2) 6.02
(3) 9.07 (4) 11.02

16. Which of the following is correct ratio of $\dfrac{H_3\overset{+}{N}—CH(CH_3)COO^-}{H_2N—CH(CH_3)COO^-}$ at pH 10?

(1) 2 : 1 (2) 5 : 8
(3) 1 : 2 (4) 8 : 5

Column Matching Type Question

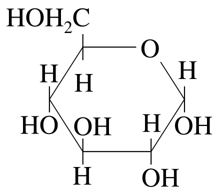
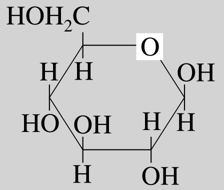
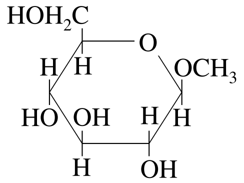
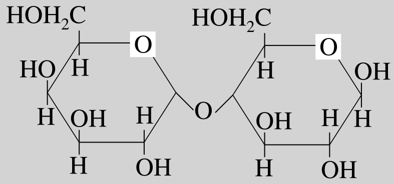
17. Match the column I with Column II and mark the correct option from the codes given below.

	Column I (Pair of molecules)		Column II (Characteristics)
i.	Glucose–fructose	p.	Anomers
ii.	Fructose–mannose	q.	Diastereomers
iii.	Glucose–mannose	r.	Functional isomers
iv.	α-D-glucopyranose β-D-glucopyranose	s.	Lobry-De-Bruyn Alberada van Ekenstein transformation

Codes

	i	ii	iii	iv
(1)	s	p, q	s	r
(2)	r, s	r, s	q, s	p, q
(3)	p, q	p, s	q, s	r
(4)	q	r	r, s	p

18. Match the Column I with Column II and mark the correct option from the codes given below.

	Column I (Compound)		Column II (Property)
i.		p.	Will form osazone
ii.		q.	Molecular mass increases by 120 when treated with Ac_2O
iii.		r. s.	Reduces Tollens' reagent Is α-D-glucopyranose
iv.		t.	Non-reducing sugar

Codes

	i	ii	iii	iv
(1)	p, q, r, s	p, q, r	t	p, r
(2)	p, q, r, s	p, s	q, t	p, r
(3)	p, q, s	p, q, r	p	p, r
(4)	p, s	s, t	r	q, t

19. Match the Column I with Column II and mark the correct option from the codes given below.

	Column I (Vitamin)		Column II (Deficiency diseases)
i.	Vitamin B_1	p.	Pernicious anaemia
ii.	Vitamin B_{12}	q.	Dermatitis, loss of hair and paralysis
iii.	Vitamin H	r.	Blood coagulation
iv.	Vitamin K	s.	Beriberi

Codes

	i	ii	iii	iv
(1)	p	s	q	r
(2)	s	p	q	r
(3)	s	p	r	q
(4)	p	s	r	q

20. Match the vitamins given in Column-I with the deficiency diseases listed in Column-II

Column-I	Column-II
(a) Vitamin A	(p) Osteomalacia
(b) Vitamin C	(q) Beriberi
(c) Vitamin D	(r) Scurvy
(d) Vitamin B_1	(s) Xerophthalmia

(1) $a \to p$; $b \to q$; $c \to s$; $d \to r$
(2) $a \to s$; $b \to r$; $c \to p$; $d \to q$
(3) $a \to s$; $b \to p$; $c \to r$; $d \to q$
(4) $a \to p$; $b \to r$; $c \to q$; $d \to s$

21. Match the items in Column-I with the names of carbohydrates in Column-II

Column-I	Column-II
(a) A carbohydrate which yields only glucose on hydrolysis	(p) Sucrose
(b) A carbohydrate which yields glucose and fructose on hydrolysis	(q) Lactose
(c) A carbohydrate which yields glucose and galactose on hydrolysis	(r) Amylose
(d) A carbohydrate which reduces Fehling's solution	(s) Mannose

(1) $a \to r$; $b \to p$; $c \to q$; $d \to q, s$
(2) $a \to p$; $b \to q$; $c \to r$; $d \to p, s$
(3) $a \to q$; $b \to p$; $c \to r$; $d \to r, s$
(4) $a \to r$; $b \to p$; $c \to q$; $d \to s$

22. Match the items given in Column-I with that given in Column-II.

Column-I	Column-II
(A) Nucleotide	(p) Linkage in carbohydrates
(B) Peptide linkage	(q) Linkage in proteins
(C) Glycoside linkage	(r) A sugar and heterocyclic base combination
(D) Nucleoside	(s) The monomeric unit in nucleic acids

(1) $A \to s$; $B \to q$; $C \to p$; $D \to r$
(2) $A \to q$; $B \to p$; $C \to s$; $D \to r$
(3) $A \to p$; $B \to s$; $C \to r$; $D \to q$
(4) $A \to s$; $B \to r$; $C \to q$; $D \to p$

Single Digit Integer Type Question

23. Some of the pairs of monosaccharides are given below:

I. Allose, altrose **II.** Glucose, fructose
III. Glucose, mannose **IV.** Mannose, fructose
V. Galactose, talose **VI.** Galactose, glucose

How many of the above pairs are C-2 epimers?

24. How many of the following undergo mutarotation?
Amylose, starch, glucose, maltose, cellulose, fructose, galactose, lactose.

25. How many acidic group/s is/are present in given amino acid?

$$\overset{\oplus}{N}H_3\text{–}\underset{\displaystyle CO_2^-}{\underset{|}{C}H}\text{–}CH_2\text{–}CH_2\text{–}CO_2H$$

EXERCISE 4

1. RNA contains **(AIEEE 2002)**
(1) Ribose sugar and thymine
(2) Ribose sugar and uracil
(3) Deoxyribose sugar and uracil
(4) Deoxyribose sugar and thymine

2. A substance forms zwitter ion. It can have functional groups **(AIEEE 2003)**
(1) $—NH_2$, $—COOH$ (2) $—NH_2$, $—SO_3H$
(3) Both (1) and (2) (4) None of the above

3. Complete hydrolysis of cellulose gives **(AIEEE 2003)**
(1) D-fructose (2) D-ribose
(3) D-glucose (4) L-glucose

4. The reason for double helical structure of DNA is operation of **(AIEEE 2003)**
(1) Van der Waals forces
(2) Dipole–dipole interaction
(3) Hydrogen bonding
(4) Electrostatic attractions

5. Which base is present in RNA, but not in DNA? **(AIEEE 2004)**
(1) Uracil (2) Cytosine

(3) Guanine (4) Thymine

6. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories? **(AIEEE 2004)**

(1) A coenzyme (2) A hormone
(3) An enzyme (4) An antibiotic

7. Identify the correct statement regarding enzymes. **(AIEEE 2004)**

(1) Enzymes are specific biological catalysts that can normally function at very high temperatures (T ~ 1000 K)
(2) Enzymes are normally heterogeneous catalysts that are very specific in their action
(3) Enzymes are specific biological catalysts that cannot be poisoned
(4) Enzymes are specific biological catalysts that possess well defined active sites

8. In both DNA and RNA, heterocyclic base and phosphate ester linkages are at **(AIEEE 2005)**

(1) C'_5 and C'_1, respectively, of the sugar molecule
(2) C'_1 and C'_5, respectively, of the sugar molecule
(3) C'_2 and C'_5, respectively, of the sugar molecule
(4) C'_5 and C'_2, respectively, of the sugar molecule

9. The pyrimidine bases present in DNA are **(AIEEE 2006)**

(1) Cytosine and adenine
(2) Cytosine and guanine
(3) Cytosine and thymine
(4) Cytosine and uracil

10. The term anomers of glucose refers to **(AIEEE 20006)**

(1) Isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4)
(2) A mixture of D-glucose and L-glucose
(3) Enantiomers of glucose
(4) Isomers of glucose that differ in configuration at carbon one (C-1)

11. The secondary structure of a protein refers to **(AIEEE 2007)**

(1) α-helical backbone
(2) hydrophobic interactions
(3) sequence of α-amino acids
(4) fixed configuration of the polypeptide backbone

12. α-D-(+)- glucose and β-D-(+)-glucose are **(AIEEE 2008)**

(1) conformers (2) epimers
(3) anomers (4) enantiomers

13. The two functional groups present in a typical carbohydrate are **(AIEEE 2009)**

(1) —OH and —COOH
(2) —CHO and —COOH
(3) C=O and —OH
(4) —OH and —CHO

14. Biuret test is not given by **(AIEEE 2010)**

(1) Carbohydrates (2) Polypeptides
(3) Urea (4) Proteins

15. The change in the optical rotation of freshly prepared solution of glucose is known as **(AIEEE 2011)**

(1) Tautomerism (2) Racemisation
(3) Specific rotation (4) Mutarotation

16. The presence of absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA? **(AIEEE 2011)**

(1) First (2) Second
(3) Third (4) Fourth

17. Which of the following statements is correct? **(AIEEE 2012)**

(1) All amino acids except lysine are optically active
(2) All amino acids are optically active
(3) All amino acids except glycine are optically active
(4) All amino acids except glutamic acids are optically active

18. Which of the following compounds can be detected by Molisch's test? **(AIEEE 2012)**

(1) Nitro compounds (2) Sugars
(3) Amines (4) Primary alcohols

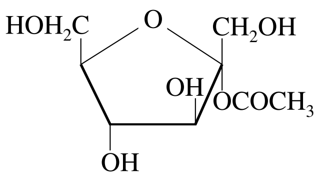
19. Synthesis of each molecule of glucose in **(JEE Main 2013)**

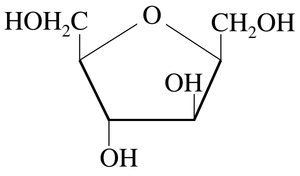
(1) 18 molecules of ATP (2) 10 molecules of ATP
(3) 8 molecules of ATP (4) 6 molecules of ATP

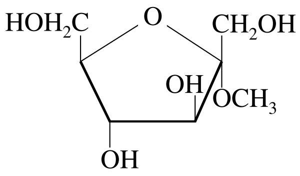
20. Which one of the following bases is not present in DNA? **(JEE Main 2014)**

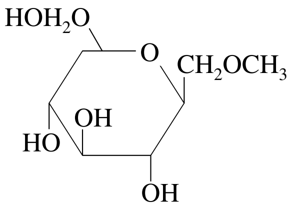
(1) Quinoline (2) Adenine
(3) Cytosine (4) Thymine

21. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? **(JEE Main 2017)**

(1) 

(2) 

(3) 

(4) 

22. Two forms of D-glucopyranose are called

(2005, Only One Option Correct Type)

(1) Enantiomers (2) Anomers
(3) Epimers (4) Diastereomers

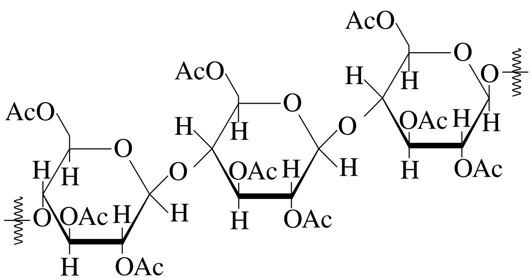
23. **Statement I:** Glucose gives a reddish-brown precipitate with Fehling's solution.

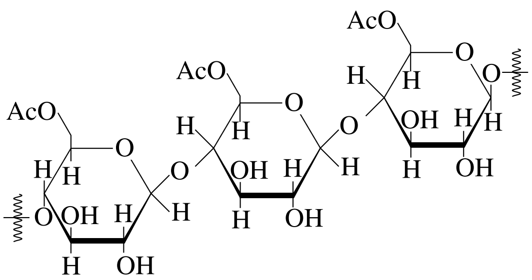
Statement II: Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

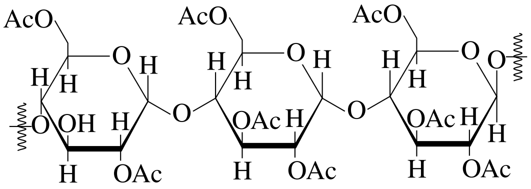
(2007, Statement Type)

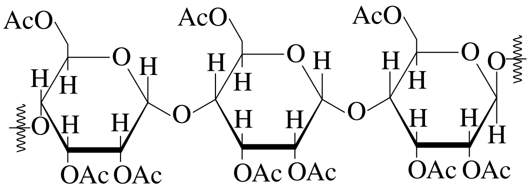
24. Cellulose upon acetylation with excess acetic anhydride/H_2SO_4 (catalytic) gives cellulose triacetate whose structure is

(2008, Only One Options Correct Type)

(1) 

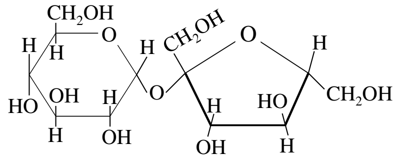
(2) 

(3) 

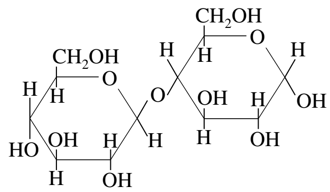
(4) 

25. The correct statement(s) about the following sugars X and Y is (are)

(2009, One or More than One Options Correct Type)



X

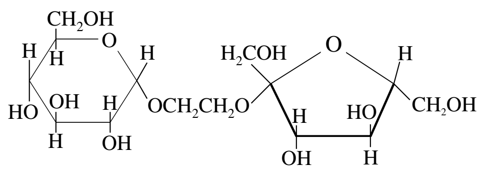


Y

(1) X is a reducing sugar and Y is a non-reducing sugar
(2) X is a non-reducing sugar and Y is a reducing sugar
(3) The glucosidic linkages in X and Y are α and β.
(4) The glucosidic linkages in X and Y are β and α, respectively

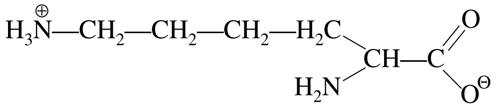
26. The correct statement about the following disaccharide is

(2010, Only One Options Correct Type)



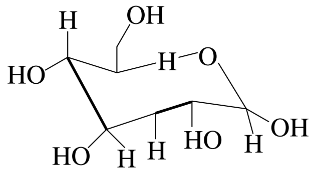
(1) Ring A is pyranose with α-glycosidic linkage
(2) Ring A is furanose with α-glycosidic linkage
(3) Ring B is furanose with α-glycosidic linkage
(4) Ring B is pyranose with β-glycosidic linkage

27. The total number of basic groups in the following form of lysine is **(2010, Integer Type)**



28. The following carbohydrate is

(2011, Only One Option Correct Type)



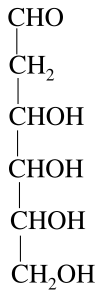
(1) a ketohexose (2) an aldohexose

(3) an α-furanose (4) an α-pyranose

29. A decapeptide (mol. wt. 796) on complete hydrolysis gives glycine (mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is

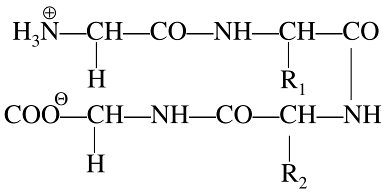
(2011, Integer Type)

30. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form is **(2012, Integer Type)**



31. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0?

(2012, Integer Type)

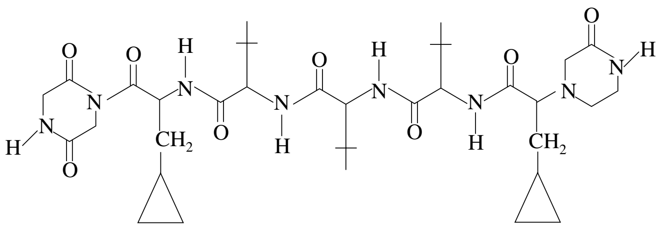


Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

32. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (Val), phenylalanine (Phe) and alanine (Ala) on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with —NH_2 group attached to a chiral centre is **(2013 Adv., Integer Type)**

33. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the people shown below is

(2014 Adv., Integer Type)



34. For 'invert sugar', the correct statement(s) is (are)

[JEE Adv. 2016]

(Given: specific rotation of (+)-sucrose, (+)-maltose, L-(–)-glucose and L-(+)-fructose in aqueous solution are +66°, + 140°, – 52° and 92°, respectively)

(1) Invert sugar is prepared by acid catalysed hydrolysis of maltose

(2) Invert sugar is an equimolar mixture of D-(+)-glucose and D-(–)-fructose

(3) Specific rotation of invert sugar is –20°

(4) On reaction with Br_2 water, invert sugar forms saccharic acid as one of the products

ANSWER KEY

EXERCISE # 1

1. (3)	2. (1)	3. (1)	4. (2)	5. (4)
6. (3)	7. (3)	8. (3)	9. (2)	10. (4)
11. (4)	12. (3)	13. (1)	14. (1)	15. (3)
16. (1)	17. (3)	18. (1)	19. (2)	20. (3)
21. (3)	22. (1)	23. (1)	24. (2)	25. (1)
26. (4)	27. (2)	28. (3)	29. (3)	30. (1)

EXERCISE # 2

1. (2)	2. (3)	3. (3)	4. (3)	5. (4)
6. (3)	7. (2)	8. (2)	9. (2)	10. (4)

11. (4)	12. (4)	13. (2)	14. (4)	15. (1)
16. (4)	17. (1)	18. (2)	19. (3)	20. (2)
21. (3)	22. (4)	23. (2)	24. (2)	25. (1)
26. (2)	27. (1)	28. (4)	29. (2)	30. (4)
31. (4)	32. (3)	33. (2)	34. (3)	35. (2)

EXERCISE # 3

1. (1,3,4)	2. (1,2,3)	3. (1,2,3,4)		4. (1,2)
5. (2,3,4)	6. (3,4)	7. (1,2,4)	8. (1,2,4)	9. (1)
10. (1)	11. (1)	12. (1)	13. (2)	14. (4)
15. (3)	16. (3)	17. (2)	18. (1)	19. (2)
20. (2)	21. (1)	22. (1)	23. (3)	24. (5)
25. (2)				

EXERCISE # 4

1. (2)	2. (3)	3. (3)	4. (3)	5. (1)
6. (2)	7. (4)	8. (2)	9. (3)	10. (4)
11. (1)	12. (3)	13. (3)	14. (1)	15. (4)
16. (2)	17. (3)	18. (2)	19. (1)	20. (1)
21. (1)	22. (2)	23. (3)	24. (1)	25. (2,3)
26. (1)	27. (2)	28. (2)	29. (6)	30. (8)
31. (4)	32. (4)	33. (4)	34. (2,3)	

HINT AND SOLUTION

EXERCISE # 1

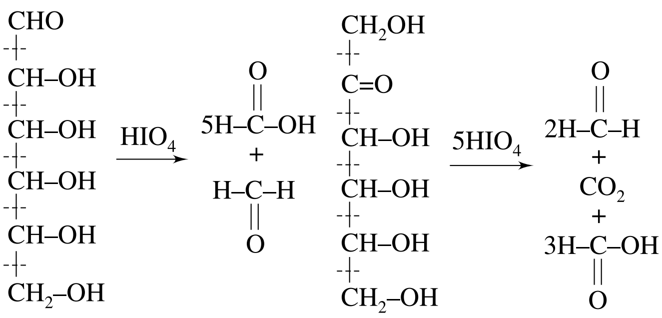
1. [3]

Refer theory

2. [1]

Theory based

3. [2]



Glucose   Glucose

4. [2]

Theory based

5. [4]

Theory based

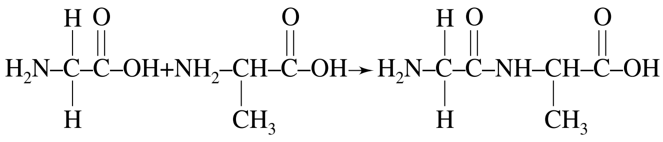
6. [2]

D-Glucose, D-Mannose, D-Fructose gives same osazone.

7. [3]

MF of ribose and 2-deoxyribose will be different. Hence they form different osazanie.

8. [3]



Glycine   Alanine   Gly-Ala link

9. [2]

Compounds which are mirror image at only annomeric carbon known as annomer.

10. [4]

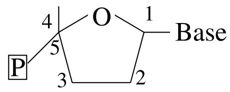
In Sucrose structure both anomeric carbon involve in glycosidic linkage formation

Thus, it gives negative test with Fehling's solution and Tollens' reagent, non-reducing sugar

11. [4]

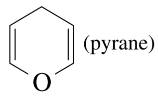
Theory based

12. [3]



13. [2]

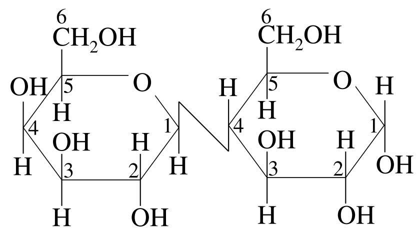
14. [1]



→ Pyrane like structure known as pyranose structure

15. [3]

Substance having –OH group at anomeric C are reducing sugar



Lactose

16. [1]

Theory based

17. [3]
Enzymes are protein natured sub.
So they contain polyamide linkage
$(-\underset{\displaystyle O}{\underset{\|}{C}}-NH)$

18. [1]
Theory based

19. [2]
Theory based

20. [3]
Theory based

21. [3]
Theory based

22. [2]
Theory based

23. [1]
Theory based

24. [2]
Theory based

25. [1]
Phosphodiester linkage formed between C'_3–C'_5

26. [4]
In RNA, Uracil base present, not thymine

27. [2]
ATP $\rightarrow$ Adenosine triphosphate

28. [3]
An enzyme catalyses only a specific reaction, like lock and key mechanism.

29. [3]
Theory based

30. [1]
Inorganic co-factor (prosthetic group) of enzyme is zinc carboxypeptidase-A

EXERCISE # 2

1. [2]

2. [3]
Theory based

3. [3]
Theory based

4. [3]
Theory based

5. [4]
I and III are mirror image at only anomeric carbon hence they are anomers.
I and II are mirror image at 4th carbon hence they are epimers.

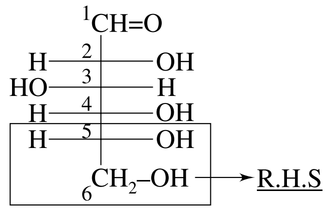
6. [3]
In sucrose, the two monosaccharides are joined together by glycosidic linkage.

7. [2]
Theory based

8. [2]
Labre-Debrawun reaction.

9. [2]
Theory based.

10. [4]



D-glucose

11. [4]
$\left(-\underset{\displaystyle O}{\underset{\|}{C}}-NH-\right)$ Present in both protein & Nylon 66

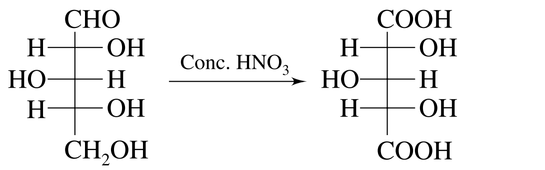
12. [4]
At anomeric carbon, OH group absent, Hence option (4) is non-reducing sugar.

13. [2]
Insulin is hormone

14. [4]
Cellulose is linear polymer of β-D glucose

15. [1]
$\left.\begin{array}{l}\text{Amide linkage} \\ (-\underset{\displaystyle O}{\underset{\|}{C}}-NH-)\end{array}\right\} \longrightarrow$ Peptide linkage

16. [4]



Plane of symmetry
(Optically inactive)

17. [1]
Theory based

18. [2]

$$pI = \frac{1}{2}(pk_{a_1} + pk_{a_2})$$
$$= \frac{2.3 + 9.7}{2} = 6$$

19. [3]

For an acidic amino acid, the pI is the average of the pk_a value of the two –COOH groups (uncharged) in its acidic form

$$pI = \frac{10.79 + 8.95}{2}$$

$$= \frac{19.74}{2} = 9.87$$

20. [2]

Each nucleotide unit are held together by phosphodiester linkage at C'_3–C'_5 position of sugar and phosphate respectively

21. [3]

A always combine with T with 2H bond

G always combines with C with 3H bond

5– A T G C C T A A G –3

↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓

2 + 2 + 3 + 3 + 3 + 2 + 2 + 2 + 3 = 22 H-bond

22. [4]

Theory based

23. [2]

Theory based

24. [2]

Theory based

25. [1]

Theory based

26. [2]

Theory based

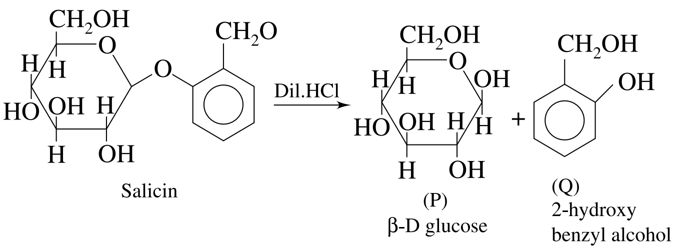
27. [1]

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose D-glucose D-fructose

(non-reducing sugar)

28. [4]



29. [2]

$$pI = \frac{Pk_1 + Pk_2}{2}$$

$$= \frac{2 + 3.90}{2} = 2.45$$

At iso electric point (PI) no migration take place.

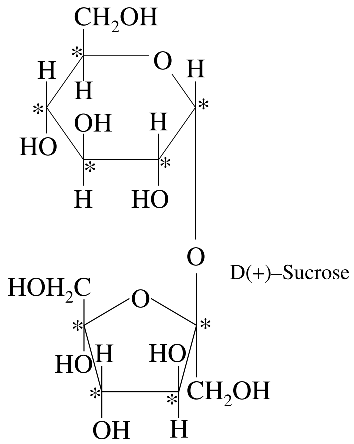
30. [4]

Both D-glucose and D-fructose form same OSAZONE with H_2N –NH–PH

31. [4]

Amylose is the linear polymer of α-D glucose formed by 1 : 4 glycosidic linkage.

32. [3]



33. [2]

Theory based

34. [3]

Theory based

35. [2]

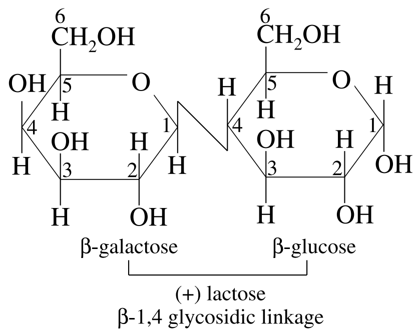
Because of the presence of five membered ring, it is a furanose structure. Oxygen is missing from 2 position, so it is β-glycoside of D-deoxyribofuranose.

EXERCISE # 3

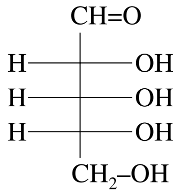
1. [1,3,4]

Cane sugar will give equimolar mixture of D glucose and D fructose

2. [1,2,3]



3. [1,2,3,4]



Ribose (5C)

4. **[1,2]**

Proteins are polymer of α-amino acid.

Glycogen is the reserved food in animals.

Cellulose is linear polymer of β-D-glucose.

Amylopectin is a branched polymer of α-D-glucose.

5. **[2,3,4]**

β-form of glucose is more stable because all the bigger groups occupy equatorial positions, in it. Since, α and β-forms are non-superimposable non-mirror images, so they are related as diastereomers, not as enantiomers.

6. **[3,4]**

D-glucose contains an aldehyde group while D-fructose contains a ketone group. So, these two are related as functional isomers.

During the osazone formation, only C_1 and C_2 are involved. Rest of the carbons retain their configuration.

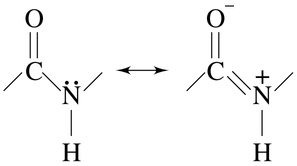
7. **[1,2,4]**

Sucrose is dextrorotatory but a non-reducing sugar. It contains a pyranose and a furanose ring linked together by 1, 1′-glycoside bond. On hydrolysis, it gives (+) D-glucose and (–) D-fructose. The α is more for later, so the solution becomes laevorotatory.

Maltose is a reducing sugar because of the presence of free hemiacetal group. It contains α-1, 4-glycosidic linkage.

8. **[1,2,4]**

Peptide linkage is in fact an amide linkage which shows resonance and hence, the C–N bond acquires partial double bond character as



The above bond is hydrophilic (i.e. water loving) and the protein chains are associated through intermolecular H-boding.

9. **[1]**

$NaHSO_3$ provide weak nucleophile. So that can't break ring structure of glucose.

10. **[1]**

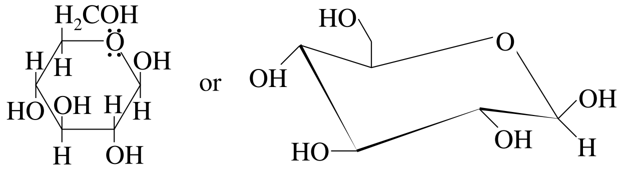
Theory based

11. **[1]**

Theory based

12. **[1]**

Structure of β-D-glucopyranose is



Since, all the ring substituents are at equatorial positions, so, it is more stable and hence, abundant aldohexose.

13. **[2]**

Because of the presence of acidic (—COOH) and basic (—NH_2) groups both, amino acids including glycine are amphoteric in nature.

In these acids ammonium ions ($-\overset{+}{N}H_3$) behaves like an acidic group and carboxylate ion ($-CO_2^-$) (with more tendency to accept a proton) behaves like a basic group.

14. **[4]**

15. **[3]**

16. **[3]**

Sol. **(14 to 16)**

$$\mathbf{pK_a = -\log K_a}$$

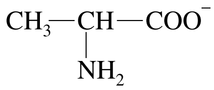
So, $pK\_a_1 = -\log K_{a_1} = -\log(4.6 \times 10^{-3}) = 2.34$

$$pK_{a_2} = -\log(2 \times 10^{-10}) = 9.69$$

$$\text{pI (isoelectric point)} = \frac{2.34 + 9.69}{2} = 6.015$$

$$pH = 10 > pI$$

At pH 10 (i.e. point 4) both the groups will be in the basic form i.e.



17. **[2]**

(i) → (r, s); (ii) → (r, s); (iii) → (q, s); (iv) → (p, q)

Glucose is an aldehyde while fructose is a ketone, although both have the same molecular formula. Thus, these are related a functional isomers.

LDBAVE transformation involves interconversion of glucose into fructose or mannose or vice-versa.

Mannose is an anomer of glucose, so it is also an aldehyde. Thus, it is also functional isomer of fructose.

α and β (cyclic) forms of glucose are related as diastereomers (i.e., non-superimposable non-mirror images).

18. **[1]**

(i) → (p, q, r, s); (ii) → (p, q, r); (iii) → (t); (iv) → (p, r)

All except (iii) because of the presence of free hemiacetal group form osazone and reduce Tollens' reagent.

(iii) is a non-reducing sugar.

(i) is a-D-glucopyranose.

And in case of (i) and (ii), molecular mass increases by 120 when treated with acetic anhydride.

19. [2]

(i) → (s); (ii) → (p); (iii) → (q); (iv) → (r)

Beriberi is a nervous disease caused by the deficiency of vitamin B.

Pernicious anaemia is the result of deficiency of vitamin B_{12}.

Deficiency of vitamin H leads to dermatitis, hair loss, etc.

Vitamin K is responsible for blood coagulation.

20. [2]

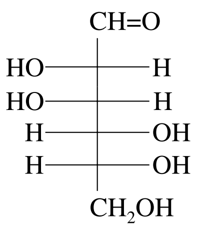
Theory based

21. [1]

α-D glucose + β-D fructose → sucrose

α-D glucose + α-D galactose → lactose

nα-D glucose → Amylose (linear polymer)



Mannose (reducing sugar)

22. [1]

Theory based

23. [3]

Only the pairs of (allose, altrose), (glucose, mannose), and (galactose, talose) contain C-2 epimers. (refer key concept)

24. [5]

Among the given only glucose, maltose, fructose, lactose galactose undergo mutarotation.

25. [2]

$\overset{\oplus}{N}H_3$ and COOH have acidic group.

EXERCISE # 4

1. [2]

RNA, ribonucleic acid.

Sugar present in RNA is D (–) ribose. It consists of cytosine and uracil as pyrimidine and guanine and adenine as purine bases.

2. [3]

For the formation of zwitter ion, basic part and acidic part both should be present in a molecule.

3. [3]

Partial hydrolysis of cellulose gives the disaccharide cellobiose ($C_{12}H_{22}O_{11}$). Cellobiose resembles maltose (which on acid catalysed hydrolysis yields two molar equivalents of D-glucose) in every respect except one: the configuration of its glycosidic linkage.

4. [3]

Hydrogen bonding is involved as a molecular force in the DNA molecule.

Watson and Crick observed the purine–pyrimidine type of hydrogen bonding (instead of purine–purine and pyrimidine–pyrimidine type).

5. [1]

Uracil is present in RNA but not in DNA.

6. [2]

Insulin is a hormone, built up of two polypeptide chains.

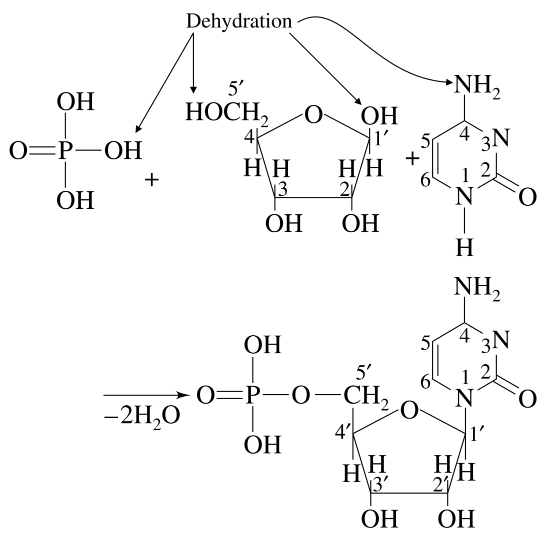
7. [4]

Normal optimum temperature of enzymes is between 25°C to 40°C. Hence, (1) is false. Enzymes are normally homogeneous catalysts that can be poisoned. Thus, (2) and (3) are also false. Enzymes have well defined active sites and their actions are specific in nature.

Enzymes have well defined active sites and their actions are specific in nature.

8. [2]

Synthesis of RNA/DNA from phosphoric acid, ribose and cytosine is given below. Thus, ester linkage formation and heterocyclic attachment place at C'_5 and C'_1 of sugar molecule.



9. [3]

In DNA, cytosine and thymine are pyrimidine bases.

10. [4]

Anomers of glucose are cyclic diastereomers (epimers) differing in configuration of the hydroxyl group at C-1, existing in two forms α and β, respectively.

11. [1]

Primary structure involves sequence of α-amino acids in a polypeptide chain.

Secondary structure involves α-helical and β-pleated sheet like structures.

12. [3]

α-D(+) glucose and β-D(+) glucose are anomers of glucose differing the configuration of hydroxyl group at C-1.

13. [3]

Carbohydrates are optically active polyhydroxy aldehyde or polyhydroxy ketones.

—C=O, —OH are the functional groups of typical carbohydrate.

14. [1]

Biuret test is characteristically given by the compound having (amide)

$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$$ functional group

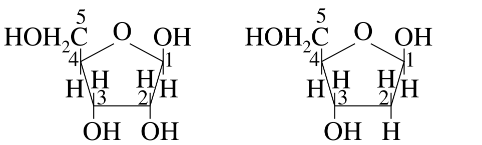
15. [4]

A spontaneous change in the specific rotation of a solution of an optically active compound is called mutarotation.

Hemiacetal forms of α-and β-D-glucose are stable in solid state but in aqueous solution, there is opening of the cyclic structure which gives solution of constant specific rotation.

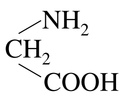
16. [2]

In RNA molecule, sugar moiety is β-D-ribose in which —OH group is present at 2nd carbon. Whereas in DNA, it is β-D-2-deoxyribose in which —OH group is absent at 2nd carbon.



β-D-ribose β-D-2-deoxyribose

17. [3]

Glycine  is α-amino acetic acid with no chiral carbon, thus optically inactive.

18. [2]

Molisch's test is used for the detection of carbohydrates. Add two drops of alcoholic solution of α-naphthol to the carbohydrate solution under study. Add conc. H_2SO_4 slowly by the side of the test tube. A violet ring is formed at the junction of the two liquids, if carbohydrate is present.

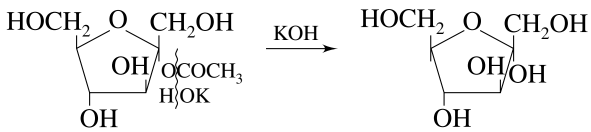
19. [1]

$6CO_2 + 12NaDPH + 18ATP \rightarrow C_6H_{12}O_6 + 12NADP + 18ADP$

20. [1]

DNA contains four nitrogenous bases: adenine, guanine, cytosine, and thymine. Quinoline is an alkaloid, hence, it is not present in DNA.

21. [1]



–OH group present at annomeric carbon so it is reducing suger.

22. [2]

α and β cyclic hemiacetals of D-glucose having difference in configuration at C-1 only are called anomers.

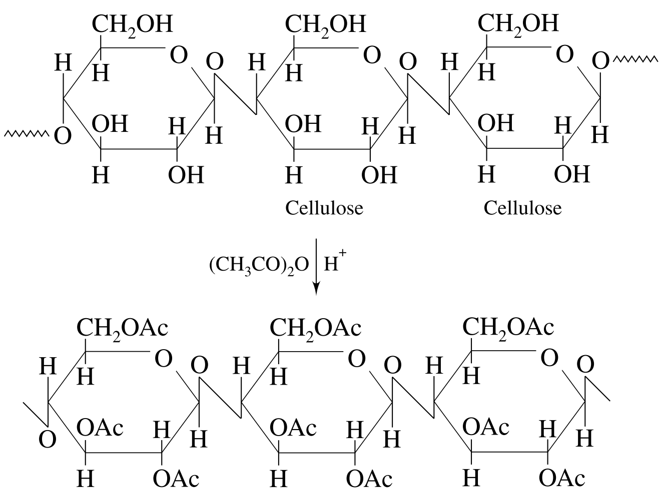
23. [3]

Statement I is correct: Presence of —CHO group in glucose is tested by Fehling's solution test where a reddish-brown precipitate of Cu_2O is formed.

Hence, Statement II is incorrect.

24. [1]

Cellulose is biopolymer of β-D-glucopyranose as



Triacetylated Cellulose

25. [2,3]

X is acetal, has no free hemiacetal, hence a non-reducing sugar while Y has a free hemiacetal group, it is reducing sugar, Also, glucosidic linkage of X is α while that of Y is β-linkage.

26. [1]

The six-membered cyclic ether is known as pyranose while the five-membered cyclic ether is known as furanose. Hence, ring (1) is a pyranose and it has ether linkage at α-position that is known as α-glycosidic linkage in carbohydrate chemistry.

27. [2]

—COO^- and —NH_2 are basic groups in lysine.

28. [2]

Here, the —OH of hemiacetal group is equatorial therefore, it is a β-pyranose of an aldohexose.

29. [6]

A decapeptide has nine peptide (amide) linkages. Therefore, on hydrolysis, it will absorb nine water molecules. Hence total mass of hydrolysis product

$$= 796 + 18 \times 9$$
$$= 958$$

Mass of glycine in hydrolysis product

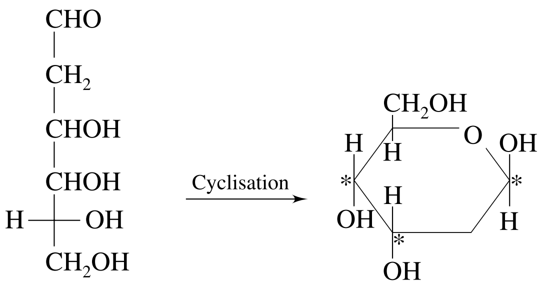
$$= \frac{958 \times 47}{100} = 450$$

Number of glycine molecule in one molecule of decapeptide

$$= \frac{450}{75} = 6$$

30. [8]

The D-form of given sugar is



D-sugar D-pyranonse

Configuration at the three chiral carbons (starred) can be changed maintaining D-configuration.

Hence, the total number of stereoisomers of D-pyranose = $2^3 = 8$

31. [4]

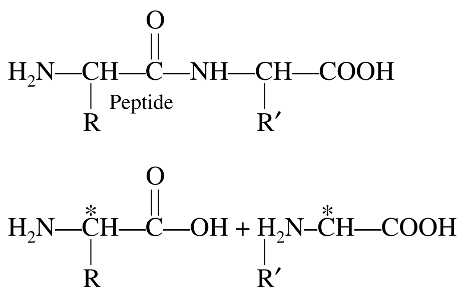
The amino acid remains completely in zwitter ionic form at its isoelectric point. Amino acids with additional acidic group have their isoelectric pH less than 7.0 and increasing pH above isoelectric point makes them anionic. On the other hand, amino acids with additional basic group have their isoelectric pH greater than 7.0 and decreasing pH below isoelectric point (by adding acid solution) makes them cationic. The given peptide with following R_1 and R_2 are basic will remain protonated (cationic) at pH = 7.0.

Peptide	R_1	R_2
IV	CH_2CONH_2	$(CH_2)_4NH_2$
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

Thus, 4 is the correct integer

32. [4]

A peptide linkage is hydrolysed to two free amino acids.



C^*f is chiral carbon. Tetrapeptide has four amino acids joined by three peptide linkages.

—COOH group is on alanine part, thus it is at fixed C-terminal position in each combination.

Glycine is optically inactive thus, it cannot be on the N-terminal side.

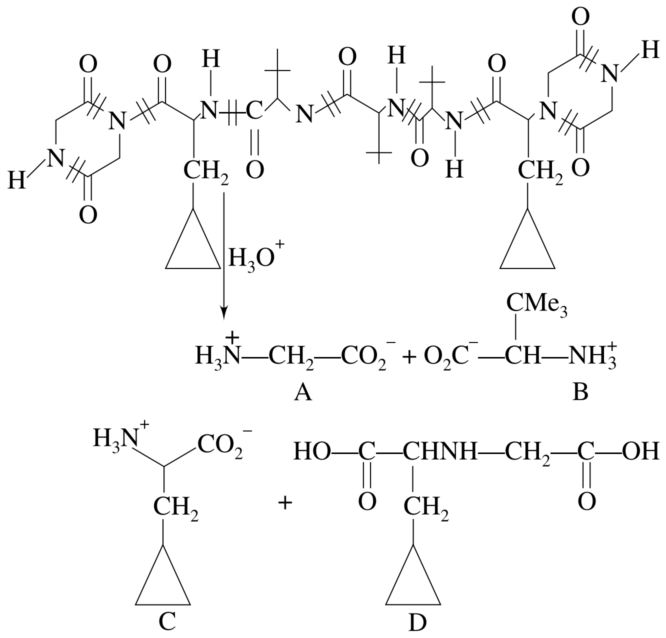
Thus, possible combinations are

Phe-Gly-Val-Ala
Phe-Val-Gly-Ala
Val-Gly-Phe-Ala
Val-Phe-Gly-Ala

Thus, in all four combinations are possible

33. [4]

Chemical reaction and product formed after hydrolysis of given peptide can be represented as



34. [2, 3]

If there is inversion of specific rotation from (+) to (–), then invert sugar is formed

(1) $\underset{\substack{\text{(+) Maltose} \\ 140°}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\substack{D(+) \\ 52°}}{\text{Glucose}}$

(2) $\underset{\substack{\text{(+) Maltose} \\ 140°}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\substack{D(+) \\ 52°}}{\text{Glucose}} + \underset{\substack{L(-) \\ -92°}}{\text{Fructose}}$

–40° for 2 moles mixture

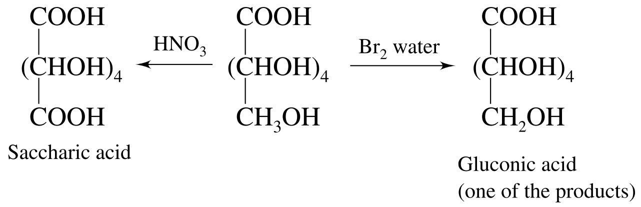
–20° for 1 mole mixture

There is formation of invert sugar, thus, correct.

(3) Specific rotation of invert sugar is –20° per mole. Thus, correct.

(4) Br_2 water is a weak oxidising agent. It oxidises –CHO to –COOH.

–CH_2OH group is not affected.



HNO_3 (a strong oxidising agent) oxidises invert sugar to saccharic acid. Thus, incorrect.

CHAPTER 7

Polymers

INTRODUCTION

- A polymer is a compound of high molecular mass formed by the combination of large number of small molecules and the process is called polymerisation.
- The small molecules which constitute the repeating units in a polymer are called monomer units.
- These large molecules have relative molecular masses in the range 10^4–10^6.

Example $\underset{\text{ethee}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{polythene}}{[-CH_2CH_2-]_n}$

CLASSIFICATION OF POLYMERS

Polymers are classified on the following bases:

1. Classification based on type of monomers unit:

(i) Homopolymer: The polymer formed from one kind of monomer is called homopolymer.

Example: Polyethylene

(ii) Copolymer or mixed polymer: Polymer formed from more than one kind of monomer unit is called copolymer.

Example: Buna-S

2. Classification based upon origin or source:

(i) Natural polymers: Polymers found in nature mostly in animal and plants sources, are called natural polymers

Example: Starch, cellulose, protein, Nucleic acids, natural rubber, etc.

(ii) Synthetic polymers: These are man-made polymers synthesised in the laboratory from low molecular weight compounds.

Example: Nylon, Dacron, Bakelite, synthetic rubber, polystyrene, etc.

(iii) Semi-synthetic polymers: These are mostly derived from naturally occurring polymers by carrying out chemical modifications. For example,

$$\text{Cellulose} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow{H_2SO_4} \text{Cellulose diacetate}$$

Cellulose diacetate is used in making threads, films, glasses, etc.

3. Classification based on structure: These are of three types based on structure

(i) Linear polymers: These are the polymers in which monomer units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure.

These polymers have high densities, high tensile strength and high melting points.

Example: Polythene, Nylon and polyesters

(ii) Branched chain polymers: These are the polymers in which monomeric units are linked to constitute long chains (called main chain). There are side chains of different lengths which constitute branches. Branched chain polymers are irregularly packed. These polymers have lower tensile strength and lower melting points as compared to linear polymers.

Example: Amylopectin (component of starch)

(iii) Cross linked polymers: These are the polymers in which monomeric units are linked together to constitute a three-dimensional network.

Cross linked polymers are hard, rigid and brittle because of their network structure.

Example: Bakelite

4. Classification based on synthesis: These are of two types based on synthesis

(i) Addition polymerisation: This involves the self-addition of several unsaturated molecules of one or two monomers without loss of any small molecule to form a single giant molecule. The polymer formed is known as addition polymer.

Example: Polythene

(ii) Condensation polymerisation: In this the monomer (same or different) units link with each other by the elimination of a small molecule (e.g., water, methyl alcohol) as a by-product. The polymer formed is known as condensation polymer.

Example: Nylon, terylene, etc.

Since the condensation polymerisation proceeds by a stepwise intermolecular condensation, it is also known as step polymerisation and the polymer formed is known as step growth polymer.

Differences between Addition and Condensation polymers

S. N.	Addition polymers	Condensation polymers
1.	Formed by addition reaction	Formed by condensation process with elimination of small molecules, like H_2O
2.	Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
3.	Generally involve one monomer unit.	Generally involve more than one monomer unit.
4.	Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
5.	They are generally chain growth polymers.	They are generally step growth polymers.

5. Classification based on intermolecular forces:

(i) Elastomers: There are the polymers having elastic character. The polymer chains in such type of polymers are held together by weakest intermolecular forces.

These forces permit the polymer to be the stretched by stress, but the polymer regains its former shape when the stress is relieved. The elasticity of such polymers can be further modified by introducing few cross links between the chains.

Example: Natural rubber

(ii) Fibres: These are the polymers that have quite strong interparticle forces, such as H-bonds.

They have high tensile strength and high modulus.

They are thread-like polymers and can be woven into fabrics.

Example: Nylon, Dacron etc.

(iii) Thermoplastics: These are the polymers which can be easily moulded into desired shapes by heating and subsequent cooling to room temperature.

The intermolecular forces in thermoplastic polymers are intermediate to those of elastomers and fibres.

Thermoplastic polymers soften on heating and become fluids, but on cooling they become hard.

Example: polyethene, polystyrene

Plasticisers: such plastics can be easily softened by the addition of some organic compounds which are known as plasticisers.

The plasticising effect is due to the solubilisation action and an accompanying reduction in intermolecular forces which permits free movement of molecules relative to each other.

Some **important** plasticisers are:

(i) Tricresyl phosphate

(ii) Dimethyl phthalate

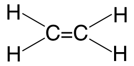
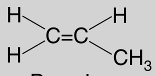
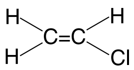
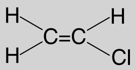
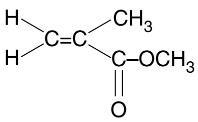
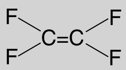
(iii) Triphenyl phosphate

(iv) Camphor

(iv) Thermosetting polymers: These are the polymers which become hard and infusible on heating. Heating results in excessive cross linking between the chains forming three dimensional network of bonds.

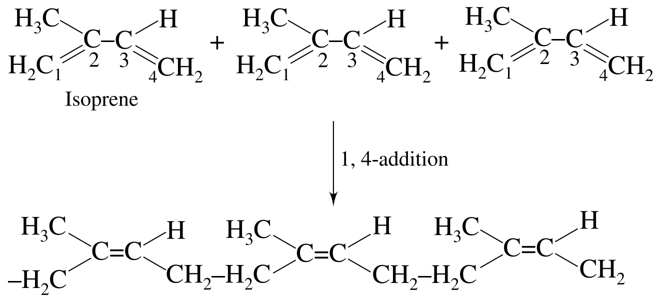
Example: Bakelite, Melamine

Some Common Addition Polymers

Monomer	Polymer	Uses
 Ethylene	Polythene $-\!\!\left[CH_2-CH_2\right]_n\!\!-$	Bags, toys, etc.
 Propylene	Polypropylene $-\!\!\left[CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\right]_n\!\!-$	Beakers, mill cartons, etc.
 Vinyl chloride	Polyvinyl chloride (PVC) $-\!\!\left[CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}\right]_n\!\!-$	Rain coats, pipes, tiles, etc.
 Acrylonitrile	Poly acrylo nitrile, (PAN) Orlon/Acrilan $-\!\!\left[CH_2-\underset{\displaystyle CN}{\underset{\vert}{CH}}\right]_n\!\!-$	Carpets, etc.
 Methyl metharcrylate	Plexiglass or poly (methyl smethacrylate), PMMA $-\!\!\left[CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle COOCH_3}{\underset{\vert}{C}}}}\right]_n\!\!-$	Transparent objects, lenses, etc.
 Tetrafluoro ethylene	Teflon or Polytetrafluoroethylene (PTFE) $-\!\!\left[CF_2-CF_2\right]_n\!\!-$	Chemical equipment, Non-stick cookware

Natural Rubber

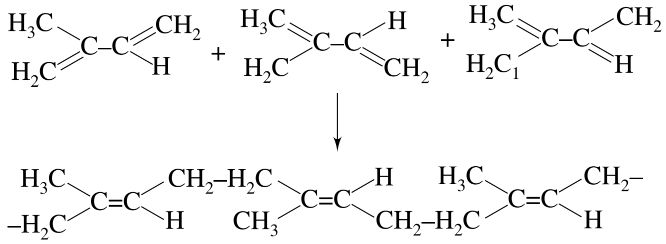
Natural rubber is a linear polymer of 2-methyl-1, 3-butadiene (isoprene). It is also called as *cis*-1, 4-polyisoprene.



Cis-polyisoprene (natural rubber)

Gutta-percha:

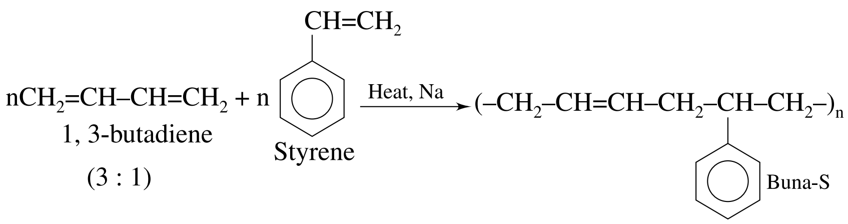
It is a naturally occurring isomer of rubber in which all the double bonds are *trans*. Like rubber, gutta percha is exuded by certain trees. It is harder and more brittle than rubber.



Trans-polyisprene (gutta-percha)

Synthetic Rubber

(i) Buna-S: It is copolymer of 1, 3-butadiene and styrene. It is obtained by the polymerisation of butadiene and styrene in the ratio of 3:1 in the presence of sodium.



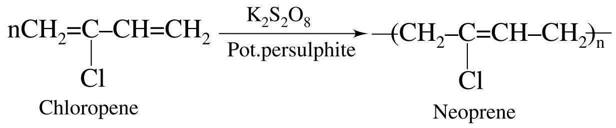
Uses: Buna-S is also vulcanised and used in making tyres for the vehicles. It is also used as rubber soles and in making water proof shoes.

(ii) Buna-N: It is obtained by the copolymerisation of 1, 3-butadiene and acrylonitrile in the presence of a peroxide catalyst.

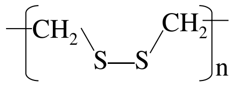
$$\underset{\text{1, 3-Butadiene}}{nCH_2{=}CH{-}CH{=}CH_2} + \underset{\text{Acrylonitrite}}{nCH_2 = \overset{\overset{CN}{|}}{C}H} \xrightarrow{\text{Copolymerzation}} \underset{\text{Buna-N}}{(CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{CN}{|}}{C}H)_n}$$

It is used in making oil seals, tank lining, etc.

(iii) Neoprene: Neoprene or polychloroprene is formed by the free radical polymerisation of chloroprene.



(iv) Thiokol: It is a synthetic rubber made by the polymerisation of ethylene dichloride and sodium polysulphide.



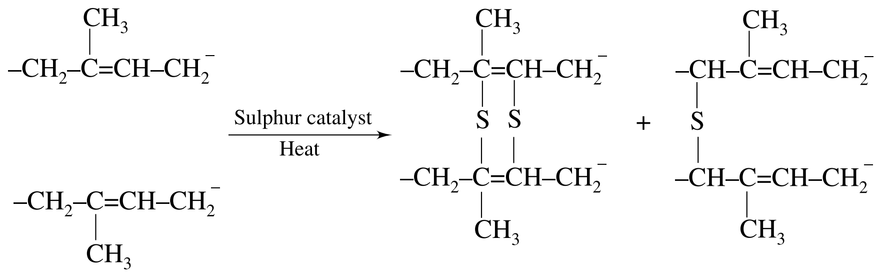
Thiokol

The presence of sulphur atoms in the polymeric chain make it inert or less reactive.

It is used in making hoses, engine gasket. The mixture of thiokol with oxidising agent is used as rocket fuel.

Vulcanisation of Rubber

In vulcanisation rubber is heated (3 hours) with sulphur (3–10%) at a temperature of 125–140°C. Rubber hydrocarbon combines with the sulphur atoms to form the sulphur bridges. The resulting product is tough, non-elastic and resistant to heat. It becomes non-abrasive and not affected by chemicals.



Natural rubber

(i) Rubber made with 1–3% sulphur is soft and stretchy and is used to make rubber bands.

(ii) Rubber made with 3–10% sulphur is more rigid and is used to manufacture tyres for automobiles, etc.

Condensation Polymers:

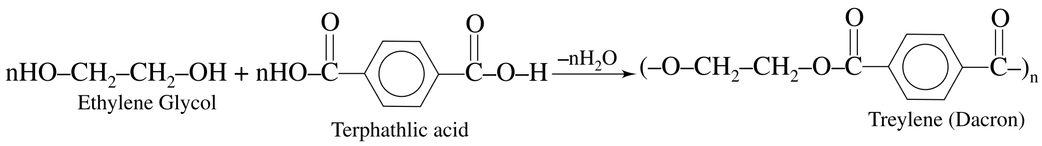
- A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecule like $-H_2O$, NH_3, etc.
- In this type, each monomer generally contains two functional groups.

  Example: Nylon 6, 6; Terylene; Bakelite.

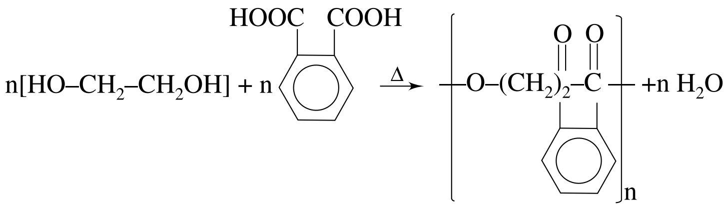
(I) Polyesters: These are the polymers having ester linkage $(-\overset{\overset{\large O}{||}}{C}\,O-)$

Example:

(i) Terylene (Dacron):



(ii) Glyptal or (alkydresin): The most simple glyptal (polyethylene phthalate) formed from the polycondensation of glycol and phthalic acid.

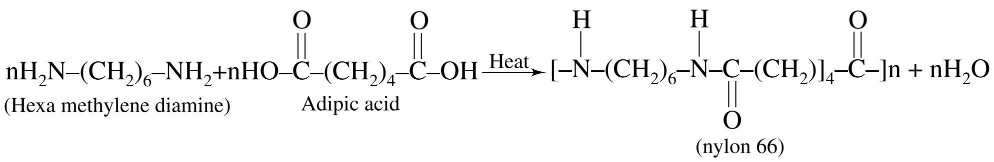


Uses: It is used in the manufacture of paints and lacquers.

(II) Polyamides: Such polymers have amide linkage (–CONH–) in the chain.

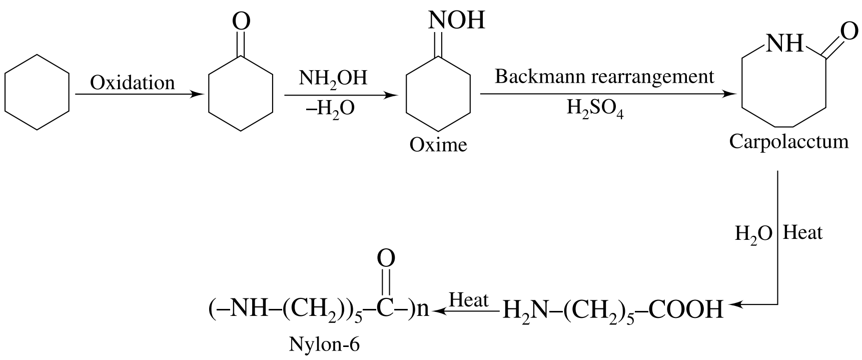
Example:

(i) Nylon 66



Uses: Nylon 66 has high tensile strength so it is used in the manufacture of carpet, textile fibres and bristles for brushes. It is used in making elastic hosiery.

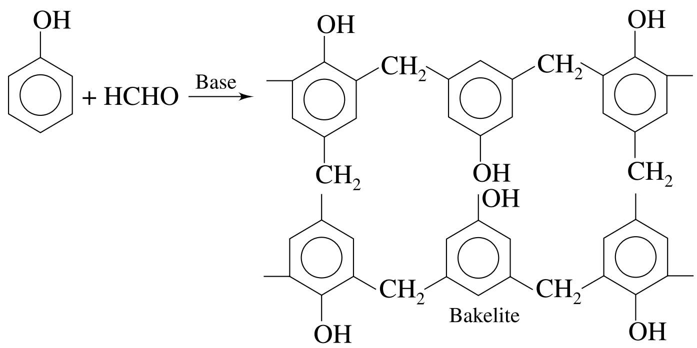
(ii) Nylon-6



Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

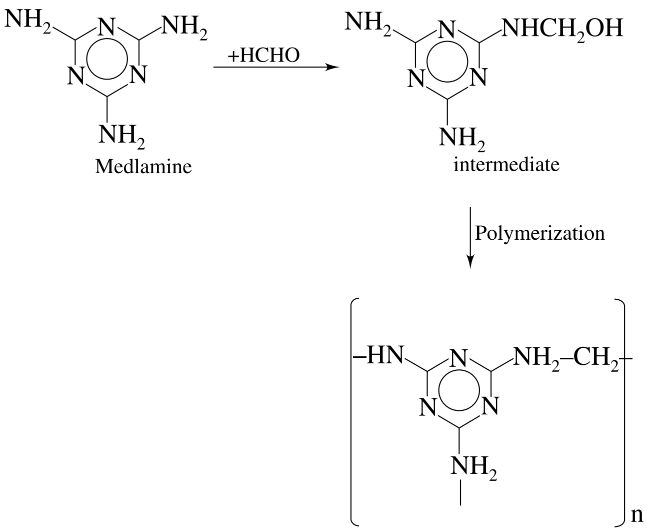
(III) Formaldehyde resins

(i) Phenol–formaldehyde resins (Bakelite)



Because Bakelite is hard and is a good electrical insulator, it is extensively used on making electrical switches, fuse holders, etc.

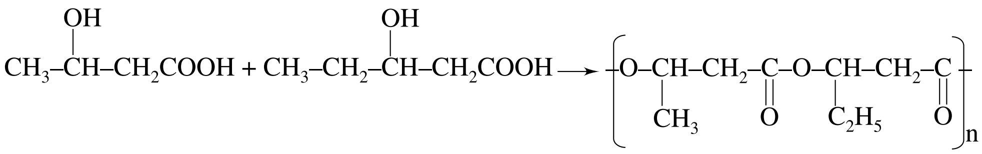
(ii) Melamine–formaldehyde resin: Melamine–formaldehyde resin is formed by the co-polymerisation of melamine and formaldehyde.



(IV) Biodegradable polymers: These are polymers that can be broken into small segments by enzyme-catalysed reaction. The required enzymes are produced by microorganism.

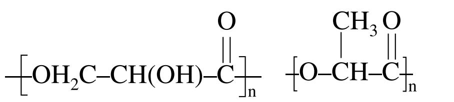
It is a known fact that the carbon–carbon bonds of chain growth polymers are inert to enzyme-catalysed reaction, and hence they are non-biodegradable.

(i) PHBV (poly-hydroxybutyrate-co-b-hydroxy valerate). It is a co-polymer of 3-hydroxy butyric acid and 3-hydroxy pentanoic acid.



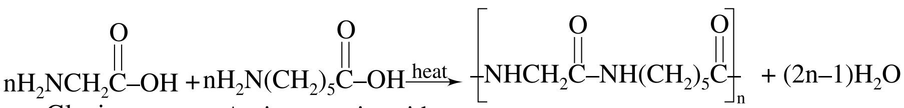
PHBV

(ii) Poly glycolic acid (PGA) and poly lactic acid (PLA): These are also biodegradable polymers and are used for post-operative stiches. These are bioabsorbable structures.



Poly glycolic acid   Poly lactic acid

(iii) Nylon-2, 6. It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid ($H_2N–(CH_2)_5COOH$) and is biodegradable.



Glycine   ε-Aminocaporic acid   Nylon 2-nylon 6

SOLVED EXAMPLE

1. Which one is used as a heterogeneous catalyst in polymerisation of ethylene into polyethene?
(1) Walker catalyst
(2) Ziegler–Natta catalyst
(3) Wilkinson's catalyst
(4) Ruthenium catalyst

Sol. **[2]**
In the polymerisation of ethylene into polyethylene Zeigler–Natta catalyst (triethyl aluminium + titanium tetrachloride) is used as the heterogeneous catalyst.

2. Which of the following is an example of natural polymer?
(1) Polyester (2) Glyptal
(3) Starch (4) Nylon-6

Sol. **[3]**
Starch is natural polymer of D-glucose.

3. Which of the following is a synthetic rubber?
(1) Buna-N (2) Buna-S
(3) Neoprene (4) All of these

Sol. **[4]**
Buna-N, Buna-S and neoprene are synthetic rubber. {refer theory}

4. Which of the following is correct about thermosetting polymers?
(1) Thermosetting polymers are cross-linked polymers.
(2) They do not melt (or soften) on heating.
(3) Cross-linking is usually developed at the time of moulding where they harden irreversibly.
(4) All of the above

Sol. **[4]**
Ex: of thermosetts is bakelite

5. Di-n-butyl phthalate is
(1) Plasticiser
(2) Thermoplastic
(3) Polymer
(4) Thermosetting plastic

Sol. **[1]**
Di-n-butylphthalate is plasticiser added to PVC to make it soft.

6. Natural rubber is
(1) *Trans* polyisoprene
(2) Cis polyisoprene
(3) *Cis* and *trans* isoprene
(4) Neoprene

Sol. **[2]**
Natural rubber is a homopolymer of *cis*-isoprene.

7. The structural formula of the monomer of poly (methylmethacrylate) (PMMA) is
(1) $CH_2{=}CHCOOCH_3$ (2) $CH_2{=}C(CH_3){-}COOCH_3$
(3) $CH_3COOCH = CH_2$ (4) $CH_3COOC(CH_3){=}CH_2$

Sol. **[2]**
Formula of option 2 is of methyl methacrylate, it is a monomer of PMMA, or Plexiglas.

8. Which one of the following compounds is polyester?
(1) Bakelite (2) Nylon 6, 6
(3) Terylene (4) Rubber

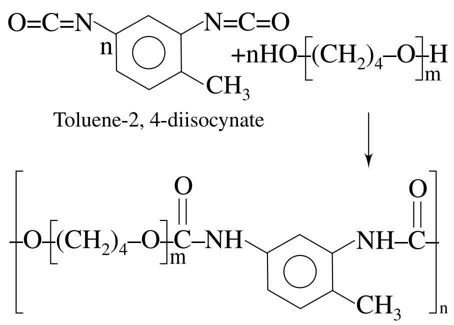
Sol. **[3]**
Terylene is a polyester fibre made up of by the polymerisation of ethylene glycol and terephthalic acid. (refer key concept)

9. Nylon is classified as a condensation polymer because
(1) in its preparation a solid is formed from liquid monomers
(2) its structure contains the peptide linkage, –CONH–
(3) it can be prepared from aqueous solutions of its monomers
(4) a small molecule is eliminated in its formation from its monomers

Sol. **[4]**
Nylon is a condensation polymer because in the reaction of adipic acid with hexamethylene diamine, small molecule H_2O is eliminated in its formation.

10. A polyurethane is the product of
(1) toluene-2,6-diisocyanate and ethylene glycol in presence of a blowing agent
(2) ∈-caprolactum and ethylene glycol
(3) terephthalic acid and ethylene glycol
(4) an isocyanate and an alcohol

Sol. Polyurethanes are obtained by the reaction of a diisocyanate with a diol,



Toluene-2, 4-diisocynate

Lycra, a polyurethane

EXERCISE 1

1. Which of the following is not a natural polymer?
(1) Natural rubber
(2) Cellulose
(3) Polymethyl methacrylate
(4) Proteins

2. The process of vulcanisation makes rubber
(1) soluble in water (2) elastic
(3) hard (4) soft

3. Plexiglasis
(1) PAN
(2) Poly (ethyl acrylate)
(3) Poly (methyl methacrylate)
(4) None of the above

4. Buna –N synthetic rubber is a copolymer of:
(1) $H_2C = CH - CN$ and $H_2C = CH - CH = CH_2$
(2) $H_2C = CH - CN$ and $H_2C = CH - C(CH_3) = CH$
(3) $H_2C = CH - C(Cl) = CH_2$ and $C_5H_6 - CH = CH_2$
(4) $H_2C = CH - CH = CH_2$ and $C_5H_6 - CH = CH_2$

5. A polymer which is used for making electrical switches is obtained from phenol by reacting with:
(1) HCHO (2) $(CH_2OH)_2$
(3) CH_3CHO (4) CH_3COCH_3

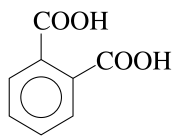
6. *Trans*-form of polyisoprene is
(1) Gutta-percha (2) Hydrochloride rubber
(3) Buna-N (4) Synthetic rubber

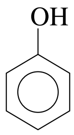
8. The polymer containing strong intermolecular forces is:
(1) Starch (2) Natural rubber
(3) Teflon (4) Nylon 6, 6

9. Which of the following is an example of condensation polymer?
(1) Teflon (2) Orlon
(3) Nylon-66 (4) Neoprene

10. Which of the following polymers would have the highest resistance to combustion?
(1) $-\!\left[CF_2-CF_2\right]\!-_n$ (2) $-\!\left[CF(Cl)-CF(Cl)\right]\!-_n$ with CF_2-CF_2 each bearing Cl
(3) $-\!\left[CF_2-CF_2(Cl)\right]\!-_n$ (4) $-\!\left[CF_2-CF_2(OCOCH_3)\right]\!-_n$

11. High density polyethylene (HDPE) can be prepared from ethylene by
(1) Ziegler–Natta process
(2) Heating with peroxides
(3) Condensing is sealed tubes
(4) Condensing with styrenes

12. Which one of the following sets forms a biodegradable polymer?
(1) $H_2N-(CH_2)_6-NH_2$ and $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$
(2) $HO-CH_2-CH_2-OH$ and 

(3) $CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH$ and $CH_3-CH_2-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH$
(4) 

and $H-\overset{O}{\overset{\|}{C}}-H$

13. Which one of the following is not a condensation polymer?
(1) Nylon 2,6 (2) PHBV
(3) Nylon-6 (4) Acrilan

14. Terylene (Dacron) is the polyester of:
(1) Hexamethylenediamine and adipic acid
(2) Vinyl chloride and formaldehyde
(3) Melamine and formaldehyde
(4) Ethylene glycol and terephthalic acid

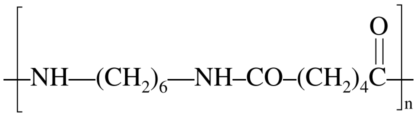
15. The basic unit of neoprene is:
(1) chloroprene (2) isoprene
(3) styrene (4) butadiene

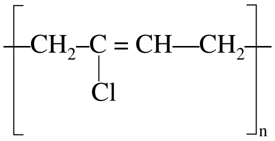
16. Which of the following is a natural polymer?
(1) Bakelite (2) Cellulose
(3) PVC (4) Neoprene

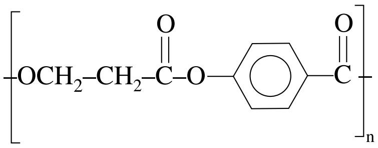
17. The chemical name of melamine is:
(1) 2,4-Diamino-1,3,5-triazine
(2) 2-Amino-1,3,5-triazine
(3) 2,4,6-Triamino-1,3,5-triazine
(4) 1,3,5-Triamino-2,4,6-triazine

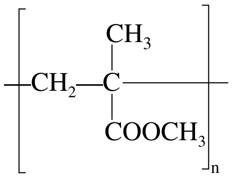
18. Which of the following is not correctly matched?

(1) Nylon-6,6:

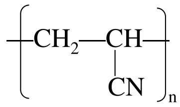


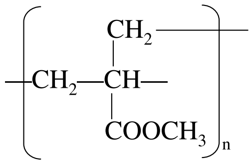
(2) Neoprene: 

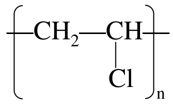
(3) Terylene: 

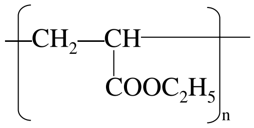
(4) PMMA: 

19. Acrilan is a hard material and has high melting point. Which of the following represents its structure?

(1) 

(2) 

(3) 

(4) 

20. Which of the following polymers can be used for lubrication and as an insulator?

(1) SBR (2) PAN

(3) PTFE (4) PVC

EXERCISE 2

1. Which of the following sets contains only thermoplastics?

(1) Glyptal, Melmac, PAN

(2) Polythene, Bakelite, Nylon-6

(3) PVC, PMMA, Polystyrene

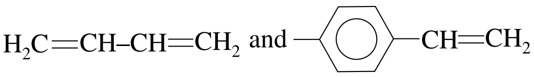
(4) Polypropylene, Urea–formaldehyde, Teflon

2. Which of the following sets forms the biodegradable polymer?

(1) $H_2C{=}CH{-}CN$ and $H_2C{=}CH{-}CH{=}CH_2$

(2) 

(3) $H_2N{-}CH_2{-}COOH$ and $H_2N{-}(CH_2)_5{-}COOH$

(4) 

3. Among cellulose, poly (vinyl chloride), nylon, and natural rubber, the polymer in which the intermolecular force of attraction is the weakest is

(1) nylon (2) poly (vinyl chloride)

(3) cellulose (4) natural rubber

4. Ebonite is

(1) polypropene

(2) natural rubber

(3) synthetic rubber

(4) highly vulcanised rubber

5. Which of the following polymers cannot be made by free radical addition polymerisation mechanism?

(1) PE (2) HDPE

(3) LDPE (4) Teflon

6. Formation of polyethylene from calcium carbide takes place as follows:

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$C_2H_2 + H_2 \longrightarrow C_2H_4$

$nC_2H_4 \longrightarrow (-CH_2-CH_2-)_n$

The amount of polyethylene obtained from 64.1 kg of CaC_2 is

(1) 7 kg (2) 14 kg

(3) 21 kg (4) 28 kg

7. Which of the following rubber is not a polydiene?

(1) Polyisoprene (2) Polychloroprene

(3) Thiokol (4) Nitrile rubber

8. Wash and wear clothes are manufactured using

(1) nylon fibres

(2) cotton mixed with nylon

(3) terylene fibres

(4) wool fibres

9. The monomer of the polymer $\sim\sim CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C^{\oplus}}}}}$ is

(1) $CH_2{=}C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$

(2) $CH_3{-}CH{=}CH{-}CH_3$

(3) $CH_3{-}CH{=}CH_2$

(4) $CH_2 - \underset{CH_3}{\underset{|}{C}} = \underset{CH_3}{\underset{|}{C}} - CH_3$

10. Which of the following sets contains only copolymers?

(1) SBR. Glyptal, Nylon-6,6

(2) Polythene, polyester, PVC

(3) Nylon-6, butyl rubber, Neoprene

(4) Melmac, Bakelite, Teflon

11. Polymerisation of propene using Ziegler–Natta catalyst is advantageous over free-radical polymerisation because:

(1) it can lead to living polymers via anionic polymerisation

(2) it permits step-growth polymerisation resulting in a highly cross-linked polymer

(3) it gives highly branched polymer with a high degree of crystallinity

(4) it gives linear polymer molecules permitting stereochemical control

12. Given the polymers, A = Nylon 6-6; B = Buna-S; C = Polythene

Arrange these in decreasing order of their intermolecular forces.

(1) A > C > B (2) B > C > A

(3) A > B > C (4) C > B > A

13. Which of the following monomers can undergo radical, cationic as well as anionic polymerisation with equal ease?

(1) $CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$ (2) $C_6H_5{-}CH{=}CH_2$

(3) $CH_2{=}CH{-}CN$ (4) $CH_2{=}CH_2$

14. Gutta-percha is

(1) *Trans*-polyisoprene

(2) Non-elastic and softens to a plastic-like material on heating

(3) Used in underwater cables and golf balls

(4) All of the above

15. What is true regarding vulcanisation of rubber?

(1) Rubber molecules are joined through S–S linkage at the ends.

(2) Rubber molecules are linked through S–S linkage at the various parts of polymer backbone.

(3) Vulcanisation makes rubber perfectly crystalline.

(4) Vulcanisation converts rubber into a thermosetting polymer.

EXERCISE 3

One and More Than One Option Correct Type Question

1. Which of the following is/are thermosetting polymers?

(1) Bakelite (2) Polystyrene

(3) PVC (4) Melmac

2. Which of the following is/are biodegradable polymers?

(1) Nylon-66 (2) PHBV

(3) Polychloroperene (4) Nylon-2-nyon-6

3. Polyacetylene is a conducting polymer and

(1) is prepared by the polymerization of acetylene using a Ziegler-Natta catalyst

(2) the conjugated double bond in polyacetylene causes it to conduct electricity

(3) is used for the manufacture of electrodes for measuring pH

(4) is not a synthetic metal

4. Which monomer would polymerise in isotactic, syndiotactic, and atactic forms?

(1) $CH_2{=}CCl_2$ (2) $CH_3{—}CH{=}CH_2$

(3) $Ph{—}CH{=}CH_2$ (4) $CH_2{=}CH_2$

5. Which of the following can be used as plasticisers?

(1) Sodium hexametaphosphate

(2) Di-n-butylphthalate

(3) Tricresyl phosphate

(4) Diethyl phthalate

6. Thermoplastic polymer are those

(1) That have ordered crystalline regions and amorphous noncrystalline regions both.
(2) That are hard at room temperature but on heating they become soft enough to be moulded
(3) That are used in combs, toys, light switch plates and telephone casting.
(4) None of these

7. Which is/are true regarding rayon?
(1) It is pure regenerated cellulose.
(2) It is obtained by dissolving wood pulp in alkaline CS_2.
(3) It is obtained by passing Na salt of cellulose xanthate through spinneret into aqueous $NaHNO_3$ solution.
(4) It is extracted as fibres of cellulose.

8. Which of the following statements is/are true?
(1) Natural rubber is a 1,4-polymer of isoprene.
(2) In vulcanization, the formation of sulphur bridges between different chains makes rubber harder and stronger.
(3) Natural rubber has the *trans*-configuration at every double bond.
(4) Buna-S is a copolymer of butadiene and styrene.

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I
(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

9. Statement I: Cellulose is not digested by human beings.
Statement II: Cellulose is a polymer of α-D glucose.

10. Statement I: Cellulose acetate is a semi-synthetic polymer.
Statement II: Chemical name of cellulose acetate polymer is rayon.

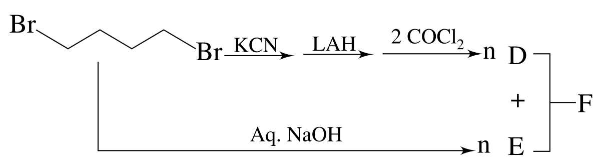
11. Statement I: Buta-1, 3-diene is the monomer of gutta-percha.
Statement II: Gutta-percha is formed through anionic addition polymerisation.

12. Statement I: Plexiglas is the commercial name of PMMA.
Statement II: It is used in making contact lens because it has an excellent light.

13. Statement I: PUF (polyurethane foam) is spongy.
Statement II: During the preparation of PUF, CO_2 is evolved, which forms bubbles that are trapped within the bulk of polymer. As it solidifies, it gives spongy product.

Comprehension Type Question

Passage based questions (Q. 14–16):



14. Compound D is
(1) $O{=}C{=}N(CH_2)_6\ N{=}C{=}O$
(2) $\overset{-}{C}{\equiv}\overset{+}{N}{-}(CH_2)_6\ \overset{+}{N}{\equiv}\overset{-}{C}$
(3) $O{=}C{=}N(CH_2)_4N{=}C{=}O$
(4) $\overset{-}{C}{\equiv}\overset{+}{N}{-}(CH_2)_4\ N{\equiv}C{=}O$

15. The polymer F is
(1) Polyurethane (2) Vinyon
(3) Perlon-L (4) Nylon-6

16. Which of the following groups does polymer F contain?
(1) Polyamide (2) Polyene
(3) Polycarbamate ester (4) Polyester

Column Matching Type Question

17. Match list I and II and select the correct answer using the codes given below the lists:

List-I	List-II
(A) Nylon	(1) Polyester
(B) Terylene	(2) Polytetra fluoroethylene
(C) Teflon	(3) Synthetic rubber
(D) Neoprene	(4) Polyamide

	A	B	C	D
(1)	2	3	1	4
(2)	2	3	4	1
(3)	4	1	3	2
(4)	4	1	2	3

18. Match the column I with Column II and mark the correct option from the codes given below.

	Column I		Column II
i.	Nylon-6 6	p.	Condensation polymerisation
ii.	Styrene	q.	Addition polymerisation
iii.	Nylon-6	r.	Homopolymer
iv.	Teflon	s.	Copolymer

Codes

	i	ii	iii	iv
(1)	p, s	q, r	p, r	q, r
(2)	q, r	p, q	r	s
(3)	q, s	p, q	s, q	r, s
(4)	s, r	q	s	p

19. Match the column I with Column II and mark the correct option from the codes given below.

	Column I		Column II
i.	HDPE	p.	An ester
ii.	Polypropene	q.	Reduction in % s-character
iii.	PVC	r.	Free radical addition polymerisation
iv.	Dacron	s.	Homopolymer

Codes

	i	ii	iii	iv
(1)	q, s	q, r, s	q, s	p
(2)	p	q, r	q	s
(3)	q	r, s	q	p
(4)	p	q, r	q	p

Single Digit Integer Type Question

20. How many of the following are condensation copolymers?

Nylon-6, nylon-66, Dacron, glyptal, buna-S, ABS, neoprene, PHBV, perlon-U.

EXERCISE 4

1. Monomers are converted to polymer by **(AIEEE 2002)**

(1) hydrolysis of monomers
(2) Condensation reaction between monomers
(3) Protonation of monomers
(4) None of the above

2. Nylon threads are made up of **(AIEEE 2003)**

(1) Polyvinyl polymer
(2) Polyester polymer
(3) Polyamide polymer
(4) Polyethylene polymer

3. Which of the following is a polyamide? **(AIEEE 2005)**

(1) Bakelite (2) Terylene
(3) Nylon-6 6 (4) Teflon

4. Which of the following is fully fluorinated polymer? **(AIEEE 2005)**

(1) PVC (2) Thiokol
(3) Teflon (4) Neoprene

5. Bakelite is obtained from phenol by reacting with **(AIEEE 2008)**

(1) $(CH_2OH)_2$ (2) CH_3CHO
(3) CH_3COCH_3 (4) HCHO

6. Buna-N synthetic rubber is a copolymer of **(AIEEE 2009)**

(1) $H_2C{=}CH{-}\underset{}{\overset{Cl}{\overset{|}{C}}}{=}CH_2$ and $H_2C{=}CH{-}CH{=}CH_2$
(2) $H_2CCH{-}CH{=}CH_2$ and $H_5C_6{-}CH{=}CH_2$
(3) $H_2C{=}CH{-}CN$ and $H_2C{=}CH{-}CH{-}CH{=}CH_2$
(4) $H_2C{=}CH{-}CN$ and $H_2C{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2$

7. The polymer containing strong intermolecular forces, e.g. hydrogen bonding, is **(AIEEE 2011)**

(1) teflon (2) nylon-66
(3) polystyrene (4) natural rubber

8. Thermosetting polymer, bakelite is formed by the reaction of phenol with **(AIEEE 2011)**

(1) CH_3CH_2CHO (2) CH_3CHO
(3) HCHO (4) HCOOH

9. The species which can best serve as an initiator for the cationic polymerisation is **(AIEEE 2012)**

(1) $LiAlH_4$ (2) HNO_3
(3) $AlCl_3$ (4) Bali

10. Which one is classified as a condensation polymer? **(JEE Main 2014)**

(1) Dacron (2) Neoprene
(3) Teflon (4) Acrylonitrile

11. Which polymer is used in the manufacture of paints and lacquers? **(JEE Main 2015)**

(1) Bakelite (2) Glyptal
(3) Polypropene (4) Polyvinyl chloride

12. The formation of which of the following polymers involves hydrolysis reaction? **(JEE Main 2017)**

(1) Nylon 6 (2) Bakelite
(3) Nylon 6, 6 (4) Terylene

13. Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH_3COCHO.

(JEE-Adv. 2005, Subjective Type)

(i) Deduce the structure of A.

(ii) Draw the structures of all *cis*/forms of polymer of compound A.

14. Match the chemical substances in column I with type of polymers/type of bond in Column II.

(JEE-Adv. 2007, Matching Type)

	Column I		Column II
i.	Cellulose	p.	Natural polymer
ii.	Nylon-6 6	q.	Synthetic polymer
iii.	Protein	r.	Amide linkage
iv.	Sucrose	s.	Glycoside linkage

Codes

	i	ii	iii	iv
(1)	s	p	q, s	q, r
(2)	p, s	q, r	p, r	s
(3)	s	p, s	q	r
(4)	p	q	s	r, s

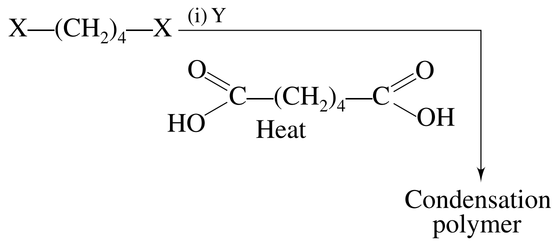
15. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is

(2009, Only One Option Correct Type)

(1) nylon (2) poly (vinyl chloride)
(3) cellulose (4) natural rubber

16. The correct functional group X and the reagent/reaction conditions Y in the following scheme are

(2011, One or More than One Options Correct Type)



(1) X = $COOCH_3$, Y = H_2/Ni/Heat
(2) X = $CONH_2$, Y = H_2/Ni/Heat
(3) X = $CONH_2$, Y = Br_2/NaOH
(4) X = CN, Y = H_2/Ni/Heat

ANSWER KEY

EXERCISE # 1

1. (3)	2. (2)	3. (3)	4. (1)	5. (1)
6. (1)	7. (4)	8. (3)	9. (1)	10. (1)
11. (1)	12. (3)	13. (4)	14. (4)	15. (1)
16. (2)	17. (3)	18. (3)	19. (1)	20. (3)

EXERCISE # 2

1. (3)	2. (3)	3. (4)	4. (4)	5. (4)
6. (4)	7. (3)	8. (3)	9. (1)	10. (1)
11. (4)	12. (1)	13. (2)	14. (4)	15. (2)

EXERCISE # 3

1. (1,4)	2. (2,4)	3. (1,2,3)	4. (2,3)	5. (2,3)
6. (1,2,3)	7. (1,2,4)	8. (1,2,4)	9. (3)	10. (2)
11. (4)	12. (1)	13. (1)	14. (1)	15. (1)
16. (3)	17. (4)	18. (1)	19. (1)	20. (5)

EXERCISE # 4

1. (2)	2. (3)	3. (3)	4. (3)	5. (4)
6. (3)	7. (2)	8. (3)	9. (3)	10. (1)
11. (2)	12. (1)	13. (*)	14. (2)	15. (4)
16. (1,2,3,4)				

HINT AND SOLUTION

EXERCISE # 1

1. [3]

Poly (methyl methacrylate) synthesised in laboratory so that it is synthetic polymer.

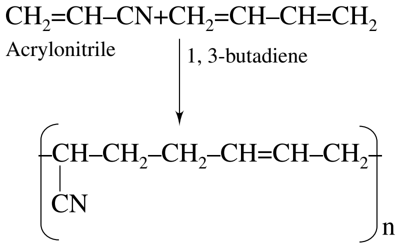
2. [2]

On vulcanisation, S introduces cross-links at the reactive sites of double bonds and makes the rubber stiffened, more elastic, and soluble in water solvents.

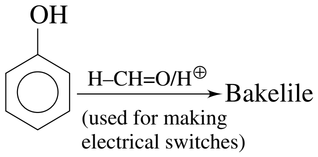
3. [3]

Plexiglas is addition polymer of poly (methyl methacrylate)

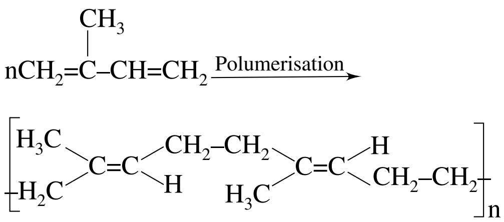
4. [1]



5. [1]



6. [1]



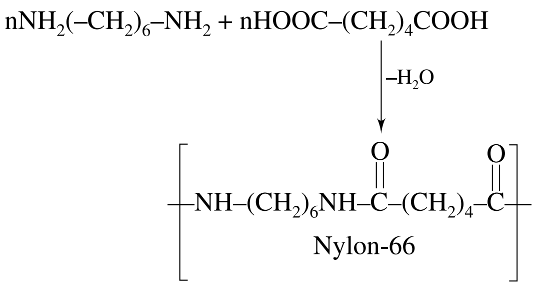
Teans-polyisoprene or gutta-percha
(soften on heating)

8. [4]

Fibres have quite strong interparticle forces such as H-bonds.

Nylon 6, 6 is an example of fibres.

9. [3]



In formation of nylon-66 loss of water molecule takes place so that it is condensation polymer.

10. [1]

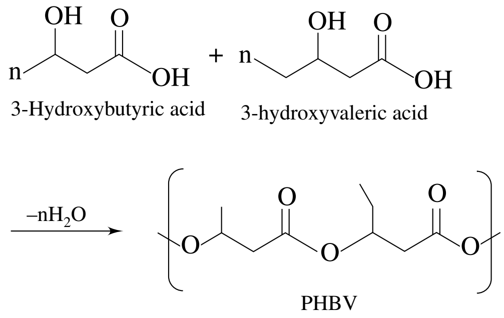
Teflon has the highest resistance to combustion

11. [1]

High density polyethylene (HDPE) can be prepared from ethylene by Ziegler–Natta process

12. [3]

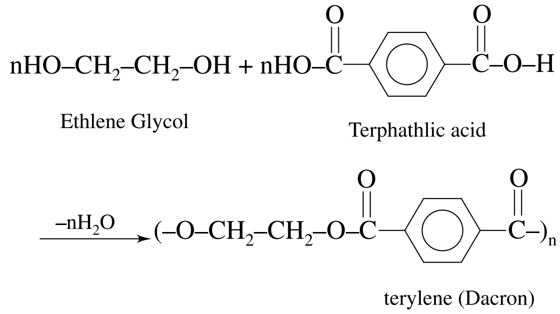
Polymer which are decomposed by biocatalyst known as biodegradable polymer



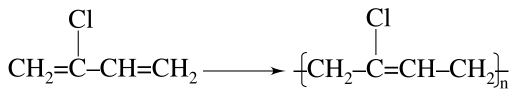
13. [4]

Acrilan is addition polymer of acrylo nitrile

14. [4]



15. [1]



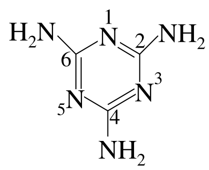
Chloroprene Neoprene

16. [2]

Cellulose is a natural polymer of β-D glucose

17. [3]

The structure of melamine is

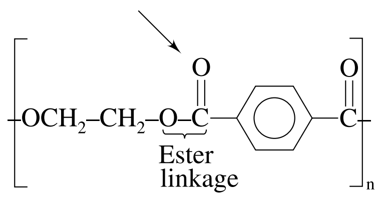


2,4,6-Triamino-1,3,5-triazine

18. [3]

Structure of terylene is

>C=O attached with the benzene ring.



19. [1]

$$\underset{\text{Acrylonitrile}}{nCH_2=CH-CN} \longrightarrow \underset{\text{acrilane}}{\left[CH_2-\underset{CN}{\underset{|}{C}}H_2 \right]_n}$$

20. [3]

PTFE $\rightarrow$ polytetraflouroethylene is used for lubrication and as an insulator

EXERCISE # 2

1. [3]

Thermoplastics are the plastics which become soft on heating and hard on cooling, i.e., they can be moulded again and again, e.g. PVC, polythene, PMMA, polystyrene. Polypropylene, Teflon, etc.

2. [3]

$$\underset{\text{Glycine}}{nH_2NCH_2\overset{O}{\overset{||}{C}}-OH} + \underset{\varepsilon\text{-Aminocaporic acid}}{nH_2N(CH_2)_5\overset{O}{\overset{||}{C}}-OH}$$

$$\xrightarrow{\text{heat}} \underset{\text{Nylon 2-nylon 6}}{\left[NHCH_2\overset{O}{\overset{||}{C}}-NH(CH_2)_5\overset{O}{\overset{||}{C}} \right]_n} + (2n-1)H_2O$$

3. [4]

In elastomers the polymer chains are held together by weakest intermolecular forces. These forces permit the polymer to be the stretched under stress but they regain their former shape when the stress is relieved.

e.g.: Natural rubber

4. [4]

Ebonite is highly vulcanised rubber.

5. [4]

Because of the presence of electron withdrawing F-atoms, $CF_2=CF_2$ undergoes anionic addition polymerisation. Others because of the absence of electron releasing or electron withdrawing groups are prepared by free radical polymerisation.

6. [4]

n mole of CaC_2 = n mole of C_2H_4 = n mole of $(-CH_2-CH_2-)$

n × 64 kg = n × 28 kg = n × 28 kg

$\rightarrow$ Amount of polyethene = 28 kg

7. [3]

It is a synthetic rubber made by the polymerisation of ethylene dichloride and sodium polysulphide.

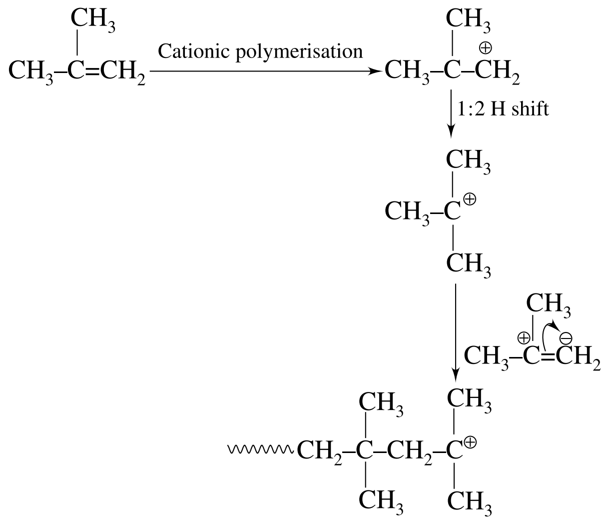
$$\left[CH_2 \diagdown S-S \diagup CH_2 \right]_n$$

Thiokol

8. [3]

Wash and wear clothes are manufactured using Terylene fibres.

9. [1]



10. [1]

Co-polymers are made up of more than one kind of monomer units. A few examples are given in the table below.

Polymer	Monomer units
SBR	Styrene + buta-1, 3-diene
Glyptal	Glycol + phthalic acid
Nylon-66	Adipic acid + hexamethylenediamine
Bakelite	Phenol + formaldehyde
Polyester	Acid + alcohol
Melmac	Melamine +HCHO

Polythene, PVC, nylon-6, butyl rubber, neoprene and Teflon all are homopolymers.

11. [4]

Polymerisation of propene using Ziegler–Natta catalyst yields isotactic polypropylene which has no chain branching. For this reason it has a crystalline structure with higher density and greater strength than the polypropylene produced by free-radical polymerisation.

12. [1]

BUNA-S $\rightarrow$ Elastomer , Nylon-66 $\rightarrow$ Fibre, Polythene $\rightarrow$ Thermoplastic

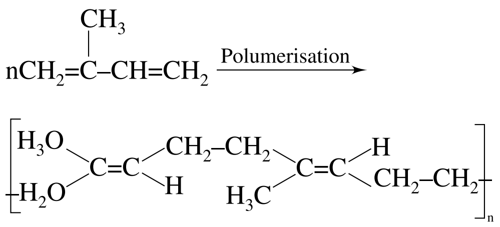
Order of intermolecular forces : Elastomer < Thermoplastic < Fibres

Thus Nylon-66(A) > Polythene (C) > BUNA-S(B)

13. [2]

Benzyl cation, anion and free radical all are stable species. So, it undergoes radical, cationic and anionic polymerisation with equal ease.

14. **[4]**



Teans-polyisoprene or gutta-percha
(soften on heating)

It is used for making underwater cables and golf balls.

15. **[2]**

Vulcanisation is a process of heating natural rubber with S. This brings about linking of polymer chains at various points of backbone through S–S linkage. This provides strength to

EXERCISE # 3

1. **[1,4]**

Polystyrene and PVC have forces intermediate of fibres and elastomers. Moreover, they can be remoulded. So, these are the examples of thermoplastics.

Bakelite and melmac because of the formation of stable cross-linked structure (on heating) are classified as thermosetting polymers.

2. **[2,4]**

Polymers degraded by microorganisms are called biodegradable polymers, e.g., PHBV, nylon-2-nylon-6, etc.

3.

Sol. **[1,2,3]**

Theory based

4. **[2,3]**

Compounds (olefins) in which two groups attached to the same carbon atom are different, give isotactic, syndiotactic or atactic forms when subjected to polymerisation.

5. **[2,3]**

The substance which lowers the melting point (softening point) of a polymer, thereby reducing the interparticle forces is called plasticiser, Generally, high boiling esters or haloalkanes are used for this purpose. Thus, di-n-butylphthalate and tricresyl phosphate are the examples of plasticisers.

6. **[**

Sol. **[1,2,3]**

Theory based.

7. **[1,2,4]**

When wood pulp is dissolved in CS_2, alkali solution, it gives sodium salt of cellulose xanthate, not the rayon. Other given statements are true.

8. **[1,2,4]**

Theory based (Refer key concept)

9. **[3]**

Theory based

10. **[2]**

Theory based

11. **[4]**

2-methylbuta-1, 3-diene (isoprene) is the monomer of gutta-percha. It is actually *trans*-polyisoprene unit.

Presence of electron releasing Me group makes it more reactive towards cationic polymerisation.

12. **[1]**

PMMA [poly (methhylmethacrylate)] is commercially called Plexiglas because it is hard and transparent, with excellent transmission property and hence, used for making contact lens.

13. **[1]**

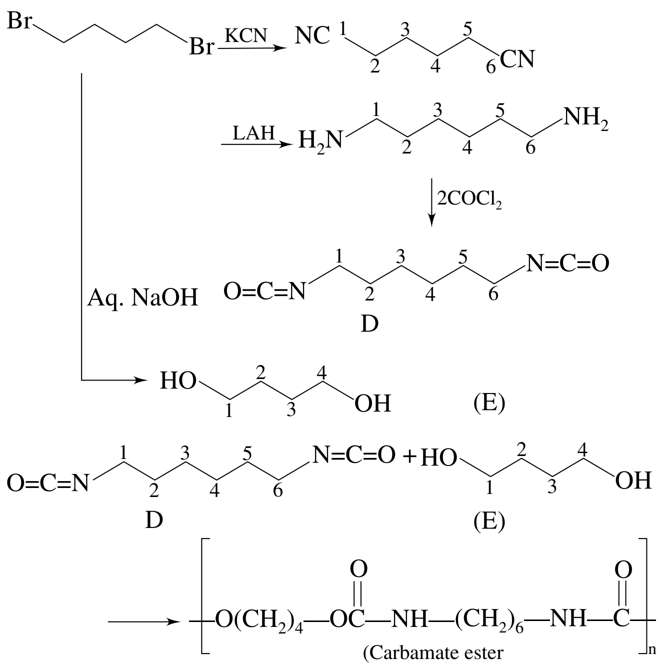
PUF is prepared by mixing a little water with diol. Some of the diisocyanate reacts with water to give carbamic acid, which spontaneously loses carbon dioxide to give an aromatic diamine. The CO_2 thus evolved forms bubbles that are trapped within the bulk of polymer. When it solidified, a spongy product PUF is formed.

14. **[1]**

15. **[1]**

16. **[3]**

Sol. **(Q. 14–16)**



(Carbamate ester
Or polyurethane
group) F
Polyurethane or perlon-U

17. [4]

Theory based

18. [1]

(i) → (p, s); (ii) → (q, r);

(iii) → (p, r); (iv) → (q, r)

Addition polymerisation involves no loss of small molecules which are lost in case of condensation polymerisation.

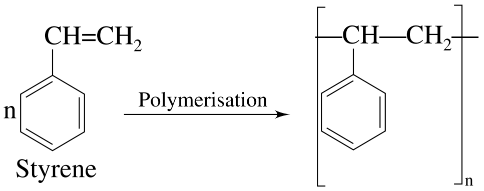
Homopolymers contain only one kind of monomer units while in case of copolymer, more than one kind of monomer unit is involved.

(i) $n\mathrm{NH_2(—CH_2)_6—NH_2 + nHOOC—(CH_2)_4COOH}$

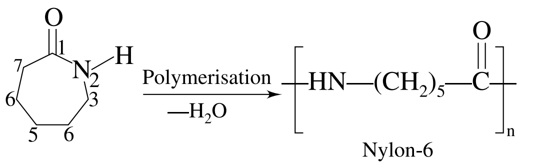
$$\xrightarrow{-\mathrm{H_2O}} \left[\mathrm{—HN—(CH_2)_6NH—\overset{O}{\overset{\|}{C}}—(CH_2)_4—\overset{O}{\overset{\|}{C}}—} \right]_n$$

Nylon-6, 6

So, it is a condensation copolymer.

(ii) 

Polystyrene or styrene
(Addition, homopolymer

(iii) 

Nylon-6
(Condensation homopoymer

(iv) $$\mathrm{n\,CF_2{=}CF_2} \xrightarrow{\text{Polymerisation}} \left[\mathrm{—\underset{F}{\overset{F}{C}}—\underset{F}{\overset{F}{C}}—} \right]_n$$

19. [1]

(i) → (q, s); (ii) → (q, r, s);

(iii) → (q, s); (iv) → (p)

$$\text{HDPE}\quad \mathrm{n(\overset{sp^2\ (s\text{-character } 33\%)}{CH_2{=}CH_2})} \longrightarrow \left[\mathrm{\overset{sp^3\ (s\text{-character } 25\%)}{—CH_2—CH_2—}} \right]_n$$

HDPE homopolymer

Polypropene same as HDPE, s-character decreases. It can be prepared by free radical mechanism, PVC is also a homopolymer in which (s)-character reduces Dacron or terylene is polyester (condensation copolymer).

20. [5]

Nylon-6 6, Dacron, glyptal, PHBV and perlon-U all are condensation copolymers.

EXERCISE # 4

1. [2]

Condensation is the process of aggregation of more than one molecule without losing any atom or group (sometimes smaller group or atoms H_2O, R—OH, etc., are released).

$$\underset{\text{Monomer}}{\mathrm{nCH_2{=}CH_2}} \longrightarrow \underset{\text{Polymer}}{\mathrm{—CH_2—(CH_2—CH_2)_n—CH_2—}}$$

2. [3]

Nylon threads are made up of polyamide. Some common are Nylon

6

$$\mathrm{H_2N—(CH_2)_5—\overset{O}{\overset{\|}{C}}—OH};\ \text{Monomer}$$

3. [3]

Nylon-66 is a polyamide of hexamethylene diamine $(CH_2)_6(NH_2)_2$ and adipic acid $(CH_2)_4(COOH)_2$. (Each reactant has six carbon chain, hence trade code 6, 6 is used.)

4. [3]

Teflon is $\left[\mathrm{—CF_2—CF_2—} \right]_n$.

5. [4]

Bakelite is obtained from phenol by reacting with HCHO in the acidic or alkaline medium.

6. [3]

Buna-N is actually abbreviated form, where Bu represents 1,3-butadiene, na represents Na, (sodium) and N represents nitrile (acrylonitrile).

Thus, buna-N is a copolymer of 1,3-butaidene and acrylonitrile usually polymerise in the presence of sodium.

7. [2]

Nylon-6 6 contains strong intermolecular forces like hydrogen bonds that are formed between $\mathrm{—\overset{O}{\overset{\|}{C}}—NH}$ group of successive chains.

8. [3]

Bakelite is a thermosetting polymer formed by the condensation reaction of phenol with HCHO in the presence of conc. H_2SO_4.

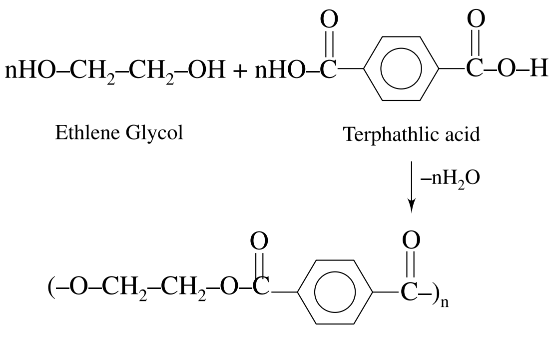
It is thus, a cross-linked polymer in which condensation takes place at o- and p-positons.

9. [3]

Electron-deficient species (Lewis acid) is used as an initiator for cationic polymerisation.

10. [1]

Dacron is a condensation polymer of ethylene glycol and methyl terephthalate.



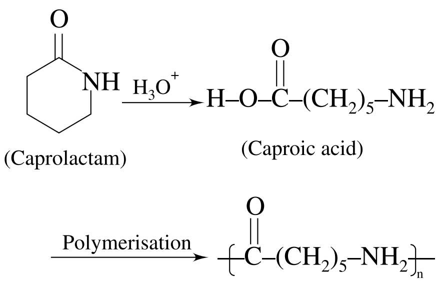
Terylene (Dacron)

11. [2]

Glyptal is used in the manufacture of paints and lacquers.

12. [1]

Caprolactam is hydrolysed to produce caproic acid which undergoes condensation to produce Nylon-6



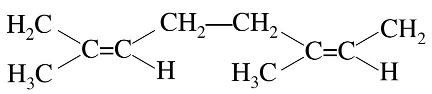
(Nylon-6)

13. (i)

$$H_2C{=}\underset{\text{Isoprene}}{C(CH_3)}{-}CH{=}CH_2 \xrightarrow[\text{Zn-}H_2O]{O_3} 2HCHO + CH_3{-}\overset{O}{\overset{\|}{C}}{-}CHO$$

Isoprene

(ii) Isoprene



Natural rubber

14. [2]

(i) Cellulose, a natural polymer of β-D-glucose, linked by glycoside linkage.

(ii) Nylon-6 6, a synthetic polymer of adipic acid and 1,6-diaminohexane. The diacid is linked with diamine through amide linkage.

(iii) Protein, a natural polymer of α-amino acids where individual amino acid units are linked by amide linkage.

(iv) Sucrose, has glycoside linkage, a disaccharide.

15. [4]

Cellulose and nylons have H-bonding type of intermolecular attraction while poly (vinyl chloride) is polar. Natural rubber is hydrocarbon and has the weakest intermolecular force of attraction, i.e. van der Waals' force of attraction.

16. [1,2,3,4]

(1) $CH_3OOC{-}(CH_2)_4{-}COOCH_3 \xrightarrow[\text{Heat}]{H_2/Ni}$

$HOCH_2{-}(CH_2)_4{-}CH_2OH{+}2CH_3OH$

$\xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH}$

$$\left[O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

Ester, (Condensation polymer)

(2) $H_2NOC{-}(CH_2)_4{-}CONH_2 \xrightarrow[\text{Heat}]{H_2/Ni} H_2N{-}(CH_2)_6$

$-NH_2 \xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH}$

$$\left[HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

Nylon, (Condensation polymer)

(3) $H_2NOC{-}(CH_2)_4{-}CONH_2 \xrightarrow[NaOH]{Br_2}$ Hofmann's bromamide reaction

$H_2N{-}(CH_2)_4{-}NH_2 \xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH}$

$$\left[HN-(CH_2)_4-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

Nylon, (Condensation polymer)

(4) When X = CN

$NC{-}(CH_2)_4{-}CN \xrightarrow[\text{Heat}]{H_2/Ni} H_2N{-}(CH_2)_6{-}NH_2$

$\xrightarrow[\text{Heat}]{HOOC-(CH_2)_4-COOH}$

$$\left[HN-(CH_2)_4-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

Nylon, (Condensation polymer)

CHAPTER 8

Chemistry in Everyday Life

1. DRUGS

Drugs are chemicals of low molecular masses (~100–500 u). These interact with macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these chemicals are called **medicines** and are used in diagnosis, prevention and treatment of diseases.

Use of chemicals for therapeutic effect is called **chemotherapy**.

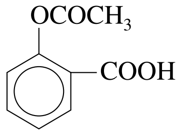
Classification of Medicines

Medicines are generally classified according to the purpose for which they are used. The different terms thus used along with examples are given below:

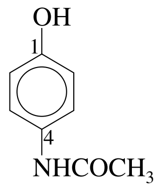
(i) Antipyretics: Chemicals which are used to bring down the body temperature during high fever are called antipyretics.

On taking these medicines, the person gets a lot of perspiration.

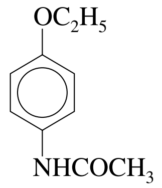
Examples: Aspirin, Phenacetin and Paracetamol



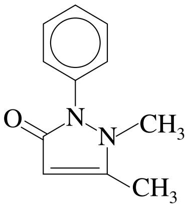
Aspirin (Acetylsalicylic acid)



Paracetamol (4-Acetamidophenol)



4-Ethoxyacetanilide (Phenacetin)



Analgin

Novalgin is another well-known antipyretic.

Quinine has also some antipyretic effect.

Paracetamol is preferred over aspirin as an antipyretic since aspirin gets hydrolysed to salicylic acid in the stomach. The salicylic acid thus produced may cause ulcer in the stomach walls where from the bleeding may take place.

(ii) Analgesics: Medicines used for getting relief from pain are called analgesics. There are of two types

(a) Narcotics and (b) Non-narcotics

(a) Narcotics

Drugs which produce sleep and unconsciousness are called narcotics.

These are mostly opium and marijuana plant products.

They cause addiction.

Example: Morphine, Heroin (Morphine diacetate), codeine, etc.

(b) Non-narcotics

They are less potent the narcotics.

They do not cause addiction.

- Aspirin, Paracetamol, Phenacetin and Novalgin act both as antipyretic as well as analgesic. They are quite effective and give immediate relief from pain and fever.
- Aspirin is also used for prevention of heart attacks as it has anti-blood clotting action.
- Novalgin is the most widely used analgesic.
- Some other analgesics are: butazoilidine and brufen or ibuprofen.

(iii) Antiseptics and Disinfectants:

(a) Antiseptics: The chemicals which kill or prevent the growth of micro-organisms are called **antiseptics.**

These are not harmful to living tissues and can be safely applied on wounds, cuts. There are also used to reduce odours resulting from bacterial decomposition of the body or in the mouth, thus they are mixed with deodorants, face powders and breath purifiers.

Common examples are:

(i) Cl_2 is used for making water fit for drinking at a concentration 0.2–0.4 ppm.

(ii) Dettol is an antiseptic. It is a mixture of chloroxylenol and terpenol in a suitable solvent.

(iii) Bithional is antiseptic which is generally added to medicated soaps to reduce the odour produced by bacterial decomposition of organic matter on the skin.

(iv) Iodine is powerful antiseptic. It is used as a tincture of iodine which is 2–3% iodine solution of alcohol–water.

(v) Some organic dyes are also effective antiseptics. These are used for the treatment of infectious disease. The common examples of antiseptic dyes are gentian violet and methylene blue.

(b) Disinfectants:

The chemical substances which are used to kill microorganisms

They cannot be applied on living tissues are called **disinfectants.**

These are commonly applied to inanimate objects such as floors, instruments, etc.

Example: Bleaching powder, chlorine, H_2O_2.

Note: The same substance can act disinfectant as well as antiseptic depending upon its concentration. For example, a 0.2% solution of phenol acts as antiseptic and is 1% solution acts as disinfectant.

(iv) Antimalarial: Chemical substances which are used to bring down the body temperature during malaria fever are called antimalarial drugs.

Originally quinine (an alkaloid) was the only drug known to be effective against malaria.

Now-a-days, a number of synthetic drugs are used for the purpose. These are Chloroquine, Paraquine, Primaquine, etc.

(v) Tranquilisers: Chemical substances used to cure mental disease are called tranquilisers.

These are used to release mental tension and reduce anxiety.

These are the constituents of sleeping pills. They act on higher centres of nervous system. These are also called **psychotherapeutic drugs.**

These drugs make the patient passive and help to control their emotional distress or depression.

These also help to restore confidence and the patients work with full capacities which they already have.

(a) Hypnotics: These are also known as tranquilisers and are used to reduce mental tension and anxiety.

These induce sleep.

These are components of sleeping pills (sedatives)

Example: Barbituric acid, Luminal, Seconal.

(b) Non-hypnotics: They reduce tension and anxiety.

(c) These do not induce sleep.

Equanil is also an important tranquilisers used in depression and hypertension.

(vi) Antidepressants: These drugs are given to patients with shattered confidence.

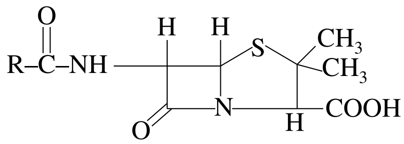
These produce a feeling of well-being and confidence in the person of depressed mood. Therefore, these are also called mood booster drugs.

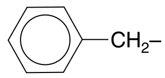
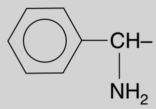
Common examples are Vitalin, Cocaine, Methedrine, etc.

(vii) Antibiotics: These are the chemical substance which are produced by micro-organisms (bacterial, fungi) They can inhibit the growth or even destroy other micro-organisms.

The first successful antibiotic produced was penicillin. It was discovered by Alexander Fleming in 1920. The general formula of penicillin in $C_9H_{11}O_4$ SN_2R where R may be different for different members. For example,

With the substitution of different R groups, about six natural penicillin have been isolated so far. For example**,**



Penicillin	Nature of R
Penicillin G or Benzyl penicillin	
Penicillin F	$CH_3–CH_2–CH=CH–CH_2–$
Penicillin K	$CH_3–(CH_2)_6–$
Ampicillin	

- Antibiotics can be broadly classified into two types:
  - **(i) Bactericidal:** Bactericidal antibiotics kill the microorganisms in the body. Some examples are: Penicillin, Ofloxacin, Aminoglycosides, etc.
  - **(ii) Bacteriostatic:** Bacteriostatic antibiotics inhibit or stop the growth of microorganisms in the body.

    Examples: Erythromycin, Tetracycline, Chloramphenicol.
- **Ampicillin and amoxicillin** are some modification of penicillin. It may be noted that many patients develop allergy to penicillin. Therefore, it is essential to test the patient for sensitivity (allergy) to penicillin before it is administered
- **Penicillin** has narrow spectrum. These can be used for curing sore throat, gonorrhoea, rheumatic fever, local infections, etc.
- **Streptomycin** is also an antibiotic used for the treatment of tuberculosis, meningitis, pneumonia, local infections, etc.
- **Broad spectrum antibiotics:** These are the antibiotics which are effective against several different types of harmful microorganisms and thus, Capable of curing several infections are called broad spectrum antibiotics.

  Examples: Tetracycline, Chloromycetin and Chloramphenicol.

  Ampicillin and Amoxicillin have broad spectrum.

(viii) Germicides: These are the chemical substances used to kill germs, fungi and virus.

The common examples of germicides are phenol, cresol, formaldehyde, DDT, potassium permanganate solution, (1%) chlorine, bleaching power, hydrogen peroxide, etc.

(ix) Anti-fertility drugs: Chemical substances which are used to cheek pregnancy in women are called anti-fertility drugs or birth control drugs or oral contraceptives.

All these drugs contain chemicals related to female sex hormones having a steroid ring structure. Most of these contain a combination of an oestrogen and progesterone. For example, a common brand name, Enovid E, contains norethindrone (a progestin) mestranol or ethenylestradiol monomethyl ether (an oestrogen). All such drugs are expected to have side effects and hence should be used only under proper medical advice.

(x) Antihistamines: The drugs which have been used to fight allergy are called **antihistamines.**

These are so called because they check the production of histamines. Thus, antihistamines are widely used for treatment to hay fever, conjunctivitis, nasal discharges, irradiation sickness, motion sickness (air, sea, and road), and nausea in pregnancy and post-operative vomiting.

The antihistamine drugs which are widely used are diphenlhydramine hydrochloride, Cetirizine, Chloropheniramine, Promethazine hydrochloride, etc. The structure of some of these are given below

(xi) Antacids:

Antacids are substances that decrease gastric acidity by neutralising hydrochloric acid. They are compared quantitatively in terms of their acid-neutralising capacity.

These usually contain salts of Al, Mg and Na. These are of the following two types:

(a) Systemic antacid (b) Non-systemic antacid

(a) Systemic antacids:

Systemic antacids like sodium bicarbonate decrease acidity but cause systemic alkalosis due to absorption of bicarbonate. Hence acid-base balance is disturbed. Further excess sodium may cause oedema and cardiac failure in patients with renal or cardiac dysfunction.

(b) Non-systemic antacids: These may contain one or more of the following compounds: $Al(OH)_3$, $Mg(OH)_2$, $MgCO_3$, $CaCO_3$, magnesium trisilicate, magaldrate, etc. These antacids are not absorbed after administration and hence acid-base imbalance is minimal

(xii) Sulpha drugs: These have great antibacterial powers and are used as medicines for various diseases. These are also antibiotics and protect the body against micro-organisms.

These are used against diseases such as pneumonia, tuberculosis, diphtheria, etc. Some important sulpha drugs are sulphadiazine, sulphanilamide, etc.

2. CLEANSING AGENTS

Soaps

(a) Sodium salts of higher fatty acids (fatty acids with number of carbon atoms more than a certain threshold) like stearic acid, oleic acid, palmitic acid, etc. are called hard soaps and the potassium salts of these fatty acids are called soft soaps.

(b) Soaps are prepared by hydrolysis of higher fatty acids.

(c) A higher proportion of salts of saturated acids (palmitic, stearic, etc.) gives hard soaps, while a higher proportion of salts of unsaturated acids (oleic acid) yields soft soaps.

(d) Alkaline hydrolysis of oils or fats by NaOH or KOH gives glycerol and sodium or potassium salt of the fatty acid. This reaction is known as saponification.

$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} \\ | \\ CH_2OCOC_{17}H_{35} \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3C_{17}H_{35}COONa \text{ (sodium stearate)}$$

Types of soaps:

(a) Hard soaps: These are obtained from cheap oils and fats using sodium hydroxide. These contains free alkali and are used for washing purposes.

(b) Soft soaps: These are obtained from good oils using potassium hydroxide. These do not contain free alkali and are used as toilet soaps, shaving cream, in shaving sticks and shampoo.

(c) Transparent soaps: These are formed by dissolving toilet soaps in alcohol and evaporating the filtrate. They contain glycerol.

(d) Medicated soaps: Toilet soaps containing some medicinal important substance are called medicated soaps.

(e) Metallic soaps: These are soaps of metals other than sodium and potassium.

Cleansing Action of Soap: When soap is rubbed with the greasy surface of clothes with water, it forms an emulsion and the dirt particles separate out form the greasy surface. Soap forms colloidal solution with water, which separate the dirt particles by absorbing them and escape out on washing with water.

Synthetic Detergents

Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap.

These can be used both in soft and hard water as they give foam even in hard water.

Some of the detergents give foam even in ice cold water.

The synthetic detergents, soap-less detergents, soap-less soaps and syndets are substitutes of soaps. Unlike soaps, they are derived from purely synthetic chemicals rather than from chemicals obtained from natural sources like oils/fats. However, like soaps they contain both hydrophilic (water-soluble) and hydrophobic (oil-soluble) parts.

Types of detergents:

Detergents are of three types

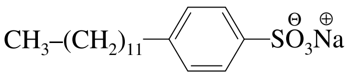
(i) Anionic detergent: These are so called because a large part of their molecules are anions. These are of two types.

(a) Sodium alkyl sulphates

Example: sodium lauryl sulphate ($C_{11}H_{23}CH_2OSO_3Na^+$)

$$\underset{\text{n-Lauryl alcohol}}{C_{11}H_{23}CH_2OH} \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\text{n-Lauryl hydrogen sulphate}}{C_{11}H_{23}CH_2OSO_3H} \xrightarrow{\text{NaOH}} \underset{\text{Sodium lauryl sulphate}}{C_{11}H_{23}CH_2OS\overset{\ominus}{O_3}\overset{\oplus}{Na}}$$

(b) Alkylbenzenesulphonates

Example:  sodium 4-(1-dodecyl) benzenesulphonate (SDS)

(ii) Cationic detergents:

Example: $[CH_3(CH_2)_{15}\overset{\oplus}{N}(CH_3)_3]\overset{\ominus}{Br}$ or $\left[CH_3-(CH_2)_{15}-\overset{\oplus}{N}(CH_3)_2-CH_3\right]\overset{\ominus}{Br}$

Cetyltrimethylammonim bromide
(Cationic detergent used in hair conditioner)

(iii) Non-ionic detergents:

Example: $CH_3(CH_3)_{16}COO(CH_2CH_2)_nCH_2CHO$

3. CHEMICALS IN FOOD

Preservatives

Such chemical substance which are added to food materials to prevent their spoilage are known as chemical preservatives.

In our country, two chemical preservatives are permitted for use.

(i) Benzoic acid (or sodium benzoate)

(ii) Potassium metabisulphite or sodium metabisulphite.

- The substance which is capable of inhibiting or arresting the process of fermentation, acidification or any other decomposition of the food

Antioxidants: Antioxidants are added to the food to retard the action of oxygen on the food.

In order to prevent rancidity antioxidants are added to oils and fats.

- Butylated hydroxyanisole (BHA) and butylated hydroxyl toluene (BHT) is a widely used antioxidant to preserve edible oils, fats, butter, etc.
- Vitamin E is a natural antioxidant.
- Ascorbic acid and citric acid also have antioxidant effect thus they are used as preservatives due to their effect on enzymes present in food.

- Sodium sulphite and calcium propionate and used as preservatives because they inhibit the growth of micro-organisms in the food.
- Sulphur dioxide and $K_2S_2O_5$ (potassium metabisulphite) are useful antioxidants for wine and beers.

Artificial Sweetening Agents: Sugar or sucrose is the natural sweetening agent. However, excess consumption of sugar leads to many diseases such as obesity, diabetes, coronary heart disease.

- Chemical which are used as substitutes for sugar in the food are called artificial sweetening agents.
- They are very helpful for diabetic patients.
- They are also low caloric substances.
- Some of the most common artificial sweetening agents are:

  (i) Saccharin (Ortho-sulphobenzimide)

  It was the first such sweetener used.

  It is 550 times sweeter than cane sugar or sucrose.

  (ii) Aspartame

  It is methyl ester of the dipeptide aspartyl phenylalanine.

  It is about 100 times sweeter than sucrose.

  It is unstable to heat and therefore, it can be used as a sugar substitute in cold drinks and cold foods only.

  (iii) Alitame

  It is about 2000 times sweeter than sucrose.

  It is more stable to heat than aspartame.

  Since Alitame is a high potency sweetener, it is difficult to control sweetness of food while using this sweetener.

  (iv) Sucralose

  It is a trichloro derivative of sucrose.

  Its appearance and taste are just like sugar.

  It is about 600 times sweeter than sucrose. It is stable at cooking temperature.

  It does not provide calories.

  Note: The use of **cyclamates** as sweetening agent has been banned in many countries in view of suspected carcinogenic effects.

SOLVED EXAMPLE

1. Which of the following chemicals can be added for sweetening of food items at cooking temperature and does not provide calories?

(1) Sucrose (2) Glucose

(3) Aspartame (4) Sucralose

Sol. **[4]**

Sucralose is a sweetening agent with zero calorific value and can be used at cooking temperature. It is a derivative of sucrose (Aspartame is also sweetening agent but is decomposed at cooking temperature).

2. Which of the following is a bacteriostatic?

(1) Penicillin (2) Erythromycin

(3) Aminoglycoside (4) Ofloxacin

Sol. **[2]**

Antibiotics have either cidal (killing) effect or static.

3. Structurally biodegradable detergent should contain

(1) Normal alkyl chain

(2) Branched alkyl chain

(3) Phenyl side chain

(4) Cyclohexyl side chain

Sol. **[3]**

Detergents with straight chain alkyl groups are biodegradable.

4. Which of the following can possibly be used as analgesic without causing addiction and modification?

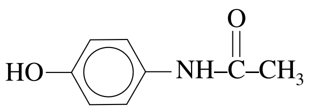
(1) Morphine

(2) N-Acetyl-para-aminophenol

(3) Diazepam

(4) Tetrahydrocatenol

Sol. **[2]**



N-acetyl-para-aminophenol can be used as an analgesic without causing addiction and modification. It is non-narcotic analgesic.

5. Which of the following enhances lathering property of soap?

(1) Sodium carbonate (2) Sodium rosinate
(3) Sodium stearate (4) Trisodium phosphate

Sol. **[2]**

Sodium rosinate is added to soap to enhance its lathering property.

6. Glycerol is added to soap. It functions:

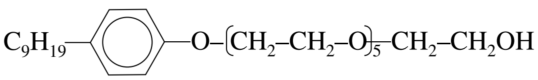
(1) As a filler
(2) To increase lathering
(3) To prevent rapid drying
(4) To make soap granules

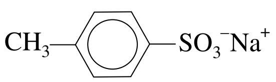
Sol. **[3]**

Soap can be prevented from rapid drying by glycerol. Glycerol (by product of soap industry) is not separated from soap to prevent it making hard.

7. Which of the following is an example of liquid dishwashing detergent?

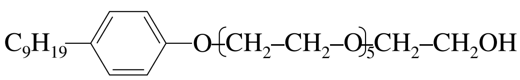
(1) $CH_3(CH_2)_{10}-CH_2OSO_3^-Na^+$

(2) 

(3) 

(4) $\left[CH_3-(CH_2)_{15}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-CH_3\right]^+ Br^-$

Sol. **[2]**



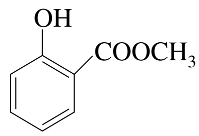
It is non-ionogenic surfactant used as liquid dishwashing detergent. These do not ionise.

8. The active chemical present in Iodex which gives relief from pain in sciatica and rheumatism is:

(1) o-hydroxybenzoic acid
(2) acetylsalicylic acid
(3) methyl salicylate
(4) ethyl salicylate

Sol. **[3]**

Methyl salicylate is the constituent of iodex.



It is also called oil at winter green

9. Dettol, an antiseptic, consists of:

(1) cresol and ethanol
(2) xylenol and terpineol
(3) chloroxylenol and terpineol
(4) phenol and cresol

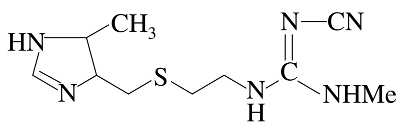
Sol. **[3]**

Dettol, an antiseptic, consists of chloroxylenol and terpineol.

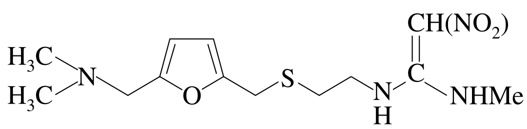
10. Select the correct statement(s) about cimetidine and ranitidine.

(1) These are antihistamine drugs
(2) These prevent the excess production of HCl in the stomach
(3) Both prevent the interaction between histamine and receptor of stomach wall
(4) All of the above are correct statements

Sol. **[4]**



Cimetidine



(1) Both are antihistamine drugs.
(2) and
(3) They prevent the interaction of histamine with the receptors present in the stomach wall and thus lesser HCl is formed.

EXERCISE 1

1. Select the correct statement(s).

(1) The antibiotics which are effective mainly against gram-positive or gram-negative bacteria are called narrow-spectrum antibiotics

(2) The antibiotics which kill or inhibit a wide range of gram-positive or gram-negative bacteria are called broad-spectrum antibiotics

(3) Penicillin G is a narrow-spectrum antibiotic while ofloxacin is a broad-spectrum antibiotics

(4) All of the above

2. Which one of the following is employed as antihistamine (anti-allergic)?

(1) Diphenylhydramine (2) Chlorpheniramine

(3) Promethazine (4) All of these

3. Which of the following statements is not correct?

(1) Allergic conditions are cured by antihistamines

(2) Hormones are continuously produced but not stored in the body

(3) The function of the white blood cells is to protect the body against infections

(4) Catabolism involves degradation of molecules

4. The oxidant which is used as antiseptic is

(1) $KBrO_3$ (2) $KMnO_4$

(3) CrO_3 (4) KNO_3

5. Which of the following analgesics are toxic to liver?

(1) Aspirin

(2) Naproxen

(3) Both Aspirin and Naproxen

(4) None of these

6. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following is not true.

(1) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant

(2) Chlorine and iodine are used as strong disinfectants

(3) Dilute solutions of boric acid and hydrogen peroxides are strong antiseptics

(4) Disinfectants harm the living tissue

7. Consider the following statements.

I. 0.2 to 0.4 ppm Cl_2 solution is used as disinfectant for drinking water.

II. Many body secretions either kill the microbes or inhibit their growth.

III. Body possesses an efficient natural defence mechanism which operates at all times against potential pathogenic microbes.

Select the correct statements.

(1) I, II and III (2) Both I and III

(3) Both II and III (4) Both I and II

8. A newer family of effective lactams antibiotics is

(1) Ampicillin (2) Amoxicillin

(3) Cephalosporins (4) Phenobarbital

9. $-COOH$ is not present as one of the functional groups in

(1) Ascorbic acid (2) Aspartame

(3) Ibuprofen (4) All of these

10. Among:

I. $CHCl_3$

II. CHI_3

III. Boric acid

IV. 0.3 ppm aqueous solution of Cl_2.

antiseptic properties are in

(1) Both II and III (2) Both III and IV

(3) Both I and II (4) II, III and IV

11. Aspirin is used to cure Alzheimer's disease which is caused by

(1) Al^{3+} (2) Mg^{2+}

(3) Fe^{3+} (4) All of these

12. Which is not the correct matching of medicine with its disease/activity?

(1) Aspirin - pain reliever

(2) Equanil - hypertension

(3) Chloramphenicol - typhoid

(4) 0.2 per cent phenol - disinfectant

13. Select True (T) and False (F) statements about tranquilisers and select the answer from the codes given.

I. Tranquilisers are narcotic drugs.

II. Some function by inhibiting the enzymes which catalyse the degradation of noradrenaline.

III. Are chemical compounds that can relieve pain and fever.

IV. Do not affect the message transfer from nerve to receptor.

Codes:

	I	II	III	IV
(1)	T	F	T	F
(2)	F	T	F	T
(3)	T	F	T	T
(4)	F	F	T	T

14. Which is the correct statement about birth control pills?
(1) Contain oestrogen only
(2) Contain progesterone only
(3) Contain a mixture of oestrogen and progesterone derivatives
(4) Progesterone enhances ovulation

15. Veronal and luminal are the derivatives of barbituric acid which are
(1) Tranquilisers
(2) Neurologically active drugs
(3) Both Tranqulisers and Neurologically active drugs
(4) None of these

16. Functional groups present in paracetamol are
(1) Alcoholic, acetylamine
(2) Phenolic, amine
(3) Phenolic, acetylamine
(4) Alcoholic, amine

17. Which of the acid is formed in the stomach and is responsible for acidity?
(1) H_2CO_3 (2) HCl
(3) H_2SO_3 (4) CH_3COOH

18. Sodium metabisulphite ($Na_2S_2O_5$) is preservative for food products such as jams, squashes, pickles, etc. It is easily converted into
(1) SO_2 and H_2SO_3 (2) Na_2SO_4 and H_2SO_4
(3) SO_3 and H_2SO_4 (4) $Na_2S_2O_3$ and $H_2S_2O_3$

19. Arsenic drugs are mainly used in the treatment of
(1) Jaundice (2) Typhoid
(3) Syphilis (4) Cholera

20. Which of the following will not enhance nutritional value of food?
(1) Carbohydrates (2) Proteins
(3) Artificial sweeteners (4) Vitamins

21. Among
I. Table salt II. Sodium bicarbonate
III. Cane sugar IV. Benzoic acid
Food preservatives are
(1) Both I and IV (2) Both II and III
(3) Both I and III (4) Both II and IV

22. Which is not an artificial sweetener?
(1) Saccharin (2) Cyclamate
(3) Aspartame (4) Saccharic acid

23. Antioxidants for wine, beers, sugar syrups, peeled fruits and vegetables are
(1) BHA (2) BHT
(3) Na_2SO_3/SO_2 (4) All of these

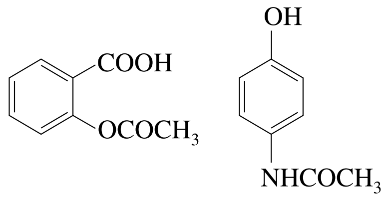
24. Relative sweeteners value (in comparison to sucrose) of the following artificial sweetener is
I. Saccharin II. Cyclamate
III. Duclin IV. Aspartame
V. Sucralose VI. Alitame
(1) I < II < III < IV < V < VI
(2) VI < V < IV < III < II < I
(3) I < III < V < IV < VI < II
(4) II < III < I < IV < V < VI

25. Which set has different class of drugs?
(1) **Analgesics** Aspirin, Naproxen, Ibuprofen, Dichlorofenan sodium
(2) **Tranquilisers** Barbiturates, Equanil, Valium, Meprobamate
(3) **Antiseptics** Chlorine, Dettol, Bithional, Boric acid
(4) **Antibiotics** Penicillin, Iodoform, Hydrogen peroxide, Serotonin

EXERCISE 2

1. Which group of class has not the correct examples of drugs/medicines?
(1) **Tranquilisers** Barbiturates, Equanil, Valium
(2) **Antibiotics** Sulphanilamide, Sulphadiazine, Sulphaguanidine
(3) **Antacids** Omeprazole, Lansoprazole, Sodium bicarbonate
(4) **Anaesthetics** Nitrogen dioxide, Ether, Halothane

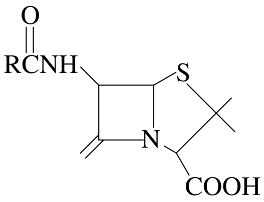
2. Among the following

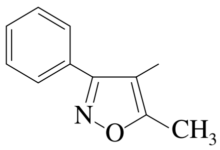
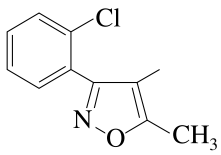


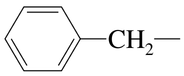
I. (aspirin) II. (acetoaminophen)

pain-killers are
(1) Both I and II (2) Only II
(3) Only I (4) None

3. Penicillin is called oxacillin if R is



(1)  (2) 

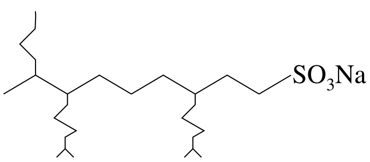
(3) $H_2C{=}CHCH_2SCH_2–$ (4) 

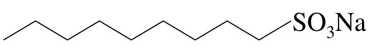
4. Aspartame is an artificial sweetener having the following functional groups
(1) Ester, peptide, amino, carboxyl
(2) Hydroxy, keto, methoxy
(3) Ester, peptide, keto, amino
(4) None of the above

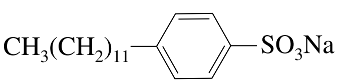
5. Antioxidants are added to many foods to prevent auto-oxidation and spoilage and allow long term storage. They function by
(1) Interrupting the chain reaction of autoxidation process
(2) Metabolising the autoxidation process
(3) Attacking active sites of autoxidation
(4) All of the above

6. Which of the following artificial sweetener will give blood red colour with $FeCl_3$ in Lassaigne's test?
(1) Saccharin (2) Cyclamate
(3) Alitame (4) All of these

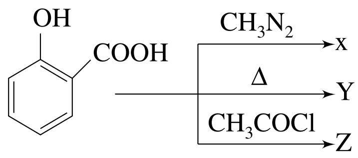
7. Which detergent can cause maximum pollution?

(1) 

(2) 

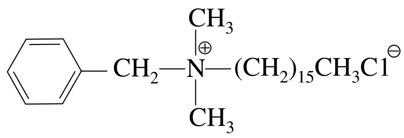
(3) 

(4) Every detergent is non-pollutant

8. 

Select the correct statements about X, Y and Z.
(1) X is used as pain-reliever in iodex
(2) Y is used as intestinal antiseptic for throat ailment
(3) Z is used as an analgesic
(4) All of the above are correct statements

9. Out of the following which is not a detergent?

(1) 

(2) $CH_3(CH_2)_{15}—\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}}—(CH_3Cl^{\ominus}$

(3) $CH_3(CH_2)_{16}\overset{O}{\overset{\|}{C}}ONa$

(4) $RCH_2(OCH_2CH_2)_nOH$

10. Hard water contains Mg^{2+} and Ca^{2+}. Which are added to detergents to complex these cations?
(1) Phosphates and silicates
(2) Sulphates and phosphates
(3) EDTA and silicates
(4) Carbonates and bicarbonates

11. Micelles from the ionic surfactants can be formed only above a certain temperature called
(1) Kraft temperature (2) Critical temperature
(3) Reduced temperature (4) Boyle's temperature

12. Among the following statements, which one is not correct?
(1) Aspirin in both an analgesic and an antipyretic
(2) Ampicillin is a natural antibiotic
(3) Sulphadiazine is a synthetic antibacterial
(4) Some disinfectants can be used as antiseptics at low concentration

13. Which of the following is used as an anaesthetic, particularly by the dentists?
(1) N_2 (2) N_2O
(3) CH_4 (4) CO_2

14. The commonly used analgesic that does not lead to addiction is:
(1) morphine
(2) pethidine
(3) diazepam
(4) N-acetyl-*p*-aminophenol

15. Which of the following is an antipyretic?
(1) Quinine (2) Luminal
(3) Paracetamol (4) Piperazine

16. Which of the following is not used as an antacid?
(1) Aluminium hydroxide gel
(2) Omeprazole
(3) Lansoprazole
(4) Codeine

17. Among the following which one is used as a painkiller?
(1) Mepacrine (2) Tetracycline
(3) Ibuprofen (4) Chlorambucil

18. A propellant for rocket engine usually consists of a fuel and an oxidiser. Which of the following combinations may serve as a liquid propellant of rocket engines?
(1) Hydrazine and liquid oxygen
(2) Hydrazine and liquid hydrogen
(3) Nitric acid and liquid oxygen
(4) Alcohol and hydrazine

19. Which of the following antibiotics are bactericidal in nature?
(I) Penicillin (II) Ofloxacin
(III) Chloramphenicol (IV) Erythromycin
Select correct code
(1) I, II (2) II, III
(3) III, IV (4) I, IV

20. Which of the following compounds is an antiseptic?
(1) Chloramphenicol (2) Streptomycin
(3) Furacin (4) Erythromycin

EXERCISE 3

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I
(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I
(3) If Statement-I is correct and Statement-II is incorrect
(4) If Statement-I is incorrect and Statement-II is correct

1. Statement I: Cimetidine and ranitidine are better antacids than $NaHCO_3$.

Statement II: Cimetidine and ranitidine prevent the interaction of histamine with the receptors present in the stomach wall, and thus results in the release of lesser amount of acid.

2. Statement I: Pickles have a long shelf life and do not get spoiled for months.

Statement II: Plenty of salt and cover of oil act as preservative.

3. Statement I: Preservatives are added to food items.

Statement II: Preservatives inhibit the growth of microorganisms.

4. Statement I: Sodium chloride is added to precipitate soap after saponification,

Statement II: Hydrolysis of esters of long chain fatty acids by alkali produces soap in colloidal form.

5. Statement I: Aspirin has been used in the prevention of heart attack.

Statement II: Aspirin has anti-blood clotting action.

6. Statement I: Bithional is added to soap to impart antiseptic property.

Statement II: It eliminates undesirable odours resulting from bacterial decomposition of organic matter on the skin.

7. Statement I: Aspirin can cause ulcer in stomach when taken empty stomach

Statement II: Aspirin prevents platelet coagulation as it has anti blood clotting action.

8. Statement I: Detergents are preferred to soaps for washing purposes.

Statement II: Detergents are non-biodegradable.

Column Matching Type Question

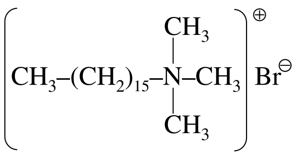
9. Match the compounds in Column I with their nature in column II and select answer from codes given below.

	Column I		Column II
i.	Saccharin	p.	Appearance and taste as sugar
ii.	Alitame	q.	Unstable at cooking
iii.	Aspartame	r.	No calorific value and entirely in cut.
iv.	Sucralose	s.	Difficult to control its sweetness.

Codes:

	i	ii	iii	iv
(1)	p	q	r	s
(2)	s	p	q	r
(3)	p	s	q	r
(4)	s	q	r	p

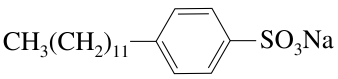
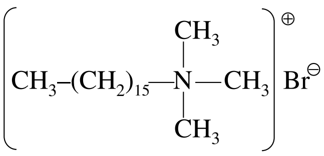
10. Match structures given in Column I with their classifications given in Column II and select answer from the codes given below.

Column I	Column II
i. $C_{17}H_{35}COO^{-}Na^{+}$	**p.** Cationic detergent
ii. $CH_3(CH_2)_{10}CH_2SO_3^{-}Na^{+}$	**q.** Anionic detergent
iii. 	**r.** Non-ionic detergent
iv. $CH_3(CH_2)_{16}COO(CH_2CH_2O)_xCH_2CH_2OH$	**s.** Soap

Codes:

	i	ii	iii	iv
(1)	p	q	s	r
(2)	p	s	q	r
(3)	s	q	p	r
(4)	r	s	p	q

11. Match the detergents in Column I with their uses in Column II.

Column I	Column II
i. 	**p.** Laundry soap
ii. $C_{17}H_{35}COONa$ + Rosin + Na_2CO_3	**q.** Dishwashing powder
iii. $CH_3(CH_2)_{16}COO(CH_2CH_2O)_x$ CH_2CH_2OH	**r.** Non-ionic detergent
iv. 	**s.** Toothpaste

Codes:

	i	ii	iii	iv
(1)	p	s	r	q
(2)	s	p	q	r
(3)	r	s	q	p
(4)	q	s	p	r

12. Match the terms in Column I with their definitions in Column II and select the answer from the codes given.

Column I		Column II	
i.	Antiseptic	p.	A drug that kills the organism of the body.
ii	Bacteriostatic	q.	That either kills or prevents the growth of micro-oganisms.
iii.	Bactericidal	r.	They kill the micro-organism
iv.	Disinfectant	s.	A substance that prevents the normal growth of micro-organisms

Codes:

	i	**ii**	**iii**	**iv**
(1)	p	q	r	s
(2)	q	s	p	r
(3)	r	p	q	s
(4)	s	q	p	r

13. Match the drugs in Column I with their activities in Column II and select the answer from the codes given.

Column I		Column II	
i.	Paracetamol	p.	Anti-pyretics
ii.	Chloramphenicol	q.	Anti-diabetic
iii.	Bithinol	r.	Antibiotic
iv.	Insulin	s.	Antiseptic

Codes:

	i	**ii**	**iii**	**iv**
(1)	p	r	s	q
(2)	p	r	q	s
(3)	q	r	p	s
(4)	r	q	s	p

14. Match the medicines given in Column-I with their types given in Column-II

Column-I	Column-II	
(a) Phenelzine	(p)	Non-narcotic analgesic
(b) Aspirin	(q)	Antifertility drug
(c) Morphine	(r)	Antidepressant drug
(d) Norethindrone	(s)	Narcotic analgesic

(1) a → r; b → s; c → q; d → p

(2) a → r; b → p; c → s; d → q

(3) a → p; b → r; c → s; d → q

(4) a → r; b → p; c → q; d → s

15. Match the following:

(i)	Malachite green	(a)	Antiseptic
(ii)	Terramycin	(b)	Basic dye
(iii)	Iodine	(c)	Acidic dye
(iv)	Martius yellow	(d)	Antibiotic

(1) (i) – (c), (ii) – (d), (iii) – (a), (iv) – (b)

(2) (i) – (b), (ii) – (a), (iii) – (d), (iv) – (c)

(3) (i) – (b), (ii) – (d), (iii) – (a), (iv) – (c)

(4) (i) – (c), (ii) – (a), (iii) – (d), (iv) – (b)

EXERCISE 4

1. Which of the following could act as a propellant for rockets? **(AIEEE 2003)**

(1) Liquid hydrogen + liquid nitrogen

(2) Liquid oxygen + liquid argon

(3) Liquid hydrogen + liquid oxygen

(4) Liquid nitrogen + liquid oxygen

2. Which one of the following types of drugs reduces fever? **(AIEEE 2005)**

(1) Tranquiliser (2) Antibiotic

(3) Antipyretic (4) Analgesic

3. Which of the following compounds is not an antacid? **(JEE Main 2015)**

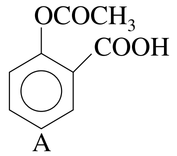
(1) Aluminium hydroxide

(2) Cimetidine

(3) Phenelzine

(4) Ranitidine

4. Compound A given below is **(AIEEE 2002, JEE Main 2015)**



A

(1) Antiseptic (2) Antibiotic

(3) Analgesic (4) Pesticide

5. Which of the following is an anionic detergent? **[JEE Main 2016]**

(1) Sodium lauryl sulphate

(2) cetyltrimethyl ammonium boromide

(3) Glyceryl oleate

(4) Sodium stearate

ANSWER KEY

EXERCISE # 1

1. (4)	2. (4)	3. (2)	4. (2)	5. (3)
6. (3)	7. (1)	8. (1)	9. (1)	10. (4)
11. (1)	12. (4)	13. (3)	14. (3)	15. (3)
16. (3)	17. (2)	18. (1)	19. (3)	20. (3)
21. (4)	22. (4)	23. (3)	24. (4)	25. (4)

EXERCISE # 2

1. (4)	2. (4)	3. (1)	4. (1)	5. (1)
6. (4)	7. (1)	8. (4)	9. (3)	10. (1)
11. (1)	12. (2)	13. (2)	14. (4)	15. (3)
16. (4)	17. (3)	18. (1)	19. (1)	20. (3)

EXERCISE # 3

1. (2)	2. (1)	3. (1)	4. (2)	5. (1)
6. (2)	7. (3)	8. (2)	9. (3)	10. (3)
11. (2)	12. (2)	13. (1)	14. (2)	15. (3)

EXERCISE # 4

1. (3)	2. (3)	3. (3)	4. (3)	5. (1)

HINT AND SOLUTION

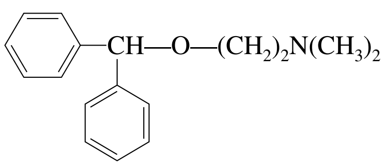
EXERCISE # 1

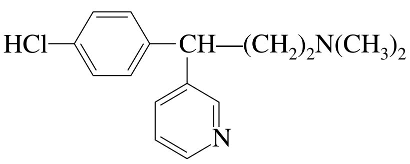
1. [4]

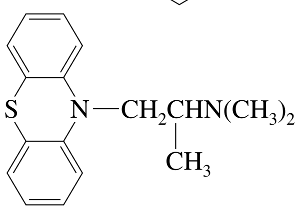
Theory based

2. [4]

Allergic reactions are caused by the generation of histamine in the body and drugs are called anti-histamines.

(1) 

(2) 

(3)  Promethazine

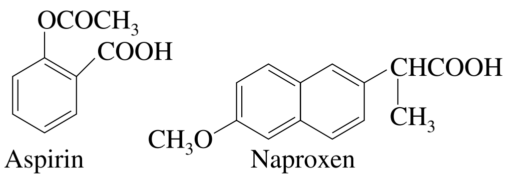
3. [2]

Hormones are not continuously produced; rather they are produced in controlled manner according to the requirement of the body.

4. [2]

$KMnO_4$ is used as an antiseptic.

5. [3]



Aspirin Naproxen

Both are analgesics but are toxic to liver and cause bleeding from stomach wall and are a gastric irritant.

6. [3]

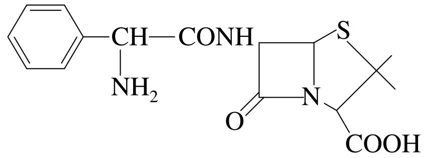
Dilute solutions of boric acid and hydrogen peroxides are mild antiseptics not strong antiseptic.

7. [1]

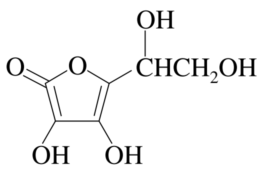
Refer key concept.

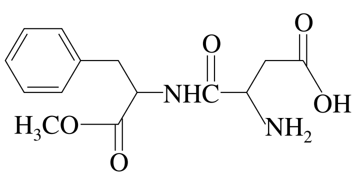
8. [1]

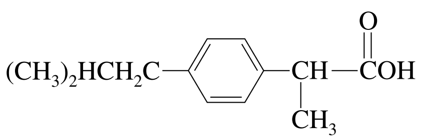
Penicillin of the type given below is newer family of antibiotic.



9. [1]

(1)  Ascorbic acid

(2)  Aspartame

(3)  Ibuprofen

10. [4]

(I) $CHCl_3$-anaesthetics

(II) CHI_3-With I_2 (in alcohol) called tincture of iodine-antiseptic

(III) Boric acid-antiseptic for eyes

11. [1]

In recent years, Al has been under suspicion as a possible cause of Alzheimer's disease. This disease causes young men and women to lose their memory.

12. [4]

0.2 per cent solution of phenol – antiseptic

1.0 per cent solution of phenol – disinfectant

13. [3]

(I) True	(II) False
(III) True	(IV) True

14. [3]

Birth control pills contain a mixture of oestrogen and progesterone derivatives.

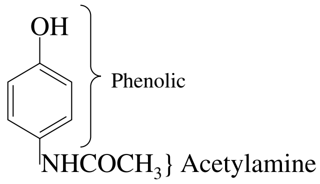
15. [3]

Veronal and luminal have

Tranquiliser activity and Neurological activity

16. [3]

Paracetamol is



17. [2]

HCl is formed in the stomach and this acid is responsible for acidity.

18. [1]

$Na_2S_2O_5 \longrightarrow Na_2SO_3 + SO_2$

$SO_2 + H_2O \longrightarrow H_2SO_3$

SO_2 and H_2SO_3 are food preservatives.

19. [3]

Arsenic drugs such as salvarsan is used for the treatment of syphilis.

20. [3]

Artificial sweeteners have zero calorific value and do not enhance nutritional value if they are used as foods.

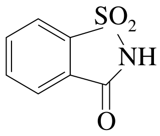
21. [4]

(II) Sodium bicarbonate ($NaHCO_3$)

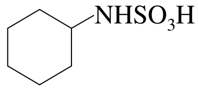
(IV) Benzoic acid (in the form of sodium salt) is food preservatives

22. [4]

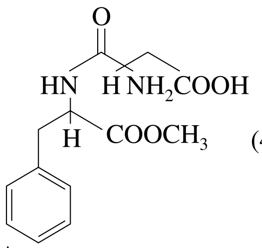
Saccharic acid is the oxidation product (by HNO_3) of glucose and is not the artificial sweetener. Others are

(1) 

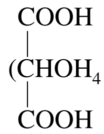
Sachharin

(2) 

Cyclamate

(3) 

Aspartame

(4) 

Saccharic acid

23. [3]

Na_2SO_3 and SO_2 are the best antioxidants for wine, beers, sugar-syrups, etc., as these are easily oxidised to SO_4^{2-} $SO_3^{2-} \xrightarrow{\text{Oxidation}} SO_4^{2-}$

24. [4]

(I) 110	(II) 20
(III) 25	(IV) 180
(V) 650	(VI) 2000

25. [4]

Penicillin – antibiotic.

Iodoform and hydrogen peroxide – antiseptics.

Serotonin – Tranquilizer.

EXERCISE # 2

1. [4]

Ether and halothane are anaesthetics.

Nitrogen dioxide is not under this class. N_2O (nitrous oxide, also called laughing gas) was used as an anaesthetic by dentists.

2. [4]

(I) aspirin, and (II) acetaminophen are pain killar

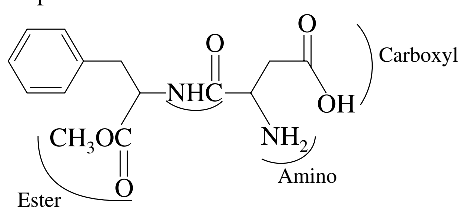
3. [1]

Refer key concept.

(1) Oxacillin	(2) Cloxacillin
(3) Penicillin–O	(4) Penicillin–G

4. [1]

Aspartame is shown below



5. [1]

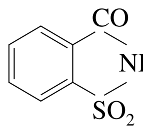
Antioxidants function by interrupting the chain reaction of autoxidation process that foods are preserved.

6. [4]

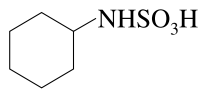
If N and S along with carbon, both are present, NaCNS is formed in Lassaigne's test which gives blood red colour with $FeCl_3$.

$FeCl_3 + NaCNS \longrightarrow [Fe(CNS)]Cl_2$

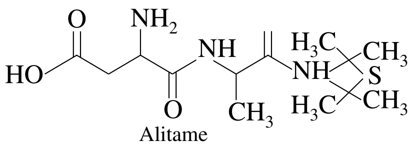
Blood red colour

(1) 

Saccharin

(2) 

Cyclamate

(3) 

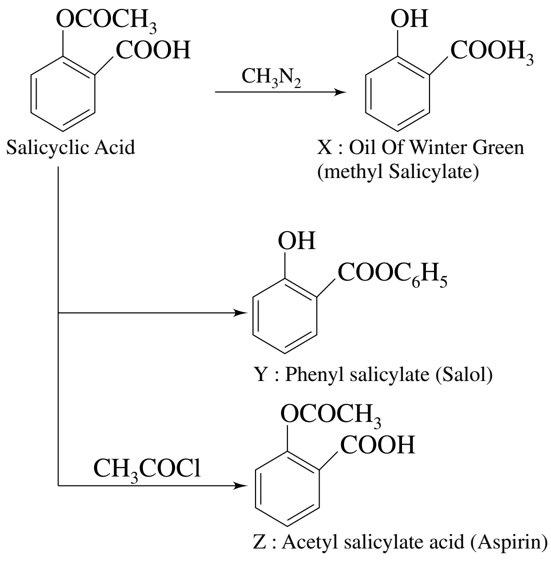
Alitame

7. [1]

Straight-chain alkyl groups are biodegradable while branched-chain alkyl groups are not.

Non-biodegradable detergents become pollutants in rivers and lakes.

8. [4]



(1) Correct (2) Correct

(3) Correct

9. [3]

Sodium stearate is a soap and not the detergent.

10. [1]

Hard water contains Ca^{2+} and Mg^{2+}. These are complexed with silicates and phosphates present in detergents. These ions are called builders.

11. [1]

Micelles formation takes place above a temperature called Kraft temperature.

12. [2]

Ampicillin is modified pencillin.

13. [2]

N_2O gas used by anaesthetic by dentist.

14. [4]

N-Acetyl p-amino phenol (paracetamol) is used for reducing temprature (analgesic).

15. [3]

Paracetamol used as antipyretic as well analgesic.

16. [4]

Codeine is narcotic analgesic not antacid.

17. [3]

Ibuprofen used as a painkillar.

18. [1]

Hydrazine & liqoxygen.

19. [1]

Refer key concept.

20. [3]

Furacin is an antiseptic.

EXERCISE # 3

1. [2]

Overproduction of an acid in the stomach causes irritation and pain. $NaHCO_3$ makes the stomach alkaline and triggers the production of more acid.

$$NaHCO_3 + H_2O \longrightarrow H_2CO_3 + \underbrace{NaOH}_{\text{Alkaline}}$$

Cimetidine and ranitidine prevent the interaction of histamine with the receptors present in the stomach wall and thus are better antacids.

Thus, Statement I and Statement I are correct but Statement II is not the correct explanation of Statement I.

2. [1]

Plenty of salt and cover of oil act as preservatives for pickles, These do not allow bacteria to thrive on them.

Thus, Statement I and Statement II are correct and Statement II is the correct explanation of Statement I.

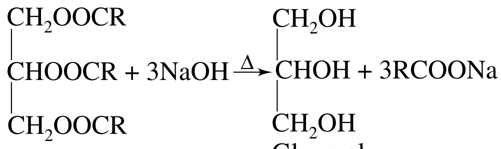
3. **[1]**

Preservatives (as sodium benzoate) are added as preservatives. They inhibit the growth of bacteria on them. Thus, they are preserved.

Thus, Statement I and Statement II are correct and Statement II is the correct explanation of Statement I.

4. **[2]**

Soap in formed by the saponification of glycerides (esters of glycerol and fatty acids).



Srearin ($R = C_{17}H_{38}$) Glycerol

$$RCOONa \rightleftharpoons RCOO^{-} + Na^{+}$$

Mixture of glycerol and soap (called spent lye) is in colloidal form, if NaCl is added.

$[R\ COO^{-}][Na^{+}] > K_{ap}$

and RCOONa is precipitated by common ion effect, It is **called salting out** of soap.

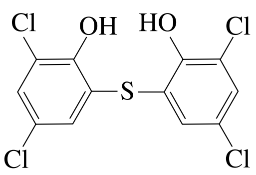
Thus, Statement I and Statement II are correct but Statement II is not the correct explanation of Statement I.

5. **[1]**

Aspirin has been used to prevent heart attack (as first-aid) as it has anti-blood clotting action.

Thus, Statement I and Statement II are correct and Statement II is the correct explanation of Statement I.

6. **[2]**



Bithional has antiseptic property. Statement I and Statement II are correct but Statement II is not the correct explanation of Statement I.

7. **[3]**

8. **[2]**

Column matching type question

9. **[3]**

(i) Saccharin appears as sugar and also having same taste.

Thus **(i)** $\rightarrow$ **(p)**

(ii) Alitame is too much in sweetness and can't be controlled.

Thus **(ii)** $\rightarrow$ **(s)**

(iii) Aspartame is unstable at cooking temperature and can't be used, it is suitable in cold drinks.

Thus **(iii)** $\rightarrow$ **(q)**

(iv) Sucralose has no calorific value and is harmless.

Thus **(iv)** $\rightarrow$ **(r)**

10. **[3]**

(i) is a type of soap formed by saponification of glyceride.

Thus **(i)** $\rightarrow$ **(s)**

(ii) is anionic detergent.

Thus **(ii)** $\rightarrow$ **(q)**

(iii) is cationoic detergent.

Thus **(iii)** $\rightarrow$ **(p)**

(iv) is non-ionic (neutral) detergent.

Thus, **(iv)** $\rightarrow$ **(r)**

11. **[2]**

(i) $\rightarrow$ (s); (ii) $\rightarrow$ (p);

(iii) $\rightarrow$ (q); (iv) $\rightarrow$ (r)

12. **[2]**

(i) $\rightarrow$ q; (ii) $\rightarrow$ s;

(iii) $\rightarrow$ p; (iv) $\rightarrow$ r

13. **[1]**

(i) Paracetamol – antipyretics.

Thus, **(i)** $\rightarrow$ **(p)**

(ii) Chloramphenicol – antibiotic.

Thus, **(ii)** $\rightarrow$ **(r)**

(iii) Bithinol – antiseptic.

Thus, **(iii)** $\rightarrow$ **(s)**

(iv) Insulin – anti-diabetic.

Thus, **(iv)** $\rightarrow$ **(q)**

14. **[2]**

(i) Phenelzine – Antidepresent drug.

Thus, **(a)** $\rightarrow$ **(r)**

(ii) Asprin $\rightarrow$ Non narcotic analgesic.

Thus, **(b)** $\rightarrow$ **(p)**

(iii) Morphine $\rightarrow$ Narcotic analgesic.

Thus, **(c)** $\rightarrow$ **(s)**

(iv) Norethindrone $\rightarrow$ Antifertility drug.

Thus, **(d)** $\rightarrow$ **(q)**

15. **[3]**

EXERCISE # 4

1. **[3]**

Liquid hydrogen and liquid oxygen are good fuels.

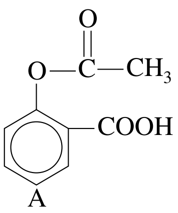
2. [3]

Antipyretic drugs reduce fever, Analgesics relieve in pain, antibiotics act against bacterial infections while tranquilisers are used against mental disorders.

3. [3]

Aluminium hydroxide $Al(OH)_3$, cimetidine and ranitidine are antacids while phenelzine is not.

4. [3]



o-acetyl salicylic acid
Aspirin (analgesic)

5. [1]

Sodium lauryl sulphate $[(CH_3(CH_2)_{10}CH_2SO_3^-Na^+)]$ = Anionic detergent

Cetyltrimethyl ammonium bromide

$$\left[\begin{array}{c} \quad\quad\quad\quad\quad\; CH_3 \\ \quad\quad\quad\quad\quad\; | \\ CH_3\text{–}(CH_2)_{15}\text{–}N\text{–}CH_3 \\ \quad\quad\quad\quad\quad\; | \\ \quad\quad\quad\quad\quad\; CH_3 \end{array}\right]^+ Br^- = \text{Cationic detergent}$$

Glyceryl oleate $[(C_{17}H_{32}COO)_3C_3H_5]$ = Non-ionic detergent

Sodium stearate $[C_{17}H_{35}COO^-Na^+]$ = Anionic soap