CHAPTER

10 ALCOHOLS, PHENOLS AND ETHERS

Syllabus

- *Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.*
- *Phenols : Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.*
- *Ethers : Nomenclature, methods of preparation, physical and chemical properties, uses.*

Chapter Analysis

List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
IUPAC Name	–	–	–	1Q (1 mark)	1Q (1 mark)
Reaction Mechanism	1Q (2 marks)	–	1Q (5 marks)*	1Q (2 marks)#	–
Conversion	–	1Q (2 marks)	–	–	–
Give reason	–	1Q (3 marks)	–	–	–
Write the products formed/reagents involved for a reaction	1Q (3 marks)	–	1Q (5 marks)*	1Q (2 marks)#	1Q (3 marks)
Properties	–	–	1Q (5 marks)*	1Q (2 marks)#	

- * One question of 5 marks was asked. One question of 2 marks on Formula of reagents involved in the reactions, one question of 2 marks on Arranging the compounds in increasing order of the property and one of 1 mark on Mechanism of the reaction was asked.
- # One question of 2 marks with two choices was asked. First choice was on Arranging the compounds in increasing acid strength and Mechanism of reaction. Second choice was on writing the structure of products formed in different conditions.

On the basis of above analysis, it can be said that from exam point of view, IUPAC name, Mechanism of Reaction and Properties are the most important topics of the chapter. Also, Write the products formed/reagents involved for a reaction type of question was also asked.

TOPIC-1
Methods of Preparation and Properties of Alcohols and Phenols

Revision Notes

- **Alcohol :** When one hydrogen atom of alkane is replaced by —OH group, the compounds obtained are called alcohols having general formula $C_nH_{2n+1}OH$.

➢ **Classification of Alcohols :**

(a) mono, di, tri and polyhydric alcohols :

(i) Those alcohols which contain one —OH group *e.g.*, CH_3OH, C_2H_5OH etc. are called monohydric alcohols.

(ii) Those alcohols which contain two —OH groups, are called dihydric alcohols. Their general formula is $C_nH_{2n}(OH)_2$. They are called diols. *e.g.*, $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ 1, 2-ethanediol.

(iii) Those alcohols which contain three hydroxyl (—OH) groups, are called trihydric alcohols. They are also called triols.

Their general formula is $C_nH_{2n-1}(OH)_3$. *e.g.*, $\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}$ 1, 2, 3-propanetriol.

(iii) Those alcohols which have more than one —OH groups are called polyhydric alcohols *e.g.*, $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ Glycol.

(b) 1°, 2° and 3° alcohols :

(i) The alcohol in which —OH group is attached to primary (1°) carbon atom is called primary alcohol *e.g.*, CH_3OH, C_2H_5OH etc.

(ii) The alcohol, in which —OH group is attached to secondary (2°) carbon atom is called secondary alcohol, *e.g.*, $CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$ (2-propanol).

(iii) The alcohol in which —OH group is attached to tertiary (3°) carbon atom is called tertiary alcohol *e.g.*,

$\begin{matrix}CH_3\\|\\CH_3—C—OH\\|\\CH_3\end{matrix}$ or $(CH_3)_3COH$ (2-methylpropan-2-ol).

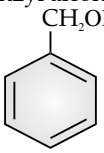
(c) Allylic and vinylic alcohols :

(i) Those alcohols in which —OH group is attached to single bonded sp^3-hybridised carbon next to carbon-carbon double bond, that is to allylic carbon are called allylic alcohols. *e.g.*, $CH_2 = CH—CH_2—OH$

(ii) Those alcohols in which —OH group is attached to double bonded sp^2-hybridised carbon atom are called vinylic alcohols. They are highly unstable and get tautomerised to form aldehydes. *e.g.*,

$$\underset{\text{(Vinyl alcohol)}}{CH_2=CHOH} \rightleftharpoons \underset{\text{(Acetaldehyde)}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$

(d) Benzyl alcohol : Those alcohols in which —OH group is attached to single bonded sp^3-hydridised carbon atom attached to aromatic ring are called benzyl alcohols. *e.g.*,

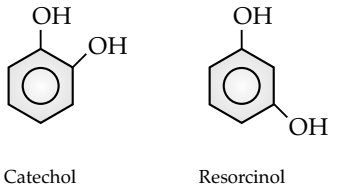


Benzyl alcohol
(Phenyl methanol)

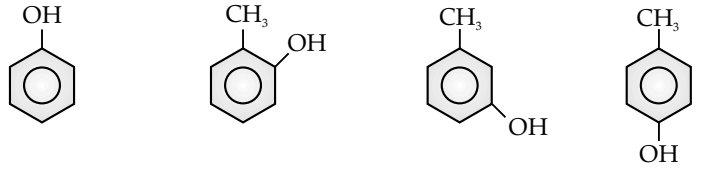
➢ **Common and IUPAC Names of Some Alcohols**

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3CHOHCH_3$	*iso*-Propyl alcohol	Propan-2-ol
$(CH_3)_2CH—CH_2OH$	*iso*-Butyl alcohol	2-Methyl propan-1-ol
$CH_3CH_2CHOHCH_3$	*sec*- Butyl alcohol	Butan-2-ol
$(CH_3)_3C—OH$	*tert*- Butyl alcohol	2-Methyl propan-2-ol
$\begin{matrix}CH_2—CH_2\\\|\quad\quad\|\\OH\quad OH\end{matrix}$	Ethylene glycol	Ethane-1, 2-diol
$\begin{matrix}CH_2—CH—CH_2\\\|\quad\quad\|\quad\quad\|\\OH\quad OH\quad OH\end{matrix}$	Glycerol or Glycerine	Propane-1, 2, 3-triol

➢ **IUPAC names of some Phenols :**

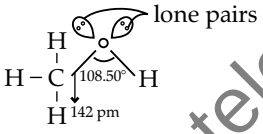


Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1, 2-diol	Benzene-1, 3-diol	Benzene-1, 4-diol



Common name	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

➢ **Structure of alcohol :** The oxygen of the —OH group is attached to sp^3 hybridised carbon by a σ bond.



➢ **Methods preparation of Alcohols :**

(1) From Haloalkanes : Haloalkanes are hydrolysed to the corresponding alcohols by treatment with aqueous alkali.

$$CH_3—Cl + KOH(aq) \rightarrow CH_3—OH + KCl$$

(2) From Aldehydes and Ketones :

(i) Reduction : Aldehyde and ketones are reduced to primary and secondary alcohols respectively. The common reducing agents are lithium aluminium hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$) or hydrogen gas in the presence of nickel or platinum as catalyst.

(a) $CH_3—\overset{O}{\overset{\|}{C}}—H + H_2 \xrightarrow{Ni \text{ or } Pt} CH_3—CH_2—OH$

Ethanal → Ethanol

(b) $CH_3—\overset{O}{\overset{\|}{C}}—CH_3 + H_2 \xrightarrow{Ni} CH_3—\overset{OH}{\overset{|}{C}}H—CH_3$

2-Propanone → 2-Propanol

(ii) Using Grignard reagent : This method is used to get all three types of alcohols. Formaldehyde (HCHO) reacts with Grignard reagent to give primary alcohol whereas other aldehydes give secondary alcohols. Ketones give tertiary alcohols. *e.g.*,

(a) $H—\overset{O}{\overset{\|}{C}}—H + CH_3MgBr \rightarrow \left[H—\overset{OMgBr}{\overset{|}{C}}H—CH_3\right] \xrightarrow{H_2O/H^+} CH_3CH_2OH + Mg\begin{matrix}OH\\Br\end{matrix}$

Methanal (Formaldehyde) + Methyl magnesium bromide → Ethanol + Hydroxy magnesium bromide

(b) $CH_3—\overset{O}{\overset{\|}{C}}—H + CH_3MgBr \rightarrow \left[CH_3—\overset{OMgBr}{\overset{|}{C}}H—CH_3\right] \xrightarrow{H_2O/H^+} CH_3—\overset{OH}{\overset{|}{C}}H—CH_3 + Mg\begin{matrix}OH\\Br\end{matrix}$

(Acetal-dehyde) + Methyl magnesium bromide → 2-propanol (Isopropyl alcohol) + Hydroxy magnesium bromide

(3) From Alkenes :

(i) $CH_2 = CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H \xrightarrow{H_2O} CH_3CH_2OH + H_2SO_4$

Ethene → Ethanol

(ii) $CH_3—CH=CH_2 + H_2SO_4 \rightarrow CH_3—\underset{\underset{OSO_3H}{|}}{CH}-CH_3 \xrightarrow{H_2O} CH_3—\underset{\underset{OH}{|}}{CH}-CH_3 + H_2SO_4$

Isopropyl alcohol

(iii) $CH_3-\underset{\text{2-methylpropene}}{\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

2-methylpropan-2-ol

(4) By hydroboration oxidation : As per anti-Markovnikov's rule -

$$3R-CH=CH_2 + (BH_3)_2 \longrightarrow (R-CH_2-CH_2)_3B \xrightarrow[OH^-, H_2O]{H_2O_2} R-CH_2-CH_2-OH + H_3BO_3$$

(5) By oxymercuration-demercuration : As per Markovnikov's rule :

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[H_2O]{(CH_3-COO)_2Hg} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-HgOOCCH_3 \xrightarrow{NaBH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propan–2–ol

(6) Reduction of carboxylic acids and esters : With the help of strong agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.

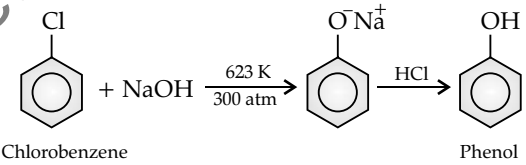
$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

Commercially, acids are reduced to alcohols by converting them to esters, followed by catalytic hydrogenation.

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

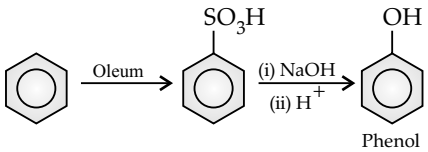
➢ **Preparation of Phenols :**

(i) From aryl halides



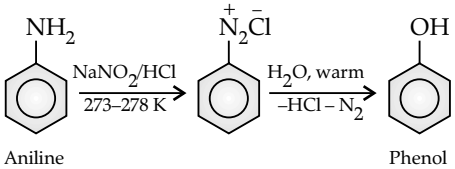
Chlorobenzene Phenol

(ii) From benzene sulphonic acid

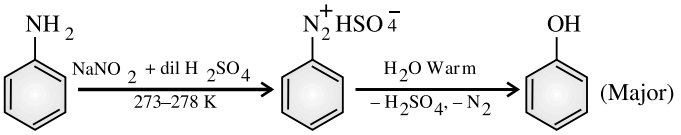


Phenol

(iii) From diazonium salts



Aniline Phenol

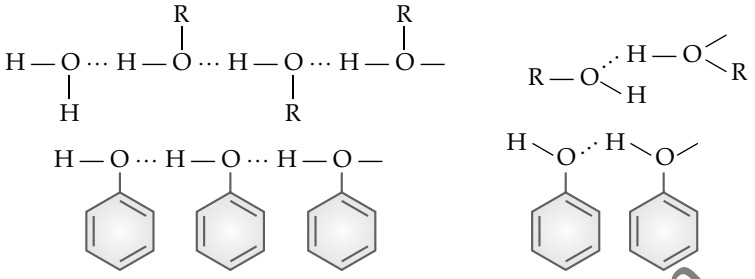


➢ **Physical and chemical properties of Alcohols and Phenols :**

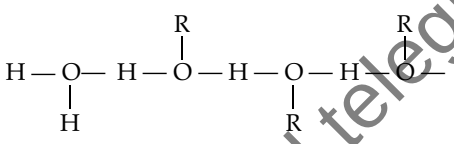
(a) Physical properties :

(i) Boiling points : The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

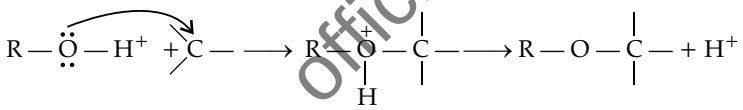
The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding resulting in high boiling point, which is lacking in ethers and hydrocarbons.



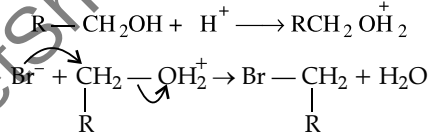
(ii) Solubility : Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.



(b) Chemical properties : Alcohols and phenols react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as *nucleophiles*.



The bond between C–O is broken when they react as *electrophiles*.



The reactions of alcohols can be classified into :

(a) Reactions involving the cleavage of O–H bond :

(i) Reaction with metals :

$$2R-O-H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R-O^{-}Na^{+}} + H_2$$

$$CH_3-CH_2-OH + Na \longrightarrow \underset{\text{Sodium ethoxide}}{CH_3-CH_2-O^{-}Na^{+}} + \frac{1}{2}H_2$$

$$\underset{\text{3° Butyl alcohol}}{6(CH_3)_3-C-OH} + 2Al \longrightarrow \underset{\text{Aluminium tert-butoxide}}{2\left((CH)_3C-O\right)_3 Al} + 3H_2$$

(ii) Esterification :

$$\underset{\text{Carboxylic acid}}{R-COOH} + \underset{\text{Alcohol}}{R'-OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R-COOR'} + H_2O$$

$$\underset{\text{Acid anhydride}}{(R-CO)_2O} + R'-OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R-COOR'} + R-COOH$$

$$\underset{\text{Acid chloride}}{R-COCl} + R'-OH \xrightarrow{\text{Pyridine}} \underset{\text{Ester}}{R-COOR'} + HCl$$

(b) Reactions involving cleavage of C–O bond :

Order of reactivity in such type of reaction is

3° Alcohol > 2° Alcohol > 1° Alcohol

(i) Reaction with hydrogen halides :

$$R-OH + H-X \xrightarrow{\text{anhyd.}ZnCl_2} \underset{\text{Alkyl halide}}{R-X} + H_2O$$

(ii) Reaction with phosphorus halides :

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$

(c) Reaction involving both the alkyl and hydroxyl group :

(i) Dehydration : 3° Alcohol > 2° Alcohol > 1° Alcohol

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2-OH} \xrightarrow[443\ K]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

$$\underset{\text{Isopropyl alcohol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3} \xrightarrow[440\ K]{85\%\ H_3PO_4} \underset{\text{Propylene}}{CH_3-CH=CH_2} + H_2O$$

$$CH_3-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow[358\ K]{20\%\ H_3PO_4} \underset{\text{Isobutylene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} + H_2O$$

(ii) Oxidation :

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} + [O] \xrightarrow[\text{or alk.}KMnO_4]{K_2Cr_2O_7/H_2SO_4} \underset{-H_2O}{R-CHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R-COOH}$$

$$\underset{\text{2° Alcohol}}{\begin{matrix}R'\\ \diagdown\\ R\diagup\end{matrix}CH-OH} \xrightarrow{CrO_3} \underset{\text{Ketone}}{\begin{matrix}R'\\ \diagdown\\ R\diagup\end{matrix}C=O}$$

$$\underset{\text{3° Butyl alcohol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\overset{|}{C}}}}-CH_3} \xrightarrow[[O],\ -H_2O]{\text{Hot conc. } HNO_3} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[[O]]{-H_2O,\ -CO_2} \underset{\text{Acetone}}{\begin{matrix}CH_3\\ \diagdown\\ CH_3\diagup\end{matrix}C=O} \xrightarrow[-H_2O,\ -CO_2]{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

(iii) Dehydrogenation :

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow[573\ K]{Cu} \underset{\text{Aldehyde}}{R-CHO} + H_2$$

$$\underset{\text{2° Alcohol}}{\begin{matrix}R\\ \diagdown\\ R'\diagup\end{matrix}CH-OH} \xrightarrow[573\ K]{Cu} \underset{\text{Ketone}}{\begin{matrix}R'\\ \diagdown\\ R\diagup\end{matrix}C=O} + H_2$$

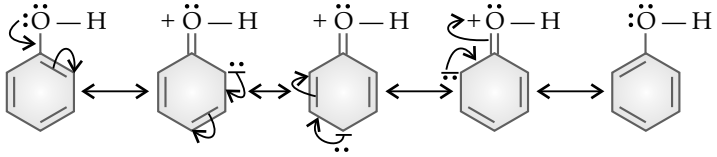
$$\underset{\text{tert-Butyl alcohol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\overset{|}{C}}}}-CH_3} \xrightarrow[-H_2O]{\text{Hot conc. } HNO_3} \underset{\text{Isobutylene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} + H_2O$$

➢ **Acidity of alcohols and phenols :** The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength. For this reason, the acid strength of alcohol decreases in the order :

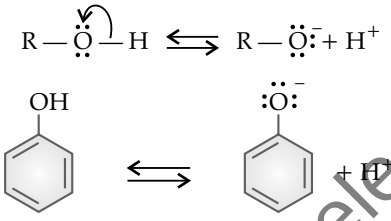
$$\underset{\text{Primary}}{R\rightarrow CH_2OH} > \underset{\text{Secondary}}{\begin{matrix}R\\ \diagdown\\ R\diagup\end{matrix}CHOH} > > \underset{\text{Tertiary}}{\begin{matrix}R\\ \diagdown\\ R\diagup\end{matrix}C-OH}$$

Alcohols can act as Bronsted acids as well as base due to donation of proton and presence of unpaired electron on oxygen respectively.

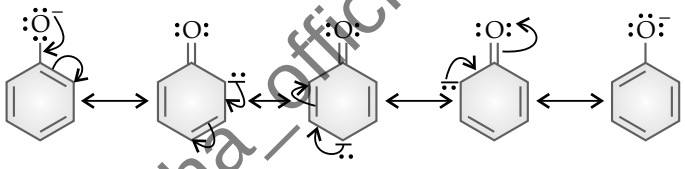
Phenols are more acidic than alcohols and water. The hydroxyl group in phenol is directly attached to the sp^2-hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.



The ionisation of an alcohol and a phenol takes place producing alkoxide and phenoxide ions as shown in equation.



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol.



➢ **Distinction between Primary, Secondary and Tertiary Alcohols :**

(i) Lucas Test : Alcohol on treating with Lucas reagent forms a clear solution. Alkyl chlorides are formed on reaction which being insoluble results in the turbidity in the solution.

$$\text{Alcohol} \xrightarrow[ZnCl_2]{HCl} \text{Alkyl chloride} + H_2O$$

Tertiary alcohol is indicated, if turbidity appears immediately. Secondary alcohol is indicated, if turbidity appears within five minutes. Primary alcohol is indicated, if turbidity appears on heating.

(ii) Iodoform test : When ethanol or any alcohol containing the group $CH_3-\underset{|}{\overset{OH}{CH}}-$ is heated with iodine and aqueous NaOH or Na_2CO_3 solution at 333 – 343 K, a yellow precipitate of iodoform is obtained.

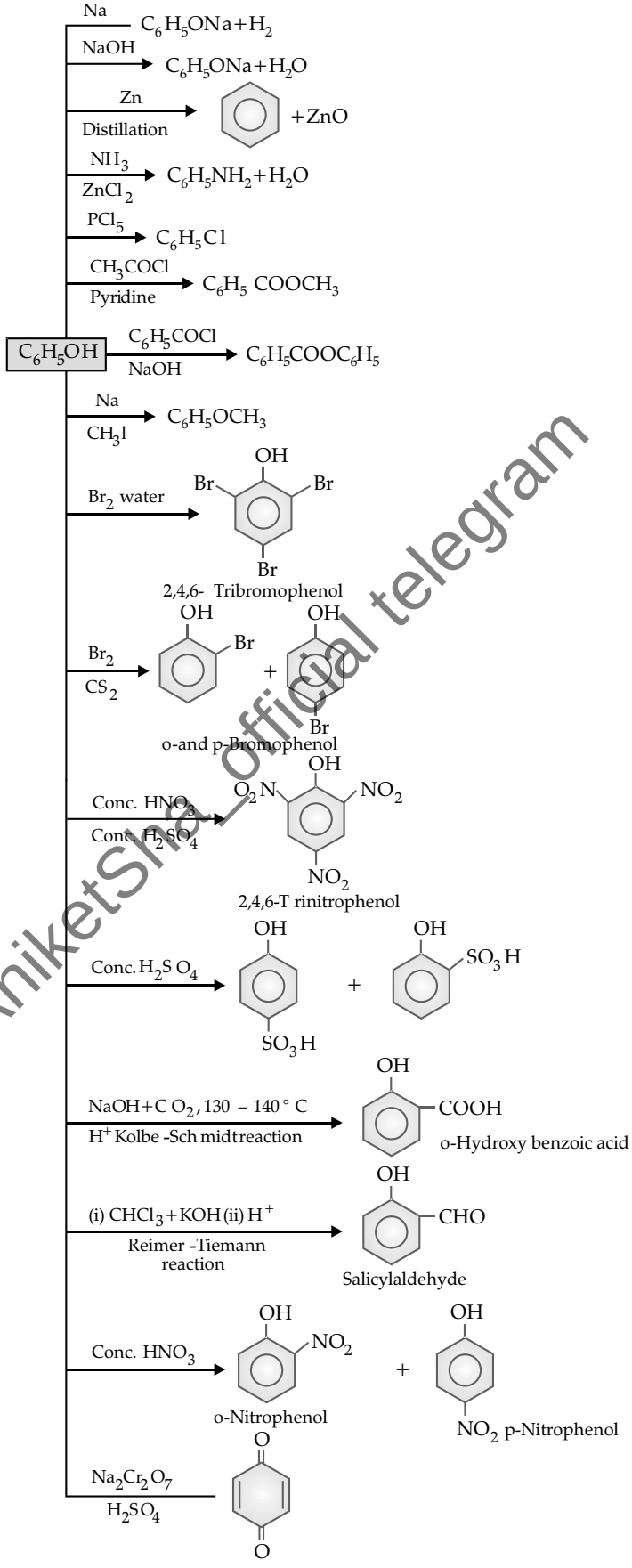
$$CH_3OH + I_2 + NaOH \xrightarrow{\Delta} \text{No reaction}$$

$$CH_3CH_2CH_2\underset{OH}{\underset{|}{C}}HCH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + CH_3CH_2CH_2COONa + 5NaI + 5H_2O$$

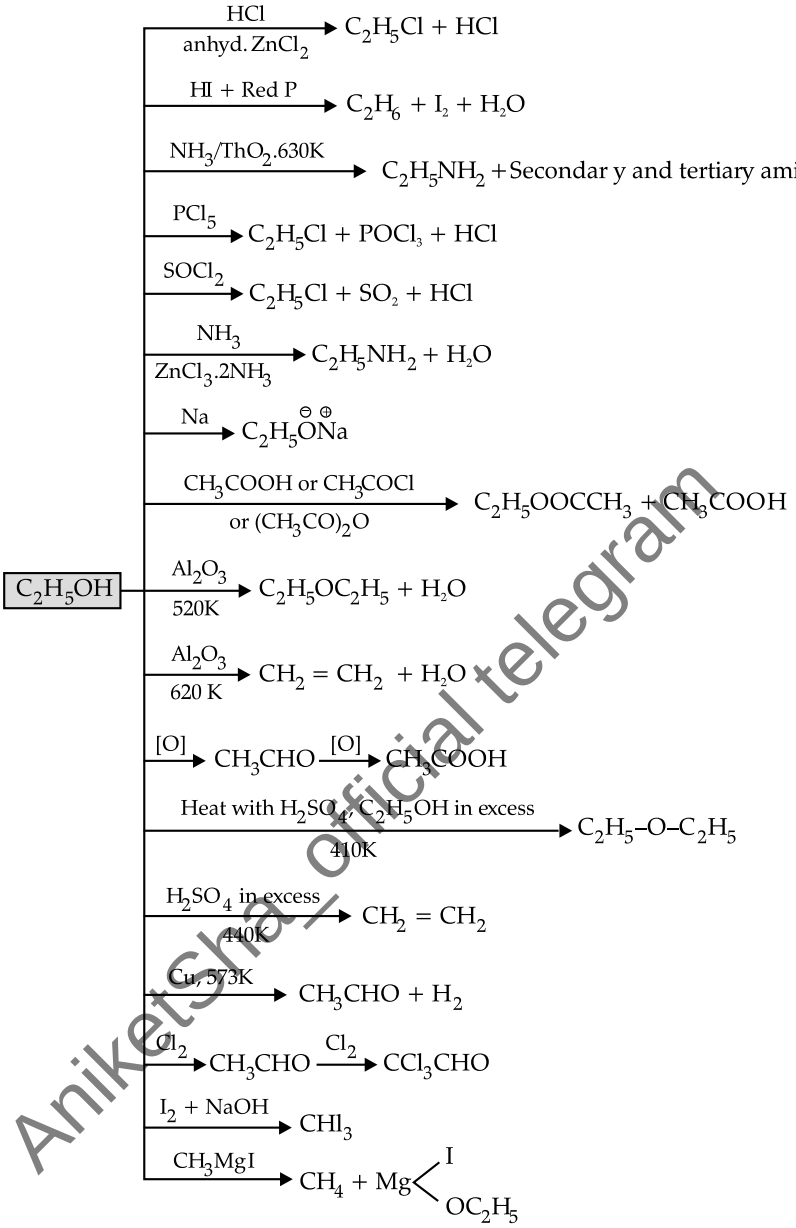
(iii) Ferric chloride test or phenols : Phenols gives a violet coloured water soluble complex with ferric chloride.

$$6C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

➢ **Reactions of Phenol :**



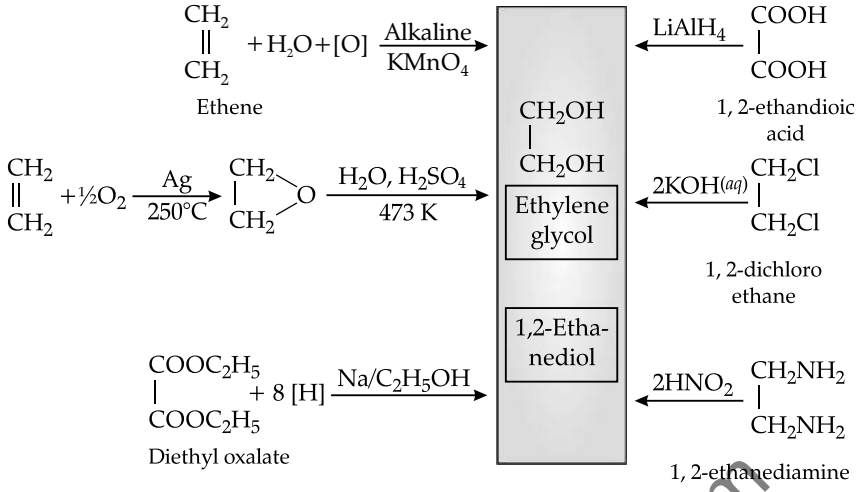
➢ **Reactions of Ethanol :**



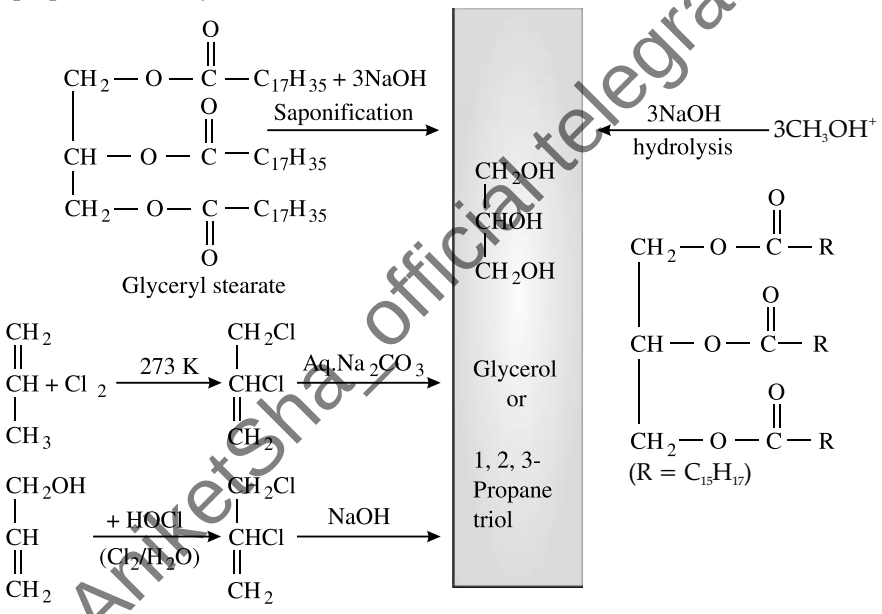
➢ **Differences between or identification of Methyl Alcohol and Ethyl Alcohol :**

S. No.	Test	Methyl alcohol	Ethyl alcohol
(i)	Boiling point	338K	351.2K
(ii)	On heating with I_2 and NaOH.	No reaction.	Iodoform is obtained.
(iii)	On heating with anhydrous sodium acetate and conc. sulphuric acid.	A specific odour of methyl acetate is produced.	Ethyl acetate is formed which has a sweet fruity odour.
(iv)	On heating with salicylic acid and conc. H_2SO_4.	Methyl salicylate (oil of winter green) is formed which has a characteristic odour.	No specific smell.
(v)	On heating with bleaching powder.	No reaction.	Chloroform with sweet smell is formed.

- **Methods of preparation of Glycol :**



- **Methods of preparation of Glycerol :**



Know the Terms

- **Lucas reagent :** An equimolar mixture of HCl and $ZnCl_2$.
- **Wood spirit :** Methanol is known as wood spirit as it is prepared by destructive distillation of wood.
- **Methylated spirit :** Denatured ethyl alcohol which is unfit for drinking purpose is called methylated spirit.
- **Fusel oil :** In the fermentation of starch, ethyl alcohol is prepared but in small amount. Some higher alcohol also form like isopentyl alcohol or isoamyl alcohol. This mixture is quite often called fusel oil.
- **Power Alcohol :** It is the mixture of 20% alcohol, and 80% petrol with ether, benzene or tetralin. It is used as a substitute for petrol for running internal combustion, engines in cars, scooters etc.
- **Lederer-Mannase reaction :** Phenol condenses with formaldehyde in presence of acid or base to give bakelite (polymer). The reaction is known as Lederer-Mannase reaction.
- **Rectified spirit :** It contains about 95.5 percent Ethyl alcohol + water (4.5%) mixture.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?

(a) 1 **(b) 2**

(c) 3 **(d) 4**

A **[NCERT Exemp. Q. 2, Page 154]**

Ans. Correct option : (a)

Q. 2. The process of converting alkyl halides into alcohols involves_____.

(a) addition reaction

(b) substitution reaction

(c) dehydrohalogenation reaction

(d) rearrangement reaction

R **[NCERT Exemp. Q. 5, Page 155]**

Ans. Correct option : (a)

Explanation : Conversion of alkyl halides into alcohols involves substitution reaction.

$RX \xrightarrow{NaOH} ROH + NaX$

Q. 3. IUPAC name of m-cresol is _____.

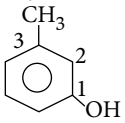
(a) 3-methylphenol **(b) 3-chlorophenol**

(c) 3-methoxyphenol **(d) benzene-1,3-diol**

A **[NCERT Exemp. Q. 8, Page 155]**

Ans. Correct option : (a)

Explanation:



(i) -OH is functional group and $-CH_3$ is substituent.

(ii) IUPAC name : 3-methylphenol.

Q. 4. What is the correct order of reactivity of alcohols in the following reaction?

$R-OH \xrightarrow{ZnCl_2} R-Cl + H_2O$

(a) 1° > 2° > 3° **(b) 1° < 2° > 3°**

(c) 3° > 2° > 1° **(d) 3° > 1° > 2°**

U **[NCERT Exemp. Q. 3, Page 154]**

Ans. Correct option : (c)

Explanation : The given reaction is nucleophilic substitution reaction in which –OH group is replaced by Cl. Tertiary alcohols, when reacts with HCl in presence of $ZnCl_2$ form tertiary carbocations. This intermediate 3° carbocation is more stable than 2° carbocation as well as 1° carbocation. The higher the stability of intermediate, the higher will be the reactivity of reactant molecule. So, the order of reactivity of alcohols in the given reaction is 3° > 2° > 1°.

Q. 5. Which of the following compounds will react with sodium hydroxide solution in water?

(a) C_6H_5OH **(b) $C_6H_5CH_2OH$**

(c) $(CH_3)_3COH$ **(d) C_2H_5OH**

R **[NCERT Exemp. Q. 11, Page 156]**

Ans. Correct option : (a)

Explanation : Phenol being more acidic reacts with sodium hydroxide solution in water to give sodium phenoxide which is resonance stabilized.

Alcohols are very weak acids.

$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

Q. 6. Phenol is less acidic than _____.

(a) ethanol **(b) o-nitrophenol**

(c) o-methylphenol **(d) o-methoxyphenol**

U **[NCERT Exemp. Q. 12, Page 156]**

Ans. Correct option : (b)

Explanation : In *o*-nitrophenol, nitro group is present at ortho position. Presence of electron withdrawing group at ortho position increases the acidic strength. On the other hand, in *o*-methylphenol and in *o*-methoxyphenol electron releasing group ($-CH_3$–O–CH_3), at ortho or para positions of phenol decreases the acidic strength of phenols. So, phenol is less acidic than *o*-nitrophenol.

B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

	Column I		Column II
(i)	Antifreeze used in car engine	(a)	Neutral ferric chloride
(ii)	Solvent used in perfumes	(b)	Glycerol
(iii)	Starting material for picric acid	(c)	Methanol
(iv)	Wood spirit	(d)	Phenol
(v)	Reagent used for detection of	(e)	Ethylene glycol phenolic group
(vi)	By product of soap industry	(f)	Ethanol used in cosmetics

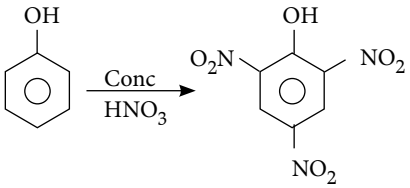
[NCERT Exemp. Q. 59, Page 162]

Ans. (i)—(e), (ii)—(f), (iii)—(d), (iv)—(c), (v)—(a), (vi)—(b)

(i) IUPAC name of ethylene glycol is ethane-1,2-diol. It is primarily used as raw material in the manufacturing of polyester fibres and the fabric industry. A small percentage of it is used in antifreeze formulations.

(ii) Ethanol is a good solvent for fatty and waxy substances. Fats and waxes provide odour to the perfumes. Apart from being a good solvent, it is less irritating to the skin. So, it is used in perfumes.

(iii) Phenol is converted into picric acid (2,4,6-trinitrophenol) by the reaction of phenol with conc. HNO_3.

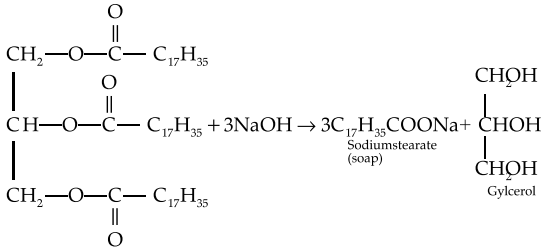


(Picric acid)

(iv) Methanol CH_3OH is also known as 'wood spirit' as it was produced by the destructive distillation of wood.

(v) Neutral ferric chloride gives purple/red colour when treated with phenols. It is the reagent used for detection of phenolic group.

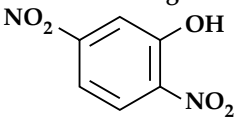
(vi) Soaps are prepared by the reactions of fatty acid with NaOH.



The glycerol (propan-1,2,3-triol) is the by-product of soap industry and used in cosmetics.

C. Answer the following:

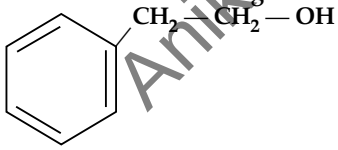
Q 1. Write the IUPAC name of the given compound :



A **[CBSE Delhi 2015]**

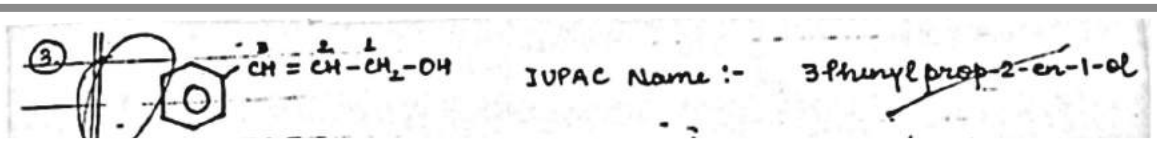
Ans. 2, 5 - dinitrophenol **1**
[CBSE Marking Scheme 2015]

Q. 2. Write the IUPAC name of the given compound :



A **[CBSE OD Central 2016]**

OR



1
[Topper's Answer 2017]

Q. 7. Write the IUPAC name of the following compound : A **[CBSE Foreign Set-1 2017]**

$C_6H_5–CH_2–CH_2–OH$

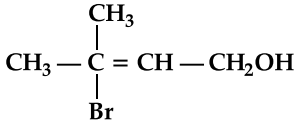
Ans. 2-Phenylethanol. **1**
[CBSE Marking Scheme 2017]

Ans. 2-Phenylethanol.**[CBSE Marking Scheme 2016] 1**

Commonly Made Error

- Students often make mistakes while using -ol suffix. Be attentive.

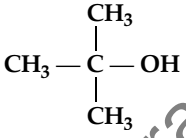
Q. 3. Write the IUPAC name of the following :



A **[CBSE Comptt. OD 2012]**

Ans. 3-Bromo-3-methyl but-2-en-1-ol. **1**

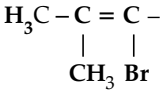
Q. 4. Write the IUPAC name of the following :



A **[CBSE Comptt. OD 2012]**

Ans. 2-Methyl-Propan-2-ol. **1**
[CBSE Marking Scheme 2017]

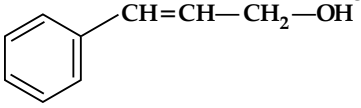
Q. 5. Write the IUPAC name of the following compound :



A **[CBSE OD Set -1 2017, 2013]**

Ans. 2-Bromo-3-methylbut-2-en-1-ol. **1**
[CBSE Marking Scheme 2017]

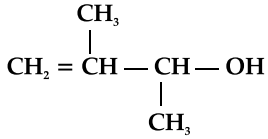
AI **Q. 6.Write the IUPAC name of the following compound:**



A **[CBSE OD Set-2 2017]**

Ans. 3 — phenyl-prop-2-en-1-ol **1**
[CBSE Marking Scheme 2017]

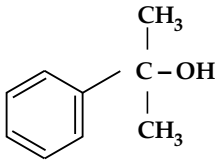
Q. 8. Write the IUPAC name of the following compound :



A **[CBSE Foreign Set-2 2017]**

Ans. 2 - Methylbut-3-en-2-ol **1**
[CBSE Marking Scheme 2017]

AI **Q. 9. Write the IUPAC name of the following compound :**

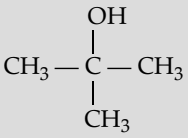


A **[CBSE Foreign Set-3 2017]**

Ans. 2 - Phenylpropan-2-ol **1**
[CBSE Marking Scheme 2017]

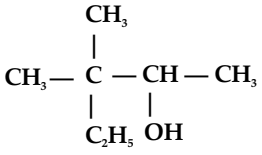
Q. 10. Draw the structural formula of 2-methyl propan-2-ol molecule. A **[CBSE Delhi 2012]**

Ans. 2-Methylpropan-2-ol



1
[CBSE Marking Scheme 2012]

Q. 11. Write the IUPAC name of the following:



A **[CBSE Delhi/OD 2018]**

Ans. 3,3 - Dimethylpentan-2-ol **1**
[CBSE Marking Scheme 2018]

Q. 12. Draw the structure of hex-1-en-3-ol compound.
A **[CBSE Delhi 2012]**

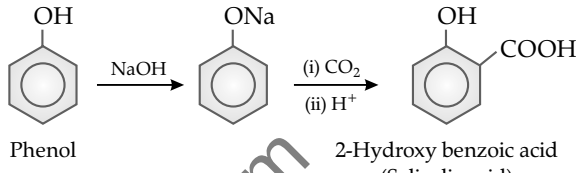
Ans. $CH_3 — CH_2 — CH_2 — \underset{\displaystyle OH}{\underset{|}{CH}} — CH = CH_2$ **1**

Q. 13. Which of the following isomers is more volatile : *o*-nitrophenol or *p*-nitrophenol ?
A **[CBSE Delhi 2014]**

Ans. *o*-nitrophenol. **1**
[CBSE Marking Scheme 2014]

Q. 14. Write the chemical reaction to explain Kolbe's reaction. R **[CBSE Comptt. Delhi 2013]**

Ans.



Phenol — 2-Hydroxy benzoic acid (Salicylic acid) **1**

Q. 15. Of the two hydroxy organic compounds ROH and R′OH, the first one is basic and other is acidic in behaviour. How is R different from R′ ?
U **[CBSE Comptt. Delhi 2013]**

Ans. R is aliphatic while R′ is aromatic. **1**

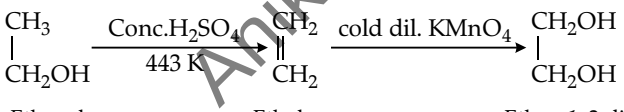
AI **Q. 16. Give a chemical test to distinguish between 2-Pentanol and 3-Pentanol.**
A **[CBSE Comptt. Delhi 2013]**

Ans. 3-pentanol immediately gives turbidity with Lucas reagent but 2-pentanol gives turbidity in around five minutes. **1**

Commonly Made Error
- Correct observations are not written in some cases although the tests given are correct.

Q. 17. How would you obtain ethane-1,2-diol from ethanol ? A **[CBSE Comptt. OD 2013]**

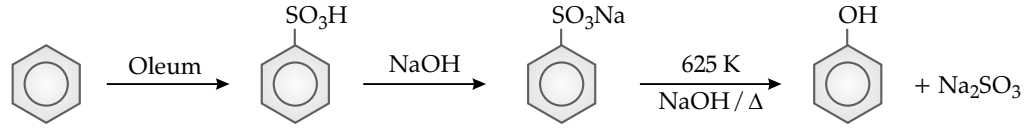
Ans.



Ethanol — Ethylene — Ethan-1, 2-diol **1**

Q. 18. How would you obtain phenol from benzene ? A **[CBSE Comptt. OD 2013]**

Ans.



Benzene — Benzene sulphonic acid — Sodium benzene sulphonate — Phenol **1**

Commonly Made Error
- In some cases, correct conditions are not shown.

Q. 19. *ortho*-nitrophenol has lower boiling point than p-nitrophenol. Why ?
A&E **[CBSE Comptt. Delhi 2012]**

Ans. *p*-nitrophenol shows intermolecular hydrogen bonding. So it has higher boiling point. Whereas o-nitrophenol shows intramolecular H-bonding hence lower boiling point. **1**

Q. 20. The C—O bond is much shorter in phenol than in ethanol. Give reason. A&E **[CBSE Comptt. Delhi 2012]**

Ans. Because in phenol, conjugation of unshared electron pair over oxygen with aromatic ring results in partial double bond character in carbon-oxygen bond. In phenol, oxygen is attached to sp^2 hybridised carbon atom while in methanol it is attached to sp^3 hybridised carbon atom. The bond formed between

oxygen and sp^2 hybridised carbon is more stable *i.e.*, shorter than that formed between oxygen and sp^3 hybridised carbon. **1**

AI **Q 21. Out of CH_3OH and  , which one is more acidic ?** U **[CBSE Comptt. Delhi 2016]**

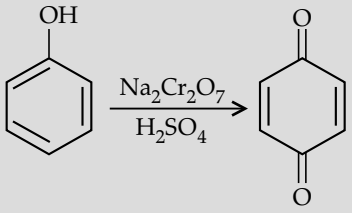
Ans.  as phenoxide ion is more stable due to resonance which is absent in alkoxide ion. **1**

[CBSE Marking Scheme 2016]

Q 22. What happens when phenol is oxidized by $Na_2Cr_2O_7 / H_2SO_4$?

R **[CBSE Comptt. OD Set-1 2017]**

Ans.

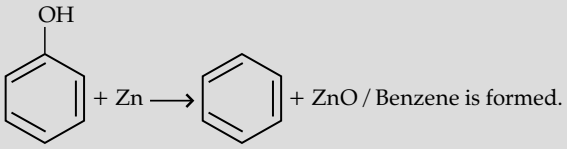


∴ Benzoquinone is formed. **1**

[CBSE Marking Scheme 2017]

Q. 23. What happens when phenol is heated with zinc dust? R **[CBSE Comptt. OD Set-2 2017]**

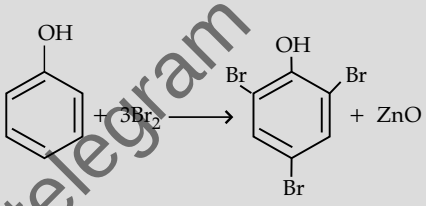
Ans.



[CBSE Marking Scheme 2017] **1**

AI **Q. 24. What happens when phenol is treated with bromine water?** R **[CBSE Comptt. OD Set-3 2017]**

Ans.



2, 4, 6- Tribromophenol is formed. **1**

[CBSE Marking Scheme 2017]

Short Answer Type Questions **(2 marks each)**

Q. 1. (i) Predict the major product of acid catalysed dehydration of 1-Methylcyclohexanol.

(ii) You are given benzene, conc. H_2SO_4, NaOH and dil.HCl. Write the preparation of phenol using these reagents.

OR

Draw the structures of any two isomeric alcohols (other than 1° alcohols) having molecular formula $C_5H_{12}O$ and give their IUPAC names. A **[CBSE SQP 2015]**

Ans. (i) 1-Methylcyclohexene **1**

(ii) $C_6H_6 \xrightarrow{conc.H_2SO_4,\Delta} C_6H_5SO_3H \xrightarrow{NaOH,fuse,575K} C_6H_5ONa \xrightarrow{dil.HCl} C_6H_5OH$ **1**

OR

Any two isomers out of the following :

(i) $CH_3—CH_2—CH_2—CH(OH)—CH_3$	Pentan-2-ol	
(ii) $CH_3—CH_2—CH(OH)—CH_2—CH_3$	Pentan-3-ol	½ + ½
(iii) $CH_3—CH(CH_3)CH(OH)—CH_3$	3-Methybutan-2-ol	
(iv) $CH_3—CH_2—C(CH_3)(OH)—CH_3$	2-Methylbutan-2-ol	½ + ½

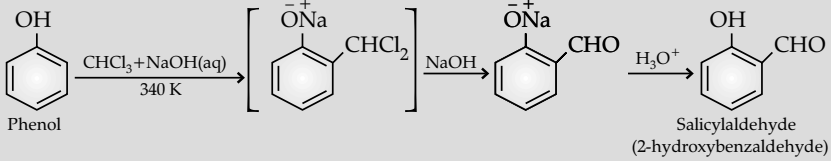
AI **Q. 2. Write the equations involved in the following reactions :**

(i) Reimer-Tiemann reaction

(ii) Williamson synthesis

R **[CBSE Delhi 2014]**

Ans. (i) Reimer - Tiemann reaction



Phenol

Salicylaldehyde (2-hydroxybenzaldehyde)

1

(ii) Williamson synthesis :

$R – X + \overset{+}{N}a – \bar{O} – R' \longrightarrow R – O – R' + NaX$

Alkyl halide Sodium alkoxide

$CH_3–CH_2–Br + \overset{+}{Na}\overset{-}{O}–CH_2–CH_3 \longrightarrow CH_3–CH_2–O–CH_2–CH_3 + NaBr$
Ethyl bromide sodium ethoxide Diethyl ether

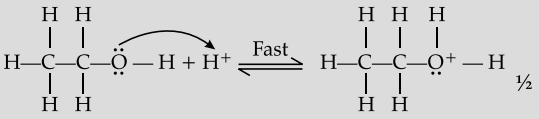
[CBSE Marking Scheme 2014] 1

Answering Tip

- While writing reactions, do not forget to write the reagents and conditions involved. Ensure that the equations are balanced.

Q. 3. Write the mechanism of acid dehydration of ethanol to yield ethene. A [CBSE SQP 2018-2019]

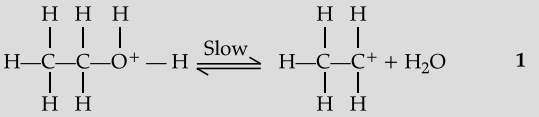
Ans. Step 1 : Formation of protonated alcohol.



½

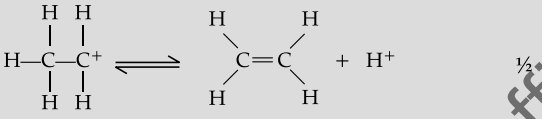
Ethanol Protonated ethanol (Ethyl oxonium ion)

Step 2 : Formation of carbocation.



1

Step 3 : Formation of ethane by elimination of a proton.



½

Ethene

[CBSE Marking Scheme 2018]

Answering Tip

- Mention each step involved in the mechanism.

Q. 4. (i) Write the mechanism of the following reaction :

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

(ii) Write the equation involved in Reimer-Tiemann reaction. A [CBSE Delhi 2014]

Ans. (i) $H–Br \rightleftharpoons H^+ + :\bar{B}r$

$CH_3–CH_2\ddot{O}H + H^+ \rightleftharpoons CH_3CH_2\overset{+}{\ddot{O}}H_2$
Ethyl oxonium ion (Protonated 1° alcohol)

$CH_3–CH_2\overset{+}{\ddot{O}}H_2 \longrightarrow CH_3–\overset{+}{C}H_2 + H_2O$

$CH_3–\overset{+}{C}H_2 + Br \longrightarrow CH_3CH_2Br$ **1**

Overall reaction :

$$CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$$

(ii) Reimer-Tiemann reaction : See S.A.T.Q. 2(i). **1**

[CBSE Marking Scheme 2014]

Q. 5. (i) Give chemical tests to distinguish between the following pairs of compounds :
Methanol and Phenol

(ii) o-nitro phenol is more acidic than o-methoxy phenol. Explain why. A&E [CBSE Comptt. OD 2013]

Ans. (i) Phenol gives a violet colouration with $FeCl_3$ solution while methanol does not. **1**

(ii) The electron withdrawing groups like $–NO_2$ increase the stability of phenoxide ion by dispersal of negative charge. The electron releasing groups like $–OCH_3$ decrease the acidic strength of phenol by destabilising the phenoxide ion by concentrating negative charge. Thus, *o*-nitrophenol is more acidic than *o*-methoxy phenol. **1**

Commonly Made Error

- Some students forget to write the observation and write only the test.

Answering Tip

- In such questions the observations should be clearly mentioned, underlining can be done to highlight it also.

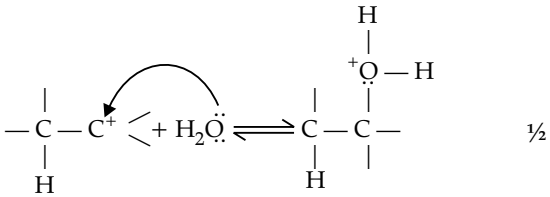
AI Q. 6. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. A [CBSE OD 2012]

Ans. $>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{C}-\underset{OH}{C}<$
Alkene

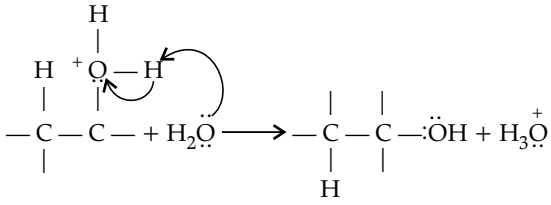
½

$H_2O + H^+ \rightarrow H_3O^+$

$>C=C< + H_3\overset{+}{O} \rightleftharpoons -\underset{H}{C}-C^+< + H_2\ddot{O}$ ½



½



½

Answering Tip

- Write in step by step manner. Ensure that the lone pairs and charges are drawn wherever required.

Q. 7. (i) Describe the mechanism of acid dehydration of ethanol to yield ethene.
(ii) Describe a chemical test to distinguish between ethanol and phenol.

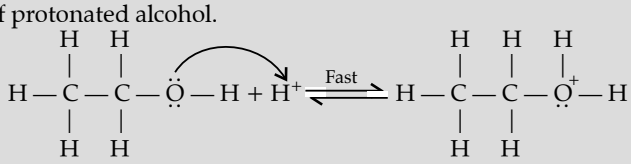
A **[CBSE Comptt. Delhi/OD 2015; Comptt. Delhi 2012]**

Ans. (i) Acid dehydration of ethanol to ethene : When ethanol is heated with concentrated sulphuric acid at 453K, it undergoes dehydration and ethene is formed.

$$CH_3CH_2OH \xrightarrow{H_2SO_4,\,453K} CH_2 = CH_2 + H_2O$$

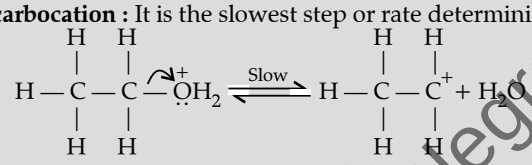
Mechanism :

Step (i) : Formation of protonated alcohol.



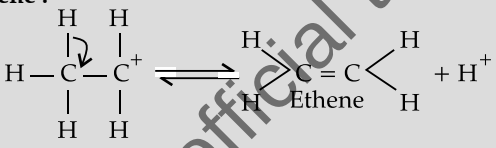
Ethanol — Protonated alcohol Ethyloxonium ion

Step (ii) : Formation of carbocation : It is the slowest step or rate determining step.



Ethyl carbocation

Step (iii) : Formation of ethene :



Ethene

1

(ii) On reaction with $FeCl_3$ phenol gives violet, blue and red colour. While ethanol give no reaction. **1**

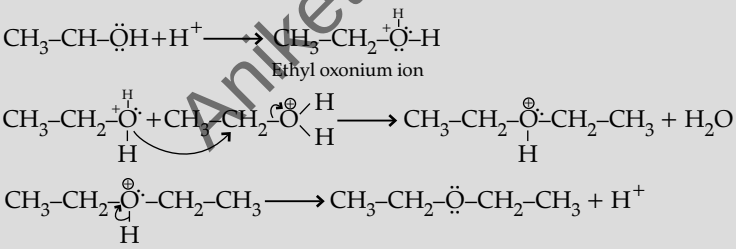
[CBSE Marking Scheme 2015]

Q. 8. Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow[413\ K]{conc.\ H_2SO_4} CH_3CH_2–O–CH_2CH_3$$

A **[CBSE Delhi 2016]**

Ans.



Ethyl oxonium ion

1

1

[CBSE Marking Scheme 2016]

Q. 9. Explain the following behaviours :

(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

(ii) ortho-nitrophenol is more acidic than ortho-methoxyphenol. A&E **[CBSE OD 2012]**

Ans. (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses because alcohols form hydrogen bonds with water. **1**

(ii) The electron withdrawing groups like $–NO_2$ increase the stability of phenoxide ion by dispersal of negative charge. The electron releasing groups like $–OCH_3$ decrease the acidic strength of phenol by destabilising the phenoxide ion by concentrating negative charge. Thus, o-nitrophenol is more acidic then o-methoxyphenol. **1**

Q. 10. (i) Arrange the following compounds in the increasing order of their acid strength:
p-cresol, p-nitrophenol, phenol

(ii) Write the mechanism (using curved arrow notation) of the following reaction;

$$CH_2 = CH_2 + H_3O^+ \rightarrow CH_3 – CH_2^+ + H_2O$$ U + A

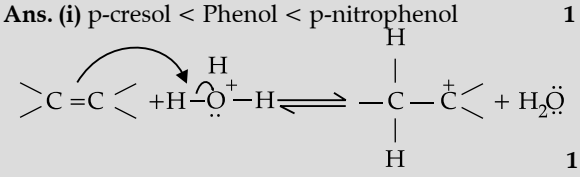
OR

Write the structures of the products when Butan-2-ol reacts with the following

(i) CrO_3

(ii) $SOCl_2$ A **[CBSE OD Set-1, 2, 3 2017]**

Ans. (i) p-cresol < Phenol < p-nitrophenol **1**



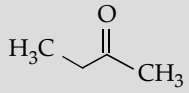
1

Answering Tip

- Use arrows to show the transfer of electrons.

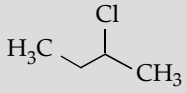
OR

(i)



1

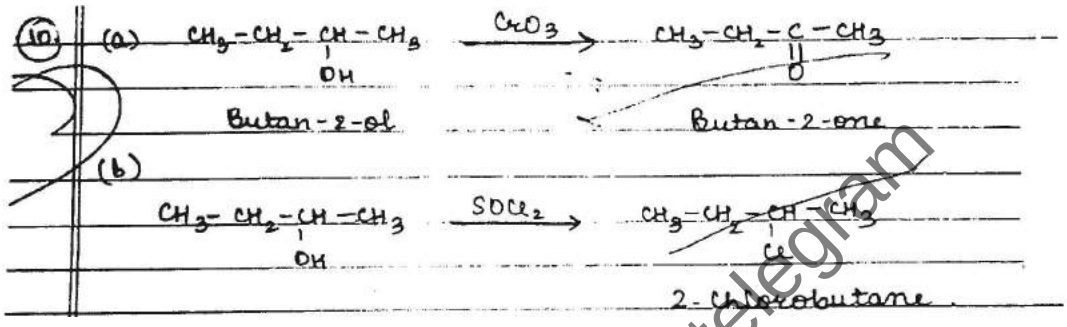
(ii)



1

[CBSE Marking Scheme 2017]

OR



2

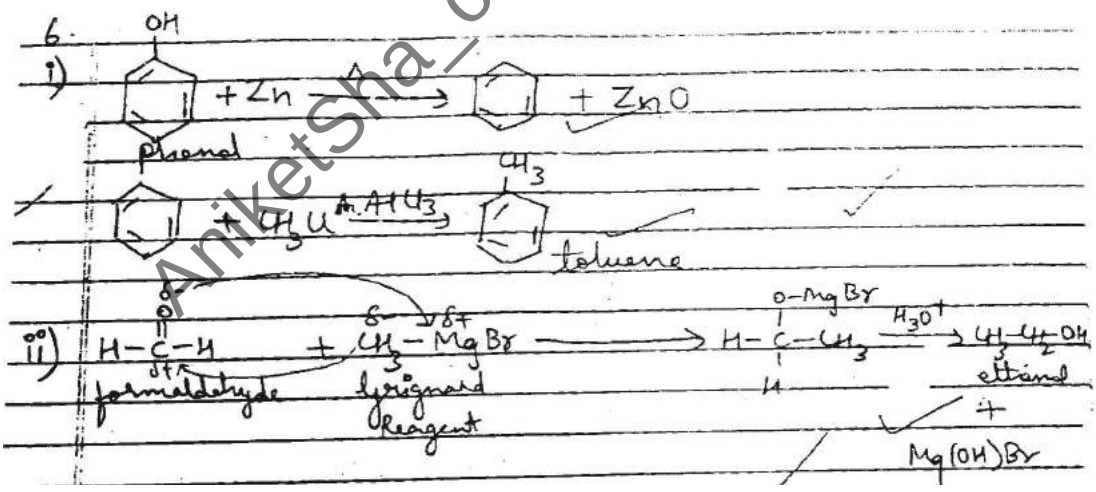
[Topper's Answer 2017]

AI Q. 11. How do you convert:

(i) Phenol to toluene

(ii) Formaldehyde to Ethanol **A [CBSE OD Set-2 2016]**

Ans.



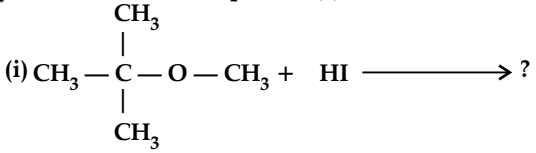
2

[Topper's Answer 2016]

Long Answer Type Questions-I

(3 marks each)

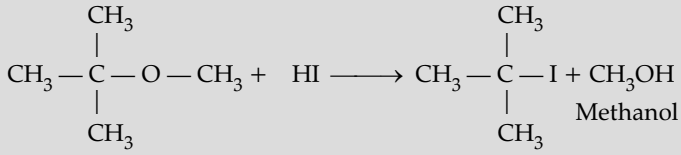
AI Q. 1. Write the main product(s) in each of the following reactions :

(i) 

(ii) $CH_3–CH = CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} ?$

(iii) C_6H_5–OH $\xrightarrow[(ii)\ CO_2, H^+]{(i)\ aq.NaOH}$ **?** **A [CBSE Delhi 2016]**

Ans.(i)

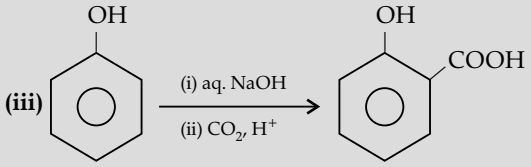


1

(ii) $CH_3 - CH = CH_2 \xrightarrow[(ii)\ 3H_2O_2 / OH^-]{(i)\ B_2H_6} CH_3CH_2CH_2OH$ **1**

Propanol

(iii)



2-Hydroxybenzoic acid (Salicylic acid) **1**

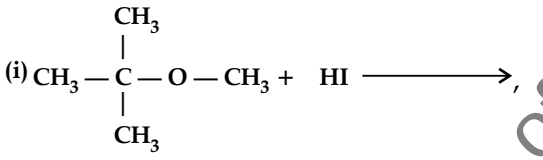
[CBSE Marking Scheme 2016]

Answering Tip

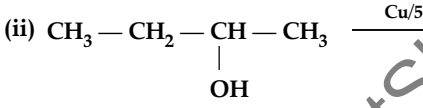
- Draw the structure and the name of the product obtained.

Q. 2. Write the final product(s) in each of the following reactions :

(i)



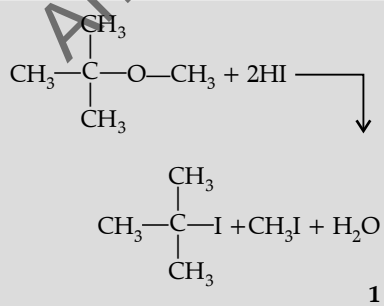
(ii)



(iii) $C_6H_5 - OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3 + aq.NaOH}$

A [CBSE OD Central 2016]

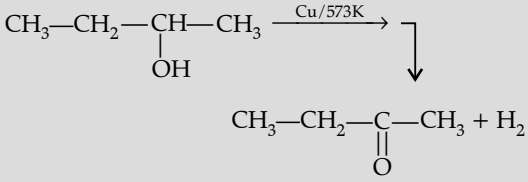
Ans. (i)



1

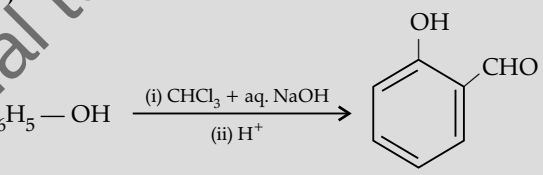
2-Iodo-2-methylpropane

(ii)



Butanone-2 **1**

(iii)



Salicylaldehyde **1**

[CBSE Marking Scheme 2016]

Answering Tip

- Draw the structure and the name of the product obtained.

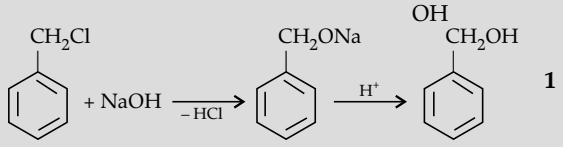
A Q. 3. How are the following conversions carried out ?
(i) Propene to propane-2-ol
(ii) Benzyl chloride to Benzyl alcohol
(iii) Anisole to p-Bromoanisole

A [CBSE Comptt. Delhi 2015]

Ans.

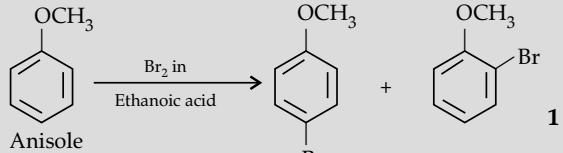
(i) $CH_3CH = CH_2 + H_2O \xrightleftharpoons{H^+} CH_3 - CH(OH) - CH_3$ **1**

(ii)



1

(iii)



Anisole — p-bromo anisole **1**

[CBSE Marking Scheme 2015]

Answering Tip

- Write the reagents involved in the conversions.

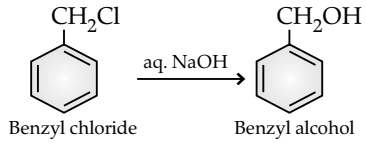
AI Q. 4. How are the following conversions carried out ?

(i) Benzyl chloride to Benzyl alcohol

(ii) Ethyl magnesium chloride to Propan-1-ol

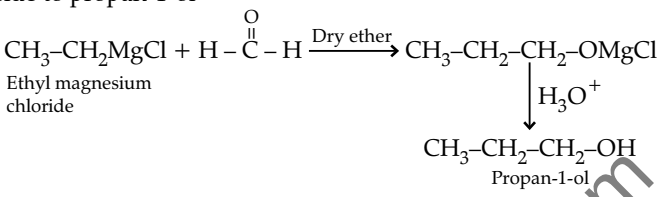
(iii) Propene to Propan-2-ol **A [CBSE Comptt. OD 2015]**

Ans. (i) Benzyl chloride to Benzyl alcohol



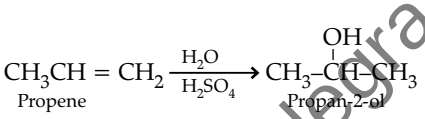
1

(ii) Ethyl magnesium chloride to propan-1-ol



1

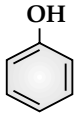
(iii) Propene to propan-2-ol



1

Q. 5. Write the major products in the following equations :

(i) $CH_3–CH_2OH \xrightarrow{PCl_5} ?$

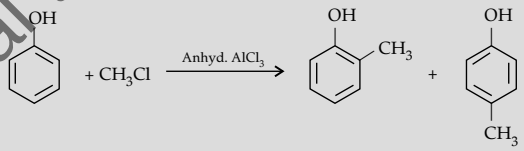
(ii)  $+ CH_3Cl \xrightarrow{anhyd.AlCl_3} ?$

(iii) $CH_3–Cl + CH_3CH_2 – ONa \longrightarrow ?$

A [CBSE Comptt. OD 2015]

Ans.(i) $CH_3–CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl$ **1**

(ii)



1

(iii) $CH_3Cl + CH_3CH_2–ONa \longrightarrow CH_3CH_2–O–CH_3$ **1**

[CBSE Marking Scheme 2015]

AI Q. 6. How do you convert the following :

(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol

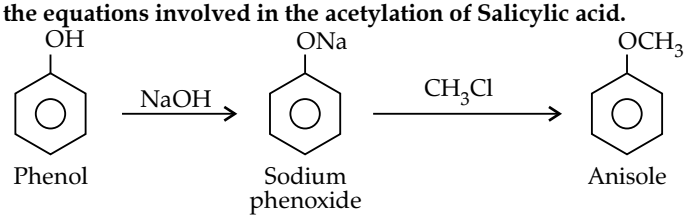
OR

(i) Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2 – O – CH_2CH_3$$

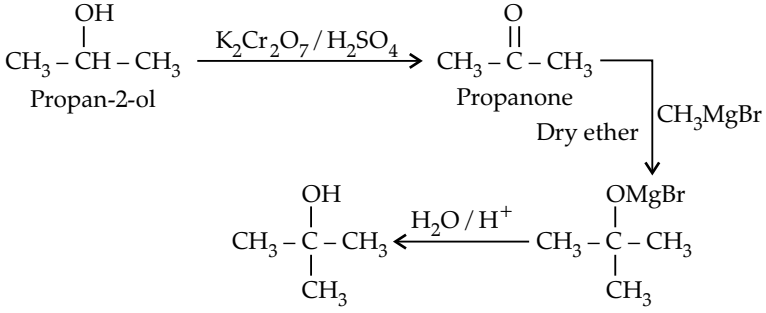
(ii) Write the equations involved in the acetylation of Salicylic acid. **A [CBSE Delhi 2015]**

Ans. (i)



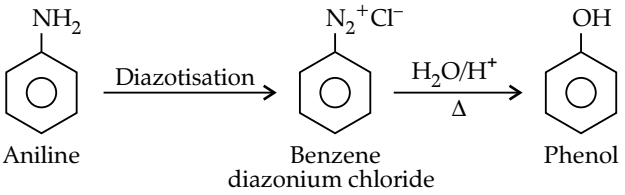
1

(ii)



1

(iii)



1

OR

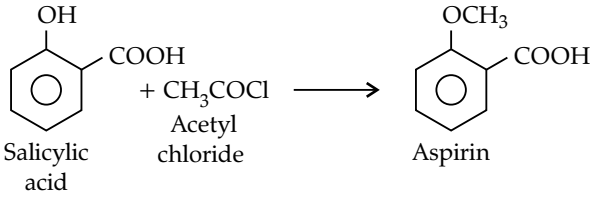
(i) $2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2 - O - CH_2CH_3$

$CH_3–CH_2–\ddot{O}H + H^+ \longrightarrow CH_3–CH_2–\overset{H}{\overset{|}{\ddot{O}}}–H$ ½

$CH_3–CH_2–\ddot{O}: + CH_2–CH_3–\overset{+}{O}\begin{matrix}H\\H\end{matrix} \longrightarrow CH_3–CH_2–\overset{+}{\underset{H}{\underset{|}{O}}}–CH_2CH_3 + H_2O$ **1**

$CH_3–CH_2–\overset{+}{\underset{H}{\underset{|}{O}}}–CH_2CH_3 \longrightarrow CH_3CH_2–O–CH_2CH_3 + H^+$ ½

(ii)



1

Answering Tip

- (i) Use arrows to show the transfer of electrons.

Q. 7. Draw the structure and name the product formed if the following alcohols are oxidized. Assume that an excess of oxidizing agent is used.

(i) $CH_3CH_2CH_2CH_2OH$

(ii) 2-butanol

(iii) 2-methyl-1-propanol A **[CBSE Delhi 2012]**

Ans. (i) $CH_3CH_2CH_2COOH$
Butanoic acid **1**

(ii) $CH_3—CH=CH—COOH$
But-2-en-1-oic acid or 2-butenoic acid **1**

(iii) $CH_3—CH(CH_3)—COOH$
2-methyl propanoic acid **1**

Q. 8. (i) Give mechanism of preparation of ethoxy ethane from ethanol.

(ii) How is toluene obtained from phenol ? A **[CBSE Comptt. Delhi 2013]**

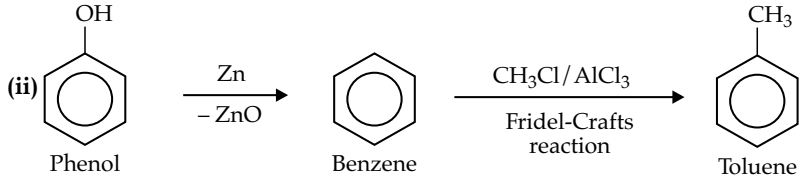
Ans. (i) $2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2 - O - CH_2CH_3$

$CH_3–CH_2–\ddot{O}H + H^+ \longrightarrow CH_3–CH_2–\overset{H}{\overset{|}{\ddot{O}}}–H$ ½

$CH_3–CH_2–\ddot{O}: + CH_2–CH_3–\overset{+}{O}\begin{matrix}H\\H\end{matrix} \longrightarrow CH_3–CH_2–\overset{+}{\underset{H}{\underset{|}{O}}}–CH_2CH_3 + H_2O$ **1**

$CH_3–CH_2–\overset{+}{\underset{H}{\underset{|}{O}}}–CH_2CH_3 \longrightarrow CH_3CH_2–O–CH_2CH_3 + H^+$ ½

(ii)



1

Q. 9. What happens when

(i) $(CH_3)_3C–OH$ is treated with Cu at 573 K,

(ii) Anisole is treated with CH_3Cl/anhydrous $AlCl_3$,

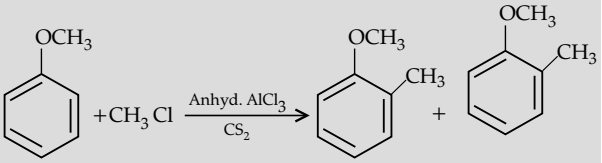
(iii) Phenol is treated with Zn dust?

Write chemical equation in support of your answer. A **[CBSE Foreign Set-1, 2, 3 2017]**

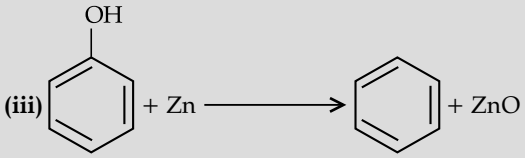
Ans. (i) $(CH_3)_3$ C-OH undergoes dehydration. ½ + ½

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - OH \xrightarrow[573\,K]{Cu} CH_3 - \overset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$$

(ii) Methyl group is introduced at ortho and para positions. ½ + ½



(iii)



½ + ½

[CBSE Marking Scheme 2017]

AI Q. 10. (i) Why phenol is more acidic than ethanol?

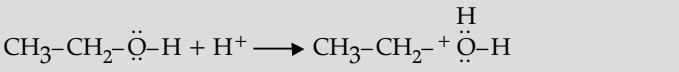
(ii) Write the mechanism of acid dehydration of ethanol to yield ether :

$$2CH_3CH_2OH \xrightarrow[413K]{H^+} CH_3CH_2OCH_2CH_3$$ AE + A **[CBSE Comptt OD Set-I, III 2017]**

Ans. (i) Due to resonance, phenoxide ion is more stable than phenol whereas there is no resonance is alkoxide ion / explained with the help of resonating structures. **1**

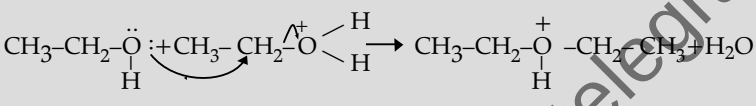
(ii)

(a)



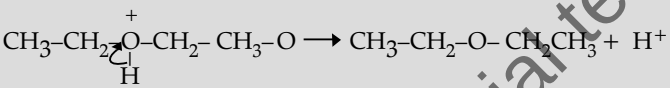
½

(b)



1

(c)



½

[CBSE Marking Scheme 2017]

Answering Tip

- (ii) Show the electron transfer mechanism by arrows.

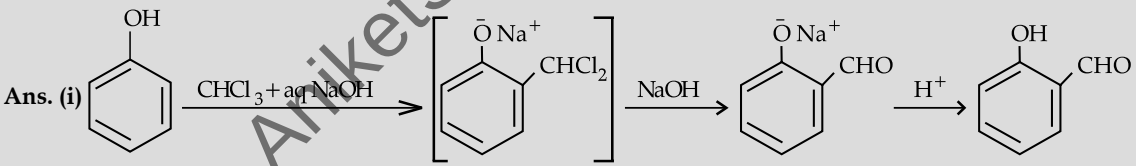
Q. 11. (i) Write Reimer-Temann reaction.

(ii) Write the mechanism of acid dehydration of ethanol to yield ethene:

$$CH_3CH_2OH \xrightarrow[443K]{H^+} CH_2 = CH_2 + H_2O$$

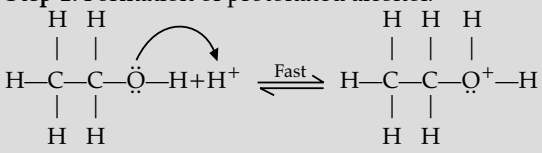
R + A **[CBSE Comptt. OD Set-2 2017]**

Ans. (i)



1

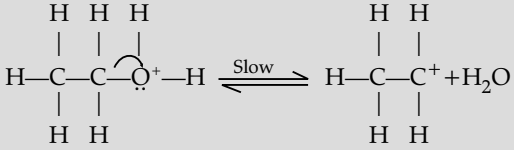
(ii) Step 1: Formation of protonated alcohol.



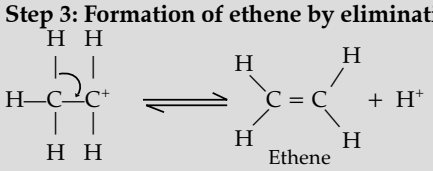
Ethanol — Protonated alcohol [Ethyl oxonium ion]

½

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction. ½



Step 3: Formation of ethene by elimination of a proton.



Ethene

1

[CBSE Marking Scheme 2017]

Q. 12. (i) Complete the following reaction and suggest a suitable mechanism for the reaction :

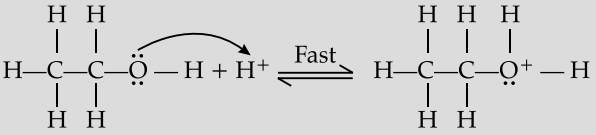
$CH_3CH_2OH \xrightarrow{H^+, 443\,K}$

(ii) Why ortho-Nitrophenol is steam volatile while para-Nitrophenol is less volatile?

A + A&E **[CBSE Comptt. Delhi/OD 2018]**

Ans. $C_2H_5OH \xrightarrow[443\,K]{H_2SO_4} CH_2 = CH_2 + H_2O$ ½

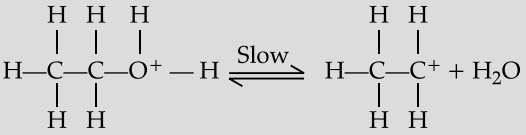
Step 1 : Formation of protonated alcohol.



½

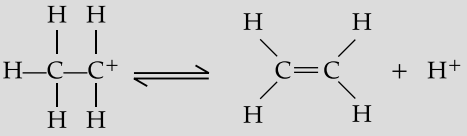
Ethanol — Protonated ethanol (Ethyl oxonium ion)

Step 2 : Formation of carbocation.



½

Step 3 : Formation of ethane by elimination of a proton.



½

Ethene

(ii) o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding. **1**

[CBSE Marking Scheme 2018]

AI **Q. 13. Explain the following behaviours:**

(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

(iii) Cumene is a better starting material for the preparation of phenol. A&E **[CBSE SQP 2017]**

Ans. (i) Because of H-bond formation between alcohol and water molecule.

(ii) Nitro being the electron withdrawing group stabilises the phenoxide ion.

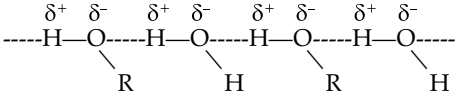
(iii) Side product formed in this reaction is acetone which is another important organic compound.

1+1+1

[CBSE Marking Scheme 2017]

Detailed Answer:

(i) Alcohols are able to form H-bonds with water due to presence of (-OH) group. Hence, they are soluble in water.



Whereas hydrocarbons are not able to form H-bonds with water hence are insoluble in water. **1**

(ii) Nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond resulting in easier loss of proton. The o-nitrophenoxide ion formed after the loss of protons is stabilised by resonance. Hence, orthonitrophenol is a stronger acid. Whereas, methoxy is an electron-releasing group which increases the electron density in the O-H bond. releasing proton difficult. Thus ortho-nitrophenol is more acidic that ortho-methoxyphenol. **1**

(iii) As oxidation of cumene results in the formation of phenol and acetone as by–product which is a commercial product used as chemical. **1**

Q. 14. Give reasons for the following:

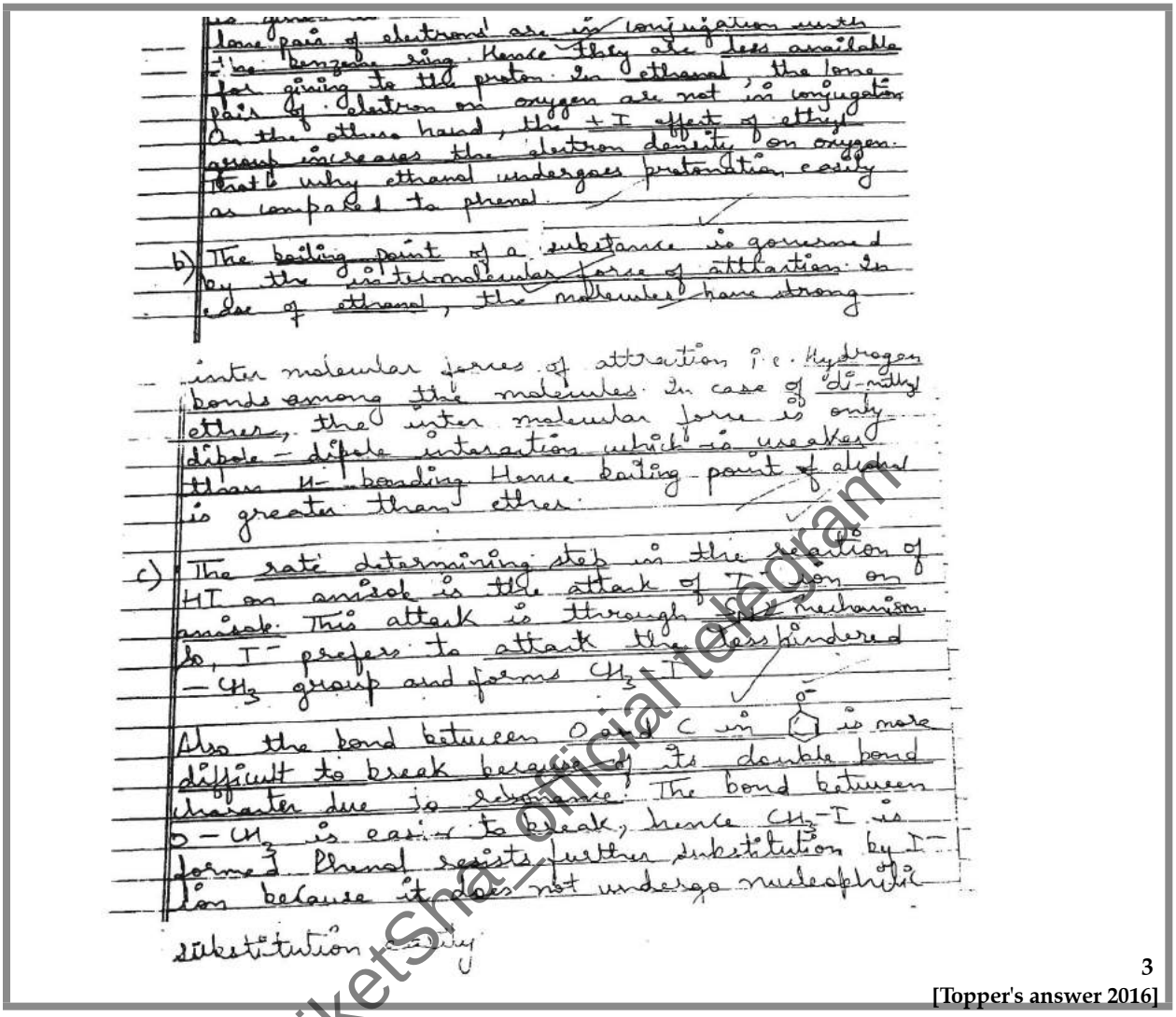
(a) Protonation of Phenols is difficult whereas ethanol easily undergoes protonation.

(b) Boiling point of ethanol is higher than that of dimethyl ether.

(c) Anisole on reaction with HI gives phenol and CH_3– I as main products and not iodobenzene and CH_3OH.

A&E **[CBSE OD Set-2 2016]**

Ans. 11. a) On protonation, the lone pair on the oxygen atom is given to the proton. In case of phenol, the



3

[Topper's answer 2016]

Detailed Answer:

(i) In phenol, the lone pair of electrons on oxygen involves in delocalization which results in their non-availability for the protonation. Whereas in ethanol, the electrons on oxygen atom are not delocalised which results in their availability for protonation. **1**

(ii) The variation can be established by intermolecular hydrogen bonding, where alcoholic hydrogen is bound to a strongly electronegative oxygen atom to give rise to dipole of the form, $Et–O^{\delta-} – H^{\delta+}$ which arises the boiling point.

Whereas, C-O bonds in dimethyl ether are polar. Carbon bonded with hydrogen is moderately electronegative compared to oxygen. In the absence of intermolecular bonding, ether becomes more volatile. **1**

(iii) Attack of I^- ion on anisole is through SN_2 mechanism, which attacks the lesser hindered CH_3 group forming CH_3I. Also, C-O bond in ether is difficult to break due to resonance. **1**

Long Answer Type Questions-II

(5 marks each)

AI **Q. 1 (i) Write the formula of reagents used in the following reactions:**

(a) Bromination of phenol to 2,4,6-tribromophenol

(b) Hydroboration of propene and then oxidation to propanol.

(ii) Arrange the following compound groups in the increasing order of their property indicated:

(a) p-nitrophenol, ethanol, phenol (acidic character)

(b) Propanol, Propane, Propanal (boiling point)

(iii) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_3 – CH_2 – \overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3 – CH_2 – \overset{+}{\underset{|}{\underset{H}{O}}} – CH_2 – CH_3 + H_2O$$

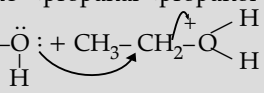
A + U **[CBSE Delhi Set-1,2,3 2017]**

Ans. (i) (a) Aq. Br_2 **1**

(b) B_2H_6, H_2O_2 and OH^- **1**

(ii) (a) ethanol<phenol<p-nitrophenol **1**

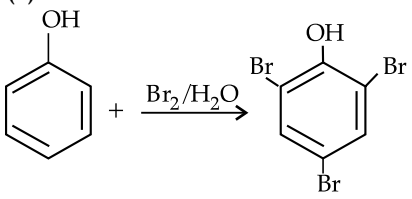
(b) propane <propanal<propanol **1**

(iii)  **1**

[CBSE Marking Scheme 2017]

Detailed Answer :

(i) (a)



Phenol 2,4,6- tribromophenol **1**

(b)

$$3CH_3-CH=CH_2 \xrightarrow{B_2H_6} (CH_3-CH_2-CH_2)_3-B \xrightarrow[H_2O_2/OH^-]{} CH_3-CH_2-CH_2OH$$ **1**

Commonly Made Error

- Some students are not able to identify all the reagents correctly.

Answering Tip

- To study organic reactions by writing the equations. Catalysts and conditions should be properly indicated.

Q. 2. Explain a process in which a biocatalyst is used in industrial preparation of a compound known to you. C **[NCERT Exemp. Q 74, Page 164]**

Ans. Biocatalysts are complex organic compounds which act as catalysts in reaction taking place in living organism. These biocatalysts (enzymes) are used in the manufacture of ethanol.

Ethanol from sugar solution (molasses):

Molasses is a non-crystalline form of sugar obtained as the mother liquor after crystallization of sugar from sugar solution. This contains about 50% sugar. It is diluted to about 10% solution and yeast is added and kept for about 2-3 days. Yeast supplies the enzymes invertase and zymase. The enzyme invertase hydrolyses sucrose to glucose and fructose to ethanol.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH}+2CO_2$$

In wine making, grapes are the source of sugar and yeast. As grapes ripen, the quantity of sugar increases and the yeast grows on the skin of the grapes. When the grapes are crushed, sugar and enzyme come in contact and fermentation starts. Fermentation takes place under anaerobic conditions (*i.e.* in the absence of air). During fermentation, CO_2 is released.

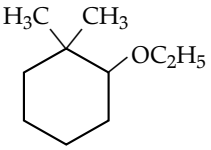
The action of enzyme is inhibited when the concentration of alcohol exceeds 14%. If air enters the fermentation mixture, the O_2 released from the air oxidizes ethanol to ethanoic acid which spoils the taste of alcoholic drinks and make it sour. **5**

TOPIC-2
Methods of Preparation and Properties of Ethers

Revision Notes

- **Ethers :** Compounds with general formula $C_nH_{2n+2}O$. They are represented by general structure, R–O–R'.
- **Nomenclature of Ethers :** Ethers are named from names of alkyl/aryl/groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix '*di*' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether. These types of ethers are called symmetrical ethers. If both the alkyl groups are different, for example, $CH_3OC_2H_5$ is ethylmethyl ether. These types of ethers are called unsymmetrical ethers. During naming ethers, the larger alkyl group is chosen as the parent hydrocarbon.

➢ **Common and IUPAC names of some Ethers are :**

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_2CH_3$	Methyl *n*-butyl ether	1-Methoxybutane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_2H_5—O—C_6H_5$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6— CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O — \underset{\displaystyle CH_3}{\underset{\vert}{CH}} — CH_3$	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5 — O — CH_2 — CH_2 — \underset{\displaystyle CH_3}{\underset{\vert}{CH}} — CH_2$	Phenyl isopentyl ether	3-Methylbutoxybenzene
$CH_3 — O — CH_2 — CH_2 — OCH_3$	—	1, 2-Dimethoxyethane
	—	2-Ethoxy-1, 1-dimethylcyclohexane

➢ **Methods of preparation of Ethers :**

(a) Williamson's synthesis : When alkyl halide reacts with sodium alkoxide, ethers are formed. *e.g.*,

$$\underset{\text{Alkyl halide}}{R – X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na} – \overset{-}{O} – R'} \longrightarrow \underset{\text{Ether}}{R – O – R'} + NaX$$

$$C_2H_5Br + CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{C}}—ONa \longrightarrow CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{C}}—OC_2H_5 + NaBr$$

2-ethoxy, 2-methyl propane

(ii) Dehydration of alcohols : Alcohols are dehydrated to ethers in presence of concentrated sulphuric acid at 413 K. The reaction involves the removal of one molecule of water from two moles of alcohols.

$$\underset{\text{Ethyl alcohol}}{C_2H_5\boxed{OH + H}OC_2H_5} \xrightarrow[413\ K]{\text{conc. } H_2SO_4} \underset{\text{Diethyl ether (Ethoxy ethane)}}{C_2H_5OC_2H_5} + H_2O$$

Alcohols can also be dehydrated by heating with alumina at 523 K and high pressure. This method is not suitable for preparation of unsymmetrical ethers.

(iii) Heating alkyl halides with dry silver oxide : Ethers can be prepared by heating alkyl halides with dry silver oxide (Ag_2O).

$$2C_2H_5Cl + Ag_2O \xrightarrow{\text{heat}} C_2H_5—O—C_2H_5 + 2AgCl$$

$$CH_3Cl + Ag_2O + C_2H_5Cl \longrightarrow CH_3—O—C_2H_5 + 2AgCl$$

Mixed ethers or unsymmetrical ethers can be prepared by this method.

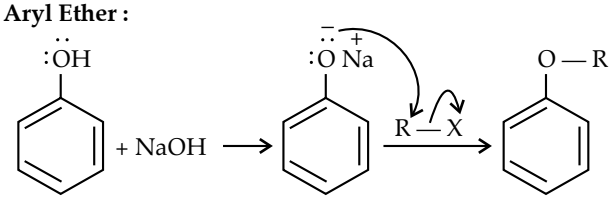
(iv) Reaction of lower halogenated ethers with Grignard reagent : Higher homologous ethers can be prepared by action of Grignard reagent on lower halogenated ethers.

$$\underset{\text{Chloromethyl ether}}{CH_3OCH_2Cl} + BrMgC_2H_5 \rightarrow \underset{\text{Methyl propyl ether}}{CH_3—O—CH_2—C_2H_5} + Mg\begin{matrix}Br\\ \diagdown\\ \diagup\\ Cl\end{matrix}$$

(v) Action of diazomethane on alcohols : Methyl ethers can be prepared by action of diazomethane on alcohols in the presence of catalysts like BF_3.

$$C_2H_5OH + CH_2N_2 \xrightarrow{BF_3} \underset{\text{Methyl ethyl ether}}{C_2H_5OCH_3} + N_2$$

(b) Preparation of Aryl Ether :

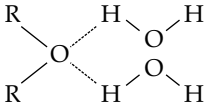


➢ **Physical Properties :**

(i) Colourless, pleasant smelling and volatile liquids.

(ii) Lower boiling points than alcohols.

(iii) Solubility is comparable to those of corresponding alcohols due to the ability of their molecules to form hydrogen bond with water molecules.



➢ **Chemical properties :**

(i) Cleavage with halogen acid :

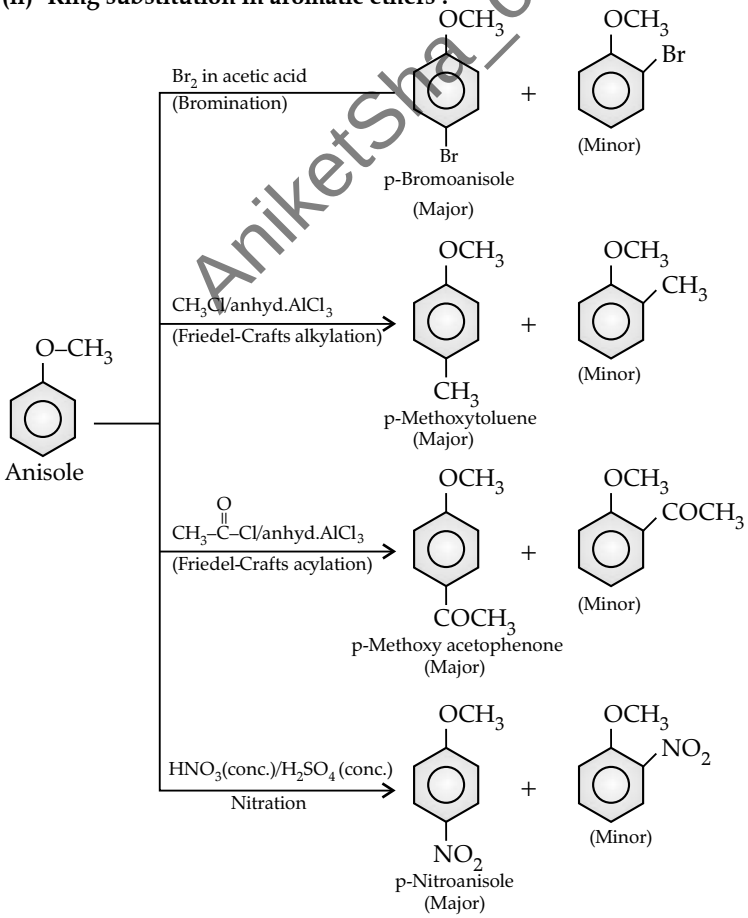
$$\underset{\text{Ether}}{R-O-R} + HX \xrightarrow{373\ K} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX\ (X = Br, I)}$$

$$C_2H_5OC_2H_5 + HI \xrightarrow{373\ K} C_2H_5OH + C_2H_5I$$

$$C_2H_5OC_2H_5 + \underset{\text{(Excess)}}{2HI} \xrightarrow{373\ K} 2C_2H_5I + H_2O$$

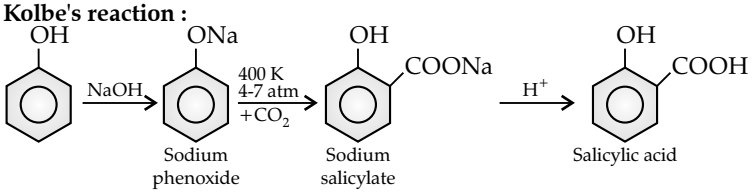
$$\underset{\text{tert-Butyl methyl ether}}{CH_3-C(CH_3)_2-OCH_3} + HI \xrightarrow{373\ K} \underset{\text{tert-Butyl iodide}}{CH_3-C(CH_3)_2-I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

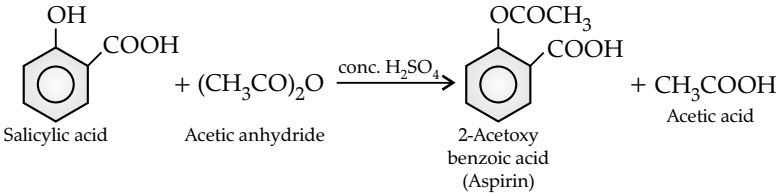
(ii) Ring substitution in aromatic ethers :



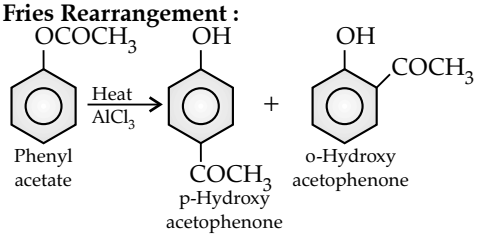
➢ **Some important name reactions :**

(i) Kolbe's reaction :





(ii) Fries Rearrangement :



(iii) Williamson synthesis :

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}-\bar{O}-R'} \longrightarrow \underset{\text{Ether}}{R-O-R'} + NaX$$

Know the Term

➢ **Alkoxyalkanes :** Ethers are named as alkoxyalkanes. The larger alkyl group forms the part of parent chain while smaller alkyl group constitutes the alkoxy group.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. IUPAC name of the compound. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OCH_3$

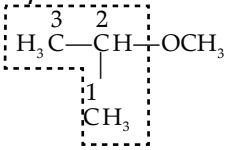
is _____.

(a) 1-methoxy-1-methylethane
(b) 2-methoxy-2-methylethane
(c) 2-methoxypropane
(d) isopropylmethyl ether

A **[NCERT Exemp. Q. 9, Page 155]**

Ans. Correct option : (a)

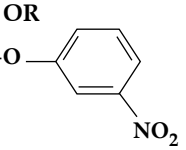
Explanation :



Q. 2. Which of the following species can act as the strongest base?

(a) – OH **(b) – OR**

(c) – OC_6H_5 **(d)**



U **[NCERT Exemp. Q. 10, Page 156]**

Ans. Correct option : (b)

Explanation : Weakest acid has the strongest conjugate base. Since R-OH is the weakest acid, therefore, –OR is the strongest base.

B. Answer the following:

Q. 1. Write the IUPAC name of the given compound :

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-CH_3$$

A **[CBSE OD 2015]**

Ans. 1-Ethoxy-2-methylpropane. **1**

Q 2. Write the IUPAC name of the following compound:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-O-CH_3$$

A **[CBSE OD Set-3 2017]**

Ans. 2-Methoxy -2- methylpropane **1**
[CBSE Marking Scheme 2017]

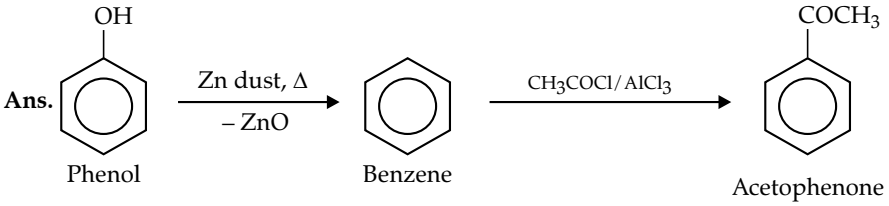
Q. 3. Write the equation involved in the reaction Williamson's ether synthesis. R **[CBSE OD 2013]**

Ans. $R-X + R'-ONa \longrightarrow R-O-R' + NaX$
Alkyl halide, Sodium alkoxide, Ether

e.g. $CH_3I + C_2H_5ONa \longrightarrow CH_3-O-C_2H_5 + NaI$
Methyl iodide, Sodium ethoxide, Ethyl methyl ether **1**

AI **Q. 4. How would you obtain acetophenone from phenol ?** A **[CBSE Comptt. OD 2013]**

Ans.



1

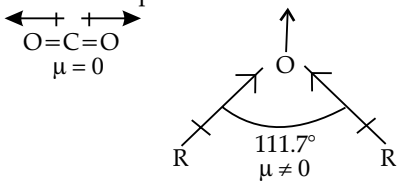
AI **Q. 5. An alkoxide is a stronger base than hydroxide ion. Justify.** A&E **[CBSE SQP 2013]**

Ans. Due to the presence of an alkyl group, higher electron density is found in alkoxide ion. **1**

Short Answer Type Questions **(2 marks each)**

Q. 1. Explain why is O=C=O nonpolar while R–O–R is polar. A&E **[NCERT Exemp. Q. 44, Page 160]**

Ans. CO_2 is a linear molecule. The dipole moment of two C = O bonds are equal and opposite. Hence, they cancel each other. So, the dipole moment of CO_2 is zero and it is a non-polar molecule.



While for ethers, two dipoles are pointing in the same direction. These two dipoles do not cancel the effect of each other. Therefore, there is a finite resultant dipole and hence, R—O—R is a polar molecule. **2**

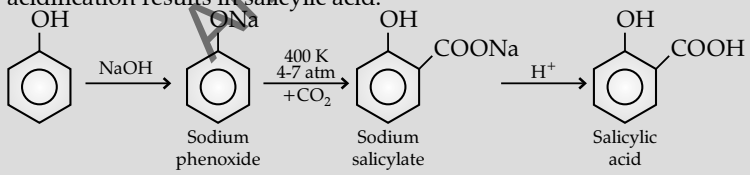
Q. 2. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason. A&E **[NCERT]**

Ans. The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed. **2**

Long Answer Type Questions-I **(3 marks each)**

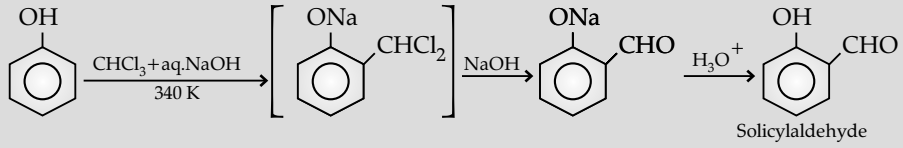
Q. 1. Explain the following with an example in each :
(i) Kolbe's reaction (ii) **Reimer-Tiemann reaction**
(iii) Williamson ether synthesis R **[CBSE Comptt. Delhi 2016]**

Ans. (i) Kolbe's reaction : Sodium phenoxide is heated with CO_2 at 400 K under a pressure of 4-7 atm which on acidification results in salicylic acid.



1

(ii) Reimer-Tiemann reaction :



1

(iii) Williamson ether synthesis : An alkyl halide reacts with sodium alkoxide or sodium phenoxide to form ether

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}-\bar{O}-R'} \longrightarrow \underset{\text{Ether}}{R-O-R'} + NaX$$

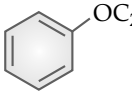
[CBSE Marking Scheme 2016] 1

Commonly Made Error

- (i) Some students write Kolbe's electrolytic reaction.

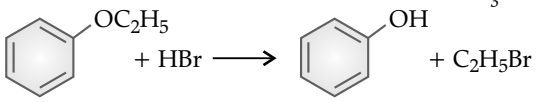
Q. 2. State the products of the following reactions :

(i) $CH_3CH_2CH_2OCH_3 + HBr \longrightarrow$

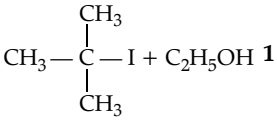
(ii)  $+ HBr \longrightarrow$

(iii) $(CH_3)_3C-OC_2H_5 \xrightarrow{HI}$ A **[CBSE Foreign 2012]**

Ans. (i) $CH_3CH_2CH_2OCH_3 + HBr \longrightarrow CH_3CH_2CH_2OH + CH_3Br$ **1**

(ii)  **1**

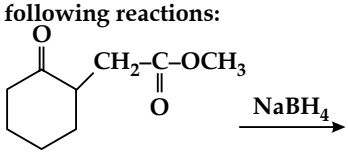
(iii) $(CH_3)_3C-O-C_2H_5 + HI \longrightarrow$

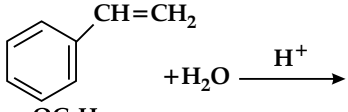
 **1**

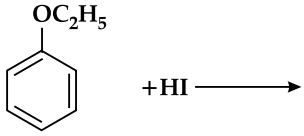
Answering Tip

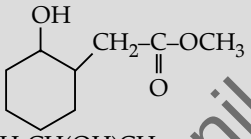
- Mention all the products formed in the chemical reaction.

AI **Q. 3. Write the structures of the main products in the following reactions:**

(i) 

(ii) 

(iii)  A **[CBSE OD 2018]**

Ans. (i)  **1**

(ii) $C_6H_5CH(OH)CH_3$ **1**

(iii) $C_2H_5I + C_6H_5OH$ (No splitting of marks) **1**

[CBSE Marking Scheme 2018]

Q. 4. The following is not an appropriate reaction for the preparation of tert-butyl ethyl ether.

$C_2H_5ONa + (CH_3)_3C-Cl \rightarrow (CH_3)_3C-OC_2H_5$

(i) What would be the major product of the given reaction ?

(ii) Write a suitable reaction for the preparation of tert-butyl ethyl ether, specifying the names of reagents used.

Justify your answer in both cases.

A **[CBSE SQP 2016]**

Ans. (i) Since the alkyl halide is a 3° halide and C_2H_5ONa is a strong base, therefore elimination occurs preferably. The product obtained is 2-Methylprop-1-ene. $[CH_3-C(CH_3)=CH_2]$. **1½**

(ii) To prepare t-Butyl ethyl ether, the alkyl halide should be 1° *i.e.,* chloroethane and the nucleophile should be sodium t-butoxide because the 3° nucleophile is able to attack 1° alkyl halide.

$(CH_3)_3C-O^-Na^+ + CH_3CH_2-Cl \rightarrow (CH_3)_3COCH_2CH_3$ **1½**

AI **Q. 5. Given reasons of the following :**

(i) Phenol is more acidic than methanol.

(ii) The C–O–H bond angle in alcohols slightly less than the tetrahedral angle (109°28′).

(iii) $(CH_3)_3C-O-CH_3$ on reaction with HI gives $(CH_3)_3C-I$ and CH_3-OH as the main products and not $(CH_3)_3C-OH$ and CH_3-I. A&E **[CBSE OD 2015]**

Ans. (i) Phenol is more acidic than methanol as the phenoxide ion formed after removal of a proton is stabilised by resonance whereas the methoxide ion formed after removal from methanol is not. **1**

(ii) Due to lone pair-lone pair repulsion on oxygen atoms. **1**

(iii) The reaction between $(CH_3)C-O-CH_3$ and HI follows S_N1 mechanism. For an S_N1 reaction, the formation of product is decided by the stability of the cabocation formed in the slowest step. As tert-butyl carbonium ion $[(CH_3)_3\overset{\oplus}{C}]$ formed after the cleavage of C—O bond in the slowest step is more stable than methyl carbonium ion therefore $(CH_3)_3$ C-I and CH_3OH are formed as main products. **1**

OSWAAL LEARNING TOOLS

***For* Suggested Online Videos**

Visit : *https://qrgo.page.link/Qj3PX* **Or Scan the Code**

Visit : *https://qrgo.page.link/2iUZq* **Or Scan the Code**

Visit : *https://qrgo.page.link/iyjzx* **Or Scan the Code**