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2ND FLOOR, SATKOUDI COMPLEX, THANA CHOWK,
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ALCOHOLS-PHENOL-ETHER
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Structural Overview:
Understand the structural characteristics of alcohols, phenols, and ethers. Explore how the presence of functional groups defines the chemical properties of these compounds.

Nomenclature Mastery:
Reinforce your knowledge of systematic nomenclature for alcohols, phenols, and ethers. Navigate through IUPAC rules, ensuring clarity in expressing compound structures.

Physical and Chemical Properties:
Explore the physical properties such as solubility, boiling points, and melting points of alcohols, phenols, and ethers. Delve into the chemical reactivity, understanding key reactions and mechanisms.

Alcohol Reactions:
Examine the various reactions involving alcohols, including oxidation, dehydration, and esterification. Understand how the functional group influences the chemical behavior.

Phenol Characteristics:
Gain insights into the unique properties of phenols, including their acidic nature and resonance stabilization. Explore their applications in industries and everyday life.

Ether Structures and Reactions:
Explore the structures and reactions of ethers. Understand their role as solvents and their importance in the synthesis of various organic compounds.

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POINTS TO REMEMBER

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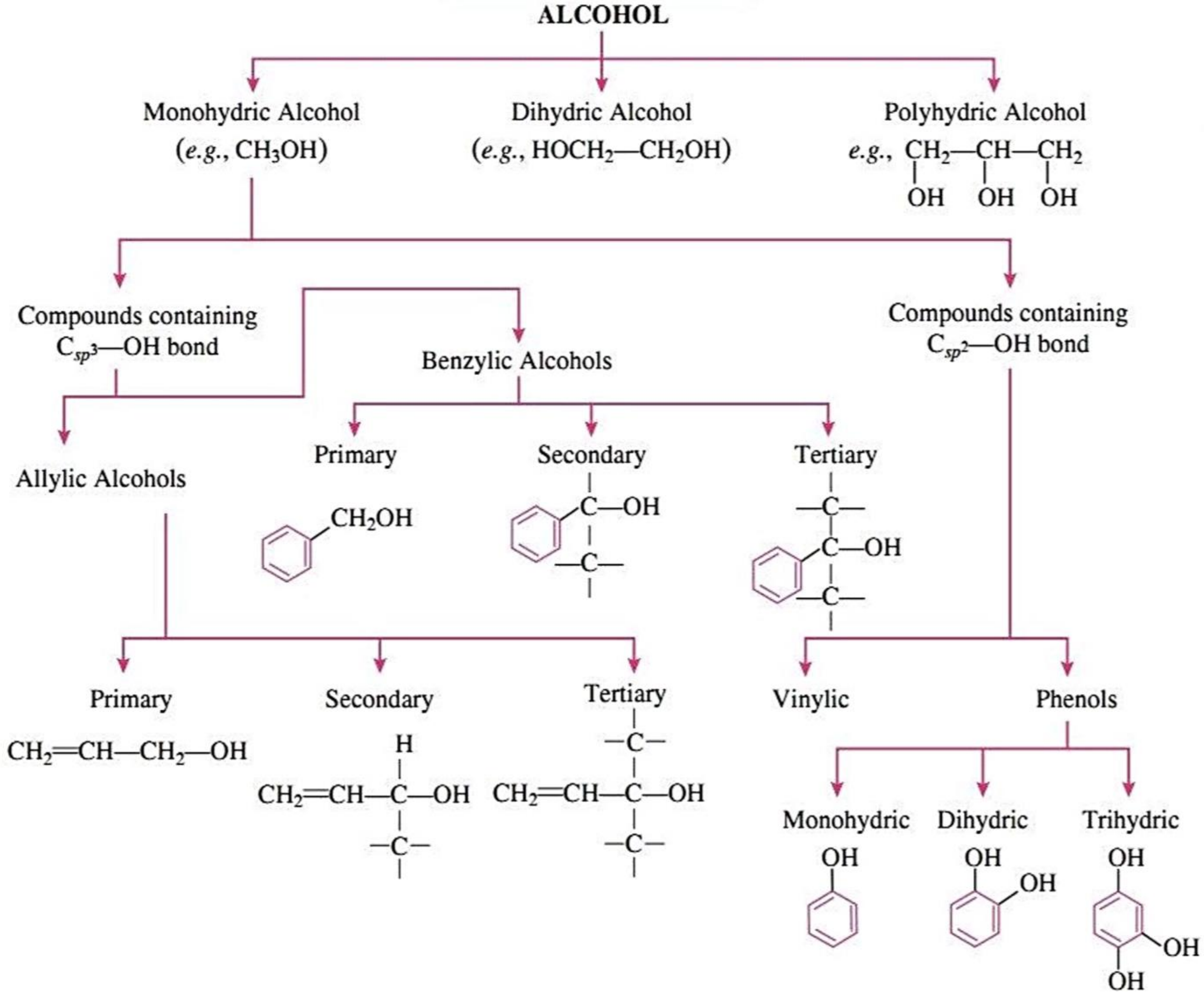
1. **Introduction:** Alcohols and phenols are the compounds containing one or more hydroxyl groups (—OH). The alcohols contain the —OH group attached to the alkyl group whereas in phenols, the —OH group is attached to the aromatic ring.

CLASSIFICATION



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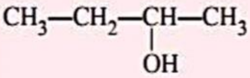
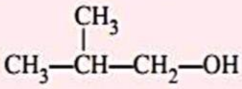
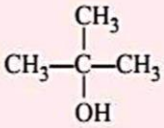
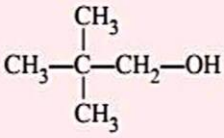
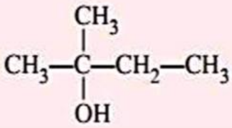
2. Common and IUPAC names of some alcohols:

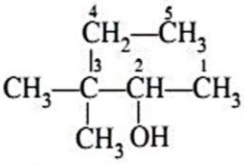
Table 7.1: Common and IUPAC Names of Some Alcohols

Common Name	Structural Formula	IUPAC Name
Ethyl alcohol	CH_3-CH_2-OH	Ethanol
n-Butyl alcohol	$CH_3-CH_2-CH_2-CH_2-OH$	Butan-1-ol
sec-Butyl alcohol	 $CH_3-CH_2-\underset{OH}{\underset{\vert}{CH}}-CH_3$	Butan-2-ol
Isobutyl alcohol	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-OH$	2-Methylpropan-1-ol
tert-Butyl alcohol	 $CH_3-\underset{OH}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_3$	2 -Methylpropan-2-ol
neo-Pentyl alcohol	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_2-OH$	2, 2-Dimethylpropan-1-ol
tert-Pentyl alcohol	 $CH_3-\underset{OH}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_2-CH_3$	2-Methylbutan-2-ol

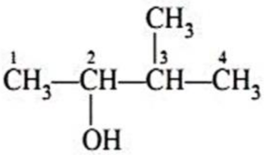
Some more examples of alcohols are given below:

$CH_2=CH-OH$

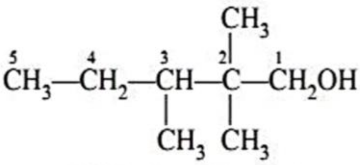
Vinyl alcohol
(Ethen-1-ol)


$CH_3-\underset{CH_3}{\underset{\vert}{\overset{\overset{4}{C}H_2-\overset{5}{C}H_3}{\overset{\vert}{\overset{3}{C}}}}}-\underset{OH}{\underset{\vert}{\overset{2}{C}H}}-\overset{1}{C}H_3$

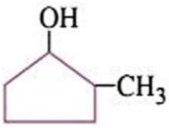
3, 3-Dimethylpentan-2-ol


$\overset{1}{C}H_3-\underset{OH}{\underset{\vert}{\overset{2}{C}H}}-\overset{CH_3}{\overset{\vert}{\overset{3}{C}H}}-\overset{4}{C}H_3$

3-Methylbutan-2-ol

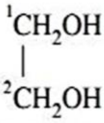

$\overset{5}{C}H_3-\overset{4}{C}H_2-\underset{CH_3}{\underset{\vert}{\overset{3}{C}H}}-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{\overset{2}{C}}}}}-\overset{1}{C}H_2OH$

2, 2, 3-Trimethylpentanol

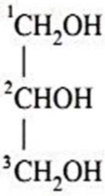


2-Methylcyclopentanol

In IUPAC system, dihydric alcohols are named as alkanediols and trihydric alcohols are named as alkanetriols.


$$\begin{array}{l} {}^1CH_2OH \\ \vert \\ {}^2CH_2OH \end{array}$$

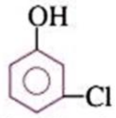
Ethylene glycol
(Ethane-1, 2-diol)

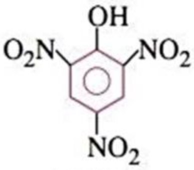

$$\begin{array}{l} {}^1CH_2OH \\ \vert \\ {}^2CHOH \\ \vert \\ {}^3CH_2OH \end{array}$$

Glycerol
(Propane-1, 2, 3-triol)

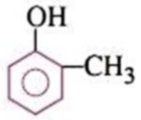
The simplest hydroxy derivative of benzene is phenol. The substituted phenols are named as derivatives of phenol.

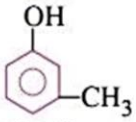

Phenol


3-Chlorophenol

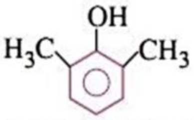

Picric acid
(2,4,6-Trinitrophenol)

Methyl phenols are known as cresols.

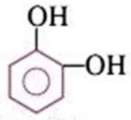

o-Cresol
(2-Methylphenol)

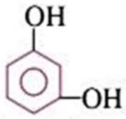

m-Cresol
(3-Methylphenol)


p-Cresol
(4-Methylphenol)

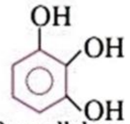

2,6-Dimethylphenol

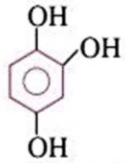
Some dihydric and trihydric phenols are given below:

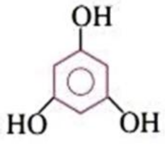

Catechol
(Benzene-1,2-diol)


Resorcinol
(Benzene-1,3-diol)

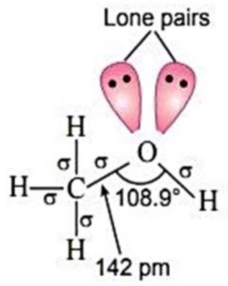

Quinol or hydroquinone
(Benzene-1,4-diol)


Pyrogallol
(Benzene-1,2,3-triol)


Hydroxyquinol
(Benzene-1,2,4-triol)


Phloroglucinol
(Benzene-1,3,5-triol)

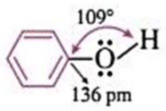
3. **Structure of R—OH:** In **alcohols**, both the carbon atoms of R, *e.g.*, —CH_3 and oxygen atom of —OH groups are sp^3 hybridised. The structure of CH_3—OH is shown below.



Structure of Methanol

The C—OH bond angle is slightly less than tetrahedral angle (109°28′) due to repulsions between lone pairs of electrons of oxygen atom. The C—O and O—H bonds are polar because of high electronegativity of oxygen atom.

In **phenols**, the –OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (*i*) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and (*ii*) sp^2 hybridised state of carbon to which oxygen is attached.



Structure of Phenol

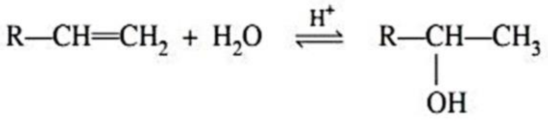
4. Methods of Preparation

Alcohols are prepared by the following methods:

(*a*) From alkenes

(*i*) By acid catalysed hydration:

Addition occurs according to Markovnikov's rule.



$$R{-}CH{=}CH_2 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

(*ii*) By hydroboration oxidation:

Addition occurs in accordance with anti-Markovnikov's rule.

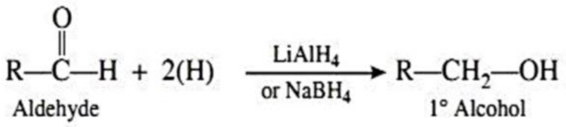
$$R{-}CH{=}CH_2 + \underset{\text{Diborane}}{\frac{1}{2}(BH_3)_2} \longrightarrow (R{-}CH_2{-}CH_2)_3B$$

$$\xrightarrow[OH^-,\ H_2O]{3H_2O_2} \underset{1^\circ\ \text{Alcohol}}{3R{-}CH_2{-}CH_2{-}OH} + H_3BO_3$$

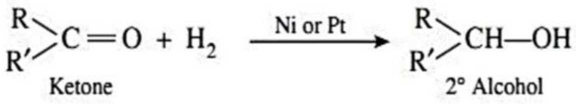
(*b*) From carbonyl compounds

(*i*) By reduction of aldehydes and ketones:

Common reducing agents used are lithium aluminium hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$), H_2 in the presence of Ni or Pt. Aldehydes on reduction give 1° alcohols whereas ketones on reduction give 2° alcohols.



$$\underset{\text{Aldehyde}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} + 2(H) \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{1^\circ\ \text{Alcohol}}{R{-}CH_2{-}OH}$$



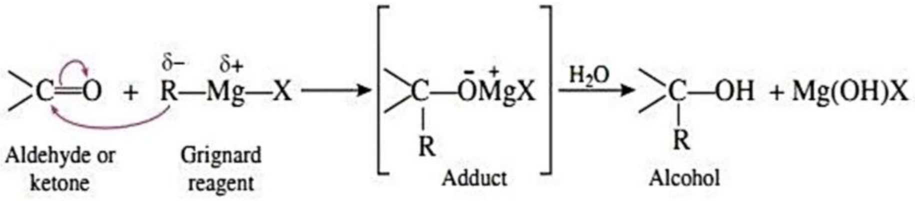
$$\underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}O} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{2^\circ\ \text{Alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>\!CH{-}OH}$$

(*ii*) By reduction of carboxylic acids and esters:

$$\underset{\text{Carboxylic acid}}{R{-}COOH} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} \underset{1^\circ\text{Alcohol}}{R{-}CH_2{-}OH}$$

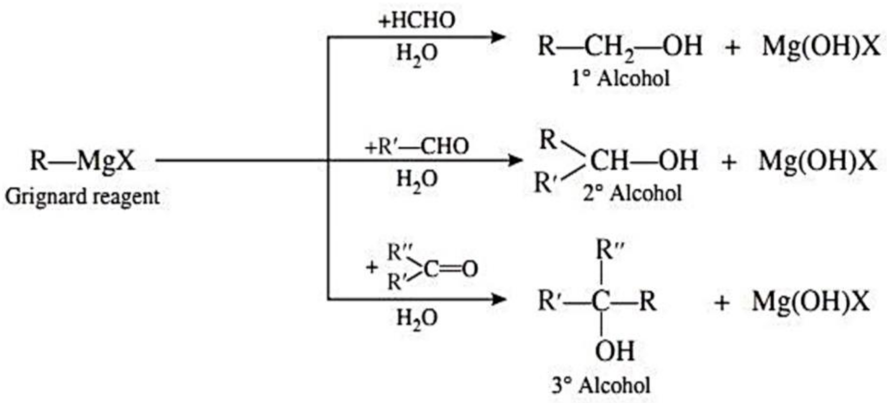
$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow[H^+]{R'OH} \underset{\text{Ester}}{R{-}COOR'} \xrightarrow{H_2/Pd} \underset{1^\circ\text{Alcohol}}{R{-}CH_2{-}OH} + R'{-}OH$$

(*c*) From Grignard's reagents



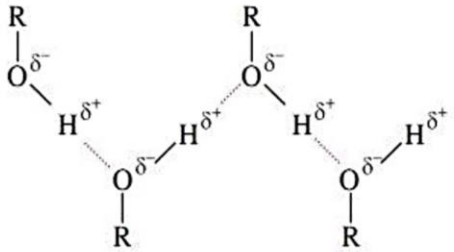
$$>C{=}O + \overset{\delta-}{R}{-}\overset{\delta+}{Mg}{-}X \longrightarrow \left[>\underset{\displaystyle R}{\underset{|}{C}}{-}\bar{O}\overset{+}{Mg}X\right] \xrightarrow{H_2O} >\underset{\displaystyle R}{\underset{|}{C}}{-}OH + Mg(OH)X$$

The reaction of Grignard's reagents with formaldehyde produces a primary alcohol, with other aldehydes it produces secondary alcohols and tertiary alcohols with ketones.



5. Physical Properties of Alcohols:

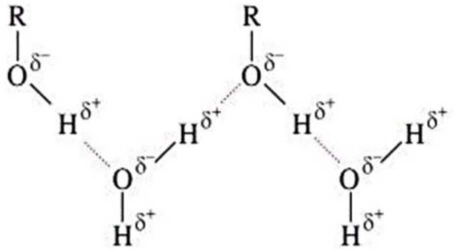
(*a*) **Boiling points:** Boiling points of alcohols are much higher than those of alkanes, haloalkanes or ethers of comparable molecular masses. This is because in alcohols strong intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.



Among isomeric alcohols, the boiling point decreases with increase in branching in the alkyl group (due to decrease in van der Waals forces with decrease in surface area). For isomeric alcohols, the boiling points generally follow the order:

Primary alcohol > Secondary alcohol > Tertiary alcohol.

(*b*) **Solubility of alcohols:** The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents like ether, benzene, etc. The solubility of lower alcohols in water is due to their ability to form hydrogen bonds with water molecules.

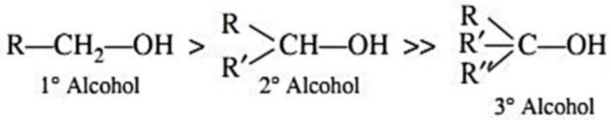


The solubility of alcohols in water decreases with increase in molecular mass because with increase in molecular mass the non-polar alkyl group becomes predominant and masks the effect of polar —OH group. In addition, among the isomeric alcohols the solubility increases with branching of chain. It is because the surface area of non-polar part in the molecule decreases, thus enhancing the solubility.

6. Chemical Properties of Alcohols:

(*a*) **Reactions involving cleavage of oxygen–hydrogen (O—H) bond**

Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O—H bond. An electron releasing group (alkyl group) 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 alcohols decreases in the following order:



$$\underset{1^\circ\ \text{Alcohol}}{R\!-\!CH_2\!-\!OH} > \underset{2^\circ\ \text{Alcohol}}{RR'CH\!-\!OH} >> \underset{3^\circ\ \text{Alcohol}}{RR'R''C\!-\!OH}$$

(*i*) **Reaction with metals:**

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

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

$$\underset{3^\circ\ \text{Butyl alcohol}}{6(CH_3)_3\!-\!C\!-\!OH} + 2Al \longrightarrow \underset{\text{Aluminium tert-butoxide}}{2((CH_3)_3\!-\!CO)_3Al} + 3H_2$$

(*ii*) **Esterification:**

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

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

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

(*b*) **Reactions involving cleavage of carbon–oxygen (C—O) bond**

In such type of reactions, the order of reactivity of alcohols is

3°Alcohol > 2°Alcohol > 1°Alcohol

(*i*) **Reaction with hydrogen halides:**

$$\underset{\text{Alcohol}}{R\!-\!OH} + H\!-\!X \longrightarrow \underset{\text{Alkyl halide}}{R\!-\!X} + H_2O$$

$$CH_3\!-\!CH_2\!-\!OH + H\!-\!Cl \xrightarrow{\text{Anhyd. } ZnCl_2} CH_3\!-\!CH_2\!-\!Cl + H_2O$$

(*ii*) **Reaction with phosphorus halides:**

$$R\!-\!OH + PCl_5 \longrightarrow R\!-\!Cl + POCl_3 + HCl$$

$$3R\!-\!OH + PCl_3 \longrightarrow 3R\!-\!Cl + H_3PO_3$$

$$3R\!-\!OH + PBr_3 \xrightarrow{\text{from } (P\ \&\ Br_2)} 3R\!-\!Br + H_3PO_3$$

$$3R\!-\!OH + PI_3 \xrightarrow{\text{from } (P\ \&\ I_2)} 3R\!-\!I + H_3PO_3$$

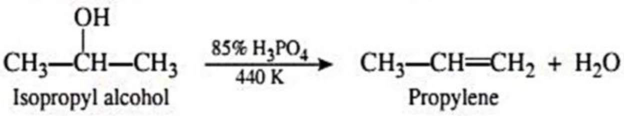
(*iii*) **Reaction with thionyl chloride:**

$$R\!-\!OH + SOCl_2 \longrightarrow R\!-\!Cl + SO_2\uparrow + HCl\uparrow$$

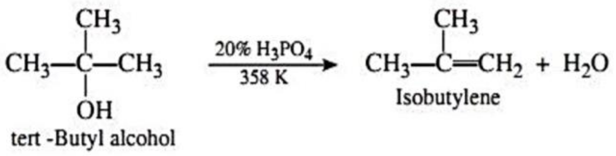
(*iv*) **Dehydration:** The ease of dehydration follows the following order:

3° Alcohol > 2° Alcohol > 1° Alcohol

$$\underset{\text{Ethyl alcohol}}{CH_3\!-\!CH_2\!-\!OH} \xrightarrow[443\ K]{\text{conc. } H_2SO_4} \underset{\text{Ethene}}{CH_2\!=\!CH_2} + H_2O$$



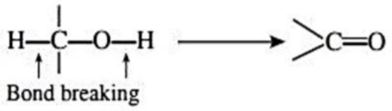
$$\underset{\text{Isopropyl alcohol}}{CH_3\!-\!\overset{\overset{\large OH}{|}}{C}H\!-\!CH_3} \xrightarrow[440\ K]{85\%\ H_3PO_4} \underset{\text{Propylene}}{CH_3\!-\!CH\!=\!CH_2} + H_2O$$



$$(CH_3)_3C{-}OH \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O$$

tert -Butyl alcohol → Isobutylene

(*v*) **Oxidation:** Oxidation of alcohols involves the formation of a carbon–oxygen double bond with the cleavage of an O—H and C—H bond.

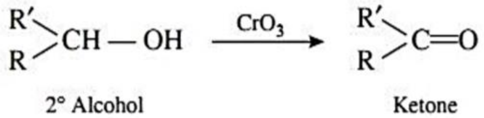


1° alcohols on oxidation give aldehydes which on further oxidation give carboxylic acids with the same number of carbon atoms.

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

$$\underset{\text{But-2-enol}}{CH_3{-}CH{=}CH{-}CH_2{-}OH} \xrightarrow{PCC} \underset{\text{But-2-enal}}{CH_3{-}CH{=}CH{-}CHO}$$

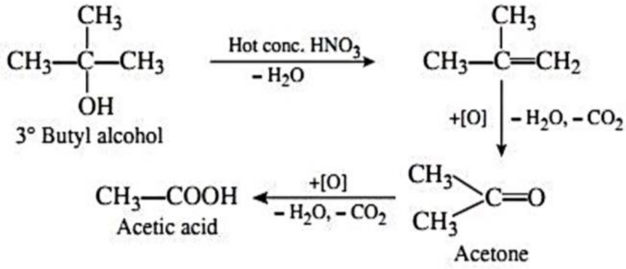
2° Alcohols are oxidised to ketones by CrO_3.



$$RR'CH{-}OH \xrightarrow{CrO_3} RR'C{=}O$$

2° Alcohol → Ketone

3° alcohols do not undergo oxidation reaction as they do not have α-hydrogens. However, when oxidation is carried under strong reaction conditions and elevated temperature, they undergo oxidation with the cleavage of C—C bond.



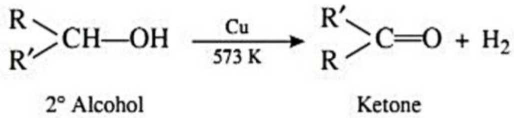
$$\underset{\text{3° Butyl alcohol}}{(CH_3)_3C{-}OH} \xrightarrow[-H_2O]{\text{Hot conc. }HNO_3} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow[-H_2O,\ -CO_2]{+[O]} \underset{\text{Acetone}}{(CH_3)_2C{=}O} \xrightarrow[-H_2O,\ -CO_2]{+[O]} \underset{\text{Acetic acid}}{CH_3{-}COOH}$$

(*vi*) **Dehydrogenation**

Primary alcohols are dehydrogenated to aldehydes.

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

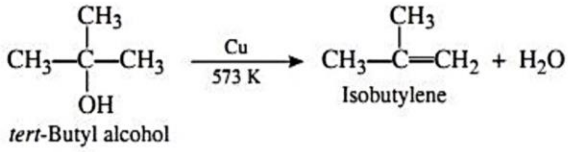
Secondary alcohols are dehydrogenated to ketones.



$$RR'CH{-}OH \xrightarrow[573\text{ K}]{Cu} RR'C{=}O + H_2$$

2° Alcohol → Ketone

Tertiary alcohols undergo dehydration to give alkenes.

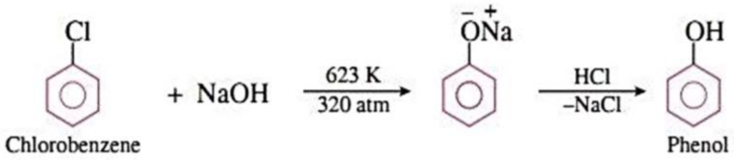


$$(CH_3)_3C{-}OH \xrightarrow[573\text{ K}]{Cu} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O$$

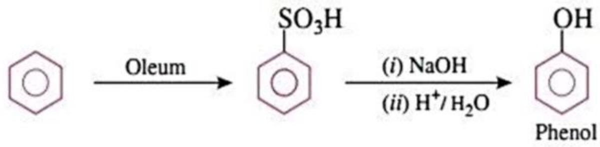
tert-Butyl alcohol → Isobutylene

7. Preparation of Phenols:

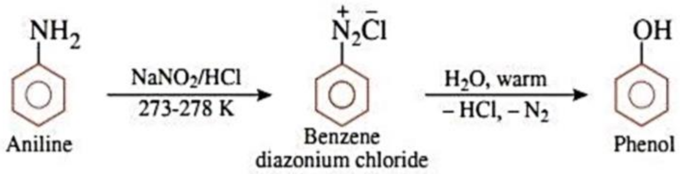
(*i*) From aryl halides



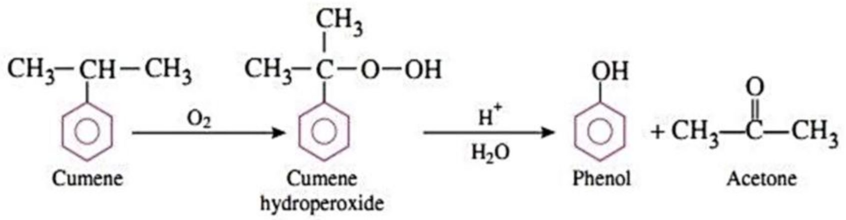
(*ii*) From benzenesulphonic acid



(*iii*) From diazonium salts

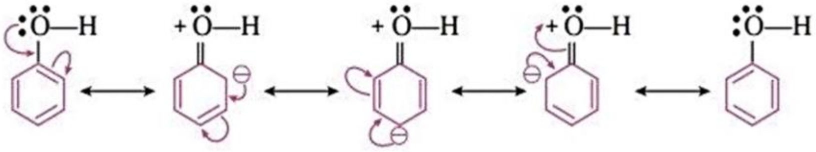


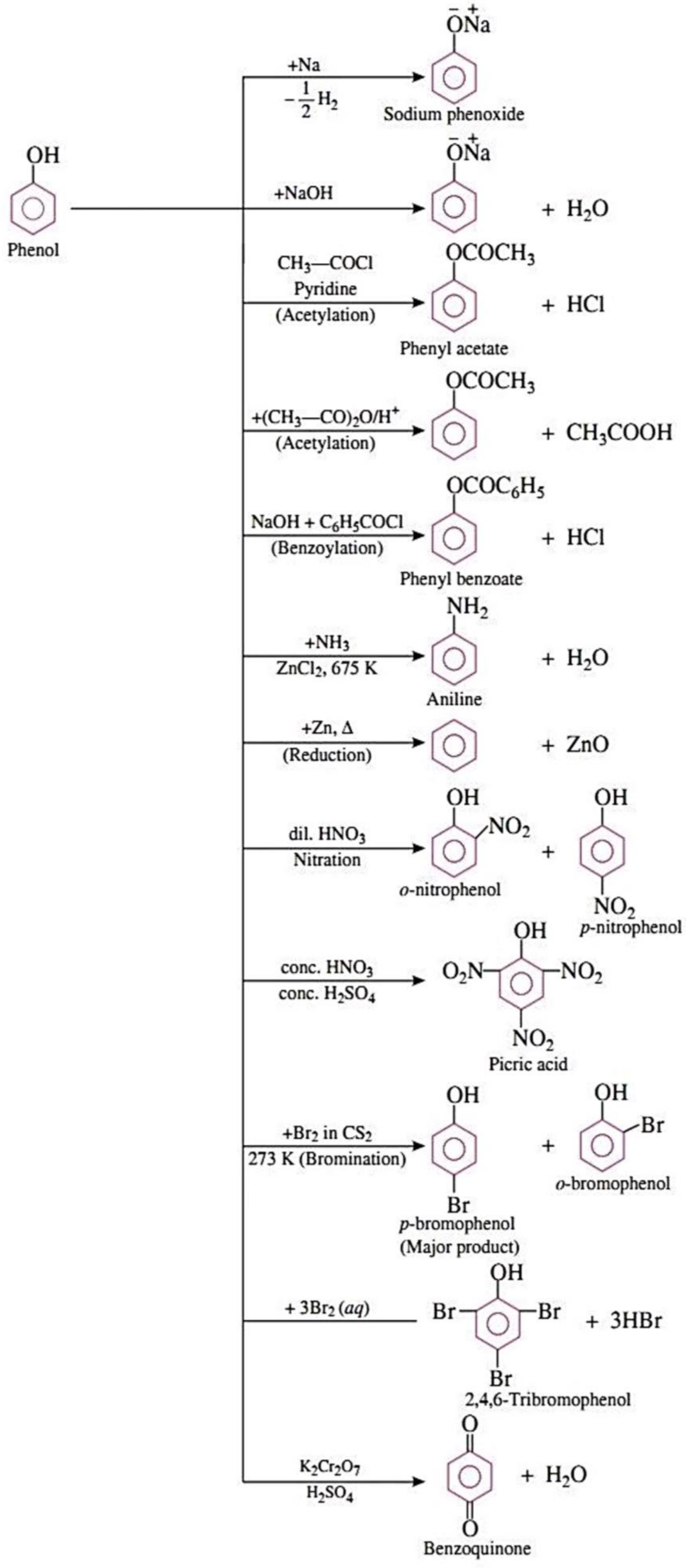
(*iv*) **From Cumene.** Cumene is oxidised in air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acids.



8. Reactions of Phenol:

Acidity of Phenol: The acidity of phenols is due to its ability to lose hydrogen ion to form phenoxide ions. In a phenol molecule, the sp^2 hybridised carbon atom of the benzene ring attached directly to the hydroxyl group acts as an electron-withdrawing group. This sp^2 hybridized carbon atom of a benzene ring attached directly to the hydroxyl group has higher electronegativity in comparison to the hydroxyl group. Due to the higher electronegativity of this carbon atom in comparison to the hydroxyl group attached, electron density decreases on the oxygen atom. The decrease in electron density increases the polarity of O—H bond and results in the increase in ionization of phenols. Thus, the phenoxide ion is formed. The phenoxide ion formed is stabilized by the delocalization of negative charge due to the resonance in the benzene ring. Phenoxide ion has greater stability than phenols, as in the case of phenol charge separation takes place during resonance. The resonance structures of phenoxide ions explain the delocalization of negative charge. In the case of substituted phenols, the acidity of phenols increases in the presence of the electron-withdrawing group. This is due to the stability of the phenoxide ion generated. The acidity of phenols further increases if these groups are attached at ortho and para positions. This is due to the fact that the negative charge in phenoxide ion is mainly delocalised at ortho and para positions of the attached benzene ring. On the other hand, the acidity of phenol decreases in the presence of electron-donating groups as they prohibit the formation of phenoxide ion.




OH
Phenol
+Na
$-\frac{1}{2}H_2$
$\overset{-}{O}\overset{+}{Na}$
Sodium phenoxide
+NaOH
$\overset{-}{O}\overset{+}{Na}$
+ H_2O
CH_3—COCl
Pyridine
(Acetylation)
$OCOCH_3$
+ HCl
Phenyl acetate
$+(CH_3—CO)_2O/H^+$
(Acetylation)
$OCOCH_3$
+ CH_3COOH
NaOH + C_6H_5COCl
(Benzoylation)
$OCOC_6H_5$
+ HCl
Phenyl benzoate
$+NH_3$
$ZnCl_2$, 675 K
NH_2
+ H_2O
Aniline
+Zn, Δ
(Reduction)
+ ZnO
dil. HNO_3
Nitration
OH
NO_2
o-nitrophenol
+
OH
NO_2
p-nitrophenol
conc. HNO_3
conc. H_2SO_4
OH
O_2N
NO_2
NO_2
Picric acid
$+Br_2$ in CS_2
273 K (Bromination)
OH
Br
p-bromophenol
(Major product)
+
OH
Br
o-bromophenol
$+ 3Br_2 (aq)$
OH
Br
Br
Br
+ 3HBr
2,4,6-Tribromophenol
$K_2Cr_2O_7$
H_2SO_4
O
O
+ H_2O
Benzoquinone

9. **Some Commercially Important Compounds:**

(*a*) **Methyl alcohol:** It is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature in presence of ZnO-Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\text{ atm}\\573\text{-}673\text{ K}}]{ZnO\text{-}Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3\text{—}OH}$$

(*b*) **Ethyl alcohol:** It is obtained commercially by fermentation.

(*i*) $$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

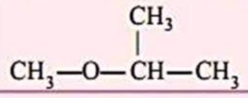
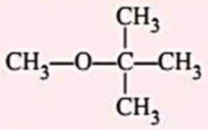
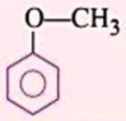
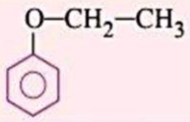
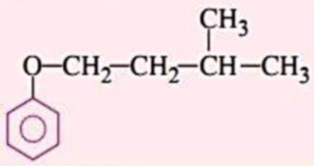
(*ii*) $$\underset{\substack{\text{Glucose}\\\text{or}\\\text{Fructose}}}{C_6H_{12}O_6} \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

10. **Ethers:** Ethers are the compounds with general formula of $C_nH_{2n+2}O$ (same as monohydric alcohols). These are represented by general structure, R—O—R′.

The groups R and R′ in ether may either be same or different. In case these groups are same, the compounds are known as simple ethers or symmetrical ethers. On the other hand, if R and R′ groups are different, the compounds are called mixed ether or unsymmetrical ethers.

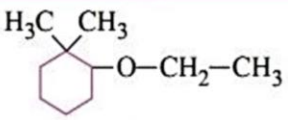
Nomenclature: According to IUPAC system, ethers are named as alkoxyalkanes. The larger alkyl group forms the part of parent chain while smaller alkyl group constitutes the alkoxy group.

Table 7.2: Common and IUPAC Names of Some Ethers

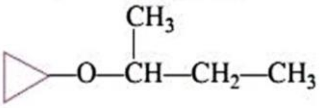
Common Name	Structural Formula	IUPAC Name
Dimethyl ether	$CH_3\text{—}O\text{—}CH_3$	Methoxymethane
Diethyl ether	$CH_3\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH_3$	Ethoxyethane
Methyl isopropyl ether	 $CH_3\text{—}O\text{—}\overset{\overset{CH_3}{\vert}}{CH}\text{—}CH_3$	2-Methoxypropane
Methyl *tert*.-butyl ether	 $CH_3\text{—}O\text{—}\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}\text{—}CH_3$	2-Methoxy-2-methylpropane
Anisole		Methoxybenzene
Phenetole		Ethoxybenzene
Phenyl isopentyl ether		3-Methylbutoxybenzene

$$CH_3\text{—}O\text{—}CH_2\text{—}CH_2\text{—}O\text{—}CH_3$$

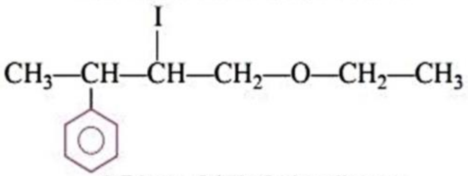
1, 2-Dimethoxyethane



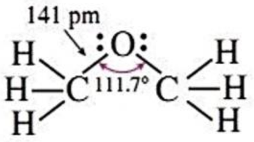
2-Ethoxy-1, 1-dimethylcyclohexane



2-Cyclopropoxybutane



1-Ethoxy -2-iodo-3-phenylbutane



Structure of Methoxymethane

Structure of ROR: In ethers, the four electron pairs, *i.e.*, the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (—R) groups. The C—O bond length (141 pm) is almost the same as in alcohols.

11. Preparation of Ethers:

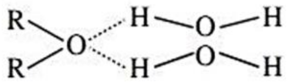
By dehydration of alcohols

$$\underset{\text{(excess)}}{2CH_3—CH_2—OH} \xrightarrow[413\text{ K}]{\text{conc. } H_2SO_4} \underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} + H_2O$$

This method is suitable for the preparation of ethers having primary alkyl groups only.

12. Physical Properties:

1. **Boiling points:** Ethers have much lower boiling points as compared to isomeric alcohols. Unlike alcohols, ether molecules are not associated by hydrogen bonds. The interparticle forces existing in their liquid states are weak dipole–dipole forces.
2. **Solubility:** The solubility of ethers is comparable to those of corresponding alcohols. The solubility of ethers is due to the ability of their molecules to form hydrogen bond with water molecules.



However, solubility of ethers in water decreases from lower members to higher members. This is because of the relative increase in the hydrocarbon portion of the molecule which decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone, etc.

13. Chemical Reactions:

Ethers are relatively inert compounds in spite of the presence of oxygen atom carrying two lone pairs of electrons in their molecules. It is because of this reason that these are used as solvents. They undergo chemical reactions under specific conditions. Some of the reactions of ethers are being described as follows:

(*a*) **Cleavage of C—O bond:** Carbon oxygen bond in ethers can be cleaved by the use of reagents like halogen acids, sulphuric acid and phosphorus pentachloride, etc.

Cleavage with halogen acid: Ethers can be cleaved by the use of hydroiodic acid or hydrobromic acid to give alkyl halide and alcohol.

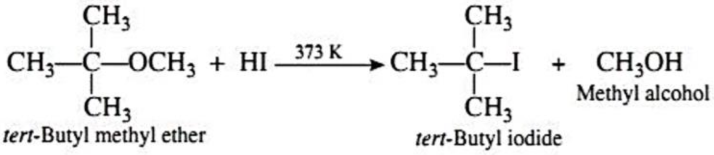
$$\underset{\text{Ether}}{R—O—R} + HX \xrightarrow{373\text{ K}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX} \quad (X = Br, I)$$

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + HI \xrightarrow{373\text{ K}} \underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Ethyl iodide}}{C_2H_5I}$$

In case excess of HI is used, the alcohol formed reacts further with HI to form alkyl iodide. The overall reaction can be written as

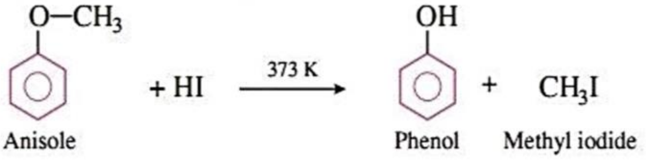
$$C_2H_5OC_2H_5 + \underset{\text{(Excess)}}{2HI} \xrightarrow{373\text{ K}} 2C_2H_5I + H_2O$$

If one group is methyl and other group is tertiary alkyl group, the main product is methyl alcohol and tertiary alkyl halide. It is because the departure of leaving group (CH_3—OH) creates a more stable tertiary carbocation.



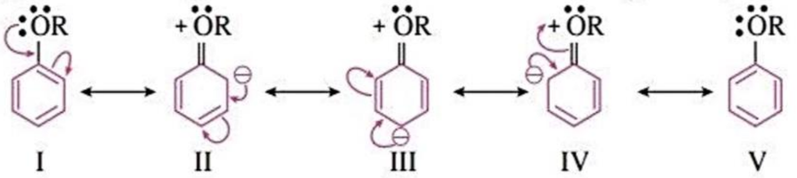
$$\underset{\textit{tert}\text{-Butyl methyl ether}}{CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—OCH_3} + HI \xrightarrow{373\text{ K}} \underset{\textit{tert}\text{-Butyl iodide}}{CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

In case of anisole, the products formed are phenol and methyl iodide.

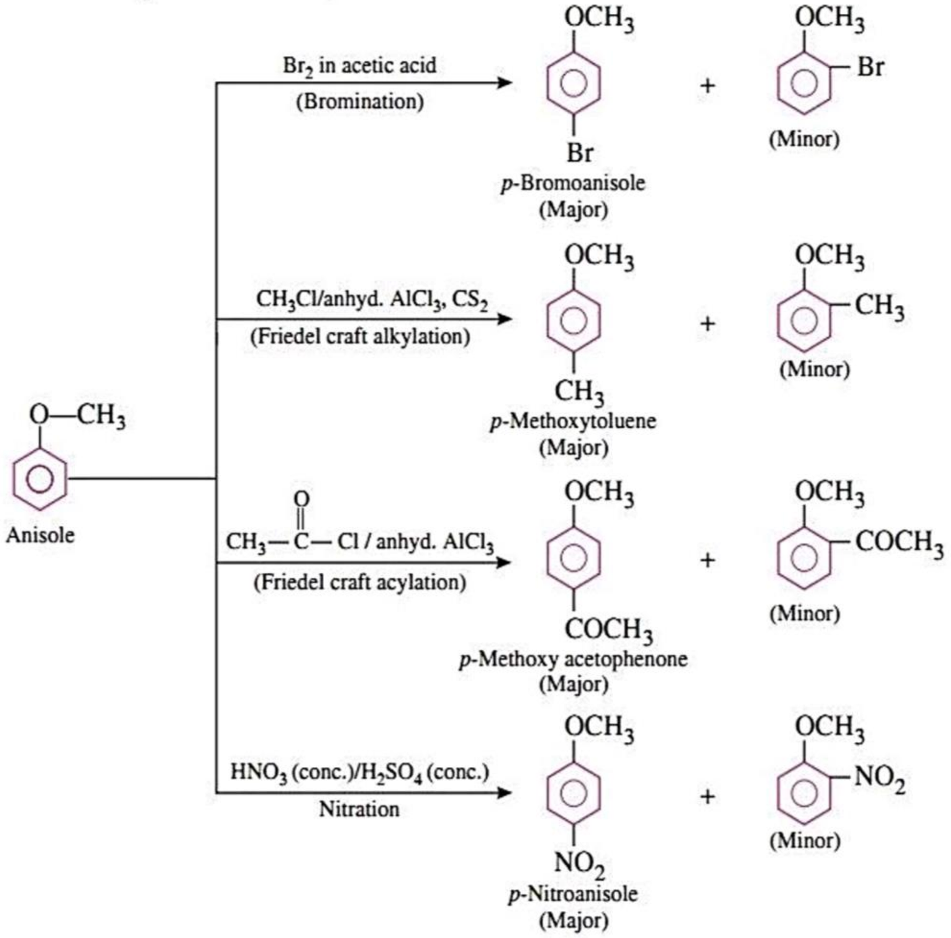


The bond between O—CH$_3$ is weaker than the bond between O—C$_6$H$_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore, the attack of I$^-$ ion breaks O—CH$_3$ bond to form CH$_3$I.

(*b*) **Ring substitution in aromatic ethers:** The alkoxy group (—OR) attached to aromatic ring activates the ring towards electrophilic substitution and directs the incoming electrophile to ortho and para positions.



The presence of negative charge at ortho and para positions indicates that electron density is more at these positions. Therefore, electrophile is likely to attack on these positions resulting in the formation of ortho and para substituted products.



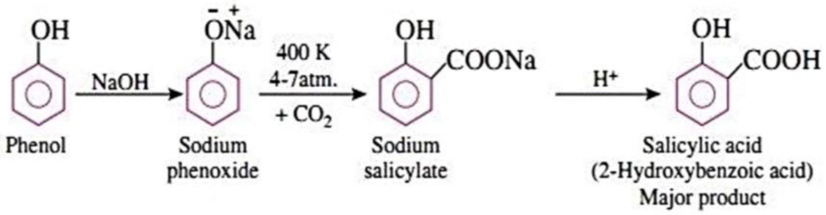
14. Uses of Ethers

Ethers are used in several ways:

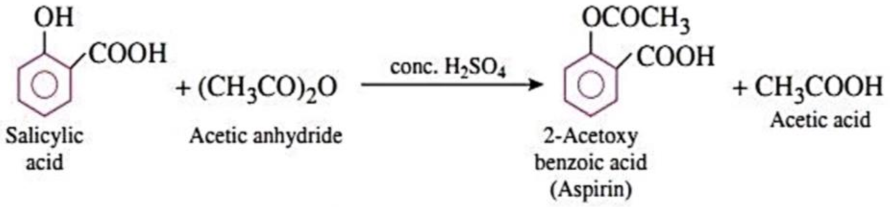
1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethyl ether is used as a solvent for organic reactions and also as an industrial solvent for oils, gums, resins, etc. It is also used as an extracting solvent.

15. Some Important Name Reactions

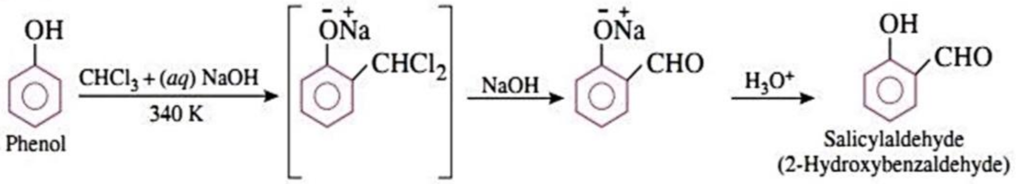
(*i*) **Kolbe's reaction:** When sodium phenoxide is heated with CO$_2$ at 400 K under a pressure of 4 –7 atm, the resulting product on acidification yields salicylic acid.



Salicylic acid is the starting material for the manufacture of 2-acetoxybenzoic acid (aspirin).



(ii) **Reimer–Tiemann reaction:** Treatment of phenol with chloroform in the presence of sodium hydroxide followed by hydrolysis of resulting product gives *o*-hydroxybenzaldehyde (salicylaldehyde) as a major product.

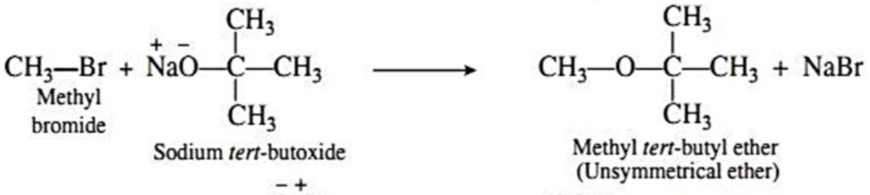


(iii) **Williamson synthesis:** It consists of reacting an alkyl halide with sodium alkoxide or sodium phenoxide to form ether.

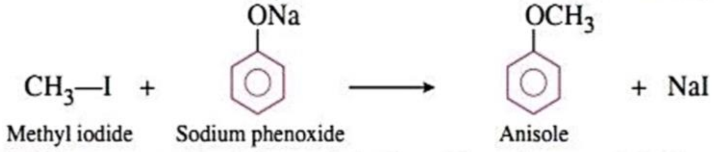
$$\underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}{-}\overset{-}{O}{-}R'} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + NaX$$

It is a convenient method for the preparation of symmetrical as well as unsymmetrical ethers.

$$\underset{\text{Ethyl iodide}}{CH_3{-}CH_2{-}I} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}{-}\overset{-}{O}{-}CH_2{-}CH_3} \longrightarrow \underset{\substack{\text{Diethyl ether}\\\text{(Symmetrical ether)}}}{CH_3{-}CH_2{-}O{-}CH_2{-}CH_3} + NaI$$



$$\underset{\substack{\text{Methyl}\\\text{bromide}}}{CH_3{-}Br} + \underset{\text{Sodium } tert\text{-butoxide}}{\overset{+}{Na}\overset{-}{O}{-}C(CH_3)_2{-}CH_3} \longrightarrow \underset{\substack{\text{Methyl } tert\text{-butyl ether}\\\text{(Unsymmetrical ether)}}}{CH_3{-}O{-}C(CH_3)_2{-}CH_3} + NaBr$$



Limitation: Williamson synthesis is used to formation of symmetrical and unsymmetrical ethers. However, for synthesis of unsymmetrical ethers a proper choice of reactants is necessary. The best yield of unsymmetrical ethers are obtained when the alkyl halides are primary. However, alkoxides may be 1°, 2° or 3°.

With 1° alkyl halide, substitution reaction takes place and ether will be formed.

With 2° alkyl halide substitution and elimination occur together giving a mixture of alkene and ethers. With 3° alkyl halide only elimination occurs giving alkenes.

16. Distinction between Primary, Secondary and Tertiary Alcohols

(a) **Lucas test:** In this test, the alcohol is treated with Lucas reagent which is an equimolar mixture of HCl and $ZnCl_2$. Alcohols are soluble in Lucas reagent and form a clear solution. On reaction, alkyl chlorides are formed which being insoluble result in turbidity in the solution.

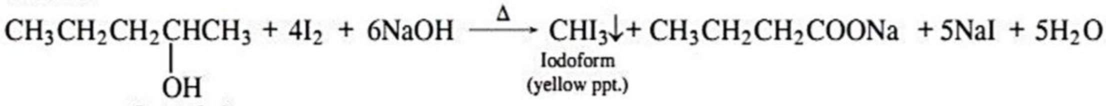
$$\text{Alcohol} \xrightarrow[ZnCl_2]{HCl} \text{Alkyl chloride} + H_2O$$

If turbidity appears immediately, tertiary alcohol is indicated.
If turbidity appears within five minutes, secondary alcohol is indicated.
If turbidity appears only upon heating, primary alcohol is indicated.

(*b*) **Iodoform test:** When ethyl alcohol or any alcohol containing the group $\boxed{CH_3-\overset{OH}{\overset{|}{C}}H-}$ or $CH_3-\overset{O}{\overset{\|}{C}}-$ group is heated with iodine and aqueous NaOH or Na_2CO_3 solution at 333–343 K, a yellow precipitate of iodoform is obtained.

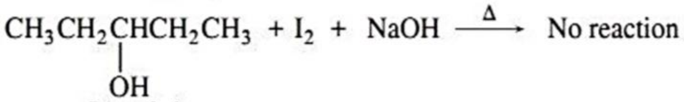
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3\downarrow} + HCOONa + 5NaI + 5H_2O$$

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



$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform}\\\text{(yellow ppt.)}}}{CHI_3\downarrow} + CH_3CH_2CH_2COONa + 5NaI + 5H_2O$$

Pentan-2-ol



$$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3 + I_2 + NaOH \xrightarrow{\Delta} \text{No reaction}$$

Pentan-3-ol

(*c*) **Ferric chloride test for phenols:** Phenol gives a violet-coloured water soluble complex with ferric chloride.

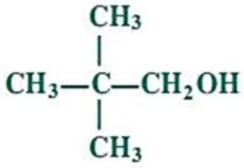
$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \xrightarrow{373\text{ K}} \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

In general, all compounds containing enolic group ($=\overset{|}{C}-OH$) respond to this test.
However, the colours of complexes are different such as green, blue, violet, etc., and depend upon the structure of phenols.

NCERT Intext Questions

Q. 1. Classify the following as primary, secondary and tertiary alcohols:

(*i*)

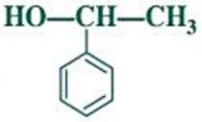


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$$

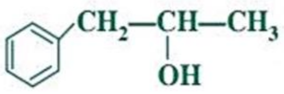
(*ii*) $H_2C=CH-CH_2OH$

(*iii*) $CH_3-CH_2-CH_2-OH$

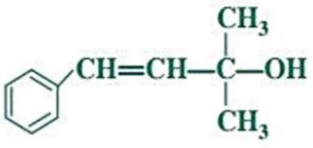
(*iv*)



(*v*)



(*vi*)

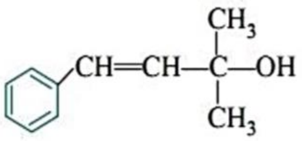


Ans. (*i*) Primary
(*ii*) Primary
(*iii*) Primary
(*iv*) Secondary
(*v*) Secondary
(*vi*) Tertiary

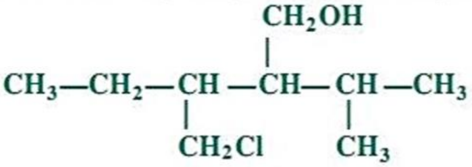
Q. 2. Identify allylic alcohols in the above examples.

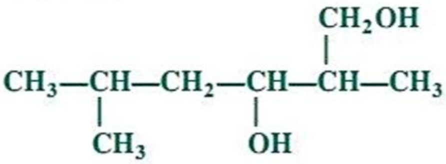
Ans. (*ii*) $H_2C=CH-CH_2OH$

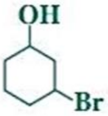
(*vi*)



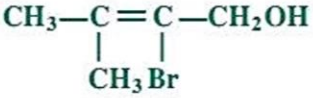
Q. 3. Name the following compounds according to IUPAC system.

(*i*) 
$CH_3-CH_2-\underset{CH_2Cl}{CH}-\overset{CH_2OH}{CH}-\underset{CH_3}{CH}-CH_3$

(*ii*) 
$CH_3-\underset{CH_3}{CH}-CH_2-\underset{OH}{CH}-\overset{CH_2OH}{CH}-CH_3$

(*iii*) 

(*iv*) 
$H_2C=CH-\underset{OH}{CH}-CH_2-CH_2-CH_3$

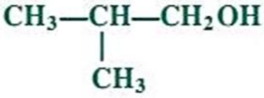
(*v*) 
$CH_3-\underset{CH_3}{C}=\underset{Br}{C}-CH_2OH$

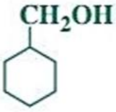
Ans. (*i*) 3-Chloromethyl-2-isopropylpentan-1-ol (*ii*) 2, 5-Dimethylhexane-1,3-diol

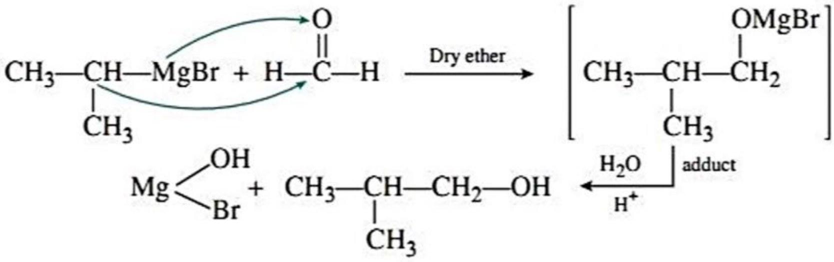
(*iii*) 3-Bromocyclohexanol (*iv*) Hex-1-en-3-ol

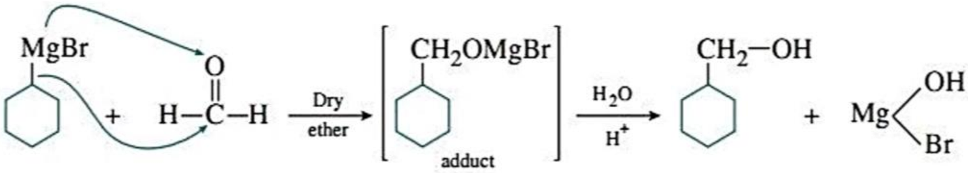
(*v*) 2-Bromo-3-methylbut-2-en-1-ol

Q. 4. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

(*i*) 
$CH_3-\underset{CH_3}{CH}-CH_2OH$

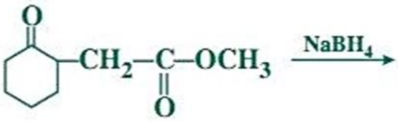
(*ii*) 

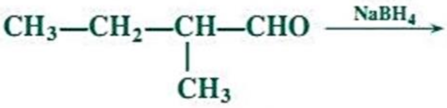
Ans. (*i*) 

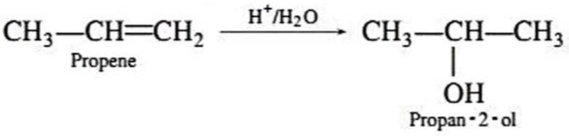
(*ii*) 

Q. 5. Write structures of the products of the following reactions.

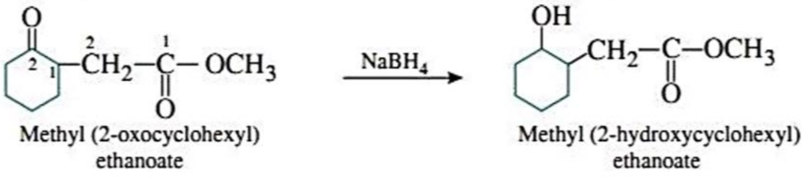
(*i*) $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$

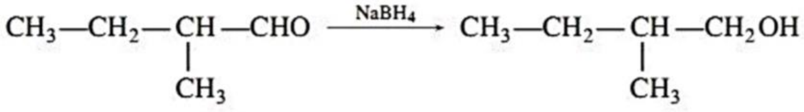
(*ii*) 

(*iii*) 
$CH_3-CH_2-\underset{CH_3}{CH}-CHO \xrightarrow{NaBH_4}$

Ans. (*i*) 
$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{H^+/H_2O} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}$

(*ii*) NaBH$_4$ is a weak reducing agent, it reduces the aldehydes/ketones and not the esters.





(*iii*) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO \xrightarrow{NaBH_4} CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

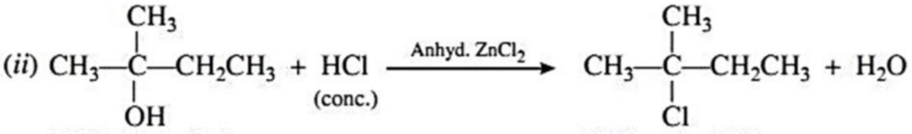
2-Methylbutanal 2-Methylbutan-1-ol

Q. 6. Give structures of the products you would expect when each of the following alcohol reacts with (*a*) HCl–ZnCl$_2$, (*b*) HBr and (*c*) SOCl$_2$.

(*i*) Butan-1-ol (*ii*) 2-Methylbutan-2-ol

Ans. (*a*) **With HCl–ZnCl$_2$ (Lucas reagent):**

(*i*) $\underset{\text{Butan-1-ol}(1^\circ)}{CH_3CH_2CH_2CH_2-OH} + \underset{\text{(conc.)}}{HCl} \xrightarrow{\text{Anhyd.}ZnCl_2}$ No reaction at room temperature

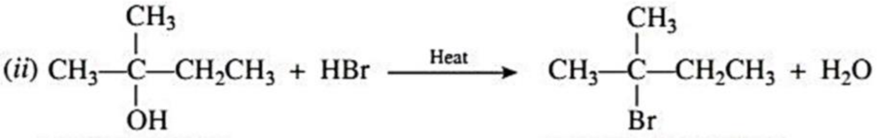


(*ii*) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_2CH_3 + \underset{\text{(conc.)}}{HCl} \xrightarrow{\text{Anhyd. }ZnCl_2} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_2CH_3 + H_2O$

2-Methylbutan-2-ol 2-Chloro-2-methylbutane

(*b*) **With HBr:**

(*i*) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + HBr \xrightarrow{\text{Heat}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} + H_2O$

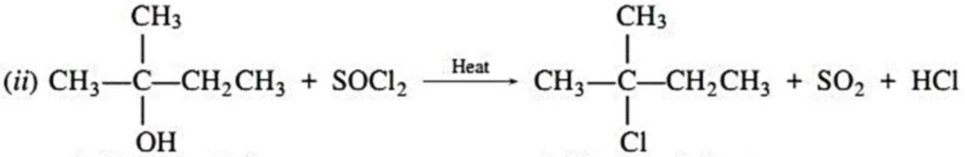


(*ii*) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_2CH_3 + HBr \xrightarrow{\text{Heat}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_2CH_3 + H_2O$

2-Methylbutan-2-ol 2-Bromo-2-methylbutane

(*c*) **With SOCl$_2$:**

(*i*) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + SOCl_2 \xrightarrow{\text{Heat}} \underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + SO_2 + HCl$

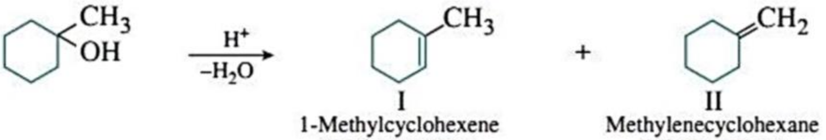


(*ii*) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_2CH_3 + SOCl_2 \xrightarrow{\text{Heat}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_2CH_3 + SO_2 + HCl$

2-Methylbutan-2-ol 2-Chloro-2-methylbutane

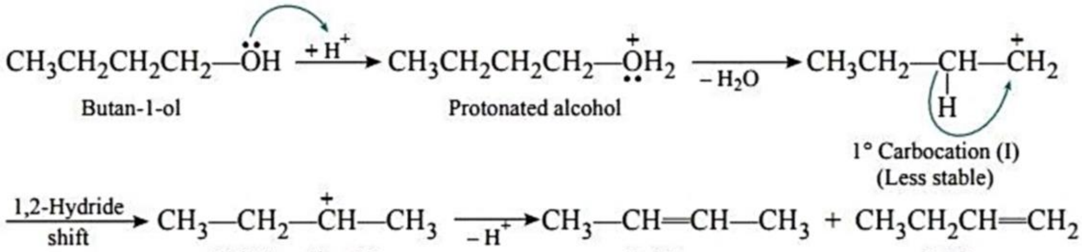
Q. 7. Predict the major product of acid catalysed dehydration of (*i*) 1-methylcyclohexanol and (*ii*) butan-1-ol.

Ans. (*i*) Acid catalysed dehydration of 1-methylcyclohexanol can give two products, I and II. Since product (I) is more substituted, according to Saytzeff rule, it is the major product.



I
1-Methylcyclohexene
(Major product)

II
Methylenecyclohexane
(Minor product)

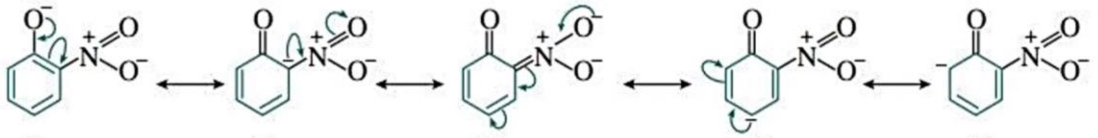


(*ii*) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2-\ddot{O}H} \xrightarrow{+H^+} \underset{\text{Protonated alcohol}}{CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}H_2} \xrightarrow[-H_2O]{} \underset{\substack{1^\circ\text{ Carbocation (I)}\\ \text{(Less stable)}}}{CH_3CH_2-\underset{H}{\underset{|}{CH}}-\overset{+}{C}H_2}$

$\xrightarrow[\text{shift}]{\text{1,2-Hydride}} \underset{\substack{2^\circ\text{ Carbocation (II)}\\ \text{(More stable)}}}{CH_3-CH_2-\overset{+}{C}H-CH_3} \xrightarrow{-H^+} \underset{\substack{\text{But-2-ene}\\ \text{(Major)}}}{CH_3-CH{=}CH-CH_3} + \underset{\substack{\text{But-1-ene}\\ \text{(Minor)}}}{CH_3CH_2CH{=}CH_2}$

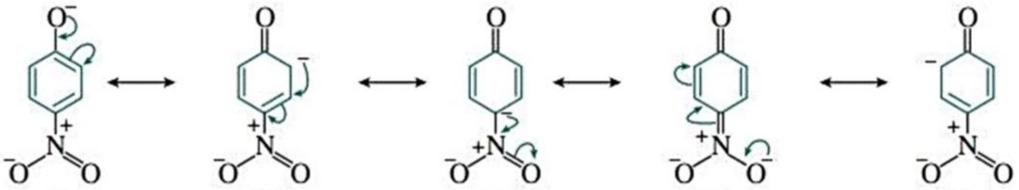
Q. 8. ***Ortho*** **and** ***para*****-nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.**

Ans. The resonance structures of *o*- and *p*-nitrophenoxide ions and phenoxide ion are given as follows:



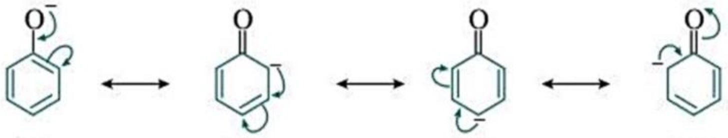
I II III IV V

Resonance structures of *o*-nitrophenoxide ion



VI VII VIII IX X

Resonance structures of *p*-nitrophenoxide ion



XI XII XIII XIV

Resonance structures of phenoxide ion

It is clear from the above structures that due to –R-effect of NO_2 group, *o*-and *p*-nitrophenoxide ions are more stable than phenoxide ion. Consequently, *o*- and *p*-nitrophenols are more acidic than phenol.

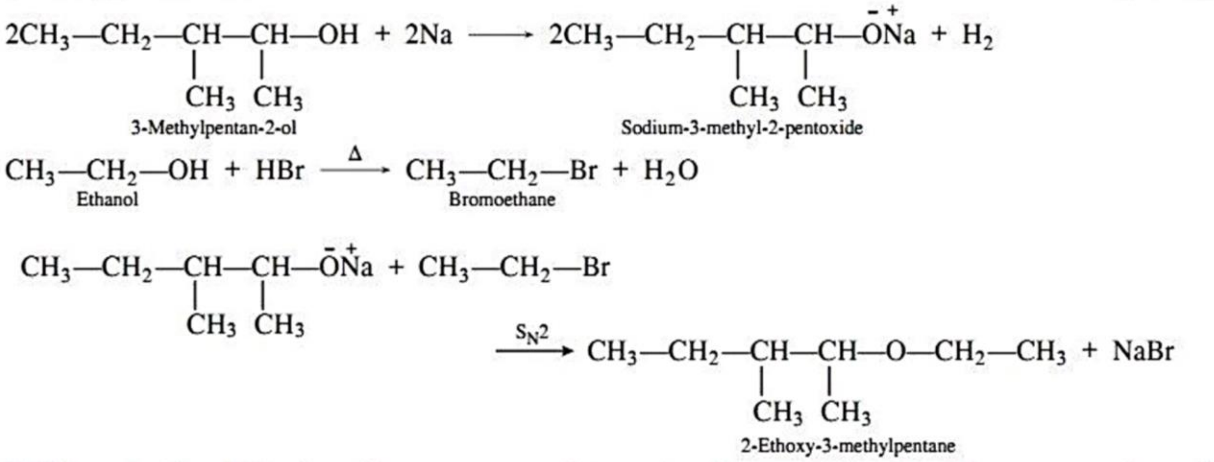
Q. 9. Write the equations involved in the following reactions:

(*i*) Reimer–Tiemann reaction **(*ii*) Kolbe's reaction**

Ans. Refer to Points to remember 15.

Q. 10. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol. **[*HOTS*]**

Ans.



$$2CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-OH + 2Na \longrightarrow 2CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\overset{-}{O}\overset{+}{Na} + H_2$$

3-Methylpentan-2-ol Sodium-3-methyl-2-pentoxide

$$CH_3-CH_2-OH + HBr \xrightarrow{\Delta} CH_3-CH_2-Br + H_2O$$

Ethanol Bromoethane

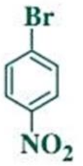
$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\overset{-}{O}\overset{+}{Na} + CH_3-CH_2-Br$$

$$\xrightarrow{S_N2} CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-O-CH_2-CH_3 + NaBr$$

2-Ethoxy-3-methylpentane

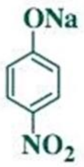
Q. 11. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(*i*)



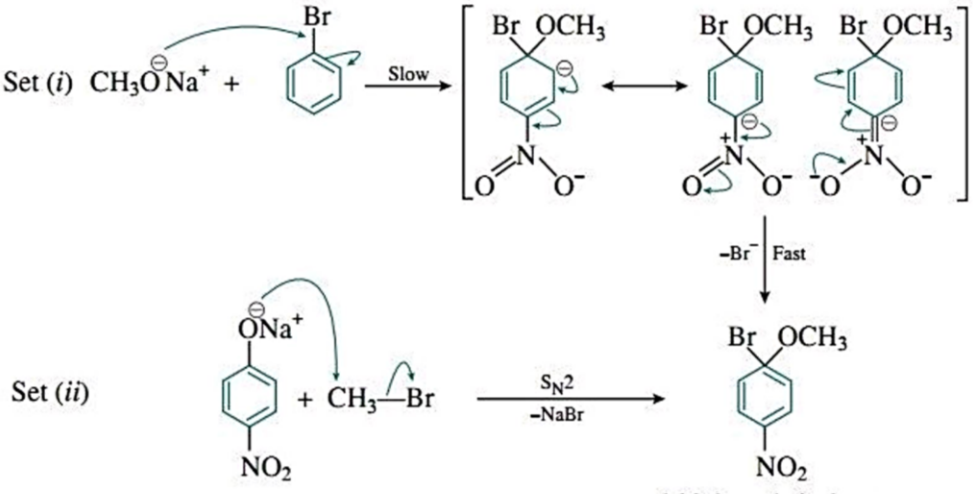
+ CH_3ONa

(*ii*)



+ CH_3Br

Ans. Chemically both sets are equally probable. In set (*i*), the Br atom is activated by the electron withdrawing effect of —NO_2 group. Therefore, nucleophilic attack by $CH_3O^-Na^+$ followed by elimination of NaBr gives desired ether, while in set (*ii*) nucleophilic attack by 4-nitrophenoxide ion on methyl bromide gives the desired ether.



1-Methoxy-4-nitrobenzene

Q. 12. Predict the products of the following reactions:

(i) $CH_3-CH_2-CH_2-O-CH_3 + HBr \longrightarrow$

(ii)

(iii)

(iv) $(CH_3)_3C-OC_2H_5 \xrightarrow{HI}$ **[*CBSE (F) 2012*]**

Ans. *(i)* $CH_3-CH_2-CH_2-O-CH_3 + H-Br \longrightarrow CH_3-Br + CH_3-CH_2-CH_2-OH$

(ii)

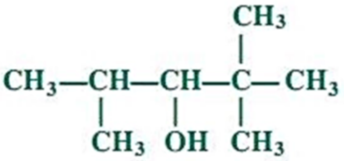
(iii)

(iv) $(CH_3)_3C-OC_2H_5 + HI \longrightarrow (CH_3)_3C-I + C_2H_5-OH$

NCERT Exercises

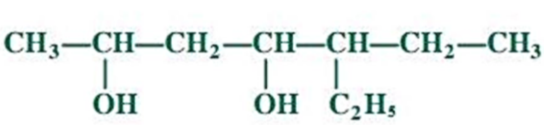
Q. 1. Write the IUPAC names of the following compounds:

(i)



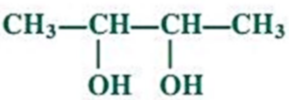
$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

(ii)



$CH_3-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-\underset{C_2H_5}{CH}-CH_2-CH_3$

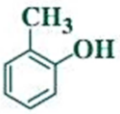
(iii)



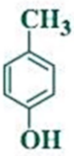
$CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$

(iv) $HOCH_2-CHOH-CH_2OH$

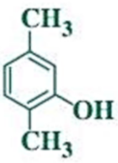
(v)



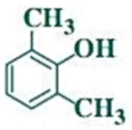
(vi)

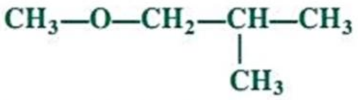


(vii)



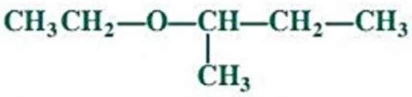
(viii)



(*ix*) 
$CH_3-O-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3$

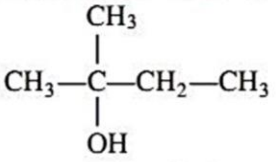
(*x*) $C_6H_5-O-C_2H_5$

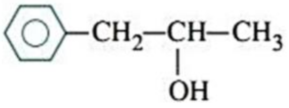
(*xi*) $C_6H_5-O-C_7H_{15}$ (*n*–)

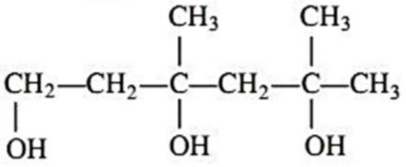
(*xii*) 
$CH_3CH_2-O-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_3$

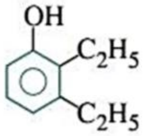
Ans. (*i*) 2, 2, 4-Trimethylpentan-3-ol
(*ii*) 5-Ethylheptane-2, 4-diol
(*iii*) Butane-2, 3-diol
(*iv*) Propane-1, 2, 3-triol
(*v*) 2-Methylphenol
(*vi*) 4-Methylphenol
(*vii*) 2, 5-Dimethylphenol
(*viii*) 2, 6-Dimethylphenol
(*ix*) 1-Methoxy-2-methylpropane
(*x*) Ethoxybenzene
(*xi*) 1-Phenoxyheptane
(*xii*) 2-Ethoxybutane

Q. 2. Write the structures of the compounds whose IUPAC names are as follows:
(*i*) 2–Methylbutan–2–ol
(*ii*) 1–Phenylpropan–2–ol
(*iii*) 3, 5–Dimethylhexane–1, 3, 5–triol
(*iv*) 2, 3–Diethylphenol
(*v*) 1–Ethoxypropane
(*vi*) 2–Ethoxy–3–methylpentane
(*vii*) Cyclohexylmethanol
(*viii*) 3–Cyclohexylpentan–3–ol
(*ix*) Cyclopent–3–en–1–ol
(*x*) 4–Chloro–3–ethylbutan–1–ol

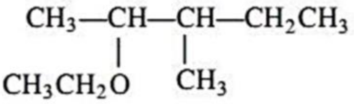
Ans. (*i*) 
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}-CH_2-CH_3$

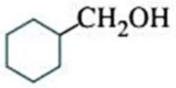
(*ii*) 

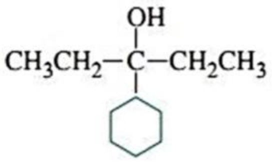
(*iii*) 
$\underset{\substack{|\\OH}}{CH_2}-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}-CH_3$

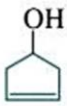
(*iv*) 

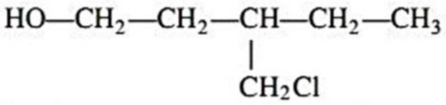
(*v*) $CH_3CH_2O - CH_2CH_2CH_3$

(*vi*) 
$CH_3-\underset{\substack{|\\CH_3CH_2O}}{CH}-\underset{\substack{|\\CH_3}}{CH}-CH_2CH_3$

(*vii*) 

(*viii*) 

(*ix*) 

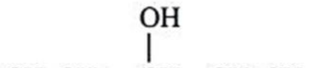
(*x*) 
$HO-CH_2-CH_2-\underset{\substack{|\\CH_2Cl}}{CH}-CH_2-CH_3$

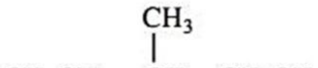
Q. 3. (*i*) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.
(*ii*) Classify the isomers in Q. 3(*i*) into primary, secondary and tertiary alcohols.

Ans. Eight isomers are possible. These are:

(*i*) $CH_3CH_2CH_2CH_2CH_2OH$
Pentan–1–ol(1°)

(*ii*) 
$CH_3CH_2CH_2-\overset{\substack{OH\\|}}{CH}-CH_3$
Pentan–2–ol(2°)

(*iii*) 
$CH_3CH_2-\overset{\substack{OH\\|}}{CH}-CH_2CH_3$
Pentan–3–ol(2°)

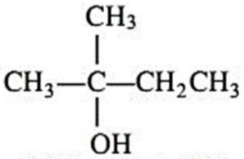
(*iv*) 
$CH_3CH_2-\overset{\substack{CH_3\\|}}{CH}-CH_2OH$
2–Methylbutan–1–ol(1°)

(v)

$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_2-OH$

3–Methylbutan–1–ol(1°)

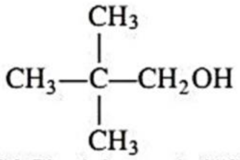
(vi)



$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_3$

2–Methylbutan–2–ol (3°)

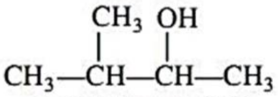
(vii)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$

2,2–Dimethylpropan–1–ol(1°)

(viii)

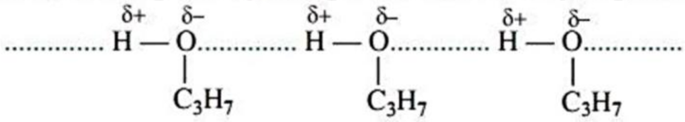


$CH_3-\overset{CH_3}{CH}-\overset{OH}{CH}-CH_3$

3-Methylbutan-2-ol(2°)

Q. 4. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

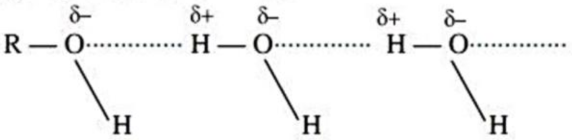
Ans. The molecules of butane are held together by weak van der Waal's forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonds.



Hence, the boiling point of propanol is much higher than that of butane.

Q. 5. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

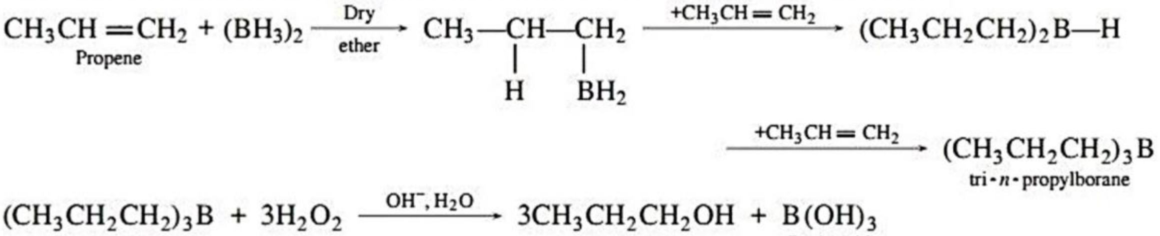
Ans. Alcohols can form H-bonds with water and break the H-bonds already existing between water molecules. Hence, they are soluble in water.



In contrast, hydrocarbons cannot form H-bonds with water and hence are insoluble in water.

Q. 6. What is meant by hydroboration–oxidation reaction? Illustrate it with an example.

Ans. The addition of diborane to alkenes to form trialkylboranes followed by their oxidation with alkaline hydrogen peroxide to form alcohols is called hydroboration–oxidation reaction.



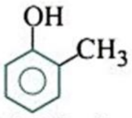
$$\underset{\text{Propene}}{CH_3CH=CH_2} + (BH_3)_2 \xrightarrow[\text{ether}]{\text{Dry}} CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2} \xrightarrow{+CH_3CH=CH_2} (CH_3CH_2CH_2)_2B-H \xrightarrow{+CH_3CH=CH_2} \underset{\text{tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B}$$

$$\underset{\text{tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B} + 3H_2O_2 \xrightarrow{OH^-,\ H_2O} \underset{n\text{-Propylalcohol}}{3CH_3CH_2CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

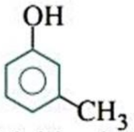
The alcohols obtained by this process is contrary to the Markovnikov's rule.

Q. 7. Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.

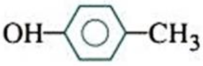
Ans. The three isomers are given as follows:



2-Methylphenol
or *o*-Cresol



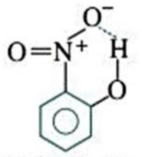
3-Methylphenol
or *m*-Cresol



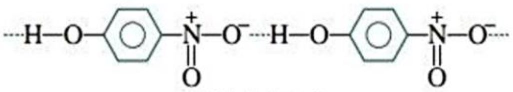
4-Methylphenol
or *p*-Cresol

Q. 8. While separating a mixture of *ortho* and *para*-nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reasons.

Ans. *o*-Nitrophenol is steam volatile as it exists as discrete molecules due to intramolecular H-bonding and hence can be separated by steam distillation from *p*-nitrophenol which is less volatile as it exists as associated molecules because of intermolecular H-bonding.



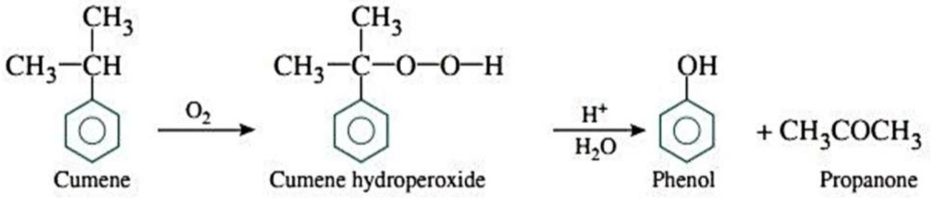
o-Nitrophenol
(Intramolecular hydrogen bonding)



p-Nitrophenol
(Intermolecular hydrogen bonding)

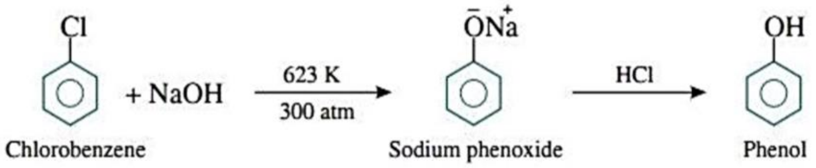
Q. 9. Give the equations of reactions for the preparation of phenol from cumene. **[*CBSE 2020 (56/3/2)*]**

Ans.



Q. 10. Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans.



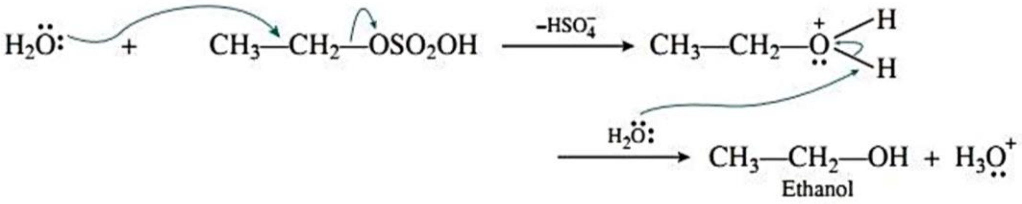
Q. 11. Write the mechanism of hydration of ethene to form ethanol. **[*CBSE 2019 (56/4/2), 2020 (56/5/1)*]**

Ans. Direct addition of H_2O to ethene in presence of an acid does not occur. Ethene is first passed through conc. H_2SO_4, when ethyl hydrogen sulphate is formed.

$$H_2SO_4 \longrightarrow H^+ + {}^-OSO_2OH$$

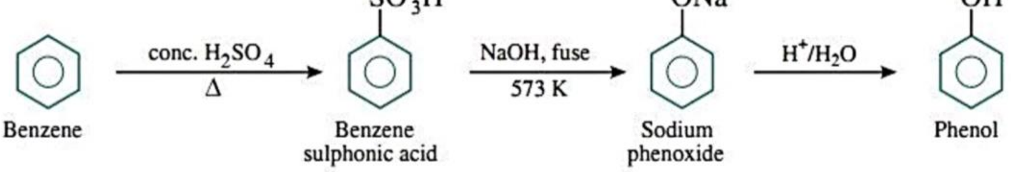
$$\underset{\text{Ethene}}{CH_2=CH_2} + H^+ \longrightarrow \underset{\text{Ethyl carbocation}}{CH_3-\overset{+}{C}H_2} \xrightarrow[\text{Fast}]{{}^-OSO_2OH} \underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-OSO_2OH}$$

Ethyl hydrogen sulphate when boiled with water undergoes hydrolysis to form ethanol.



Q. 12. You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

Ans.



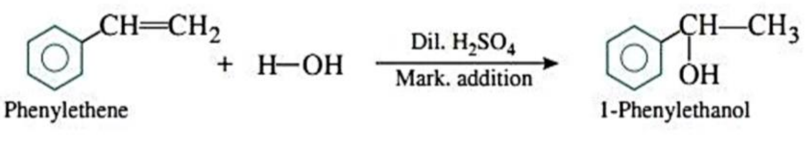
Q. 13. Show how will you synthesise:

(*i*) 1-phenylethanol from a suitable alkene?

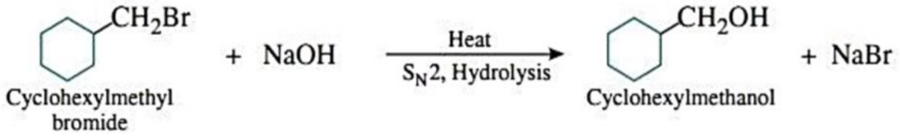
(*ii*) cyclohexylmethanol using an alkyl halide by an S_N2 reaction?

(*iii*) pentan-1-ol using a suitable alkyl halide?

Ans. (*i*) Addition of H_2O to ethenylbenzene in presence of dil. H_2SO_4 gives 1-phenylethanol.



(*ii*) Hydrolysis of cyclohexylmethyl bromide by aqueous NaOH gives cyclohexylmethanol.



(*iii*) Hydrolysis of 1-bromopentane by aqueous NaOH gives pentan-1-ol.

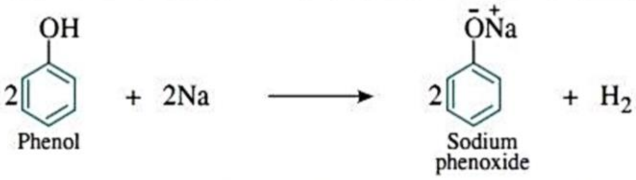
$$\underset{\text{1-bromopentane}}{CH_3—CH_2—CH_2—CH_2—CH_2—Br} + NaOH \xrightarrow[S_N2,\ \text{Hydrolysis}]{\text{Heat}}$$

$$\underset{\text{Pentan-1-ol}}{CH_3CH_2—CH_2—CH_2—CH_2—OH} + NaBr$$

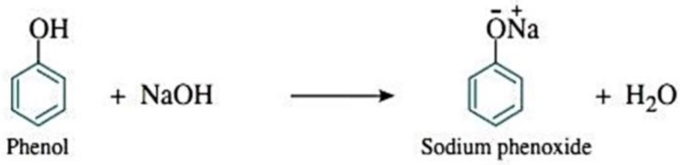
Q. 14. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Ans. The reactions showing acidic nature of phenol are:

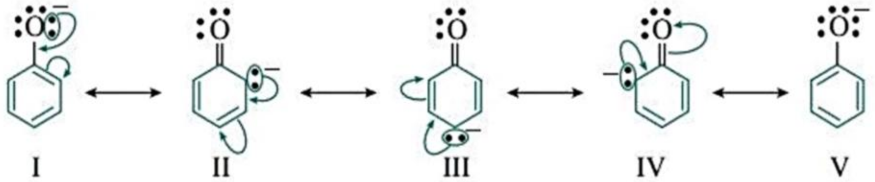
(*i*) **Reaction with sodium:** Phenol reacts with active metals like sodium to liberate H_2 gas.



(*ii*) **Reaction with NaOH:** Phenol dissolves in NaOH to form sodium phenoxide and water.

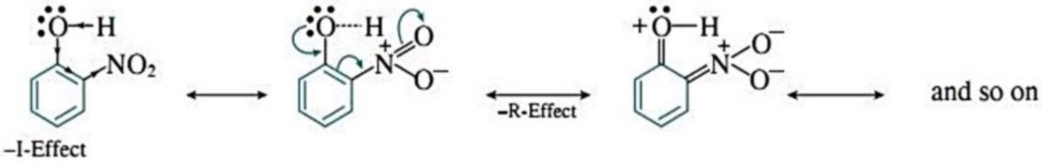


Comparison of acidic character of phenol and ethanol: Phenol is more acidic than ethanol. This is due to the reason that phenoxide ion left after the loss of a proton from phenol is stabilised by resonance while ethoxide ion left after loss of a proton from ethanol is not stabilised by resonance.

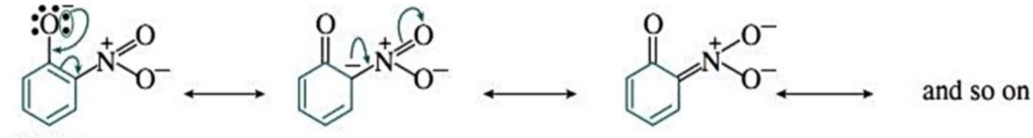


Q. 15. Explain why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol. **[*HOTS*]**

Ans. Due to strong –R and –I-effect of the NO_2 group, electron density in the O—H bond decreases and hence the loss of a proton becomes easy.



Moreover, after the loss of a proton, the *o*-nitrophenoxide ion left behind is stabilised by resonance.



This makes *o*-nitrophenol a stronger acid.

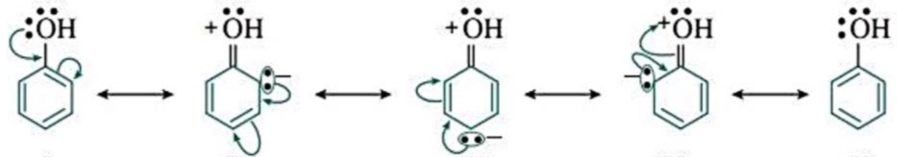
In contrast, due to + R effect, OCH_3 group increases the electron-density in the O—H bond thereby making the loss of proton difficult.

Moreover, the *o*-methoxyphenoxide ion left after the loss of a proton is destabilised by resonance as the two negative charges repel each other thereby making *o*-methoxyphenol a weaker acid.

Hence, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

Q. 16. Explain how does —OH group attached to a carbon of benzene ring activate it towards electrophilic substitution.

Ans. Phenol may be regarded as a resonance hybrid of following structures:



Thus, due to +R-effect of the —OH group, the electron density in the benzene ring increases thereby facilitating the attack of an electrophile. In other words, presence of —OH group, activates the benzene ring towards electrophilic substitution reactions. Now, since the electron density is relatively higher at the two *o*- and one *p*-position, electrophilic substitution occurs mainly at *o*- and *p*-positions.

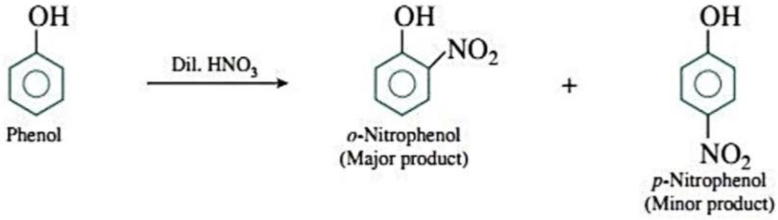
Q. 17. Give equations of the following reactions:

- **(*i*) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.**
- **(*ii*) Bromine in CS_2 with phenol.**
- **(*iii*) Dilute HNO_3 with phenol.**
- **(*iv*) Treating phenol with chloroform in presence of aqueous NaOH.**

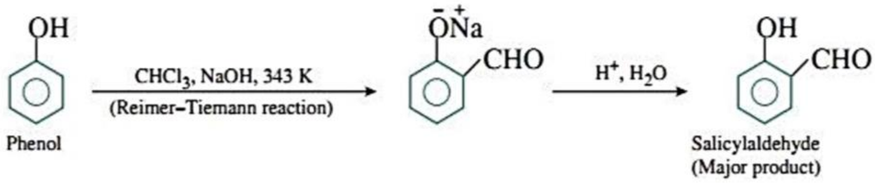
Ans. (*i*) $$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + 2[O] \xrightarrow[H^+/H_2O]{\text{Alk. } KMnO_4 \text{ (Oxidation)}} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(*ii*)

(*iii*)



(*iv*)



A small amount of *p*-hydroxybenzaldehyde is also formed.

Q. 18. Explain the following with an example:

(*i*) Kolbe's reaction **(*ii*) Reimer–Tiemann reaction**

(*iii*) Williamson ether synthesis **(*iv*) Unsymmetrical ether**

Ans. (*i*) Refer to Points to remember 15 (*i*).

(*ii*) Refer to Points to remember 15 (*ii*).

(*iii*) Refer to Points to remember 15(*v*).

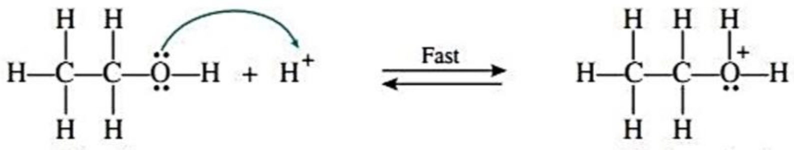
(*iv*) **Unsymmetrical ether:** If the alkyl or aryl groups attached to the oxygen atom are different, ethers are called unsymmetrical ethers. For example, ethyl methyl ether, methyl phenyl ether, etc.

Q. 19. Write the mechanism of acid catalysed dehydration of ethanol to yield ethene.

[CBSE 2019 (56/4/1)][CBSE 2023 (56/1/1)]

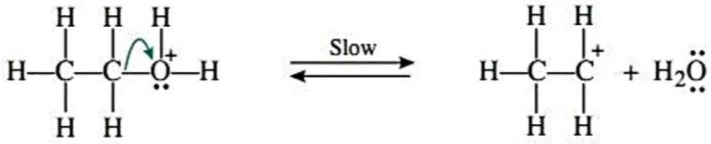
Ans. The mechanism of dehydration of ethanol involves the following steps:

Step 1: Formation of protonated alcohol

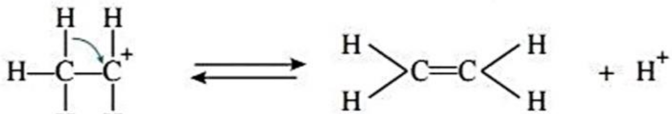


Ethanol Ethyl oxonium ion

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



Step 3: Formation of ethane by elimination of a proton



Ethene

The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

Q. 20. How are the following conversions carried out?

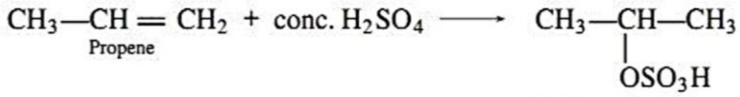
(*i*) Propene ⟶ Propan - 2 - ol

(*ii*) Benzyl chloride ⟶ Benzyl alcohol

(*iii*) Ethyl magnesium chloride ⟶ Propan - 1 - ol

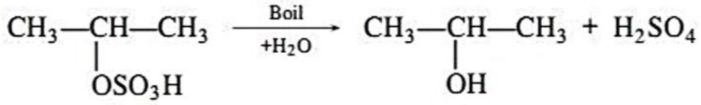
(*iv*) Methyl magnesium bromide ⟶ 2 - Methylpropan - 2 - ol

Ans. (*i*) Propan-2-ol can be prepared from propene by hydration as shown below:



$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + \text{conc. } H_2SO_4 \longrightarrow CH_3{-}\underset{OSO_3H}{\underset{|}{CH}}{-}CH_3$$

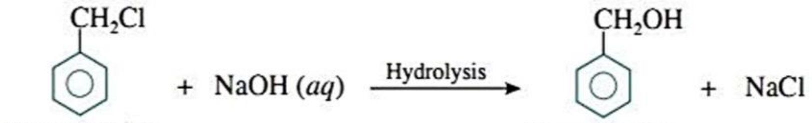
Isopropyl hydrogen sulphate



$$CH_3{-}\underset{OSO_3H}{\underset{|}{CH}}{-}CH_3 \xrightarrow[+H_2O]{\text{Boil}} CH_3{-}\underset{OH}{\underset{|}{CH}}{-}CH_3 + H_2SO_4$$

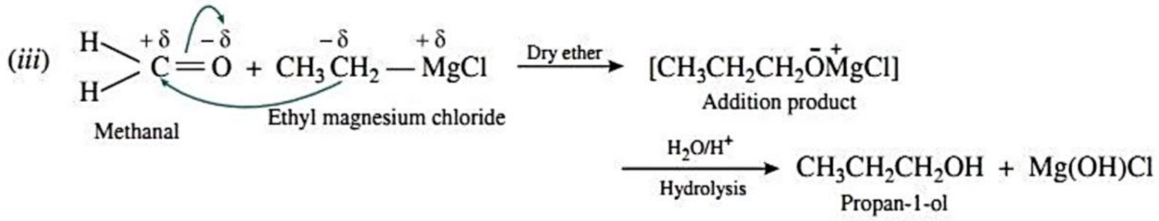
Propan - 2 - ol

(*ii*)

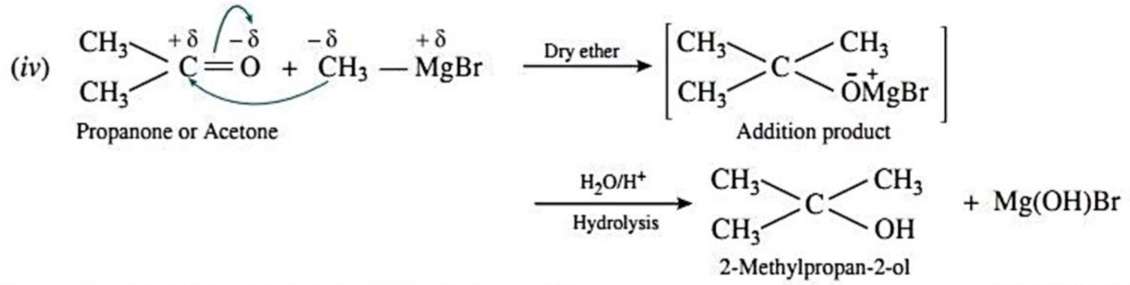


Benzyl chloride Benzyl alcohol

(*iii*)



(*iv*)



Q. 21. Name the reagents used in the following reactions: **[*CBSE (F) 2014*]**

(*i*) Oxidation of primary alcohol to carboxylic acid

(*ii*) Oxidation of a primary alcohol to aldehyde

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

(*iv*) Benzyl alcohol to benzoic acid

(*v*) Dehydration of propan-2-ol to propene

(*vi*) Butan-2-one to butan-2-ol

Ans. (*i*) Acidified potassium dichromate solution ($K_2Cr_2O_7/H_2SO_4$) or alkaline potassium permanganate solution ($KMnO_4/OH^-$) followed by hydrolysis with dil. H_2SO_4.

(*ii*) Pyridinium chlorochromate (PCC), $C_5H_5\overset{+}{N}HClCrO_3^-$ in CH_2Cl_2

(*iii*) Aqueous bromine (Br_2/H_2O)

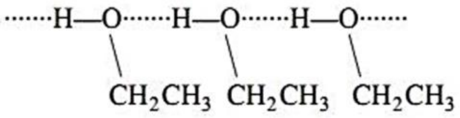
(*iv*) Acidified or alkaline potassium permanganate.

(*v*) Conc. H_2SO_4 at 433–443 K.

(*vi*) Lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$)

Q. 22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

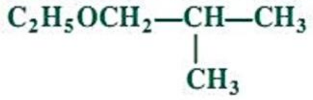
Ans. Ethanol undergoes intermolecular H-bonding due to the presence of a hydrogen attached to the electronegative oxygen atom. As a result, ethanol exists as associated molecules.



Consequently, a large amount of energy is required to break these hydrogen bonds. Therefore, the boiling point of ethanol is higher than that of methoxymethane which does not form H-bonds.

Q. 23. Give the IUPAC names of the following ethers:

(*i*)



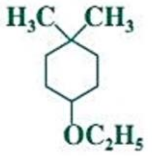
$$C_2H_5OCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

(*ii*) $CH_3OCH_2CH_2Cl$

(*iii*) $O_2N-C_6H_4-OCH_3$ (*p*)

(*iv*) $CH_3CH_2CH_2OCH_3$

(*v*)



(*vi*)

Ans. (*i*) 1-Ethoxy-2-methylpropane

(*ii*) 2-Chloro-1-methoxyethane

(*iii*) 4-Nitroanisole

(*iv*) 1-Methoxypropane

(*v*) 4-Ethoxy-1, 1-dimethylcyclohexane

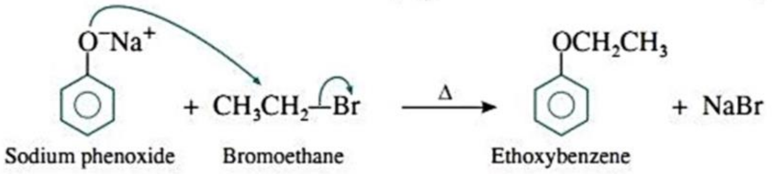
(*vi*) Ethoxybenzene

Q. 24. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

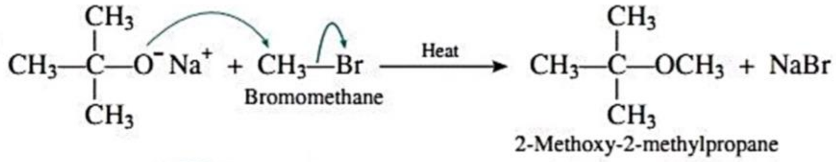
(*i*) 1-Propoxypropane **(*ii*) Ethoxybenzene**
(*iii*) 2-methoxy-2-methylpropane **(*iv*) 1-Methoxyethane** [*CBSE 2020 (56/4/2)*]

Ans. (*i*) $\underset{\text{Sodium propoxide}}{CH_3CH_2CH_2O^-Na^+} + \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2-Br} \xrightarrow{\text{Heat}} \underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3} + NaBr$

(*ii*)



(*iii*)

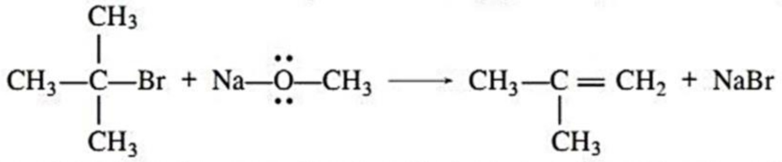


$CH_3-C(CH_3)_2-O^-Na^+ + \underset{\text{Bromomethane}}{CH_3-Br} \xrightarrow{\text{Heat}} \underset{\text{2-Methoxy-2-methylpropane}}{CH_3-C(CH_3)_2-OCH_3} + NaBr$

(*iv*) $\underset{\text{Sodium ethoxide}}{CH_3CH_2O^-Na^+} + \underset{\text{Bromomethane}}{CH_3-Br} \xrightarrow{\text{Heat}} \underset{\text{1-Methoxyethane}}{CH_3-CH_2-O-CH_3} + NaBr$

Q. 25. Illustrate with examples the limitations of Williamson synthesis for the preparation of certain type of ethers.

Ans. (*i*) Williamson's synthesis cannot be employed for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of CH_3ONa with $(CH_3)_3C-Br$ gives exclusively 2-methylpropene.



$CH_3-C(CH_3)_2-Br + Na-\ddot{O}-CH_3 \longrightarrow CH_3-C(CH_3)=CH_2 + NaBr$

(*ii*) Aryl halides and vinyl halides cannot be used as substrates because of their low reactivity in nucleophilic substitution.

Q. 26. How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

Ans. The following method can be used:

Williamson's synthesis

(*i*) $\underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH} + PBr_3 \longrightarrow \underset{\text{1-Bromopropane}}{3CH_3CH_2CH_2Br} + H_3PO_3$

(*ii*) $\underset{\text{Propan-1-ol}}{2CH_3CH_2CH_2OH} + 2Na \longrightarrow \underset{\text{Sodium propoxide}}{2CH_3CH_2CH_2O^-Na^+} + H_2$

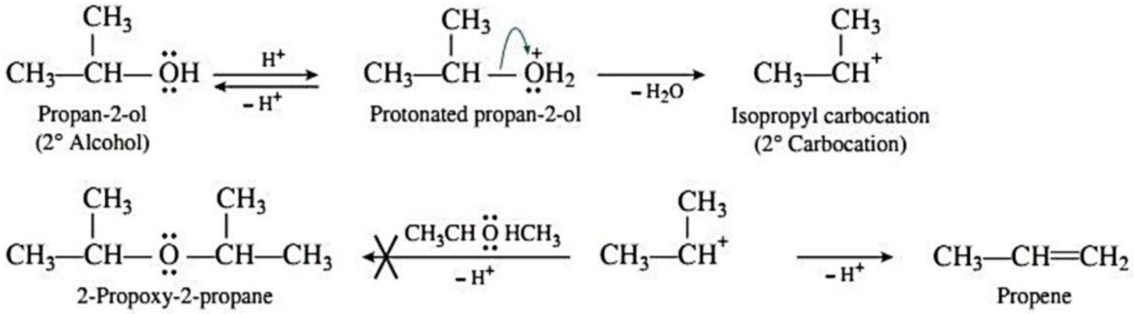
Mechanism: $CH_3CH_2CH_2O^-Na^+ + CH_3CH_2CH_2-Br \xrightarrow[\text{Heat}]{\text{Dry ether}} \underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3} + NaBr$

Q. 27. Preparation of ethers by acid-catalysed dehydration of secondary and tertiary alcohols is not a suitable method. Give reason.

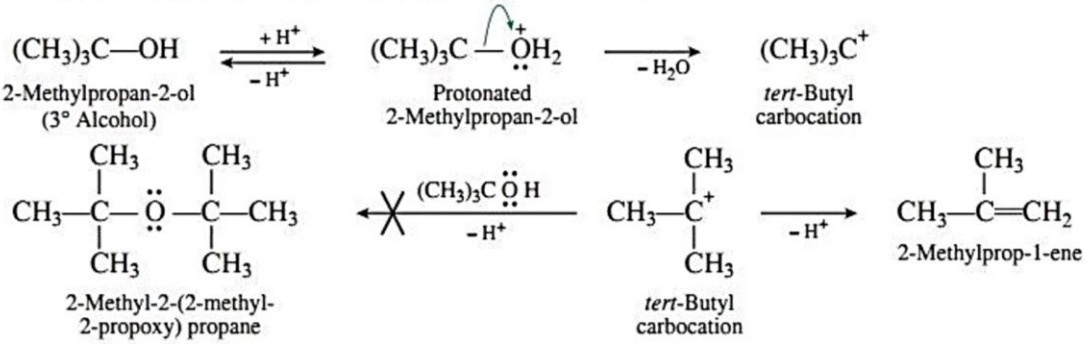
Ans. Acid-catalysed dehydration of primary alcohols to ethers occurs by S_N2 reaction involving nucleophilic attack of the alcohol molecule on the protonated alcohol molecule.

$$CH_3CH_2CH_2\ddot{O}H + CH_3CH_2CH_2-\overset{+}{O}H_2 \xrightarrow[-H_2O]{S_N2} CH_3CH_2CH_2-\ddot{O}-CH_2CH_2CH_3$$

Under these conditions, secondary and tertiary alcohols, however, give alkenes rather than ethers. This is because due to steric hindrance, nucleophilic attack of the alcohol molecule on the protonated alcohol molecule does not occur. Instead, protonated secondary and tertiary alcohols lose a molecule of water to form stable secondary and tertiary carbocations. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.



Similarly, tertiary alcohols give alkenes rather than ethers.



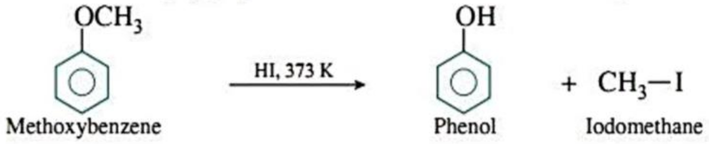
Q. 28. Write the equation for the reaction of hydrogen iodide with

(*i*) 1-propoxypropane (*ii*) methoxybenzene (*iii*) benzyl ethyl ether

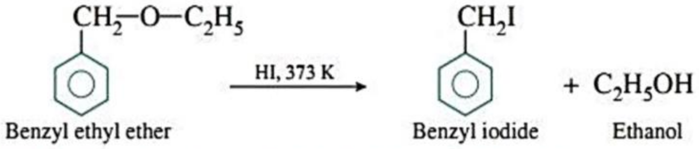
Ans. (*i*)

$$\underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} \xrightarrow[373\ K]{HI} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2—OH} + \underset{\text{Iodopropane}}{CH_3CH_2CH_2—I}$$

(*ii*)

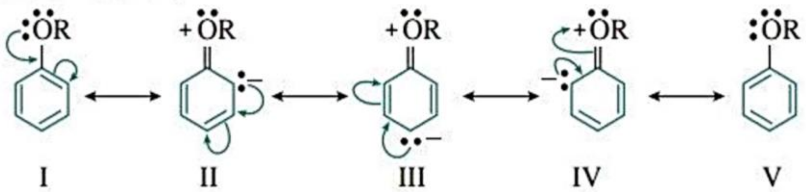


(*iii*)

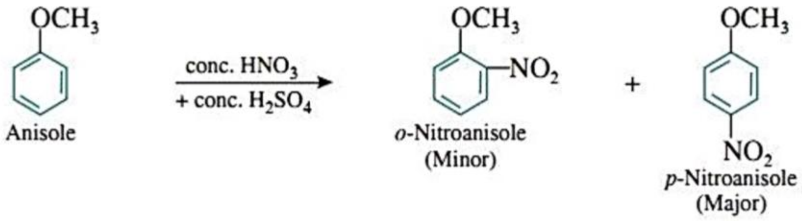


Q. 29. Explain the fact that in aryl alkyl ethers (*i*) the alkoxy group activates the benzene ring towards electrophilic substitution and (*ii*) it directs the incoming substituents to ortho and para positions in benzene ring.

Ans. Electrophilic substitution reactions: In aryl alkyl ethers, the +R-effect of the alkoxy group (OR) increases the electron density in the benzene ring thereby activating the benzene ring towards electrophilic substitution reactions.



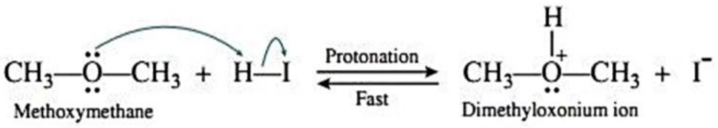
Since the electron density increase more at the two ortho and one para position as compared to *m*-positions, electrophilic substitution reactions mainly occur at *o*-and *p*-positions. For example,



Q. 30. Write mechanism of the reaction of HI with methoxymethane.

Ans. With equimolar amounts of HI and methoxymethane, a mixture of methyl alcohol and methyl iodide are formed by the following mechanism:

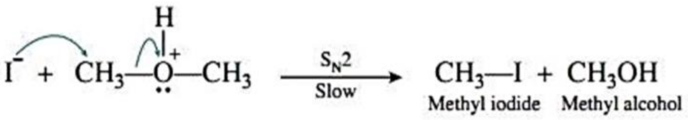
Step I:



$$CH_3-\ddot{O}-CH_3 + H-I \underset{\text{Fast}}{\overset{\text{Protonation}}{\rightleftharpoons}} CH_3-\overset{H}{\overset{|}{\ddot{O}^+}}-CH_3 + I^-$$

Methoxymethane Dimethyloxonium ion

Step II:

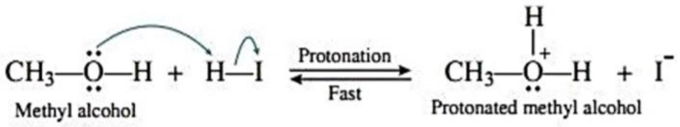


$$I^- + CH_3-\overset{H}{\overset{|}{\ddot{O}^+}}-CH_3 \xrightarrow[\text{Slow}]{S_N2} CH_3-I + CH_3OH$$

Methyl iodide Methyl alcohol

If excess of HI is used, methyl alcohol formed in step II is also converted into methyl iodide by the following mechanism:

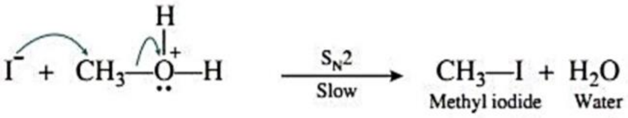
Step III:



$$CH_3-\ddot{O}-H + H-I \underset{\text{Fast}}{\overset{\text{Protonation}}{\rightleftharpoons}} CH_3-\overset{H}{\overset{|}{\ddot{O}^+}}-H + I^-$$

Methyl alcohol Protonated methyl alcohol

Step IV:



$$I^- + CH_3-\overset{H}{\overset{|}{\ddot{O}^+}}-H \xrightarrow[\text{Slow}]{S_N2} CH_3-I + H_2O$$

Methyl iodide Water

Q. 31. Write equations of the following reactions:

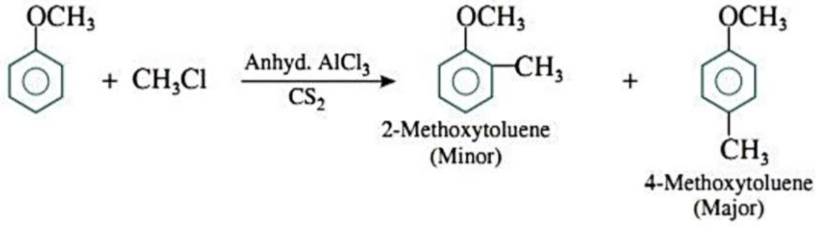
(*i*) Friedel–Crafts reaction—alkylation of anisole

(*ii*) Nitration of anisole

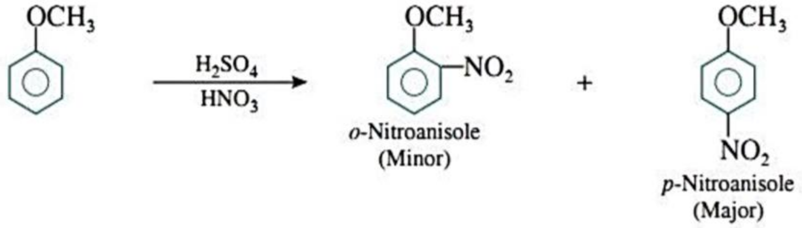
(*iii*) Bromination of anisole in ethanoic acid medium

(*iv*) Friedel–Crafts acetylation of anisole.

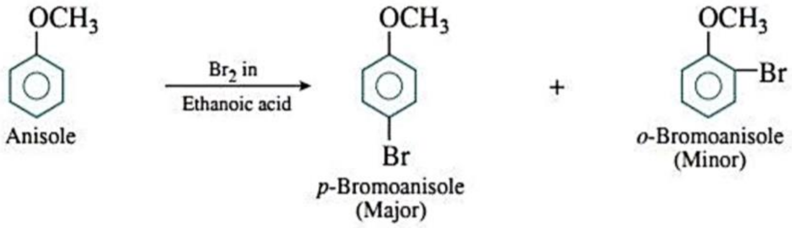
Ans. **(*i*) Friedel–Crafts reaction (Alkylation):**



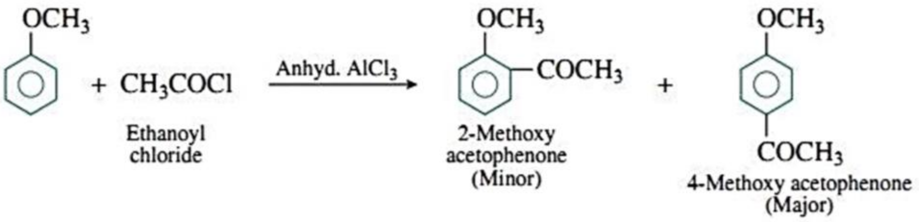
(*ii*) Nitration of anisole: Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



(*iii*) Halogenation:



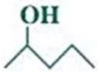
(*iv*) Friedel–Crafts acetylation of anisole:

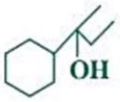


Q. 32. Show how would you synthesise the following alcohols from appropriate alkenes? **[*HOTS*]**

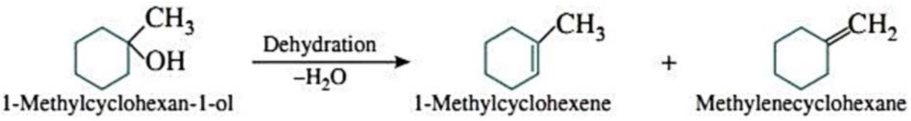
(*i*) 

(*ii*) 

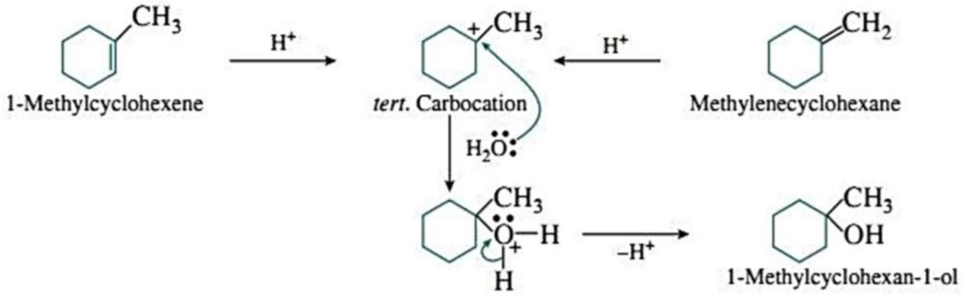
(*iii*) 

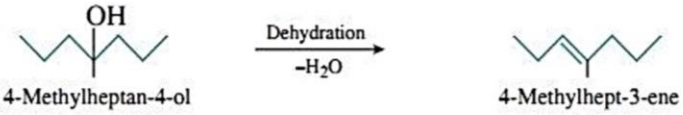
(*iv*) 

Ans. As addition and elimination are opposite to each other, the general strategy is to first dehydrate alcohol to give either a single alkene or a mixture of alkenes. If a mixture of alkenes is possible, then find out which of the alkenes will give the desired product.

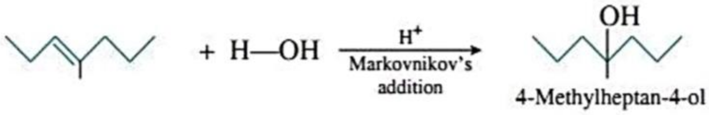
(*i*) 

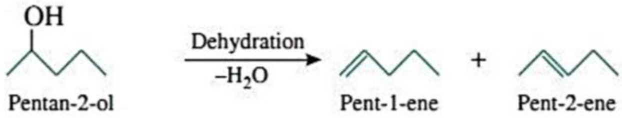
Addition of H_2O to both these alkenes gives 1-methylcylohexan-1-ol.



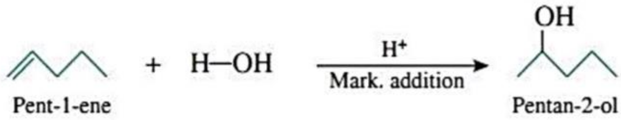
(*ii*) 

Addition of H_2O to 4-methylhept-3-ene in presence of an acid gives the desired alcohol.

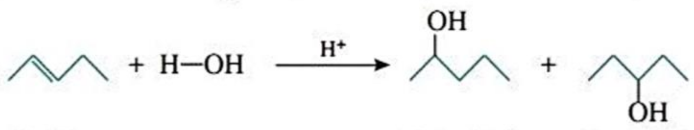


(*iii*) 

Addition of H_2O to pent-1-ene gives pentan-2-ol.

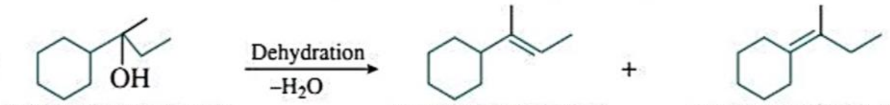


Now, addition of H_2O to pent-2-ene gives a mixture of pentan-2-ol, pentan-3-ol.



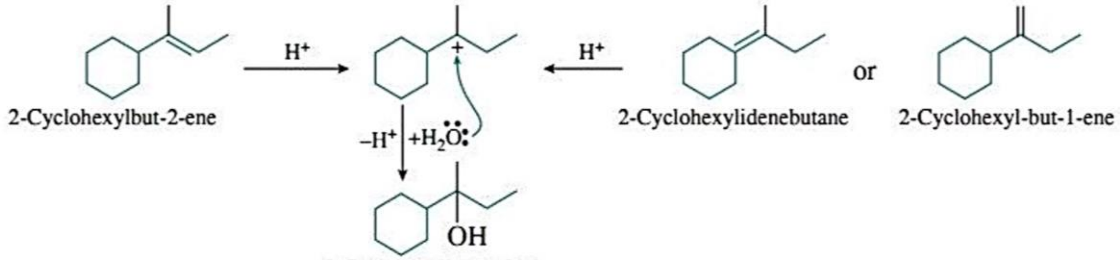
Pent-2-ene Pentan-2-ol Pentan-3-ol

Hence, the desired alkene is pent-1-ene and not pent-2-ene.

(*iv*)


2-Cyclohexylbutan-2-ol 2-Cyclohexylbut-2-ene 2-Cyclohexylidenebutane

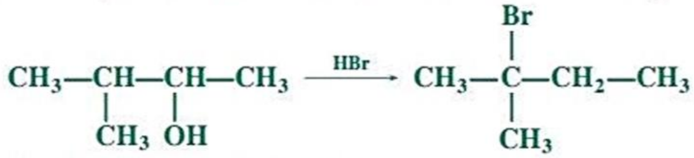
Now addition of H_2O to both 2-cyclohexylbut-2-ene and 2-cyclohexylidenebutane in presence of an acid gives 2-cyclohexylbutan-2-ol.



2-Cyclohexylbut-2-ene 2-Cyclohexylidenebutane 2-Cyclohexyl-but-1-ene

2-Cyclohexylbutan-2-ol

Q. 33. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place.



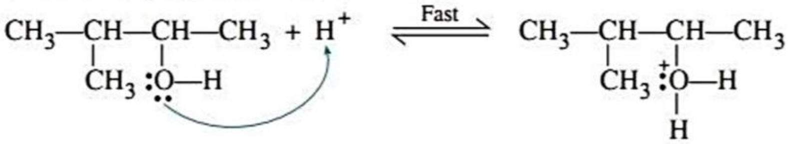
$$CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\OH\end{array}}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{\begin{array}{c}Br\\|\end{array}}{\underset{\begin{array}{c}|\\CH_3\end{array}}{C}}-CH_2-CH_3$$

Give a mechanism for this reaction.

(**Hint:** The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.)

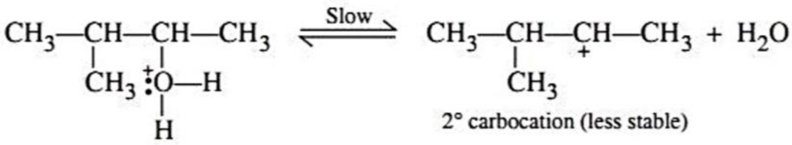
Ans. Mechanism: The reaction takes place through the following mechanism:

Step I: Formation of protonated alcohol.



$$CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\:\ddot{O}-H\end{array}}{CH}-CH_3 + H^+ \xrightleftharpoons{\text{Fast}} CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\:\overset{+}{O}-H\\|\\H\end{array}}{CH}-CH_3$$

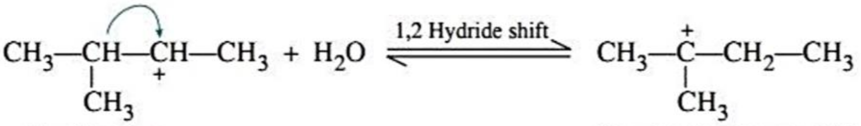
Step II: Formation of carbocation.



$$CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{\begin{array}{c}|\\:\overset{+}{O}-H\\|\\H\end{array}}{CH}-CH_3 \xrightleftharpoons{\text{Slow}} CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{+}{CH}-CH_3 + H_2O$$

2° carbocation (less stable)

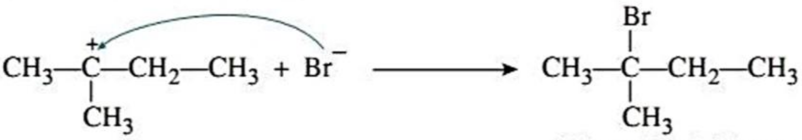
2° carbocation being less stable undergoes 1, 2 hydride shift to form more stable 3° carbocation.



$$CH_3-\underset{\begin{array}{c}|\\CH_3\end{array}}{CH}-\underset{+}{CH}-CH_3 + H_2O \xrightleftharpoons{\text{1,2 Hydride shift}} CH_3-\overset{+}{\underset{\begin{array}{c}|\\CH_3\end{array}}{C}}-CH_2-CH_3$$

2° carbocation 3° carbocation (more stable)

Step III: Attack of nucleophile



$$CH_3-\overset{+}{\underset{\begin{array}{c}|\\CH_3\end{array}}{C}}-CH_2-CH_3 + Br^- \longrightarrow CH_3-\overset{\begin{array}{c}Br\\|\end{array}}{\underset{\begin{array}{c}|\\CH_3\end{array}}{C}}-CH_2-CH_3$$

2-Bromo-2-methylbutane

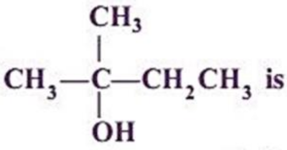
Multiple Choice Questions

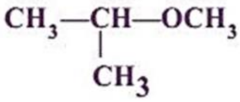
Choose and write the correct option(s) in the following questions.

1. **The C—O—H bond angle in alcohol is** [CBSE 2022 (56/3/4)]
(*a*) slightly greater than 109°28′. (*b*) slightly less than 109°28′.
(*c*) slightly greater than 120°. (*d*) slightly less than 120°.

2. **How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?** [*NCERT Exemplar*]
(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 4

3. **IUPAC name of *m*-cresol is ______________.** [*NCERT Exemplar*]
(*a*) 3-methylphenol (*b*) 3-chlorophenol (*c*) 3-methoxyphenol (*d*) benzene-1, 3-diol

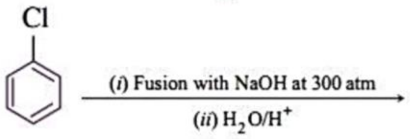
4. **The correct IUPAC name of**  $CH_3—\overset{CH_3}{\underset{OH}{C}}—CH_2CH_3$ **is** [CBSE 2020 (56/2/1)]
(*a*) *tert*-butyl alcohol (*b*) 2, 2-Dimethylpropanol
(*c*) 2-Methylbutan-2-ol (*d*) 3-Methylbutan-3-ol

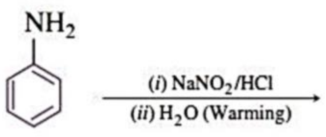
5. **IUPAC name of the compound**  $CH_3—\underset{CH_3}{CH}—OCH_3$ **is ______________.** [*NCERT Exemplar*]
(*a*) 1-methoxy-1-methylethane (*b*) 2-methoxy-2-methylethane
(*c*) 2-methoxypropane (*d*) isopropylmethyl ether

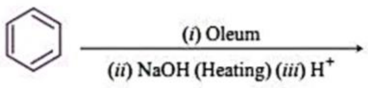
6. **The C—O bond length in phenol is less than that in methanol due to**
(*a*) partial double bond character of oxygen with aromatic ring
(*b*) sp^2 hybridised carbon to which oxygen attached
(*c*) sp^3 hybridised carbon
(*d*) both (*a*) and (*b*)

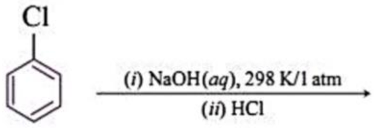
7. **Which of the following are not used to convert RCHO into RCH_2OH?**
(*a*) H_2/Pd (*b*) $LiAlH_4$
(*c*) $NaBH_4$ (*d*) Reaction with RMgX followed by hydrolysis

8. **Which of the following reactions will not yield phenol?**

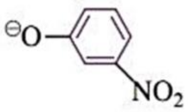
(*a*) 

(*b*) 

(*c*) 

(*d*) 

9. **Which of the following alcohols will not undergo oxidation?** [CBSE 2023 (56/5/2)]
(*a*) Butanol (*b*) Butan-2-ol
(*c*) 2-Methylbutan-2-ol (*d*) 3-Methylbutan-2-ol

10. **Which of the following species can act as the strongest base?** [*NCERT Exemplar*]
(*a*) $^{\ominus}OH$ (*b*) $^{\ominus}OR$ (*c*) $^{\ominus}OC_6H_5$ (*d*) 

11. Phenol is less acidic than _______________. *[NCERT Exemplar]*

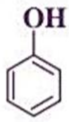
(*a*) ethanol (*b*) *o*-nitrophenol (*c*) *o*-methylphenol (*d*) *o*-methoxyphenol

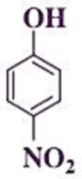
12. Which is the correct order of acid strength of the following?

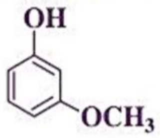
(*a*) $C_6H_5OH > H_2O > ROH > HC\equiv CH$ (*b*) $C_6H_5OH > ROH > H_2O > HC\equiv CH$

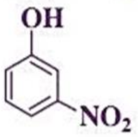
(*c*) $C_6H_5OH > HC\equiv CH > H_2O > ROH$ (*d*) $C_6H_5OH > H_2O > HC\equiv CH > ROH$

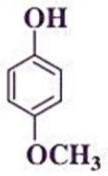
13. Mark the correct order of decreasing acid strength of the following compounds. *[NCERT Exemplar]*


(*i*)


(*ii*)


(*iii*)


(*iv*)


(*v*)

(*a*) (*v*) > (*iv*) > (*ii*) > (*i*) > (*iii*) (*b*) (*ii*) > (*iv*) > (*i*) > (*iii*) > (*v*)

(*c*) (*iv*) > (*v*) > (*iii*) > (*ii*) > (*i*) (*d*) (*v*) > (*iv*) > (*iii*) > (*ii*) > (*i*)

14. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is: *[CBSE Sample Paper 2022]*

(*a*) protonation of alcohol molecule (*b*) formation of carbocation

(*c*) elimination of water (*d*) formation of an ester

15. Which of the following reactions are feasible? *[CBSE 2023 (56/2/1)]*

(*a*) $CH_3CH_2Br + Na^+ \, {}^-OC(CH_3)_3 \longrightarrow CH_3CH_2—O—C(CH_3)_3$

(*b*) $(CH_3)_3C—Cl + Na^+ \, {}^-OCH_2CH_3 \longrightarrow CH_3CH_2—O—C(CH_3)_3$

(*c*) Both (*a*) and (*b*)

(*d*) Neither (*a*) nor (*b*)

16. The synthesis of alkyl fluoride is best obtained from: *[CBSE 2023 (56/1/1)]*

(*a*) Free radicals (*b*) Swarts reaction

(*c*) Sandmeyer reaction (*d*) Finkelstein reaction

17. The compound that reacts fastest with Lucas reagent at room temperature is

(*a*) butan-1-ol (*b*) butan-2-ol

(*c*) 2 methylpropan-1-ol (*d*) 2-methylpropan-2-ol

18. CH_3CH_2OH can be converted into CH_3CHO by _______________. *[NCERT Exemplar]*

(*a*) catalytic hydrogenation (*b*) treatment with $LiAlH_4$

(*c*) treatment with pyridinium chlorochromate (*d*) treatment with $KMnO_4$

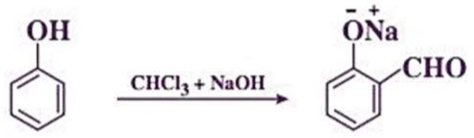
19. An alcohol on oxidation is found to give CH_3COOH and CH_3CH_2COOH. The structure of the alcohol is:

(*a*) $CH_3CH_2CH_2OH$ (*b*) $(CH_3)_2C(OH)CH_2—CH_3$

(*c*) $CH_3(CH_2)_3CH_2OH$ (*d*) $CH_3CHOHCH_2CH_2CH_3$

20. Which of the following compounds will react with sodium hydroxide solution in water? *[NCERT Exemplar]*

(*a*) C_6H_5OH (*b*) $C_6H_5CH_2OH$ (*c*) $(CH_3)_3\,COH$ (*d*) C_2H_5OH

21. 

The electrophile involved in the above reaction is:

(*a*) ${}^+CHO$ (*b*) ${}^+CHCl_2$ (*c*) ${}^-CCl_3$ (*d*) $:CCl_2$

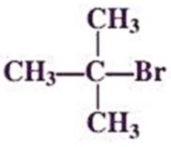
22. Monochlorination of toluene in sunlight followed by hydrolysis with *aq*. NaOH yields. *[NCERT Exemplar]*

(*a*) *o*-Cresol (*b*) *m*-Cresol

(*c*) 2, 4-Dihydroxytoluene (*d*) Benzyl alcohol

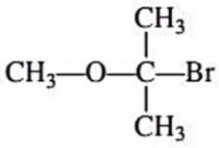
23. Which of the following compounds is oxidised to methyl ethyl ketone?

(*a*) 2-Propanol (*b*) 1-Butanol (*c*) 2-Butanol (*d*) *tert*. Butyl alcohol

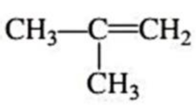
24. The reaction of 

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

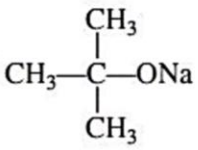
with $NaOCH_3$ forms the product

(*a*) 

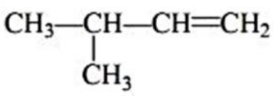
$CH_3-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

(*b*) 

$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

(*c*) 

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-ONa$

(*d*) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

25. Which of the following analogue is correct?

(*a*) *o*-nitrophenol : pk_a value (7.2) :: *m*-nitrophenol : pk_a value (7.1)

(*b*) Benzene-1, 2-diol : Catechol :: Benzene-1, 4-diol : Quinol

(*c*) $C_6H_5(OH)CHO$: Salicylaldehyde :: $C_6H_5(OH)COO^-Na^+$: Salicylic acid

(*d*) *n*-pentane : B.P. (309.1 K) :: Ethoxy ethane : B.P. (390 K)

26. Williamson's synthesis of preparing dimethyl ether is an: [*CBSE Sample Paper 2022*]

(*a*) S_N1 reaction (*b*) Elimination reaction

(*c*) S_N2 reaction (*d*) Nucleophilic addition reaction

27. Match the species in column I with the corresponding boiling point in column II and choose the correct answer using the codes given below:

Column–I	Column–II
(*i*) CH_3CH_2OH	**A.** 373 K
(*ii*) CH_3-O-CH_3	**B.** 348 K
(*iii*) H_2O	**C.** 351 K
(*iv*) $CH_3CH_2-O-CH_2CH_3$	**D.** 248 K

(*a*) (*i*) — C, (*ii*) — D, (*iii*) — A, (*iv*) — B (*b*) (*i*) — A, (*ii*) — B, (*iii*) — C, (*iv*) — D

(*c*) (*i*) — B, (*ii*) — D, (*iii*) — A, (*iv*) — C (*d*) (*i*) — D, (*ii*) — B, (*iii*) — A, (*iv*) — C

Answers

1. (*b*)	**2.** (*a*)	**3.** (*a*)	**4.** (*c*)	**5.** (*c*)	**6.** (*d*)	**7.** (*d*)	**8.** (*d*)	**9.** (*c*)	**10.** (*b*)
11. (*b*)	**12.** (*a*)	**13.** (*b*)	**14.** (*a*)	**15.** (*a*)	**16.** (*b*)	**17.** (*d*)	**18.** (*c*)	**19.** (*d*)	**20.** (*a*)
21. (*d*)	**22.** (*d*)	**23.** (*c*)	**24.** (*b*)	**25.** (*b*)	**26.** (*b*)	**27.** (*a*)			

COMPETENCY-FOCUSED QUESTIONS AS PER NEP

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

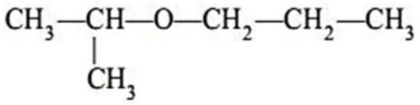
(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion** (*A*) : IUPAC name of the compound



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—CH_2—CH_2—CH_3$$ is 2-Ethoxy-2-methylethane.

Reason (*R*) : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group].

2. **Assertion** (*A*) : The boiling point of ethanol is higher than methoxymethane.

Reason (*R*) : There is intramolecular hydrogen bonding in ethanol.

3. **Assertion** (*A*) : C_2H_5OH is a weaker base than phenol but is a stronger nucleophile than phenol.

Reason (*R*) : In phenol the lone pair of electrons on oxygen is withdrawn towards the ring due to resonance. [*CBSE Sample Paper 2020*]

4. **Assertion** (*A*) : *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason (*R*) : *m*- and *p*- Nitrophenols exist as associated molecules.

5. **Assertion** (*A*) : *o*-nitrophenol is a weaker acid than *p*-nitrophenol.

Reason (*R*) : Intramolecular hydrogen bonding makes *ortho* isomer weaker than *para* isomer. [*CBSE 2020 (56/2/1)*]

6. **Assertion** (*A*) : *p*-nitrophenol is more acidic than phenol.

Reason (*R*) : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

7. **Assertion** (*A*) : In lucas test, 3° alcohols react immediately.

Reason (*R*) : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

8. **Assertion** (*A*) : Phenol on oxidation with chromic acid gives benzoquinone.

Reason (*R*) : Pure phenol is colourless but turn pink due to oxidation to phenoquinone.

9. **Assertion** (*A*) : Phenol is more reactive than benzene towards electrophilic substitution reaction.

Reason (*R*) : In the case of phenol, the intermediate carbocation is more resonance stabilized.

10. **Assertion** (*A*) : Phenols give *o*- and *p*-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

Reason (*R*) : —OH group in phenol is *o*–, *p*–directing.

11. **Assertion** (*A*) : Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason (*R*) : Lewis acid polarises the bromine molecule.

12. **Assertion** (*A*) : The reaction of phenol with acid chloride to form ether occurs in the presence of pyridine.

Reason (*R*) : Pyridine is a base so it neutralises the HCl formed and proceeds the reaction.

13. **Assertion** (*A*) : The C–O–H bond angle in alcohols is slightly less than the tetrahedral angle.

Reason (*R*) : This is due to the repulsive interaction between the two lone electron pairs on oxygen. [*CBSE 2020 (56/3/1)*]

14. **Assertion** (*A*) : Methoxy ethane reacts with HI to give ethanol and iodomethane

Reason (*R*) : Reaction of ether with HI follows S_N2 mechanism [*CBSE Sample Paper 2021*]

15. **Assertion** (*A*) : $(CH_3)_3\,C—O—CH_3$ gives $(CH_3)_3\,C—I$ and CH_3OH on treatment with HI.

Reason (*R*) : The reaction occurs by S_N1 mechanism. [*CBSE 2020 (56/4/1)*]

Answers

1. (*d*) **2.** (*c*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*a*) **7.** (*b*) **8.** (*b*) **9.** (*a*) **10.** (*d*)
11. (*d*) **12.** (*a*) **13.** (*a*) **14.** (*a*) **15.** (*a*)

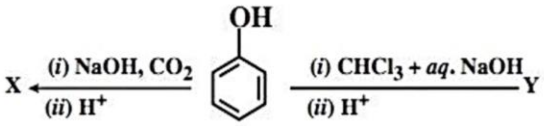
Passage-based/Case-based/ Source-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Alcohols and Phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron donating groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to give alkyl halides. On oxidation primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. The presence of —OH groups in phenols activates the ring towards electrophilic substitution. Various important products are obtained from phenol like salicylaldehyde, salicylic acid, picric acid etc.

1. **Give the structure of an alcohol which is resistant to oxidation?**
2. **Name any one group that increases the acidic character of phenol?**
3. **Consider the following reaction:**

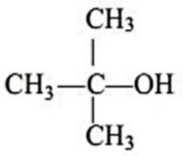


Identify X and Y.

OR

***p*-nitrophenol is a stronger acid than phenol while *p*-cresol is a weaker acid. Why?**

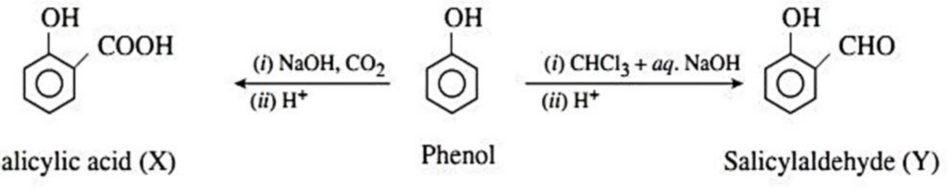
Answers

1. 

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

3° alcohols do not undergo oxidation because they do not have α-hydrogens.

2. NO_2 is electron withdrawing group, due to which it increase the stability of phenoxide ion.

3. 

OR

This is because —NO_2 decreases electron density on oxygen of O—H group making *p*-nitrophenol a stronger acid. While —CH_3 group increases electron density.

PASSAGE–2

Williamson synthesis is one of the best methods for the preparation of ethers. It involves the treatment of an alkyl halide with a suitable sodium alkoxide. Williamson's synthesis involves nucleophilic substitution of the halogen atom of an alkyl halide by an alkoxide group as shown below:

$$R-O^-Na^+ + R'X \longrightarrow R-O-R' + NaX$$

When alkyl halide used in the reaction is primary, Williamson's synthesis proceeds via S_N2 mechanism leading to the formation of an ether. This method is a versatile method for the synthesis of both symmetrical and unsymmetrical ethers.

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1. **Name the alkyl halide and sodium alkoxide used to synthesise tert-butyl ethyl ether.**
2. **What happens when benzyl ethyl ether reacts with HI?**
3. **Why is Williamson's synthesis not applicable when the alkyl halide used is tertiary?**

OR

$(CH_3)_3C—O—CH_3$ on reaction with HI gives $(CH_3)_3C—I$ and $CH_3—OH$ as the main products and not $(CH_3)_3C—OH$ and $CH_3—I$. Give reason.

Answers

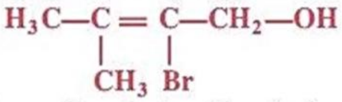
1. Ethyl bromide and sodium *tert*-butoxide.
2. Benzyl iodide and ethyl alcohol will be formed after the reaction of benzyl ethyl ether with HI.
3. This is because 3° alkyl halides are highly susceptible to dehydrohalogenation in the presence of sodium alkoxides and elimination reaction occurs.

OR

The reaction between $(CH_3)_3COCH_3$ and HI follows S_N1 mechanism. For an S_N1 reaction, the formation of product is controlled by stability of the carbocation formed in the slowest step. Since *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 $(\overset{\oplus}{C}H_3)$ therefore $(CH_3)_3C—I$ and CH_3OH are the main products.

CONCEPTUAL QUESTIONS

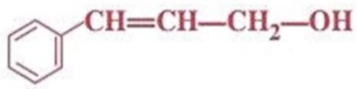
Q. 1. Write the IUPAC name of the following compound: **[*CBSE (AI) 2017*]**



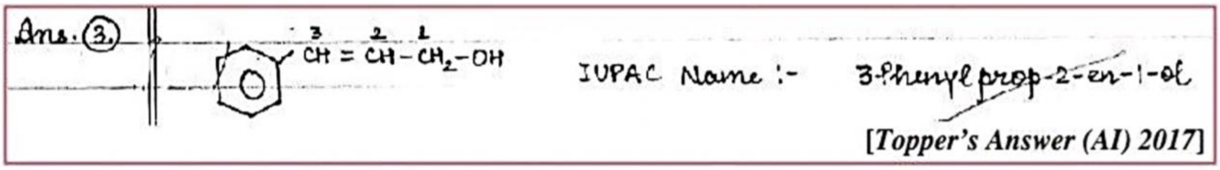
$$H_3C—\underset{CH_3}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}—CH_2—OH$$

Ans. 2-Bromo-3-methylbut-2-en-1-ol

Q. 2. Write the IUPAC name of the following compound: **[*CBSE (AI) 2017*]**



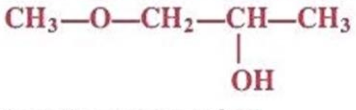
Ans.



Ans. ③ 3 2 1 CH = CH - CH₂-OH IUPAC Name :- 3-Phenyl prop-2-en-1-ol

[*Topper's Answer (AI) 2017*]

Q. 3. Write the IUPAC name of the following compound: **[*CBSE Chennai 2015*]**



$$CH_3—O—CH_2—\underset{OH}{\underset{|}{CH}}—CH_3$$

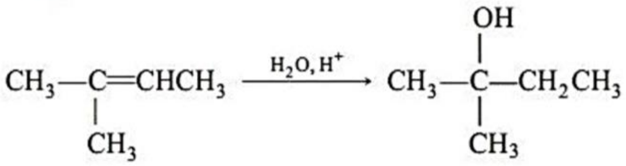
Ans. 1-methoxypropan-2-ol

Q. 4. How would you convert ethanol to ethene? **[*CBSE (AI) 2011*]**

Ans. $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[443\ K]{conc.H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$

Q. 5. How will you synthesise the following alcohol from appropriate alkene: **[*CBSE 2019 (56/4/1)*]**

Ans.



$$CH_3—\underset{CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow{H_2O, H^+} CH_3—\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—CH_2CH_3$$

Q. 6. Why *ortho*-nitrophenol is steam volalite while *para*-nitrophenol is not? *[CBSE 2023 (56/2/1)]*

Ans. Due to intramolecular H-bonding *o*-nitrophenol exists as a discrete molecule whereas due to intermolecular H-bonding *p*-nitrophenol exists as associated molecules. As a result of this *p*-nitrophenol has higher boiling point than *o*-nitrophenol.

Q. 7. Of the two hydroxy organic compounds ROH and R′OH, the first one is basic and the other is acidic in behaviour. How is R different from R′?

Ans. R is an alkyl group whereas R′ is an aryl group.

Q. 8. Arrange the following compounds in the increasing order of their acid strengths:

4-nitrophenol, phenol, 2, 4, 6-trinitrophenol *[CBSE (F) 2013]*

Ans. Phenol < 4-nitrophenol < 2,4,6-trinitrophenol

Q. 9. Phenol is an acid but does not react with sodium bicarbonate solution. Why? *[HOTS]*

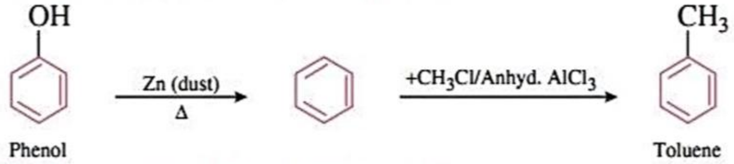
Ans. Phenol is a weaker acid than carbonic acid (H_2CO_3) and hence does not liberate CO_2 from sodium bicarbonate.

Q. 10. Suggest a reagent for conversion of ethanol to ethanoic acid. *[NCERT Exemplar]*

Ans.
(*i*) $CrO_3 - H_2SO_4$
(*ii*) $KMnO_4/OH^-$
(*iii*) H_3O^+
(*iv*) Acidified $KMnO_4$ or $K_2Cr_2O_7$

Q. 11. How is toluene obtained from phenol? *[CBSE Delhi 2013C]*

Ans.



Q. 12. Suggest a reagent for the following conversion:

[NCERT Exemplar]

Ans. CrO_3, Pyridine and HCl (Pyridinium chlorochromate)

Q. 13. What is denatured alcohol? *[NCERT Exemplar]*

Ans. Alcohol is made unfit for drinking by mixing some copper sulphate and pyridine in it. This is called denatured alcohol.

Q. 14. Explain why sodium metal can be used for drying diethyl ether but not ethyl alcohol. *[HOTS]*

Ans. Due to presence of an active hydrogen atom, ethyl alcohol reacts with sodium metal.

$$2CH_3—CH_2—OH + 2Na \longrightarrow 2CH_3—CH_2—\overset{-}{O}\overset{+}{Na} + H_2$$

Diethyl ether, on the other hand, does not have replaceable hydrogen atom therefore does not react with sodium metal hence can be dried by metallic sodium.

Q. 15. What is the order of dehydration of primary, secondary and tertiary alcohols?

Ans. Tertiary alcohols > Secondary alcohols > Primary alcohols

Q. 16. Name the reagents used in the following reactions: *[CBSE (F) 2014]*

Friedel–Crafts alkylation of anisole

Ans. Anhydrous aluminium chloride (anhyd. $AlCl_3$)

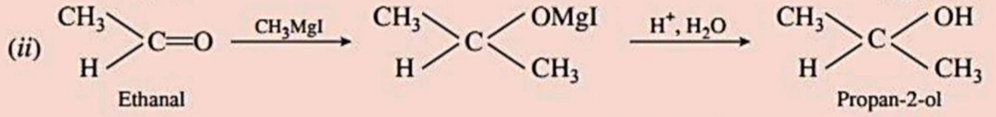
Short Answer Questions–I

Each of the following questions are of 2 marks.

Q. 1. How will you convert:

(*i*) Propene to Propan-1-ol? **(*ii*) Ethanal to Propan-2-o1?** [*CBSE Delhi 2013*]

Ans. (*i*) $\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br \xrightarrow[\Delta]{KOH\,(aq)} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$ 1

(*ii*)  1

[*CBSE Marking Scheme Delhi 2013 (56/5/1)*]

Q. 2. Which is a stronger acid—phenol or cresol? Explain.

Ans. All the cresols are weaker acids than phenols. Methyl group has +I effect (positive inductive effect) as well as hyperconjugation effect but the hyperconjugation effect predominates over the +I effect. Since both these effects increase the electron density on the O—H bond and hence all the cresols are weaker acids than phenols.

As hyperconjugation effect can operate only through *ortho* and *para* positions and not through meta positions, therefore, meta-cresol is stronger acid than *ortho* and *para*-cresols. However, due to stronger +I effect at *ortho* position than at *para* position (+I effect decreases with distance), *ortho*-cresol is a weaker acid than *para*-cresol. Thus, the order of acidic strength in increasing order is:

ortho-cresol < *para*-cresol < *meta*-cresol < phenol

Q. 3. Arrange: water, ethanol and phenol in increasing order of acidity and give reason for your answer. [*NCERT Exemplar*]

Ans. Increasing order of acidity is ethanol < water < phenol. The phenoxide ion obtained after the removal of a proton is stabilised by resonance whereas the ethoxide ion obtained after the removal of a proton is destabilised by +I effect of —C_2H_5 group. Therefore, phenol is stronger acid than ethanol. On the other hand, ethanol is weaker acid than water because electron releasing —C_2H_5 group in ethanol increases the electron density on oxygen and hence the polarity of O—H bond in ethanol decreases which results in the decreasing acidic strength. Hence, acidic strength increases in the order given above.

Q. 4. Account for the following:

(*i*) Phenol is a stronger acid than an alcohol.

(*ii*) The boiling point of alcohol decreases with increase in branching of alkyl chain.

[*CBSE 2023 (56/1/1)*]

Ans. (*i*) 

Phenoxide ion

$$R-\ddot{\underset{\cdot\cdot}{O}}-H + H_2\ddot{O}: \rightleftharpoons \underset{\substack{\text{Alkoxide ion}\\\text{(Less stable)}}}{R-\ddot{\underset{\cdot\cdot}{O}}^{-}} + H_3\ddot{O}^+$$

Phenol is stronger acid than alcohol because the phenoxide ion left-after the release of a proton is stabilised by resonance but alkoxide ion is not, moreover, the +I effect of alkyl group destabilizes the alkoxide ion by intensifying negative charge on oxygen atom.

(*ii*) In alcohols with increase of branching in carbon chain surface area decreases which results in decrease in vander Waals forces and hence decrease in boiling point.

Q. 5. Account for the following:

(*i*) Phenol does not react with $NaHCO_3$ whereas carboxylic acids react.

(*ii*) Phenol is more easily nitrated than benzene. [*HOTS*]

Ans. (*i*) $$RCOOH + NaHCO_3 \longrightarrow RCOONa + \underset{\text{Weaker acid than RCOOH}}{H_2CO_3}$$

Such acid–base reaction takes place only if the acid formed is weaker than the reacting acid. In other words, phenol is not a strong enough acid to react with $NaHCO_3$.

(*ii*) Nitration involves attack of electrophile nitronium ion ($\overset{+}{N}O_2$) on benzene ring. Due to +R effect of —OH group electron density on benzene increases. Therefore, phenol is more easily nitrated as compared to benzene.

Q. 6. Answer the following questions:

(*i*) Dipole moment of phenol is smaller that of methanol. Why?

(*ii*) In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

[*NCERT Exemplar*]

Ans. (*i*) In phenol, C—O bond is less polar due to electron-withdrawing effect of benzene ring whereas in methanol, C—O bond is more polar due to electron-releasing effect of —CH_3 group.

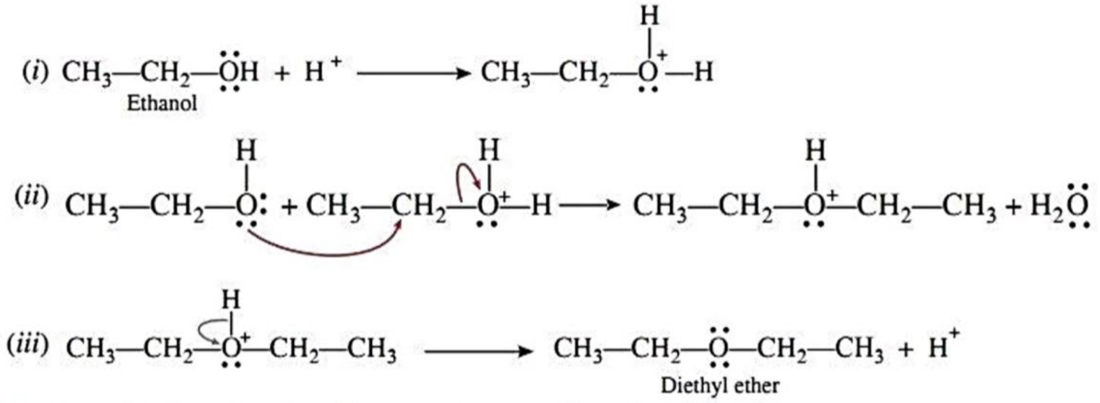
(*ii*) Phenoxide ion is more reactive than phenol towards electrophilic aromatic substitution and hence undergoes electrophilic substitution with carbon dioxide which is a weak electrophile.

Q. 7. Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow[413\ K]{\text{conc. } H_2SO_4} CH_3—CH_2—O—CH_2—CH_3$$

[*CBSE Delhi 2016, 2019 (56/4/3), 2020 (56/3/2)*] [*HOTS*]

Ans. The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on protonated alcohol as shown below:

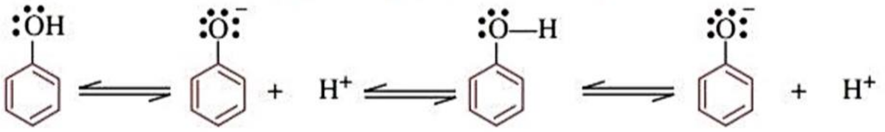


Q. 8. For the pair phenol and cyclohexanol, answer the following:

(*i*) Why is phenol more acidic than cyclohexanol?

(*ii*) Give one chemical test to distinguish between the two. [*CBSE 2023 (56/5/2)*]

Ans. (*i*)



Due to higher electronegativity of sp^2 hybridised carbon of phenol to which —OH groups is attached, electron density decreases on oxygen.

This increases the polarity of O—H bond and results in an increase in ionisation of phenols than that of cyclohexanol where —OH group is attached to sp^3 hybridised carbon atom.

(*ii*) Phenol gives a violet colouration with $FeCl_3$ solution while cyclohexanol does not.

$$\underset{\text{Cyclohexanol}}{6C_6H_{11}OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{[Fe(OC_6H_{11})_6]^{3-}} + 3H^+ + 3HCl$$

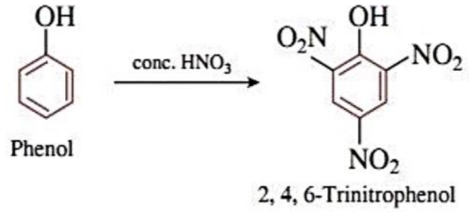
Q. 9. What happens when

(*i*) Phenol reacts with Conc. HNO_3?

(*ii*) Ethyl chloride reacts with $NaOC_2H_5$?

Write the chemical equations involved in the above reactions. [*CBSE 2019 (56/4/3)*]

Ans. (*i*)

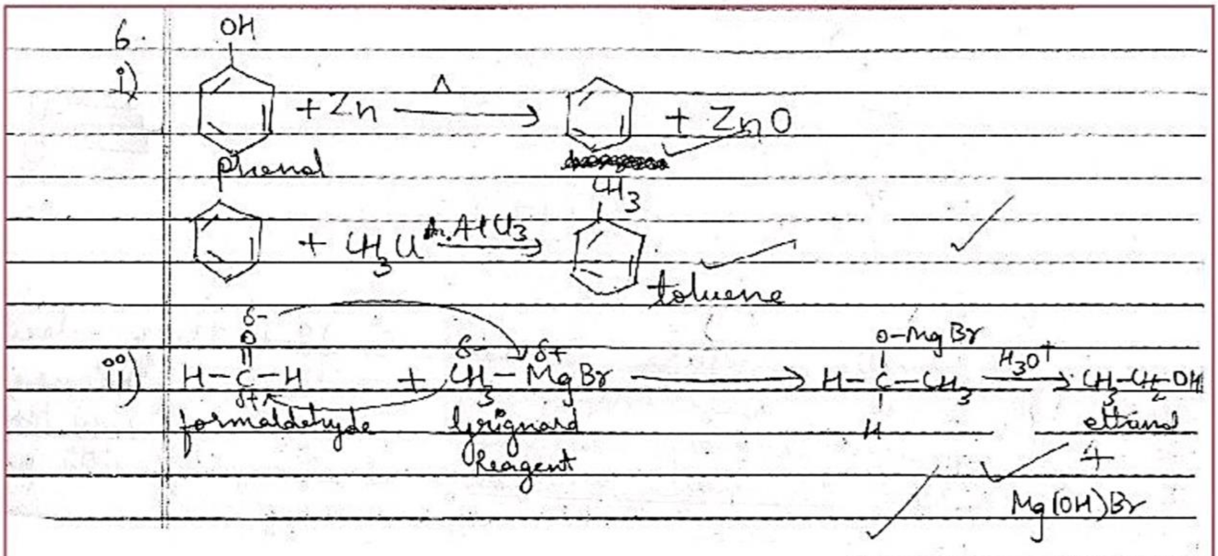


(*ii*) $$\underset{\text{Ethyl chloride}}{CH_3CH_2—Cl} + \underset{\text{Sodium ethoxide}}{CH_3—CH_2\bar{O}\overset{+}{Na}} \longrightarrow \underset{\text{Diethyl ether}}{CH_3CH_2—O—CH_2—CH_3} + NaCl$$

Q. 10. How do you convert

(*i*) phenol to toluene **(*ii*) formaldehyde to ethanol ?** [*CBSE North 2016*]

Ans.



[*Topper's Answer North 2016*]

Short Answer Questions–II

Each of the following questions are of 3 marks.

Q. 1. Explain the mechanism of the following reactions:

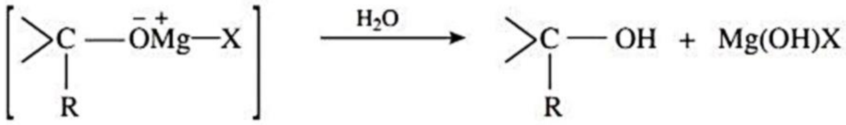
(*i*) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.

(*ii*) Acid catalysed dehydration of an alcohol forming an alkene. [*CBSE 2020 (56/1/2)*]

(*iii*) Acid catalysed hydration of an alkene forming an alcohol.

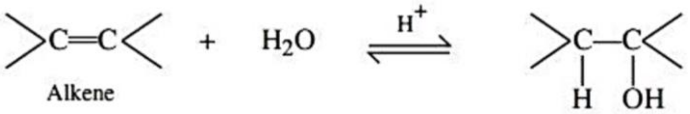
Ans. (*i*) **Step I:** Nucleophilic addition of Grignard reagent to carbonyl group.

Step II: Hydrolysis



(*ii*) Refer to NCERT Exercises, Q. 19.

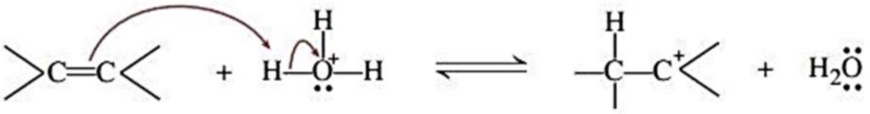
(*iii*)



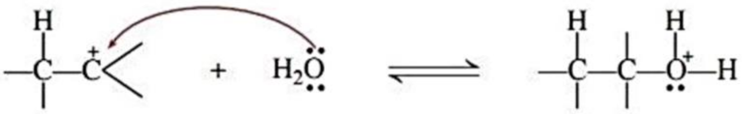
Mechanism:

Step I: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

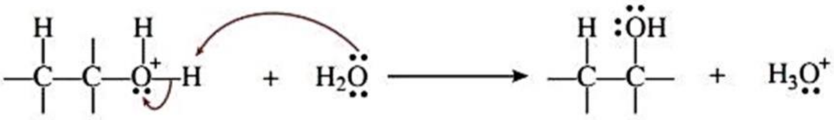
$$H_2\ddot{O} + H^+ \longrightarrow H_3\ddot{O}^+$$



Step II: Nucleophilic attack of water on carbocation.



Step III: Deprotonation to form an alcohol



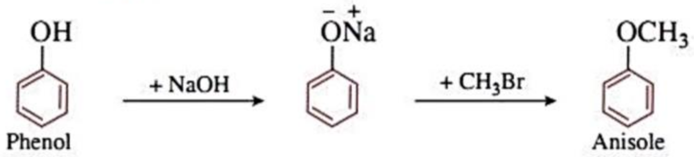
Q. 2. How do you convert the following:

(*i*) Phenol to anisole

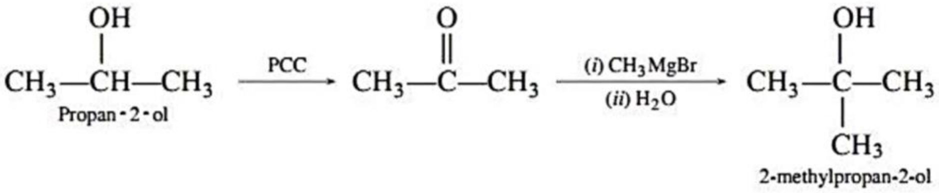
(*ii*) Propan-2-ol to 2-methylpropan-2-ol

(*iii*) Aniline to phenol [*CBSE Delhi 2015*]

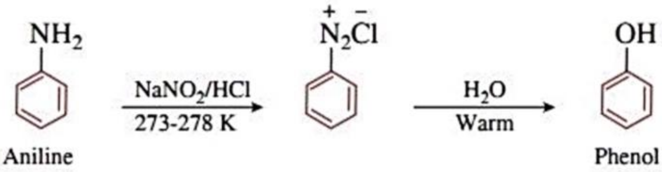
Ans. (*i*)



(*ii*)

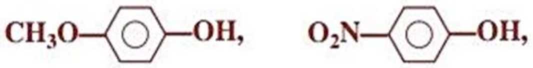


(*iii*)



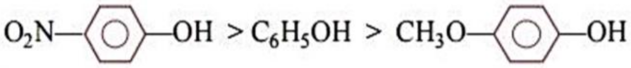
Q. 3. Arrange the following compounds in decreasing order of acidity. **[*NCERT Exemplar*]**

(*i*) H_2O, ROH, $HC \equiv CH$

(*ii*) 
C_6H_5OH

(*iii*) CH_3OH, H_2O, C_6H_5OH

Ans. (*i*) $H_2O > ROH > HC \equiv CH$

(*ii*) 

(*iii*) $C_6H_5OH > H_2O > CH_3OH$

Q. 4. Give one chemical test to distinguish between the following: **[*CBSE 2019 (56/5/1)*]**

(*i*) Phenol and propan-1-ol **(*ii*) Ethanol and dimethyl ether**

(*iii*) propan-1-ol and 2-Methyl-propan-2-ol

Ans. (*i*) Add neutral $FeCl_3$ to both the compounds. Phenol gives violet colouration while, 1 – propanol does not. **1**

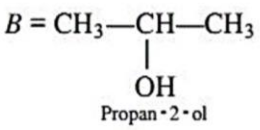
(*ii*) Add I_2/ NaOH(*aq*) to both the compounds, Ethanol gives yellow precipitate while ether does not **1**

(*iii*) Add HCl and $ZnCl_2$ to both the compounds, 2-methyl-2-propanol gives turbidity immediately while 1-propanol does not **1**

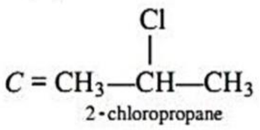
(Or any other suitable chemical test) **[*CBSE Marking Scheme 2019 (56/5/1)*]**

Q. 5. An organic compound '*A*' having molecular formula C_3H_6 on treatment with aqueous H_2SO_4 gives '*B*' which on treatment with HCl/$ZnCl_2$ gives '*C*'. The compound *C* on treatment with ethanolic KOH gives back the compound '*A*'. Identify the compounds *A*, *B*, *C*. **[*HOTS*]**

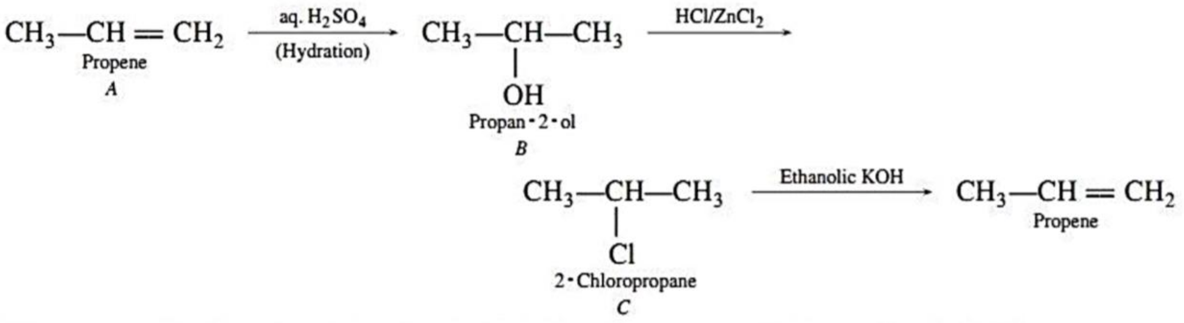
Ans. $A = \underset{\text{Propene}}{CH_3-CH=CH_2}$



$B = CH_3-\underset{\underset{\text{OH}}{|}}{CH}-CH_3$ Propan-2-ol



$C = CH_3-\overset{\overset{\text{Cl}}{|}}{CH}-CH_3$ 2-chloropropane

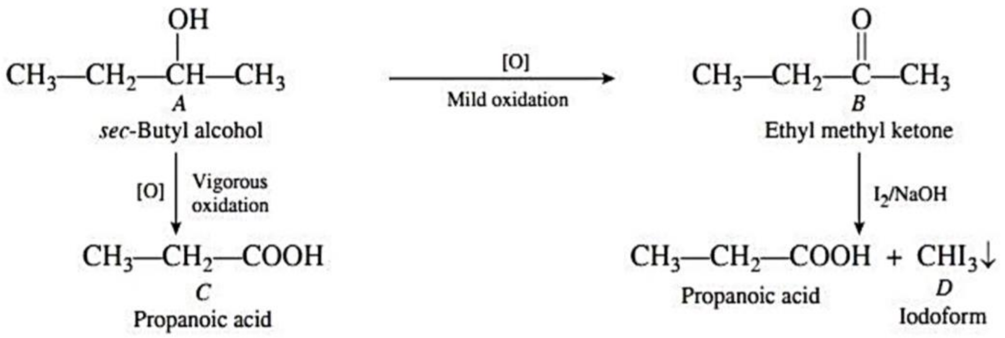


$$\underset{\substack{\text{Propene}\\ A}}{CH_3-CH=CH_2} \xrightarrow[\text{(Hydration)}]{\text{aq. } H_2SO_4} \underset{\substack{\text{Propan-2-ol}\\ B}}{CH_3-\underset{\underset{\text{OH}}{|}}{CH}-CH_3} \xrightarrow{HCl/ZnCl_2}$$

$$\underset{\substack{\text{2-Chloropropane}\\ C}}{CH_3-\underset{\underset{\text{Cl}}{|}}{CH}-CH_3} \xrightarrow{\text{Ethanolic KOH}} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

Q. 6. A compound '*A*' is optically active. On mild oxidation, it gives a compound '*B*' but on vigorous oxidation gives another compound '*C*'. *C* along with *D* is also formed from *B* by reaction with iodine and alkali. Deduce the structures of *A*, *B*, *C*, *D*. **[*HOTS*]**

Ans.



$$\underset{\substack{A\\ \textit{sec}\text{-Butyl alcohol}}}{CH_3-CH_2-\overset{\overset{\text{OH}}{|}}{CH}-CH_3} \xrightarrow[\text{Mild oxidation}]{[O]} \underset{\substack{B\\ \text{Ethyl methyl ketone}}}{CH_3-CH_2-\overset{\overset{\text{O}}{\|}}{C}-CH_3}$$

$$\underset{\substack{A}}{} \xrightarrow[\text{Vigorous oxidation}]{[O]} \underset{\substack{C\\ \text{Propanoic acid}}}{CH_3-CH_2-COOH}$$

$$B \xrightarrow{I_2/NaOH} \underset{\text{Propanoic acid}}{CH_3-CH_2-COOH} + \underset{\substack{D\\ \text{Iodoform}}}{CHI_3\downarrow}$$

Q. 7. Account for the following:

(*i*) Rectified spirit cannot be converted into absolute alcohol by simple distillation.

(*ii*) Diethyl ether does not react with sodium.

(*iii*) Phenols do not undergo substitution of the —OH group like alcohols.

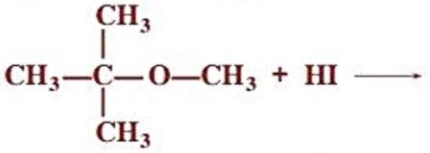
Ans. (*i*) Rectified spirit containing 95% ethyl alcohol and 5% water forms an azeotropic mixture which distils at a constant temperature of 351.13 K.

(*ii*) Since diethyl ether does not contain an active hydrogen attached to oxygen like alcohols and phenols, it does not react with sodium.

(*iii*) The C—O bond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by nucleophile. In contrast, the C—O bond in alcohols is a pure single bond and hence can be easily cleaved by nucleophile.

Q. 8. Write the main product(s) in each of the following reactions: **[*CBSE Delhi 2016*]**

(*i*)

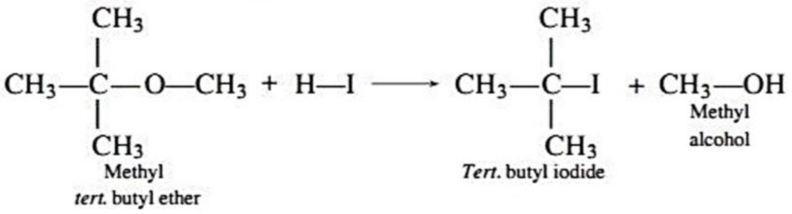


$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3 + HI \longrightarrow$$

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

(*iii*) $C_6H_5—OH \xrightarrow[(ii)\ CO_2,\ H^+]{(i)\ aq.\ NaOH}$

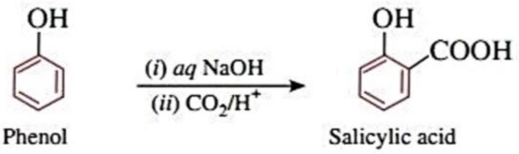
Ans. (*i*)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-CH_3 + H-I \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I + CH_3-OH$$

(*ii*) $\underset{\text{Propene}}{CH_3—CH{=}CH_2} \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} \underset{n\text{-}\ \text{propyl alcohol}}{CH_3—CH_2—CH_2—OH}$

(*iii*)

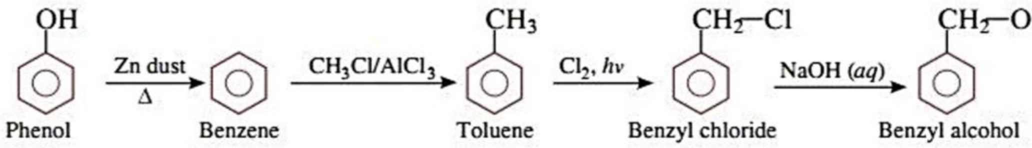


Q. 9. How will you bring the following conversions?

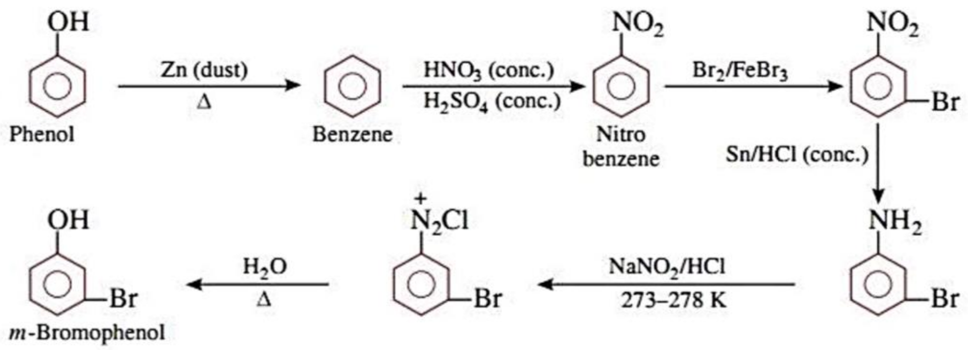
(*i*) Phenol to benzyl alcohol **(*ii*) Phenol to *m*-bromophenol**

(*iii*) Phenol to aspirin. **[*HOTS*]**

Ans. (*i*)



(*ii*)



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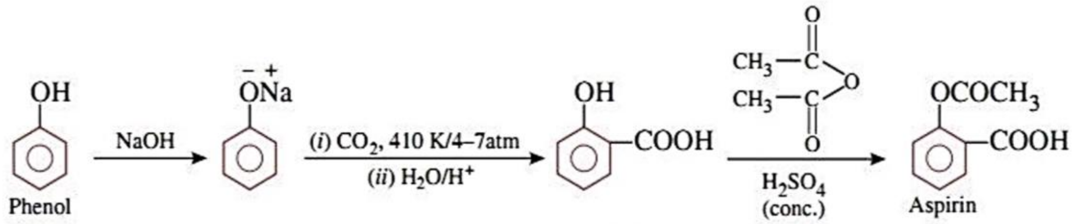


Q. 10. **(i) Why is the C—O bond length in phenols less than that in methanol?**

(ii) Arrange the following in order of increasing boiling point:
Ethoxyethane, Butanal, Butanol, *n*-butane

(iii) How can phenol be prepared from anisole? Give reaction. [*CBSE 2023 (56/5/2)*]

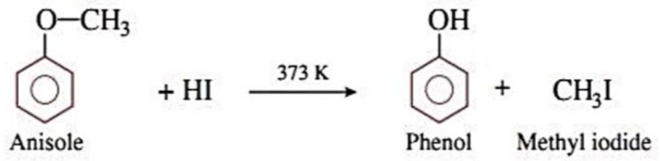
Ans. (i) This is due to

— partial double bond character on account of the conjugation of unshared electron pairs of oxygen with the aromatic ring and

— sp^2 hybridised state of carbon to which oxygen is attached.

(ii) n-Butane < ethoxyethane < butanal < butanol

(iii)

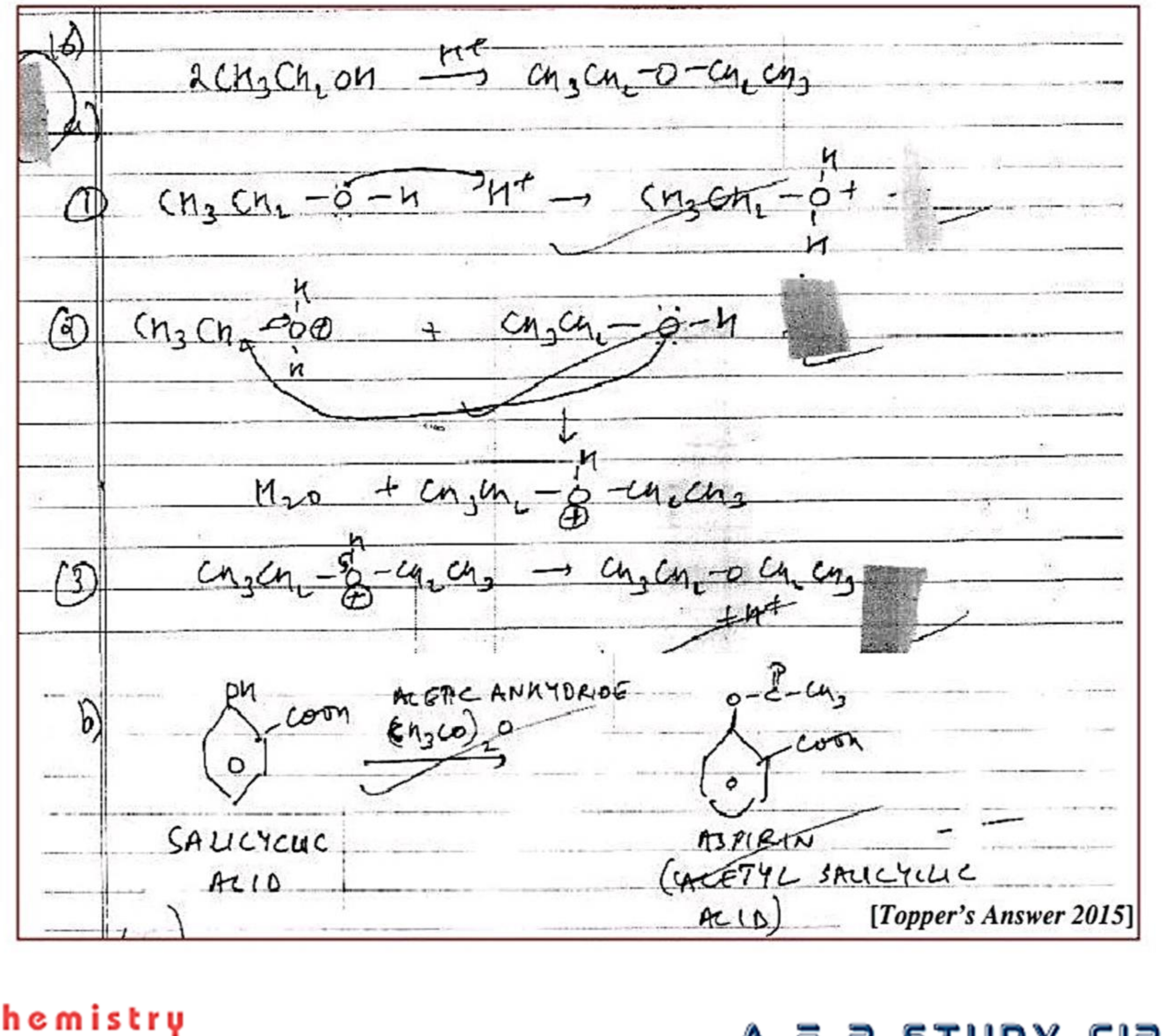


Q. 11. **(i) Write the mechanism of the following reaction:**

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

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

Ans.



(i)

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

① $CH_3CH_2-\ddot{O}-H \; H^+ \rightarrow CH_3CH_2-\overset{H}{O^+}-H$

② $CH_3CH_2-\overset{H}{O^+}-H + CH_3CH_2-\ddot{O}-H$

$\downarrow$

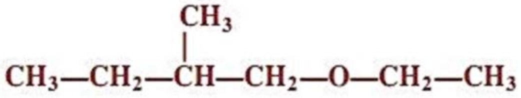
$H_2O + CH_3CH_2-\overset{H}{O^+}-CH_2CH_3$

③ $CH_3CH_2-\overset{H}{O^+}-CH_2CH_3 \rightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

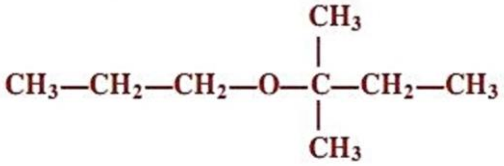
b) SALICYLIC ACID, ACETIC ANHYDRIDE $(CH_3CO)_2O$, ASPIRIN (ACETYL SALICYLIC ACID)

[*Topper's Answer 2015*]

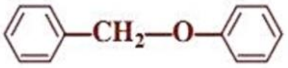
Q. 12. **Give the major products that are formed by heating each of the following ethers with HI.**

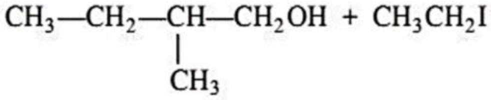
(*i*) 

$CH_3—CH_2—CH(CH_3)—CH_2—O—CH_2—CH_3$

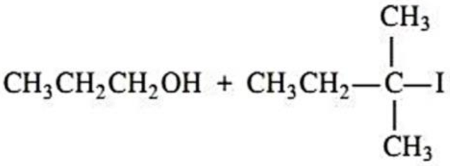
(*ii*) 

$CH_3—CH_2—CH_2—O—C(CH_3)_2—CH_2—CH_3$

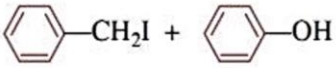
(*iii*)  **[*HOTS*]**

Ans. (*i*) 

$CH_3—CH_2—CH(CH_3)—CH_2OH + CH_3CH_2I$

(*ii*) 

$CH_3CH_2CH_2OH + CH_3CH_2—C(CH_3)_2—I$

(*iii*) 

Q. 13. **The following is not an appropriate reaction for the preparation of *tert*-butyl ethyl ether:**

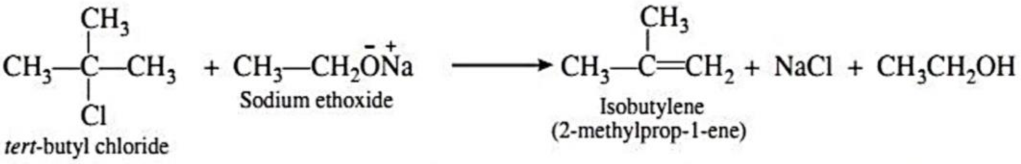
$$C_2H_5\overset{-}{O}\overset{+}{Na} + (CH_3)_3C—Cl \longrightarrow (CH_3)_3C—OC_2H_5$$

(*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.**

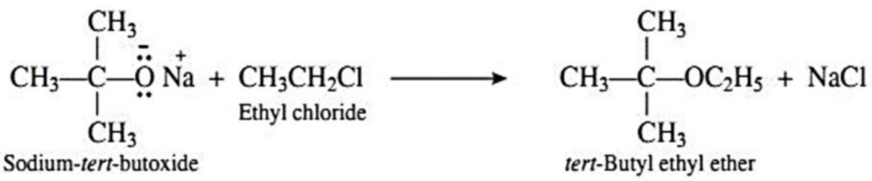
Justify your answer in both cases. [*CBSE Sample Paper 2016*] [*HOTS*]

Ans. (*i*) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide ($CH_3—CH_2\overset{-}{O}\overset{+}{Na}$) is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution reaction.



$$CH_3—C(CH_3)(Cl)—CH_3 + CH_3—CH_2\overset{-}{O}\overset{+}{Na} \longrightarrow CH_3—C(CH_3)=CH_2 + NaCl + CH_3CH_2OH$$

(*ii*) To prepare tertiary butyl ethyl ether, the alkyl halide should be primary, *i.e.*, ethyl chloride and the nucleophile should be tertiary, *i.e.*, tertiary butoxide ion. It is because the reaction occurs by S_N2 mechanism and primary alkyl halides are most reactive in S_N2 reactions.



$$CH_3—C(CH_3)_2—\ddot{\underset{..}{O}}\overset{+}{Na} + CH_3CH_2Cl \longrightarrow CH_3—C(CH_3)_2—OC_2H_5 + NaCl$$

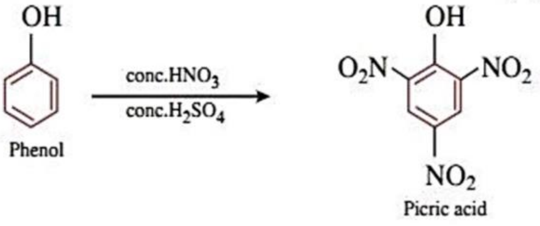
Q. 14. **How do you convert the following: (*Any three*)**

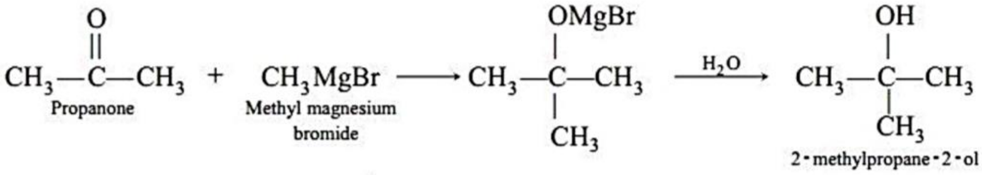
(*i*) **Phenol to picric acid**

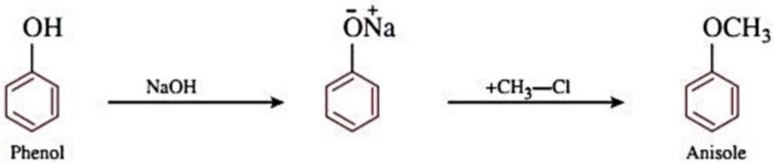
(*ii*) **Propanone to 2-Methylpropan-2-ol**

(*iii*) **Phenol to anisole**

(*iv*) **Propene to Propan-1-ol** [*CBSE 2023 (56/1/1)*]

Ans. (*i*) 

(ii) 

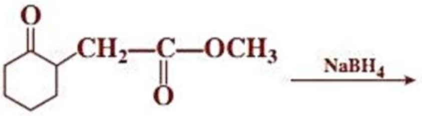
(iii) 

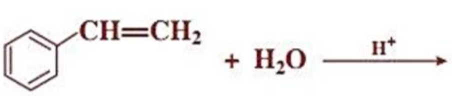
(iv) $CH_3-CH=CH_2 \xrightarrow{+(BH_3)_2} (CH_3CH_2CH_2)_3B \xrightarrow[3H_2O_2, \bar{O}H]{+H_2O} 3CH_3-CH_2-CH_2-OH$

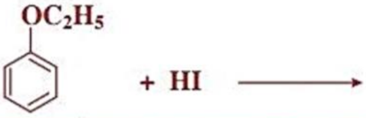
Propene Propan-1-ol

(Any three)

Q. 15. Write the structures of the main products in the following reactions:

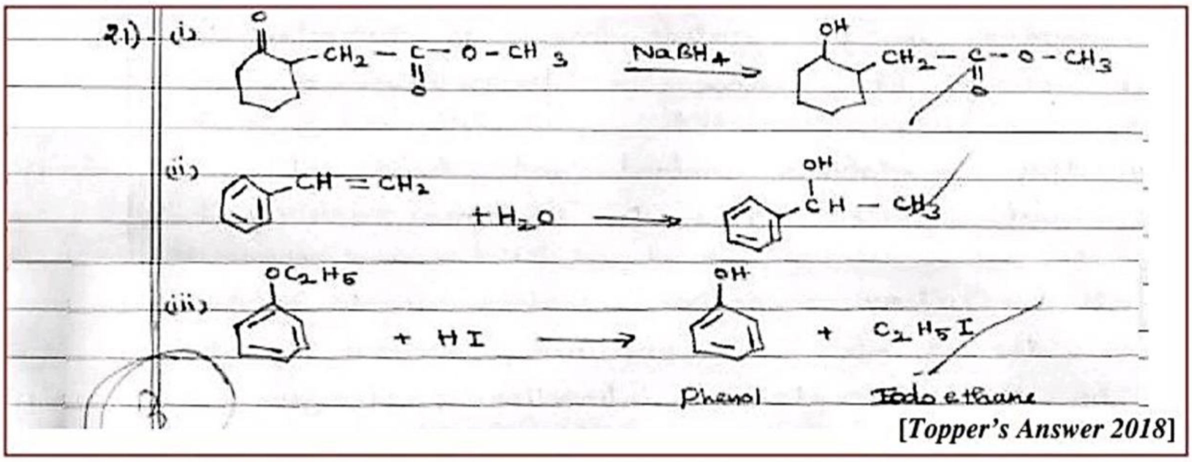
(i) 

(ii) 

(iii) 

[*CBSE 2018*]

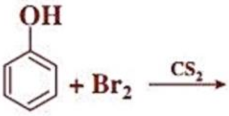
Ans.



[*Topper's Answer 2018*]

Q. 16. Write the products of the following reactions:

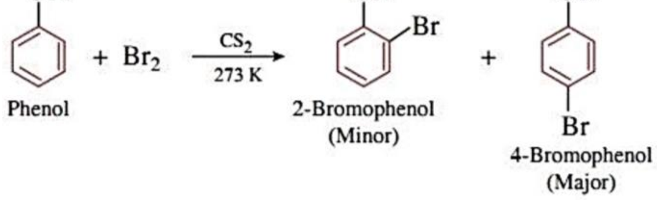
(i) $CH_3-CH_2-O-CH_3 + HI \longrightarrow$

(ii) 

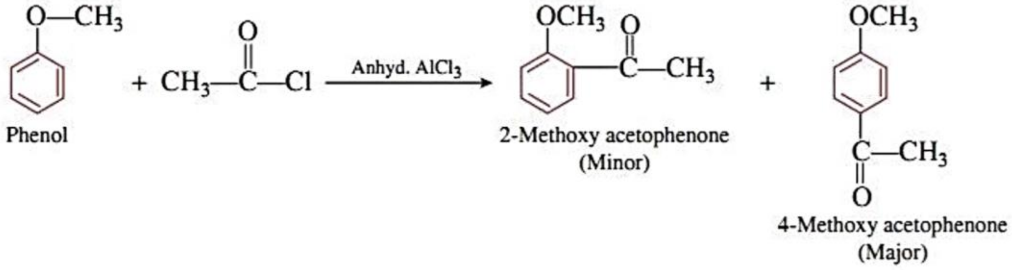
(iii) 

Ans. (i) $CH_3-CH_2-O-CH_3 + HI \longrightarrow CH_3-I + CH_3-CH_2-OH$

Ethyl methyl ether Methyl iodide Ethyl alcohol

(ii) 

(iii)

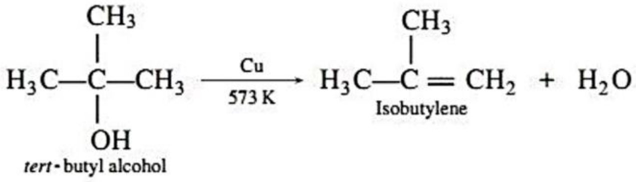


Q. 17. **What happens when**

- *(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?**

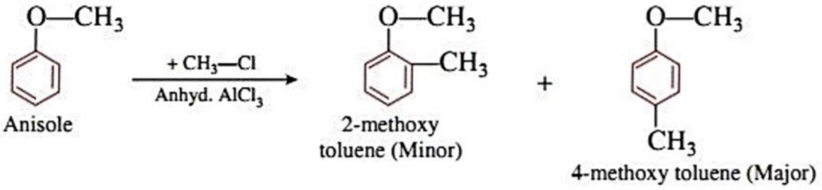
Write chemical equations in support of your answer. ***[CBSE (F) 2017]***

Ans. *(i)*

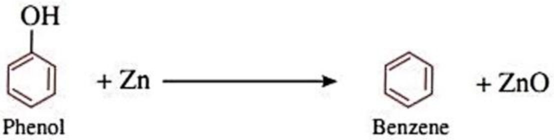


$$(CH_3)_3C{-}OH \xrightarrow[573\text{ K}]{Cu} H_3C{-}C(CH_3){=}CH_2 + H_2O$$

(ii)



(iii)

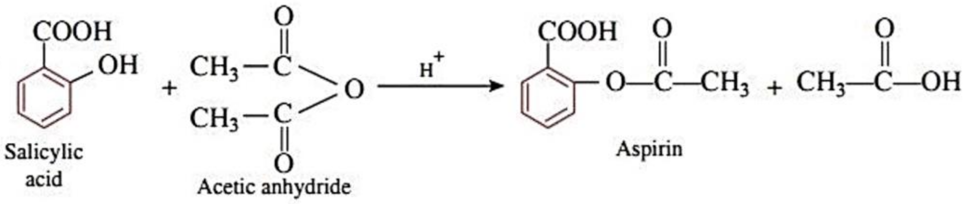


Q. 18. **What happens when**

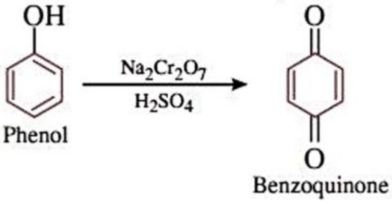
- *(i)* **Salicylic acid is treated with $(CH_3CO)_2O/H^+$?**
- *(ii)* **Phenol is oxidised with $Na_2Cr_2O_7/H^+$?**
- *(iii)* **Anisole is treated with CH_3Cl/anhydrous $AlCl_3$?**

Write chemical equation in support of your answer. ***[CBSE 2019 (56/3/1)]***

Ans. *(i)*



(ii)



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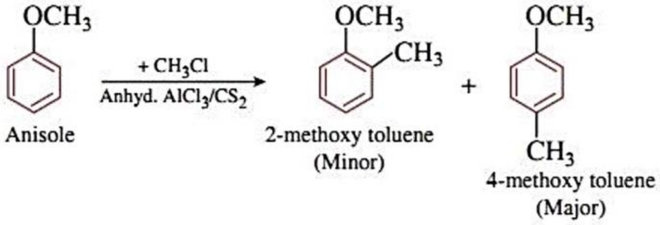


Long Answer Questions

Each of the following questions are of 5 marks.

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

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

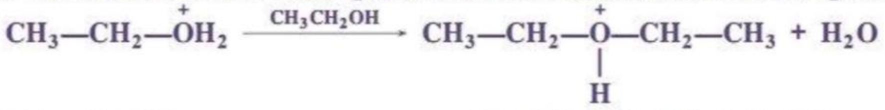
(b) Hydroboration of propene and then oxidation to propanol.

(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:



$$CH_3—CH_2—\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3—CH_2—\underset{\displaystyle H}{\overset{+}{O}}—CH_2—CH_3 + H_2O$$

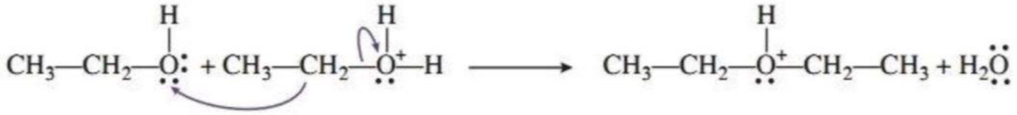
[*CBSE Delhi 2017*]

Ans. (i) (a) $Br_2(aq)$ (b) B_2H_6, H_2O, H_2O_2 and OH^-

(ii) (a) Ethanol < Phenol < *p*-nitrophenol

(b) Propane < Propanal < Propanol

(iii)

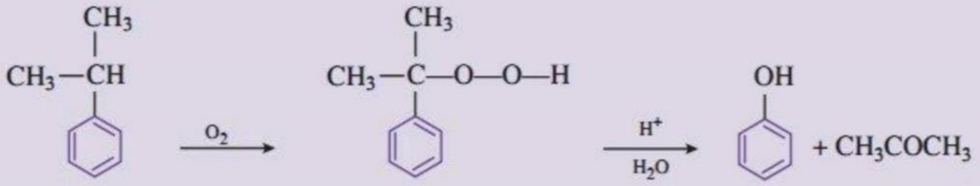


Q. 2. (i) How can you obtain phenol from (a) Cumene, (b) Benzene sulphonic acid, (c) Benzene diazonium chloride?

(ii) Write the structure of the major product obtained from dinitration of 3-methylphenol.

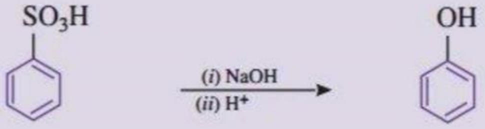
(iii) Write the reaction involved in Kolbe's reaction. [*CBSE 2019 (56/2/1)*]

Ans. (i) (a)



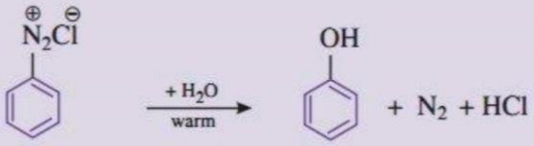
1

(b)



1

(c)



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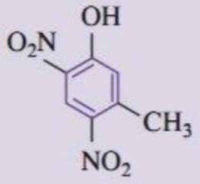
(ii)



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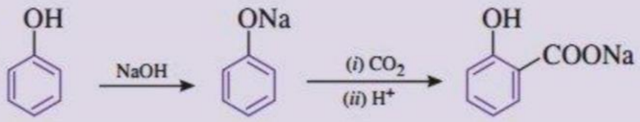
(iii)

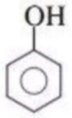


1

[*CBSE Marking Scheme 2019 (56/2/1)*]

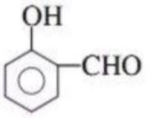
Q. 3. **An aromatic compound '*A*' on treatment with $CHCl_3/KOH$ gives two compounds '*B*' and '*C*'. Both *B* and *C* give the same product '*D*' when distilled with zinc dust. Oxidation of *D* gives *E* having molecular formula $C_7H_6O_2$. The sodium salt of *E* on heating with sodalime gives *F* which may also be obtained by distilling *A* with zinc dust. Identify *A* to *F*.** **[*HOTS*]**

Ans. *A* =



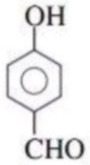
Phenol

B =



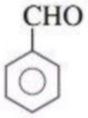
o-Hydroxy benzaldehyde

C =



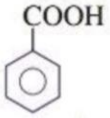
p-Hydroxy benzaldehyde

D =



Benzaldehyde

E =

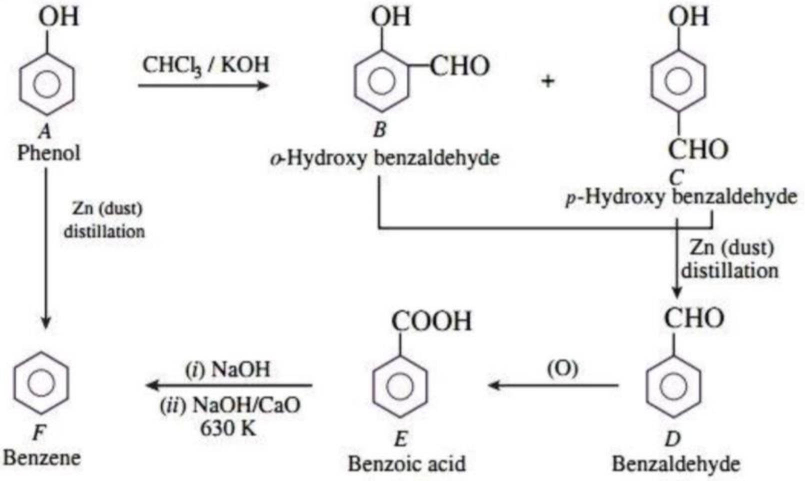


Benzoic acid

F =

Benzene

Reactions involved:



Q. 4. **(*i*) Give equations of the following reactions:**

(*a*) Phenol is treated with conc. HNO_3.

(*b*) Propene is treated with B_2H_6 followed by H_2O_2/OH^-.

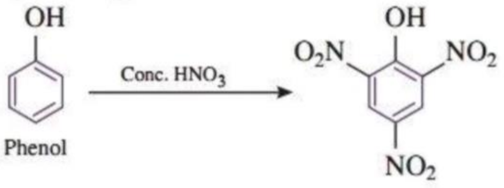
(*c*) Sodium *t*-butoxide is treated with CH_3Cl.

(*ii*) How will you distinguish between butan-1-ol and butan-2-ol?

(*iii*) Arrange the following in increasing order of acidity:

Phenol, ethanol, water **[*CBSE 2019 (56/2/1)*]**

Ans. (*i*) (*a*)

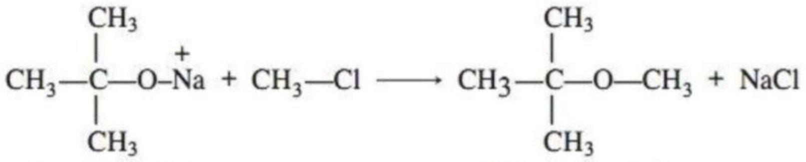


2, 4, 6-Trinitrophenol

(*b*) $CH_3—CH═CH_2 \xrightarrow[(ii)\ H_2O_2/\overline{O}H]{(i)\ B_2H_6} CH_3CH_2CH_2OH$

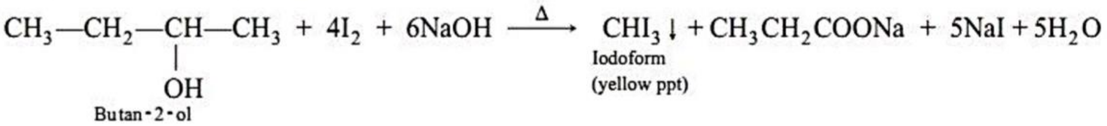
Propene Propanol

(*c*)



$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—O—\overset{+}{Na} + CH_3—Cl \longrightarrow CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—O—CH_3 + NaCl$$

Sodium tert.butoxide Methyl tert. butyl ether (*ii*) Butan-2-ol when warmed with I_2 in NaOH (NaOI) gives yellow precipitate of iodoform while butan-1-ol does not respond to this test.



$$\underset{\text{Butan-2-ol}}{CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3\downarrow} + CH_3CH_2COONa + 5NaI + 5H_2O$$

(*iii*) Ethanol < water < phenol

Q. 5. (*i*) **What happens when**

(*a*) **phenol reacts with bromine water?**

(*b*) **ethanol reacts with CH_3COCl/pyridine?**

(*c*) **anisole reacts with HI?**

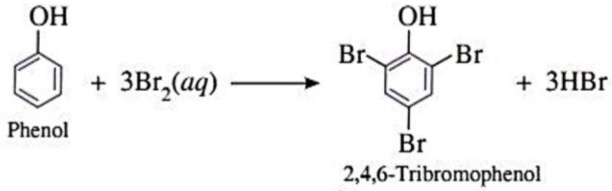
Write the chemical equations involved in the above reactions.

(*ii*) **Distinguish between:**

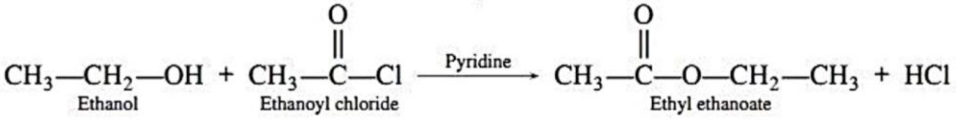
(*a*) **Ethanol and phenol**

(*b*) **Propan-2-ol and 2-methylpropan-2-ol** [*CBSE (F) 2016*]

Ans. (*i*) (*a*)

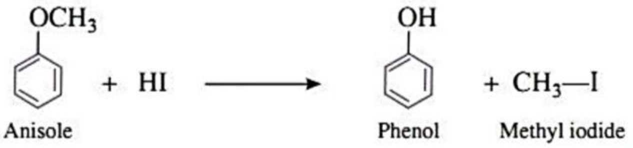


(*b*)



$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + \underset{\text{Ethanoyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl ethanoate}}{CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3} + HCl$$

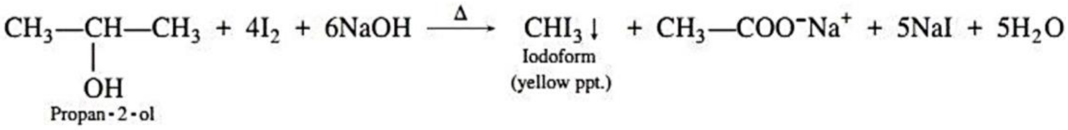
(*c*)



(*ii*) (*a*) Phenol gives violet colouration with $FeCl_3$ solution but ethanol does not.

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

(*b*) Propan-2-ol when warmed with I_2 in NaOH gives yellow precipitate of iodoform while 2-methylpropan-2-ol does not respond to this test.



$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt.)}}}{CHI_3\downarrow} + CH_3-COO^-Na^+ + 5NaI + 5H_2O$$

Q. 6. (*i*) **Write equations of the following reactions:**

(*a*) **Bromine in CS_2 with phenol**

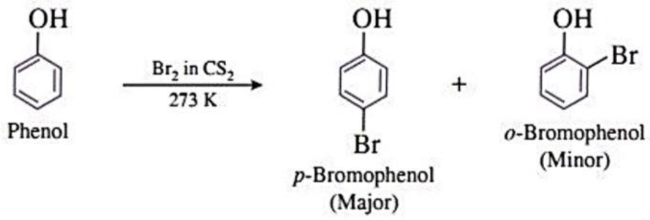
(*b*) **Treating phenol with chloroform in the presence of aq. NaOH**

(*c*) **Anisole reacts with HI**

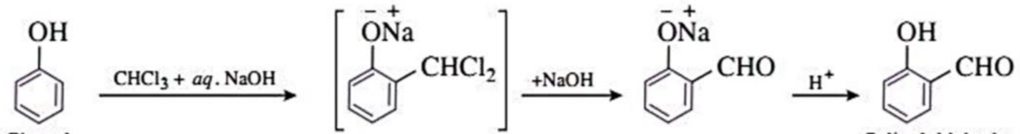
(*ii*) **Distinguish between**

(*a*) **Ethanol and Diethyl ether** (*b*) **Propanol and *t*-butyl alcohol** [*CBSE South 2016*]

Ans. (*i*) (*a*)



(*b*)



Phenol Salicylaldehyde

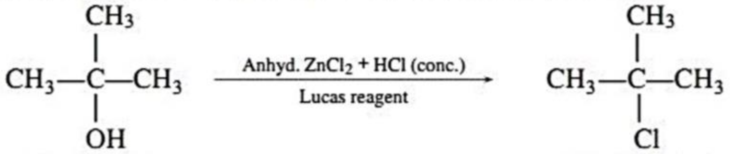
(*c*)

Anisole Phenol Methyl iodide

(*ii*) (*a*) Ethanol when warmed with I_2 in NaOH gives yellow precipitate of iodoform while diethyl ether does not.

$$CH_3—CH_2—OH + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform}\\\text{(yellow ppt.)}}}{CHI_3\downarrow} + HCOONa + 5NaI + 5H_2O$$

(*b*) *tert*-butyl alcohol on treatment with the Lucas reagent immediately gives turbidity while propanol does not produce turbidity at room temperature.



tert-butyl alcohol *tert*-butyl chloride
(Turbidity appears immediately)

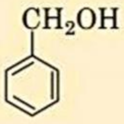
Questions for Practice

Choose and write the correct answer for each of the following.

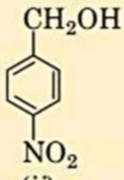
1. **The order of reactivity of the alkenes, (*i*) $(CH_3)_2C{=}CH_2$, (*ii*) $CH_3CH{=}CH_2$, (*iii*) $CH_2{=}CH_2$, when subjected to acid catalysed hydration is:**
   (*a*) (*i*) > (*iii*) > (*ii*) (*b*) (*i*) > (*ii*) > (*iii*)
   (*c*) (*ii*) > (*i*) > (*iii*) (*d*) (*iii*) > (*ii*) > (*i*)

2. **Alcohols are soluble in water because**
   (*a*) alcohol forms ionic bond with water.
   (*b*) alcohol forms hydrogen bond with water.
   (*c*) alcohol forms covalent bond with water.
   (*d*) alcohol forms interstitial compound with water.

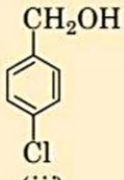
3. **Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.**



(*i*)



(*ii*)



(*iii*)

   (*a*) (*i*) < (*ii*) < (*iii*) (*b*) (*ii*) < (*i*) < (*iii*)
   (*c*) (*ii*) < (*iii*) < (*i*) (*d*) (*iii*) < (*ii*) < (*i*)

4. **In the reaction given below, X is:**

   Neopentyl alcohol $\xrightarrow{H_2SO_4}$ X

   (*a*) 2-methylpent-2-ene (*b*) 2-methylpentane
   (*c*) 2-methylbut-2-ene (*d*) neopentane

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

$$\text{R—OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{R—Cl} + \text{H}_2\text{O}$$ [*NCERT Exemplar*]

(*a*) 1° > 2° > 3°
(*b*) 1° < 2° > 3°
(*c*) 3° > 2° > 1°
(*d*) 3° > 1° > 2°

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement.

6. **Assertion** (*A*) : Phenol is more reactive than benzene towards electrophilic substitution reaction.
Reason (*R*) : In the case of phenol, the intermediate carbocation is more resonance stablized.

7. **Assertion** (*A*) : Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol.
Reason (*R*) : Addition of water in acidic medium proceeds through the formation of primary carbocation.

8. **Assertion** (*A*) : Ethers behave as bases in the presence of mineral acids.
Reason (*R*) : Due to the presence of lone pairs of electrons on oxygen.

9. **Assertion** (*A*) : The bond angles in alcohols is slightly less then 109°28'.
Reason (*R*) : Lone pair – lone pair repulsion decreases the bond angles.

10. **Assertion** (*A*) : Alkyl aryl ethers are cleaved at the alkyl–oxygen bond.
Reason (*R*) : More stable aryl oxygen bond responsible for this.

Answer the following questions:

11. (*i*) While separating a mixture of ortho and para-nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.
(*ii*) Give a chemical test to distinguish between ethyl alcohol and methyl alcohol.

12. Write the chemical equation involved in the following reactions: [*CBSE 2023 (56/2/2)*]
(*i*) Reimer-Tiemann reaction
(*ii*) Acetylation of Salicylic acid

13. (*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:

$$\text{CH}_2\text{=CH}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{—CH}_2^+ + \text{H}_2\text{O}$$ [*CBSE (AI) 2017*]

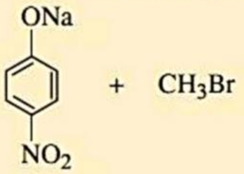
14. Give reasons for the following:
(*i*) Anisole reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol.
(*ii*) *o*-Nitrophenol is less soluble in water than *p*-nitrophenol.

15. Write the structures of the products when Butan-2-ol reacts with the following:
(*i*) CrO_3
(*ii*) SOCl_2 [*CBSE (AI) 2017*]

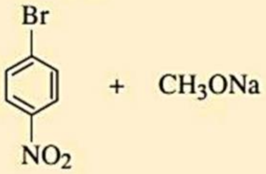
16. Alcohols react both as nucleophiles as well as electrophiles. Write one reaction of each type and describe its mechanism.

17. Which of the following is an appropriate set of reactant for the preparation of 1-methoxy-4-nitrobenzene and why? ***[CBSE 2023 (56/4/2)]***

(*i*)



(*ii*)



18. (*i*) What happens when phenol reacts with

(*a*) Conc. HNO_3, and

(*b*) $CHCl_3$ in presence of aqueous NaOH followed by acidification?

(*ii*) Why does the reaction of CH_3ONa with $(CH_3)_3C—Br$ give 2-methylpropene and not $(CH_3)_3C—OCH_3$? ***[CBSE 2023 (56/4/2)]***

19. (*i*) Write the mechanism of the following reaction: ***[CBSE 2023 (56/2/1)]***

$$2CH_3CH_2OH \xrightarrow[413\,K]{H^+} CH_3—CH_2—O—CH_2—CH_3 + H_2O$$

(*ii*) Why *ortho*-nitrophenol is steam volatile while *para*-nitrophenol is not.

20. A compound 'A' having molecular formula $C_4H_{10}O$ is found to be soluble in concentrated sulphuric acid. It does not react with sodium metal or potassium permanganate. On heating with excess of HI, it gives a single alkyl halide. Deduce the structure of compound A and explain all the reactions. ***[HOTS]***

21. How would you obtain the following?

(*i*) Benzoquinone from phenol ***[CBSE 2020 (56/1/2)]***

(*ii*) 2-Methylpropan-2-ol from methylmagnesium bromide

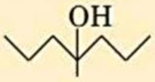
(*iii*) Propan-2-ol from propene ***[CBSE (AI) 2011, (F) 2011]***

22. Answer the following questions:

(*i*) Why are ethers insoluble in water?

(*ii*) Complete the reaction equation:

? $\longrightarrow$



(*iii*) How will you know whether a given OH group is alcoholic or phenolic in nature?

23. (*i*) Arrange the following sets of compounds in order of their increasing boiling points:

(*a*)Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol

(*b*)Pentan-1-ol, *n*-butane, pentanal, ethoxyethane.

(*ii*) Arrange the following compounds in increasing order of acidity and give a suitable explanation.

Phenol, *o*-nitrophenol, *o*-cresol ***[NCERT Exemplar]***

24. Name the reagents which are used in the following conversions:

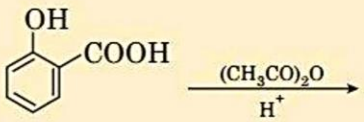
(*i*) A primary alcohol to aldehyde

(*ii*) Butan-2-one to butan-2-ol

(*iii*) Benzyl alcohol to benzoic acid

25. (*i*) Write the product(s) in the following reactions:

(*a*)



(*b*) $CH_3—CH_2—O—CH_2—CH_3 \xrightarrow{HI} ?$

(*c*) $CH_3—CH{=}CH—CH_2—OH \xrightarrow{PCC} ?$

(*ii*) Give simple chemical tests to distinguish between the following pairs of compounds:

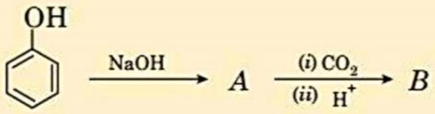
(*a*) Ethanol and Phenol

(*b*) Pentan-2-ol and pentan-3-ol

26. (*i*) Write mechanism of the reaction of HI with methoxymethane.

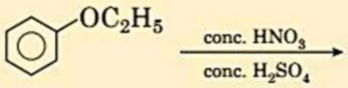
(*ii*) Identify *A* and *B* in the following reactions:

(*a*)



(*b*) $C_2H_5OH \xrightarrow[H_3O^+]{Cu,\ 573\ K} A \xrightarrow[H_2O/H^+]{CH_3MgBr} B$

(*iii*) Give the structure and the IUPAC name of the major product obtained in the following reaction:



[*CBSE Sample Paper 2015*]

Answers

1. (*b*) **2.** (*b*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*a*) **7.** (*c*) **8.** (*a*) **9.** (*a*) **10.** (*a*)