11 Alcohols, Phenols and Ethers

LESSON AT A GLANCE

- **Alcohols:** The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. Organic compounds contain the –OH group. In systematic chemical nomenclature alcohol names end in the sufix –ol.
- **Dihydric alcohols:** Two —OH group must be attached to different carbon atoms.
- **Trihydric alcohols:** Alcohols which contain three hydroxyl groups (–OH) are called trihydric alcohols.
- **Carbonium ion (Carbocation):** An atom or group of atoms in which carbon atom has positive charge due to incomplete octet is called carbonium ion.
- **Carbanion:** An atom or group of atoms in which carbon atom carries a negative charge due to its complete octet is called carbanion.
- **Fermentation:** A form of anaerobic respiration occurring in certain microorganisms *e.g.*, yeasts. It comprises a series of biochemical reactions by which sugar is converted to ethanol and carbon dioxide. Fermentation is the basis of the baking, wine and bear industries.
- **Important reaction of alcohols and phenols:**
  (*i*) Nucleophilic substitution with hydrogen halides to yield alkyl halides.
  (*ii*) Dehydration of alcohols yields alkenes.
  (*iii*) On oxidation gives aldehyde with mild oxidising agent.
  (*iv*) With strong oxidising agent carboxylic acid.
  Tertiary alcohols are resistant to oxidation.

- **Nomenclature of Alcohols**

Alcohols

(*i*) Common system: In this system alcohols (R—OH) are named as alkyl alcohols. The alkyl group attached to the —OH group is named and alcohol is added as a separate word. For example,

CH_3—OH	CH_3CH_2—OH	$CH_3CH_2CH_2$—OH
Methyl alcohol	ethyl alcohol	*n*–propyl alcohol

(*ii*) IUPAC System: In this system alcohols are named as Alkanols. The IUPAC rules are:

(*a*) Select the longest continuous carbon chain containing the –OH group.

(*b*) Change the name of the alkane corresponding to this chain by dropping the ending –e and adding the suffix –ol.

(*c*) Number the chain so as to give the carbon carrying the –OH group, the lowest possible number. The position of the –OH group is indicated by this number.

(*d*) Indicate the positions of other substituents or multiple bonds by numbers.

- **Lucas Test:** Distinguish between 1°, 2° and 3° alcohols.

In this test alcohols are treated with a solution of HCl and zinc chloride to form alkyl halides. Zinc chloride acts as a catalyst.

$$\underset{\text{Alcohol}}{R\text{—}OH} + HCl \xrightarrow{\text{Anhy.}ZnCl_2} \underset{\text{Alkyl halide}}{R\text{—}Cl} + H_2O$$

The three types of alcohols undergo this reaction at different rates.

Tertiary alcohols react with lucas reagent very rapidly.

Secondary alcohols react with somewhat slower.

- **Ethers:** Organic compounds containing the group –O– in their molecules. Examples are dimethyl ether, CH_3OCH_3 and diethyl ether, $C_2H_5OC_2H_5$. They are volatile, highly flammable compounds made by dehydrating alcohols using sulphuric acid.

TEXTBOOK QUESTIONS SOLVED

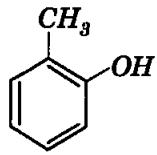
11.1 *Write IUPAC names of the following compounds:*

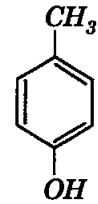
(*i*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$

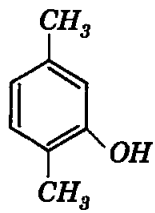
(*ii*) $H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-CH_3$

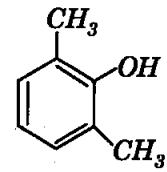
(*iii*) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(*iv*) $HO-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-OH$

(*v*) 

(*vi*) 

(*vii*) 

(*viii*) 

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

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

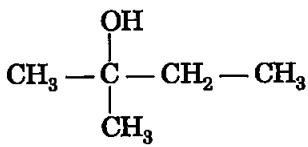
(*xi*) $C_6H_5-O-C_7H_{15}$ (*n*–)

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

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

11.2 *Write 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*) *3-Chloromethylpentan-1-ol.*

Ans. (*i*)



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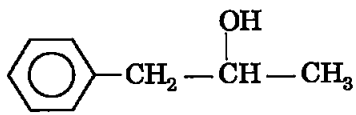

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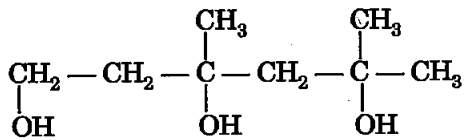
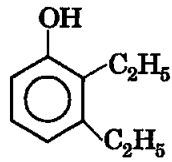
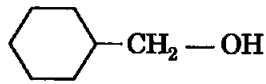
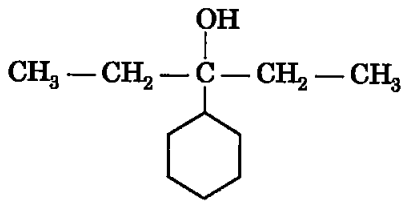


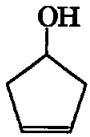
(*iv*) 

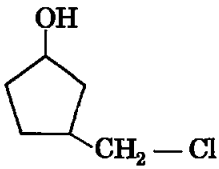
(*v*) $CH_3 - CH_2 - O - CH_2 - CH_2 - CH_3$

(*vi*) $CH_3 - CH_2 - O - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_3$

(*vii*) 

(*viii*) 

(*ix*) 

(*x*) 

11.3 (*i*) *Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.*

(*ii*) *Classify the isomers alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.*

Ans. Various isomeric alcohols with molecular formula $C_5H_{12}O$ are given below:

Structure	*IUPAC Name*	*Classification*
$CH_3–CH_2–CH_2–CH_2–CH_2–OH$	Pentan-1-ol	Primary
$CH_3—CH_2—CH_2—\underset{\displaystyle OH}{\underset{\vert}{CH}}—CH_3$	Pentan-2-ol	Secondary
$CH_3—CH_2—\underset{\displaystyle OH}{\underset{\vert}{CH}}—CH_2—CH_3$	Pentan-3-ol	Secondary
$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—OH$	2-Methylbutan-1-ol	Primary
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—CH_2—OH$	3-Methylbutan-1-ol	Primary
$CH_3—CH_2—\underset{\displaystyle OH}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}—CH_3$	2-Methylbutan-2-ol	Tertiary
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—\underset{\displaystyle OH}{\underset{\vert}{CH}}—CH_3$	3-Methylbutan-2-ol	Secondary
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}—CH_2—OH$	2,2-Dimethylpropan-1-ol	Primary

11.4 *Explain why propanol has higher boiling point than that of the hydrocarbon, butane?*

Ans. Propanol contains an —OH group due to which propanol molecules are held to each other by hydrogen bonds whereas the molecules of butane are held just by weak van der Waals' forces. Since more energy is needed to separate the molecules of propanol so it has higher boiling point than butane.

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

Ans. The solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. Hydrocarbons cannot form such hydrogen bonds, hence they are insoluble in water.

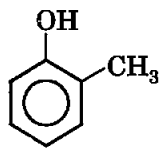
11.6 *What is meant by hydroboration-oxidation reaction? Illustrate it with an example.*

Ans. This reaction is used for the preparation of alcohols from alkenes. In this method, alkenes are treated with diborane followed by oxidation with H_2O_2. Although the reaction proceeds according to Markownikov's rule, but the final alcohol obtained is such as if addition of water has occurred anti to the Markownikov's rule. Such as propene undergoes this reaction to yield propan-1-ol

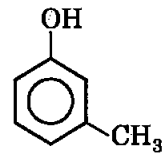
$$\underset{\text{Propene}}{3CH_3-CH=CH_2} + \frac{1}{2}\underset{\text{Diborane}}{B_2H_6} \longrightarrow (CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O_2} 3\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH} + H_3BO_3$$

11.7 *Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.*

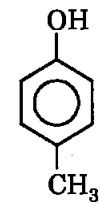
Ans. Three isomeric phenols with molecular formula C_7H_8O are possible whose structures and names are given below:



2-Methylphenol



3-Methylphenol

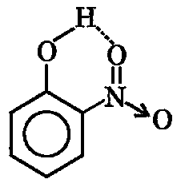


4-Methylphenol

11.8 *While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.*

Ans. Amongst the *ortho* and *para* nitrophenols, the *ortho*-isomer will be steam volatile because in this, the nitro and phenolic groups are close and can form intramolecular hydrogen bonds. So the molecules themselves are held by weaker

forces. Whereas in *para*-isomer, the molecules are held by intermolecular hydrogen bonding, so they are not easily volatile.

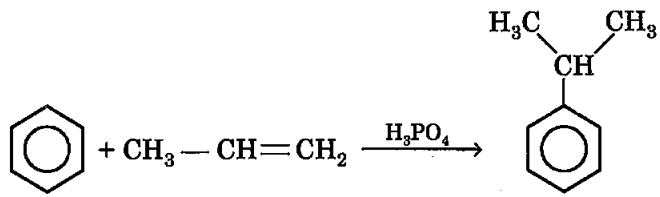


o-Nitrophenol

11.9 *Give the equations of reactions for the preparation of phenol from cumene.*

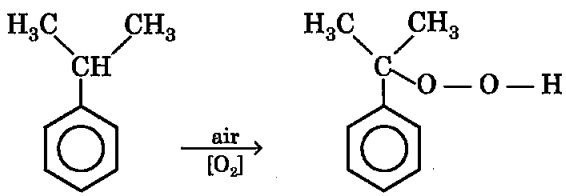
Ans. The process of obtaining phenol from cumene is described as following steps:

(*i*) Cumene is prepared by treating benzene with propene in the presence of phosphoric acid.



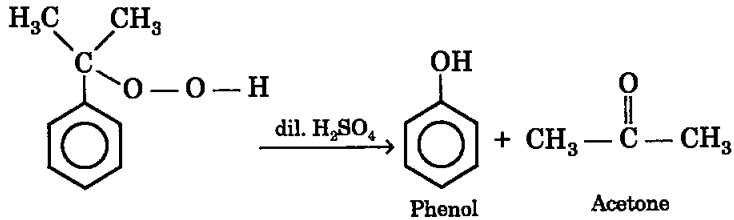
Benzene Propene Cumene (2-Phenylpropane)

(*ii*) Cumene is oxidised in presence of air to form cumene hydroperoxide.



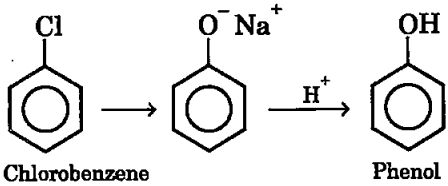
Cumene (2-Phenylpropane) Cumene hydroperoxide

(*iii*) Finally, cumene hydroperoxide is hydrolysed by dilute sulphuric acid which gives phenol. Acetone is obtained as a byproduct in this process.



11.10 *Write chemical reaction for the preparation of phenol from chlorobenzene.*

Ans.



11.11 *Write the mechanism of hydration of ethene to yield ethanol.*

Ans. $CH_2 = CH_2 + H^+ \rightleftharpoons H_3C - \overset{\oplus}{C}H_2 \xrightarrow{H_2O}$

Ethene

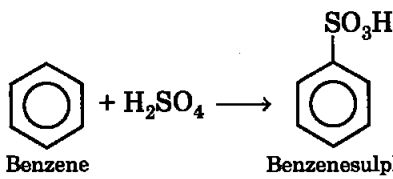
$$H_3C - \underset{\oplus OH_2}{CH_2} \xrightarrow{-H^{\oplus}} H_3C - CH_2 - OH$$

Ethanol

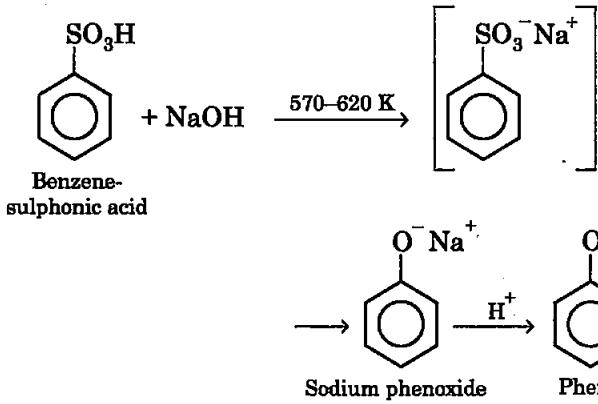
11.12 *You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.*

Ans. Phenol can be obtained by using the given reagents as follows:

Benzene on treatment with concentrated H_2SO_4 yields benzene sulphonic acid.



Benzenesulphonic acid on heating with NaOH to a temp. of 570–620 K yields sodium phenoxide which on acidification gives phenol.



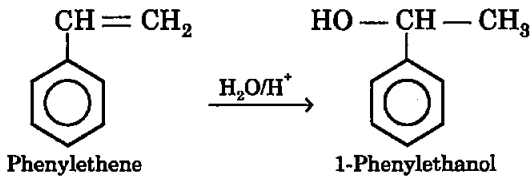
11.13 *Show how will you synthesise:*

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

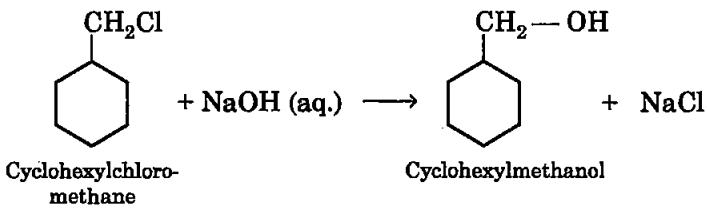
(*ii*) *cyclohexylmethanol using an alkyl halide by an* S_N2 *reaction,*

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

Ans. (*i*) 1-Phenylethanol can be obtained by addition of water to phenylethene (styrene) in presence of acid.



(*ii*) Cyclohexylmethanol can be obtained from cyclohexylchloromethane by treating with aqueous sodium hydroxide.



(*iii*) Pentan-1-ol can be obtained from 1-bromopentane by treating with aqueous sodium hydroxide.

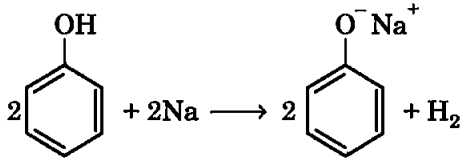
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - Br \xrightarrow{NaOH(aq.)} CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$$

1-Bromopentane — Pentan-1-ol

11.14 *Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.*

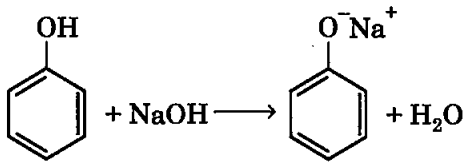
Ans. Following reactions show the acidic nature of phenol:

(*i*) Phenol reacts with sodium metal to form sodium phenoxide and hydrogen.



Phenol — Sodium phenoxide

(*ii*) Phenol also reacts with aq. NaOH to form sodium phenoxide and water.

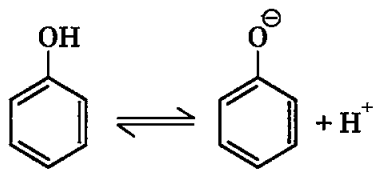


Phenol — Sodium phenoxide

Phenol is more acidic than ethanol. It can be explained on the basis that ethanol on losing H^+ ion forms ethoxide ion and phenol forms phenoxide ion.

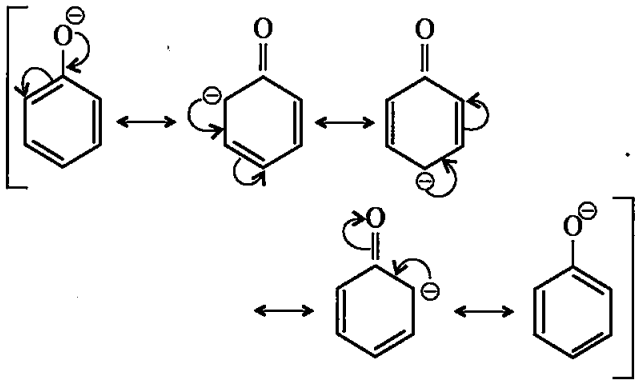
$$CH_3 - CH_2 - OH \rightleftharpoons CH_3 - CH_2 - O^{\ominus} + H^+$$

Ethyl alcohol — Ethoxide ion



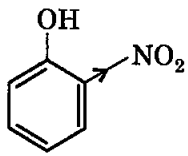
Phenol — Phenoxide ion

Phenoxide ion is stabilised due to resonance, so in this case, the equilibrium lies more towards right side, hence phenol behaves as a stronger acid than ethanol. Resonance stabilisation of phenoxide is shown as follows:

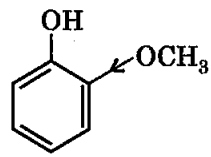


11.15 *Explain why is ortho-nitrophenol more acidic than ortho-methoxyphenol?*

Ans. As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion. Nitro group is an electron withdrawing group whereas methoxy group is an electron releasing group, so *o*-nitrophenol is more acidic than *o*-methoxyphenol.



o-Nitrophenol

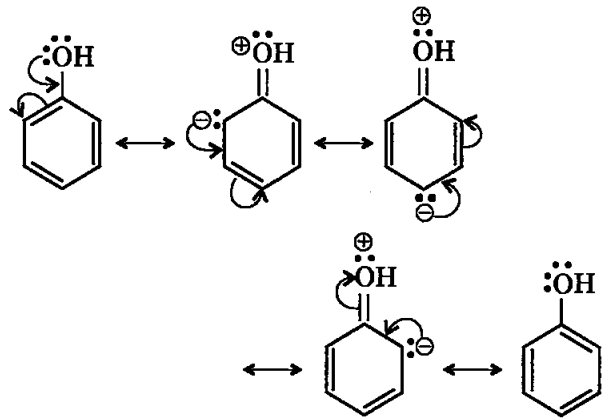


o-Methoxyphenol

11.16 *Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?*

Ans. The —OH group when attached to benzene ring, activates it towards electrophilic substitution reaction. It does so by increasing the electron density on the benzene ring by releasing of electrons due to mesomeric effect as shown below:

It is observed that the electron density increasing more at *ortho* and *para* positions, so the electrophilic substitution occurs mainly at these positions in preference to *meta* position.



11.17 *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.

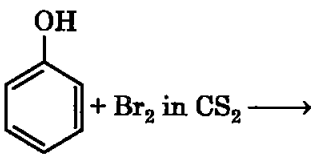
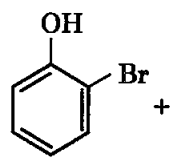
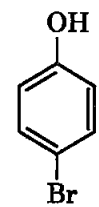
(iv) Treating phenol with chloroform in presence of aqueous NaOH.

Ans. (*i*) $CH_3 - CH_2 - CH_2 - OH \xrightarrow{\text{alk. } KMnO_4}$

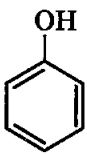
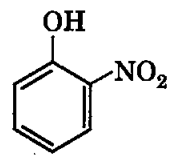
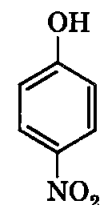
Propan-1-ol

$[CH_3 - CH_2 - CHO] \longrightarrow CH_3 - CH_2 - COOH$

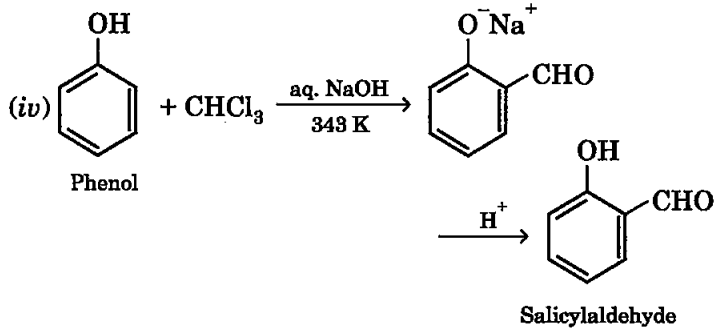
Propanal Propanoic acid

(*ii*)  + Br_2 in CS_2 ⟶  + 

Phenol 2-Bromophenol 4-Bromophenol

(*iii*)  $\xrightarrow{\text{dilute } HNO_3}$  + 

Phenol 2-Nitrophenol 4-Nitrophenol



Phenol

Salicylaldehyde

11.18 *Explain the following with an example:*

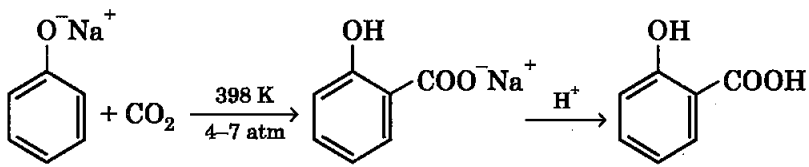
(i) Kolbe's reaction.

(ii) Reimer-Tiemann reaction.

(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

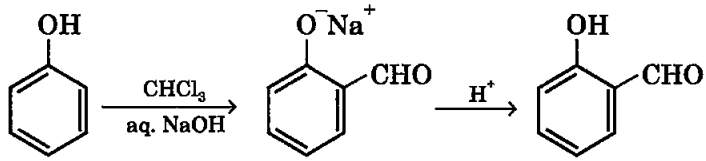
Ans. (*i*) **Kolbe's reaction.** When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



Sodium phenoxide

Salicylic acid

(*ii*) **Reimer-Tiemann reaction.** This involves the treatment of phenol with chloroform in aqueous sodium hydroxide solution followed by acid hydrolysis. Salicylaldehyde is obtained as the major product along with small amount of *para* product.



Phenol

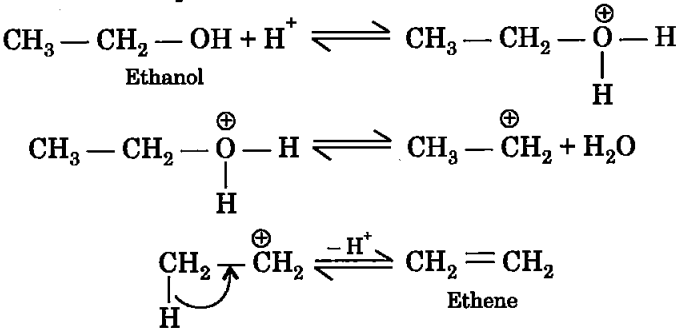
Salicylaldehyde (major)

(*iii*) **Williamson ether Synthesis:** $C_2H_5ONa + CH_3I \longrightarrow C_2H_5OCH_3 + NaI$

(*iv*) The ether which has two different alkyl groups are called unsymmetrical ether *e.g.* $CH_3CH_2CH_2OCH_3$.

11.19 *Write the mechanism of acid dehydration of ethanol to yield ethene.*

Ans. The first step in dehydration of ethanol is protonation followed by loss of water molecule to form ethyl carbocation which loses a proton to form ethene.



11.20 *How are the following conversions carried out?*

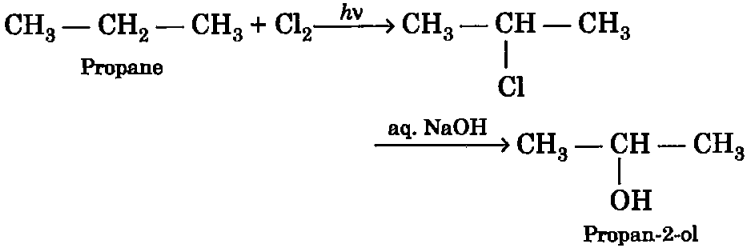
(i) Propene → Propan-2-ol.

(ii) Benzyl chloride → Benzyl alcohol.

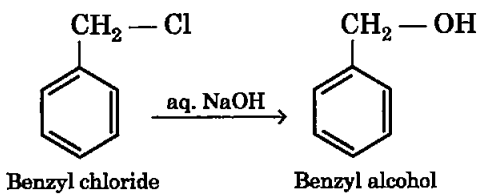
(iii) Ethyl magnesium chloride → Propan-1-ol.

(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

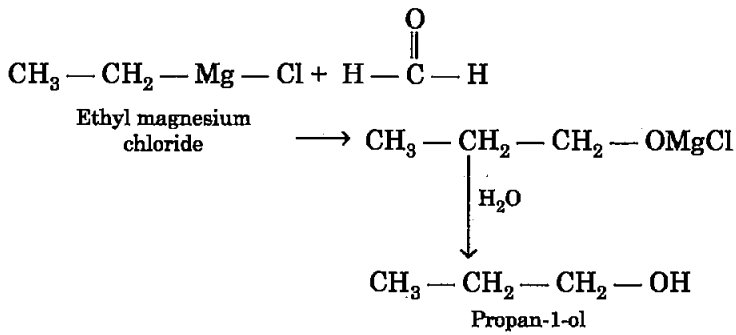
Ans. (*i*) Propane can be converted into propan-2-ol by treating it with chlorine in the presence of sunlight followed by treatment of aq. NaOH solution.



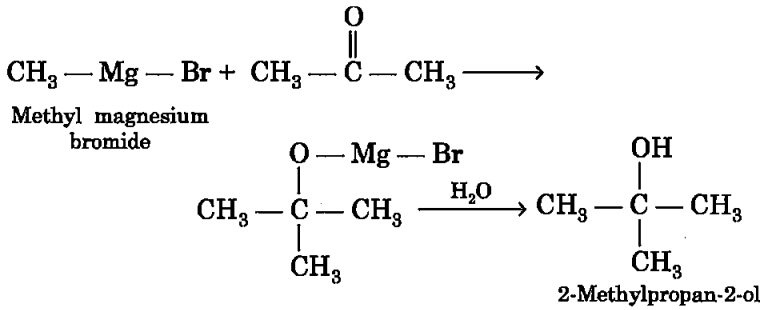
(*ii*) Benzyl chloride can be converted into benzyl alcohol by treating it with aq. NaOH solution.



(*iii*) Ethyl magnesium chloride on addition to formaldehyde followed by hydrolysis leads to the formation of propan-1-ol.



(*iv*) Methyl magnesium bromide on addition to propanone followed by hydrolysis leads to the formation of 2-Methylpropan-2-ol



11.21 *Name the reagents used in the following reactions:*

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2, 4, 6-tribro-mophenol.

(iv) Benzyl alcohol to benzoic acid.

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

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

Ans. (*i*) Potassium permanganate in the presence of dilute sulphuric acid.

(*ii*) Chromium trioxide (CrO_3) in the presence of acetic anhydride.

(*iii*) Bromine water.

(*iv*) Potassium permanganate in alkaline medium.

(*v*) Concentrated sulphuric acid.

(*vi*) Lithium aluminium hydride ($LiAlH_4$).

11.22 *Give reason for the higher boiling point of ethanol in comparison to methoxymethane.*

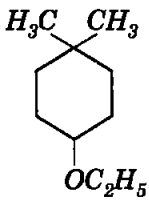
Ans. Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole forces only.

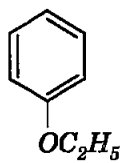
11.23 *Give IUPAC names of the following ethers:*

(*i*) $C_2H_5OCH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$

(*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-ethylpropane

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

(*iii*) 4-Nitromethoxybenzene

(*iv*) 1-Methoxypropane

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

(*vi*) Ethoxybenzene

11.24 *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

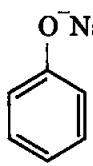
(iv) 1-Methoxyethane

Ans. (*i*)

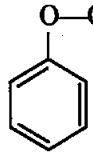
$$CH_3-CH_2-CH_2-O^-Na^+ + CH_3-CH_2-CH_2-Br \longrightarrow CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3 + NaBr$$

Sodium propoxide — 1-Bromopropane — 1-Propoxypropane

(*ii*)



Sodium phenoxide + CH_3-CH_2-Br (Bromoethane) $\longrightarrow$



Ethoxybenzene + NaBr

(*iii*) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O^-Na^+ + CH_3-Br$

Sodium 2-methyl-2-propoxide — Bromomethane

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

2-Methoxy-2-methylpropane

(*iv*) $CH_3-CH_2-O^-Na^+ + CH_3-Br \longrightarrow$

Sodium ethoxide — Bromomethane

$$CH_3-CH_2-O-CH_3 + NaBr$$

Methoxyethane

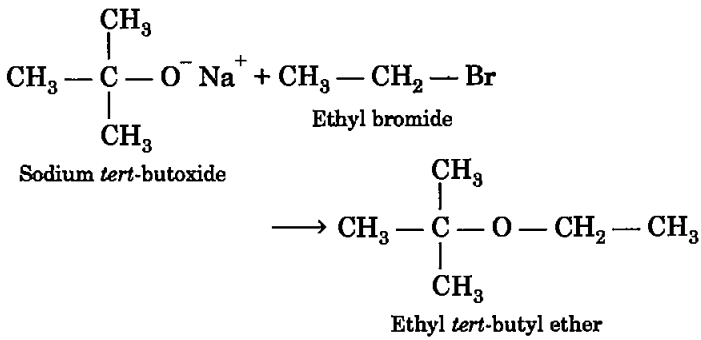
11.25 ***Illustrate with examples the limitations of Williamson's synthesis for the preparation of certain types of ethers.***

Ans. In Williamson's synthesis, an alkyl halide is treated with sodium or potassium salt of an alcohol or phenol to give ethers.

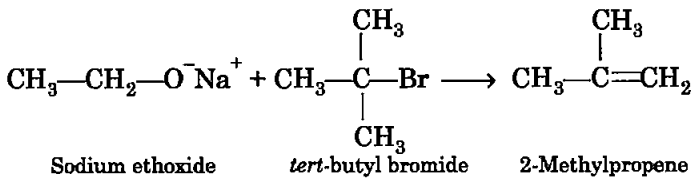
$$R-O^-Na^+ + R'-X \longrightarrow R-O-R' + NaX$$

The reaction involves the nucleophilic substitution of the halogen atom by an alkoxide ion. For the preparation of aliphatic ethers by this method, the alkyl halides used should be primary because secondary or tertiary alkyl halides may undergo elimination to form alkenes due to strongly basic nature of alkoxides.

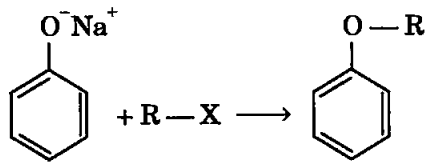
For example, if ethyl *tert*-butyl ether is to be prepared, then better yields are obtained by reacting ethyl bromide with sodium *tert*-butoxide.



But if the reaction between sodium ethoxide and *tert*-butyl bromide is carried out then 2-methylpropene is obtained as the major product.



Another limitation is in the preparation of aliphatic-aromatic ethers where the reaction proceeds by the treatment of sodium phenoxide with alkyl halide.



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

Ans. Propan-1-ol on treatment with conc. H_2SO_4 at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.

$$2CH_3-CH_2-CH_2-OH + H_2SO_4 \xrightarrow{413\ K}$$

Propan-1-ol

$$CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$$

1-Propoxypropane

Mechanism:

$$CH_3-CH_2-CH_2-OH + H^+ \rightleftharpoons$$

Propan-1-ol

$$CH_3-CH_2-CH_2-\overset{\oplus}{O}(H)-H$$

$$CH_3-CH_2-CH_2-\overset{\oplus}{O}(H)-H \rightleftharpoons CH_3-CH_2-\overset{\oplus}{C}H_2 + H_2O$$

$$CH_3-CH_2-CH_2-\ddot{O}-H + CH_3-CH_2-\overset{\oplus}{C}H_2 \longrightarrow$$

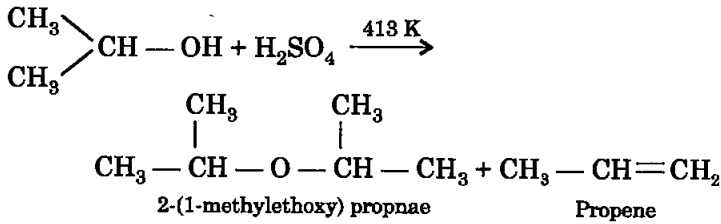
Propan-1-ol

$$CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$$

1-Propoxypropane

11.27 *Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.*

Ans. Ethers are prepared by the dehydration of alcohols using sulphuric acid at 413 K but this method does not give good yields when secondary or tertiary alcohols are used. The reason being that secondary or tertiary alcohols undergo dehydration to form alkenes preferably. Such as 2-propanol (isopropyl alcohol) on treatment with conc. H_2SO_4 at 413 K gives 2-(1-methylethoxy) propane (di-isopropyl ether) as a minor product whereas propene is obtained as a major product.



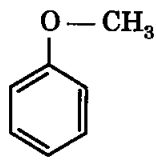
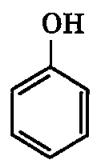
11.28 *Write the equation of the reaction of hydrogen iodide with: (i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether.*

Ans. (*i*) $CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3 \xrightarrow{HI}$

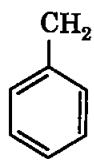
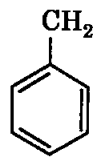
1-Propoxypropane

$CH_3-CH_2-CH_2-OH + CH_3-CH_2-CH_2-I$

Propan-1-ol 1-Iodopropane

(*ii*)  $\xrightarrow{HI}$  + CH_3-I

Methoxybenzene Phenol Methyl iodide

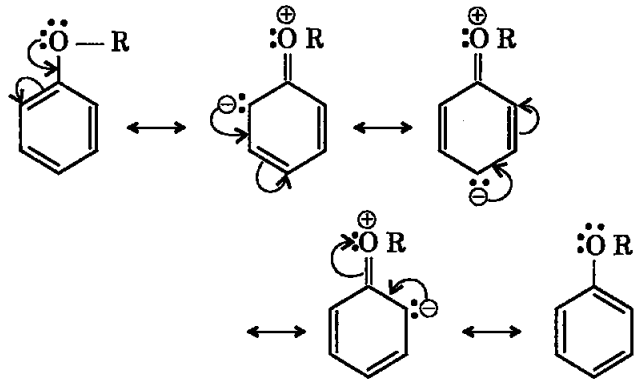
(*iii*)  $\xrightarrow{HI}$  + CH_3-CH_2-OH

Benzyl ethyl ether Benzyl iodide Ethanol

11.29 *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.*

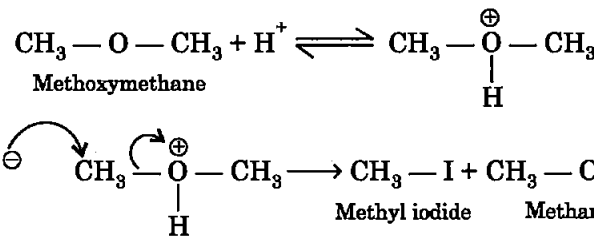
Ans. In alkyl aryl ethers, the alkoxy group is electron releasing due to mesomeric effect, so it activates the benzene ring towards electrophilic substitution. It is also observed from the following canonical structures that the electron density is increased more at *ortho* and *para* positions, so the

incoming electrophiles preferably go to *ortho* or *para* position.



11.30 *Write the mechanism of the reaction of HI with methoxymethane.*

Ans. Methoxymethane gets cleaned into methanol and methyl iodide on treatment with HI. The reaction proceeds in the following steps:



11.31 *Write equations of the following reactions:*

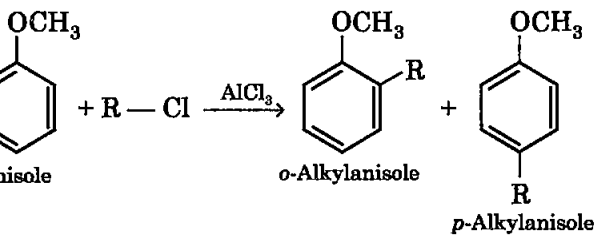
(i) Friedel-Crafts reaction—alkylation of anisole.

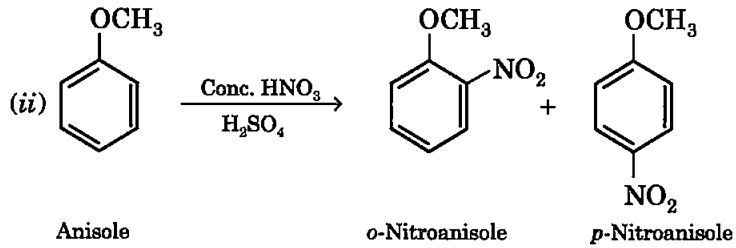
(ii) Nitration of anisole.

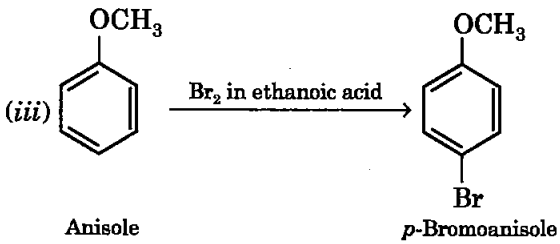
(iii) Bromination of anisole in ethanoic acid medium.

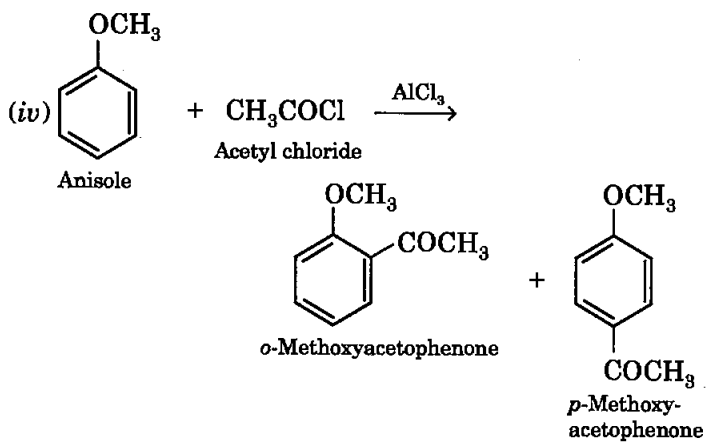
(iv) Friedel-Crafts acetylation of anisole.

Ans. (*i*)

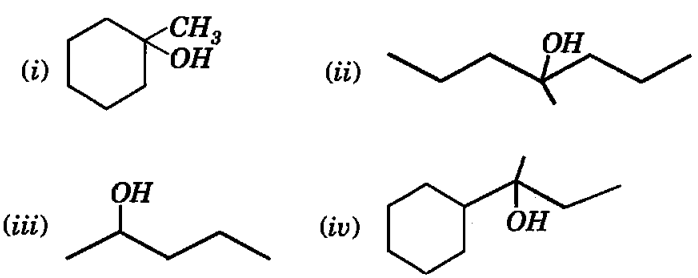




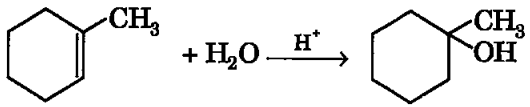




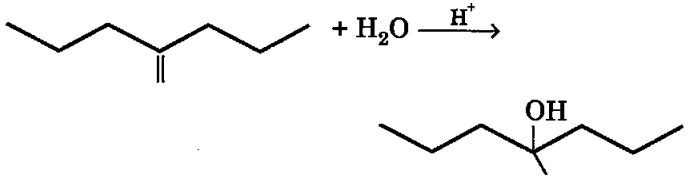
11.32 *Show how would you synthesise the following alcohols from appropriate alkenes?*



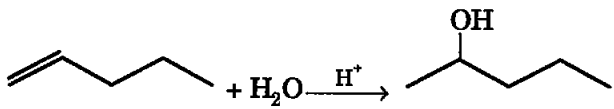
Ans. (*i*)



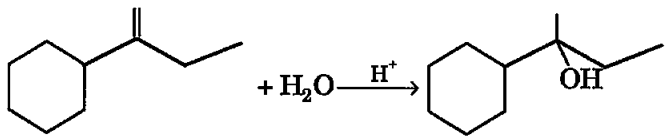
(*ii*)



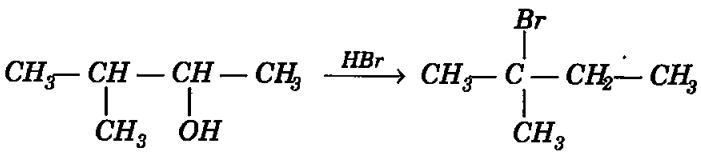
(*iii*)



(*iv*)



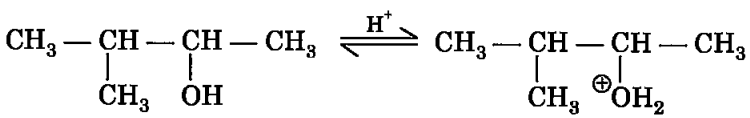
11.33 *When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:*



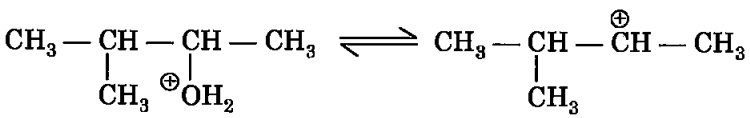
Give a mechanism for this reaction.

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

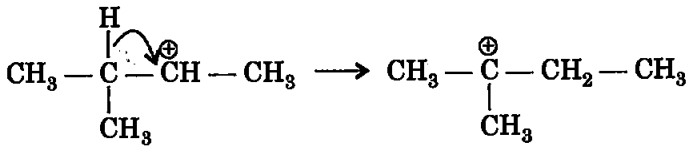
Ans. This reaction proceeds through the rearrangement of the 2° carbocation formed into a more stable 3° carbocation. The mechanism is as follows:



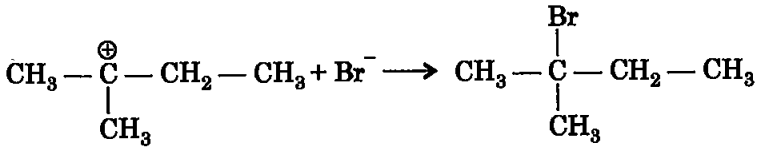
3-Methylbutan-2-ol



2° Carbocation



3° Carbocation



2-Bromo-2-methylbutane

❑❑❑