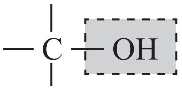
11. ALCOHOLS, PHENOLS AND ETHERS

Can you recall ?

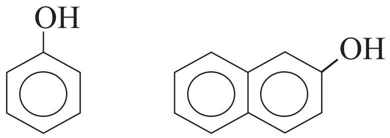
1. What is the name and formula of 2nd member of homologous series of alcohols?
2. What is the structural formula of functional group of ether?
3. What is the name of the compound having -OH group bonded to benzene ring?

11.1 Introduction :

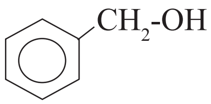
Alcohols are organic compounds whose molecules contain hydroxyl group, (-OH) attached to a saturated carbon atom.



Hydroxyl group can also be present in aromatic compounds. There are two types of aromatic hydroxy compounds: **phenols** and **aromatic alcohols.** Phenols contain a hydroxyl group directly attached to the carbon atom of benzene ring. When the hydroxyl group is present in the side chain of aromatic ring, the compound is termed as aromatic alcohol.



Phenols



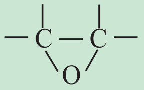
Aromatic alcohol

Ethers are compounds which contain an oxygen atom bonded to two alkyl groups or two aryl groups or one alkyl and one aryl group. Ethers are organic oxides. Ethers are considered as anhydrides of alcohols.

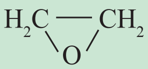
R-O-R', R-O-Ar, Ar-O-Ar'.

Do you know ?

Epoxide are cyclic ethers in which the ethereal oxygen is a part of a three membered ring.



(Ethylene oxide)



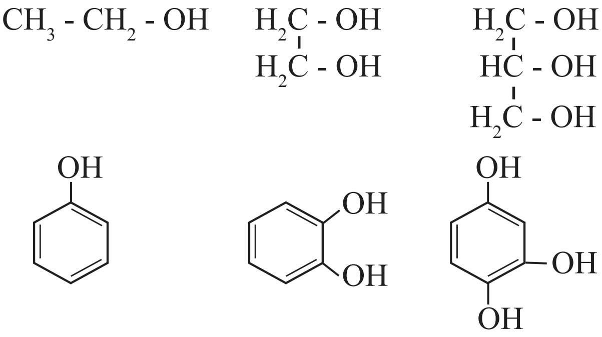
(1,2-Epoxyethane)

11.2 Classification :

Let us first consider classification of alcohols, phenols and then ethers.

11.2.1 Mono, di, tri and polyhydric compounds :

Alcohols and phenols are classified as mono, di-, tri, or polyhydric compounds on the basis of one, two, three or more hydroxyl groups present in their molecules as :



Monohydric alcohols/phenols	**Dihydric alcohols/ phenols**	**Trihydric alcohols/phenols**

Monohydric alcohols are further classified on the basis of hybridisation state of the carbon atom to which hydroxyl group is attached.

a. Alcohols containing sp^3C - OH bond : In these alcohols -OH group is attached to a sp^3 hybridised carbon atom of alkyl group. These alcohols are further classified as primary (1^0), secondary (2^0) and tertiary (3^0) alcohols in which -OH group is attached to primary, secondary and teriary carbon atom respectively. (see Fig. 11.1), also refer to Std. XI Chemistry Textbook Chapter 14, sec. 14.3.2)

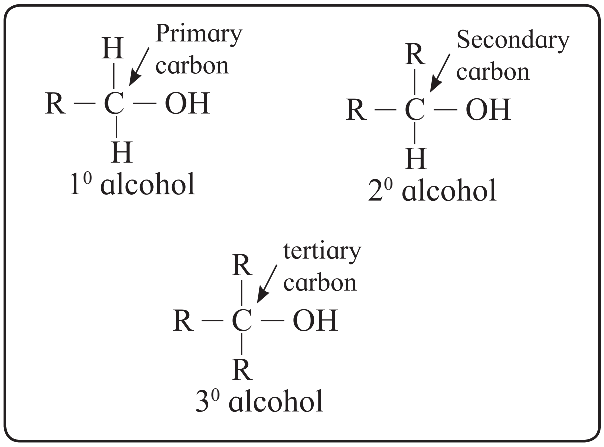


Fig. 11.1 : Primary, secondary and tertiary alcohols

Each of these three types of alcohols can also be either allylic or benzylic if the sp^3 carbon carrying -OH is further bonded to sp^2 carbon.

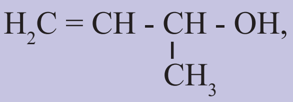
- **Allylic alcohols** : In this type of alcohols -OH group is attached to sp^3 hybridised carbon atom which is further bonded to a carbon-carbon double bond. Allylic alcohol may be primary, secondary or tertiary.
- **Benzylic alcohols** : In this type of alcohols -OH group is attached to sp^3 hybridised carbon atom which is further bonded to an aromatic ring. Benzylic alcohol may be primary, secondary or tertiary.

Use your brain power

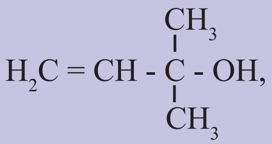
Classifiy the following

alcohols as 1^0 / 2^0 / 3^0 and allylic/ benzylic

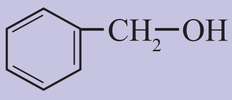
$H_2C = CH - CH_2 - OH$,

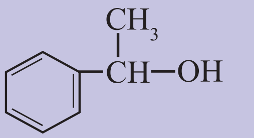


$H_2C = CH - \underset{CH_3}{CH} - OH$,



$H_2C = CH - \overset{CH_3}{\underset{CH_3}{C}} - OH$,





b. Alcohols contianing sp^2C -OH bonds :

In these alcohols -OH group is attached to a sp^2 hybridised carbon atom which is part of a carbon-carbon double bond. These alcohols are known as **vinylic alcohols**. For example

$CH_2 = CH - OH$ (Vinyl alcohol)

11.2.2 Classification of Ethers : Ethers are classified as **symmetrical ethers** (**simple ethers**) or **unsymmetrical ethers** (**mixed ethers**) depending on whether the two alkyl/ aryl groups bonded to oxygen atom are same or different respectively. For example :

$$R - O - R / Ar - O - Ar$$

$$CH_3 - O - CH_3$$

symmetrical ethers (simple ethers)

$$R - O - R' / Ar - O - Ar'$$

$$CH_3 - O - C_2H_5,\ C_6H_5 - O - CH_3$$

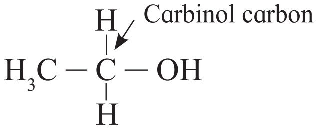
unsymmetrical ethers (mixed ethers)

11.3 Nomenclature :

11.3.1 Alcohols : There are three systems of nonmenclature of monohydric alcohols.

a. Common/trivial names : The common or trivial names of alcohols are obtained by adding word alcohol after the name of alkyl group bonded to -OH. Names of higher alkyl groups also include prefixes like normal, iso, secondary, tertiary (see. Table 11.1).

b. Carbinol system : In this system alcohols are considered as derivatives of **methyl alcohol** which is called **carbinol**. The alkyl group attached to the carbon carrying -OH group are named in alphabetical order. Then the suffix carbinol is added. For example :



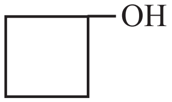
$H_3C - \overset{H}{\underset{H}{C}} - OH$

Methyl carbinol

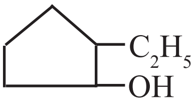
Use your brain power

Name t-butyl alcohol using carbinol system of nomenclature.

c. IUPAC system : Acording to IUPAC system (Std XI Chemistry Text book, Chapter 14), alcohols are named as **alkanols**. The ending 'e' in the name of the parent alkane, alkene or alkyne is replaced by the suffix 'ol'. For naming polyhydric alcohol, 'e' in the ending of alkane is retained, the ending 'ol' is added and number of -OH groups is indicated by prefix di, tri, etc., before 'ol'. The positions of -OH groups are indicated by appropriate locants. For example ethane -1,2-diol (see. Table 11.1). Similarly cyclic alcohols are named by using prefix cyclo to the parent alkane and considering -OH group attached to C-1 carbon atom.



Cyclobutanol



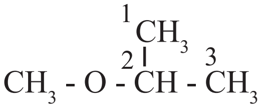
2- Ethylcyclopentanol

11.3.2 Nomenclature of phenols :

The hydroxyl derivative of benzene is called phenol. The IUPAC system name of phenol is benzenol. The common name phenol is also accepted by IUPAC. The common names have prefixes ortho, meta and para in subsituted phenols. IUPAC system uses the locant 2-, 3-, 4-, etc. to indicate the positions of substituents (see Table 11.2).

11.3.3 Nomenclature of Ethers :

In the **common system** of nomenclature, the ethers are named by writing names of the alkyl groups attached to the oxygen atom in alphabetical order and word ether is added. If two alkyl groups are same, prefix di- is used. According to the **IUPAC system** of nomenclature, ethers are named as **alkoxyalkanes** (see Table 11.3). The larger alkyl group is considered to be the parent alkane. The name of the smaller alkane is prefixed by the name of alkoxy group and its locant. For example :



$$CH_3 - O - \overset{\substack{^{1}CH_3 \\ |}}{^{2}CH} - {}^{3}CH_3$$

2-Methoxypropane

Some alkoxy group	
CH_3-CH_2O-	Ethoxy
$CH_3-CH_2-CH_2-O-$	n-Propoxy
$CH_3-\underset{\substack{\mid \\ CH_3}}{CH}-O-$	Isopropoxy

Table 11.1 Common/Trivial and IUPAC Names of some alcohols

Structural formula	Common/ Trivial Name	IUPAC Name
H_3C-OH	Methyl alcohol	Methanol
H_3C-CH_2-OH	Ethyl alcohol	Ethanol
$H_3C-CH_2-CH_2-OH$	n -Propyl alcohol	Propan -1-ol
$H_3C-CH_2-\underset{\substack{\mid \\ CH_3}}{CH}-OH$	sec-Butyl alcohol	Butan -2-ol
$H_3C-\underset{\substack{\mid \\ CH_3}}{CH}-CH_2-OH$	Isobutyl alcohol	2- Methylpropanol
$H_3C-\overset{\substack{CH_3 \\ \mid}}{\underset{\substack{\mid \\ CH_3}}{C}}-OH$	tert-Butyl alcohol	2-Methylpropan-2-ol
$\underset{\substack{\mid \\ OH}}{H_2C}-\underset{\substack{\mid \\ OH}}{CH_2}$	Ethylene glycol	Ethane-1, 2-diol
$\underset{\substack{\mid \\ OH}}{H_2C}-\underset{\substack{\mid \\ OH}}{CH}-\underset{\substack{\mid \\ OH}}{CH_2}$	Propylene glycerol	Propane-1,2,3-triol
$H_3CCH=CHCH_2OH$	Crotonyl alcohol	But-2-en-1-ol

Table 11.2 Common and IUPAC names of some phenols

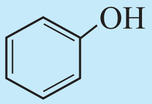
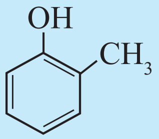
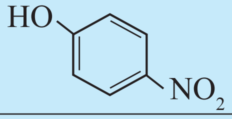
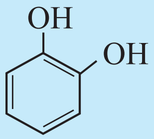
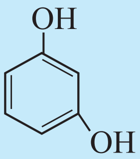
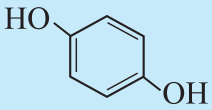
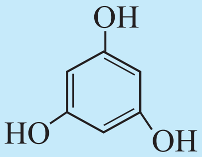
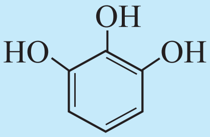
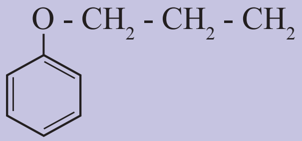
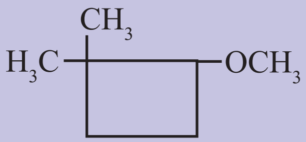
Structural formula	Common name	IUPAC Name
	Phenol	Benzenol/Phenol
	o- Cresol	2-Methylphenol
	p-Nitrophenol	4-Nitrophenol
	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone/ quinol	Benzene -1,4-diol
	Phloroglucinol	Benzene-1,3,5-triol
	Pyrogallol	Benzene-1,2,3-triol

Table 11.3 Common and IUPAC Names of some Ethers

Structural formula	Common Name	IUPAC Name
$H_3C - O - CH_3$	Dimethyl ether	Methoxymethane
$H_3C - O - CH_2 - CH_3$	Ethyl methyl ether	Methoxyethane
$H_3C - O - CH_2 - CH_2 - CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5 - O - CH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene
	Phenyl n-propyl ether	1- Propoxybenzene
	-	2- Methoxy-1,1- dimethylcyclobutane

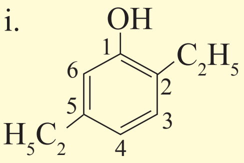
Problem 11.1 : Draw structures of following compounds.

i. 2,5-Diethylphenol ii. Prop-2-en-1-ol

iii. 2-methoxypropane iv. Phenylmethanol

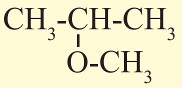
Solutuion :

i.



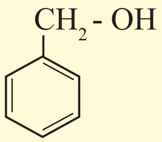
ii. $\overset{3}{H_2C}=\overset{2}{CH}-\overset{1}{CH_2}-OH$

iii.



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

iv.

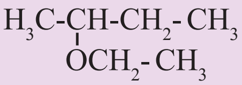


Try this...

Write IUPAC names of the following compounds.

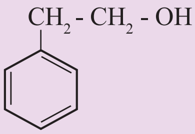
i.

ii.

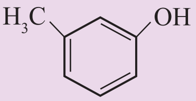


$H_3C-\underset{OCH_2-CH_3}{CH}-CH_2-CH_3$

iii.



iv.



11.4 Alcohols and Phenols :

11.4.1 Prepartion of alcohols :

a. From alkyl halide by hydrolysis with aqueous alkali or moist silver oxide (refer to section 10.6.2)

b. By acid catalyzed hydration of alkenes :

Alkene reacts with sulfuric acid to produce alkyl hydrogen sulfate, which on hydrolysis gives alcohol (Refer to Std XI Chemistry Textbook, section 15.2.4). This reaction follows **Markownikoff's rule**.

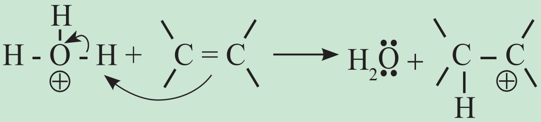
c. Hydroboration - Oxidation of alkenes :

With diborane (B_2H_6) alkene undergoes addition reaction (Hydroboration) to give to trialkylborane (R_3B), which on oxidation with hydrogen peroxide in alkaline medium gives alcohol. (Refer to Std. XI Chemistry Textbook section 15.2.4). This is an **antimarkownikoff hydration** of alkene.

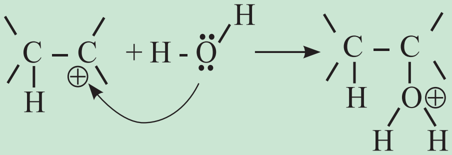
Do you know ?

The mechanism of acid catalyzed hydration of alkene involves the following three steps:

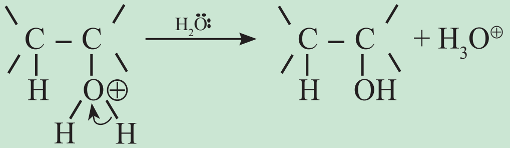
Step 1: Formation of carbocation intermediate.



Step 2: Nucleophilic attack of $H_2\ddot{O}$ on $C^{\oplus}$



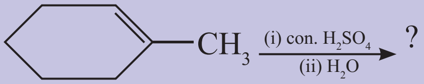
Step 3: Deprotonation



Use your brain power

Predict the major product of the following reactions :

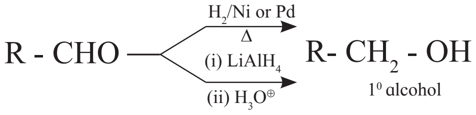
- $CH_3-CH=CH_2 \xrightarrow[(ii)H_2O_2,\ ^{\ominus}OH]{(i)B_2H_6\text{ - THF}} ?$
-

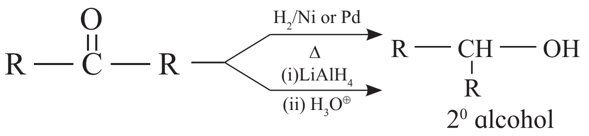


d. By reduction of carbonyl compounds :

i. By reduction of aldehydes and ketones :

Aldehydes on reduction by H_2/Ni or $LiAlH_4$ give primary alcohols (1^0). Similarly ketones on reduction with H_2/Ni or $LiAlH_4$ give secondary alcohols (2^0).

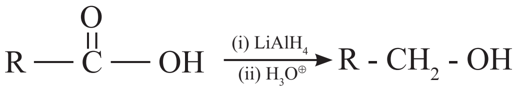




$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\Delta]{H_2/Ni\ or\ Pd} R-\underset{R}{CH}-OH \quad ; \quad R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[(ii)\ H_3O^{\oplus}]{(i) LiAlH_4} R-\underset{R}{CH}-OH$$

2^0 alcohol

ii. By reduction of carboxylic acids : Caboxylic acids require strong reducing agent $LiAlH_4$ to form primary alcohols.



$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} R-CH_2-OH$$

However $LiAlH_4$ is an expensive reagent. Therefore, commercially acids are first transformed into esters which on catalytic hydrogenation give primary alcohols.

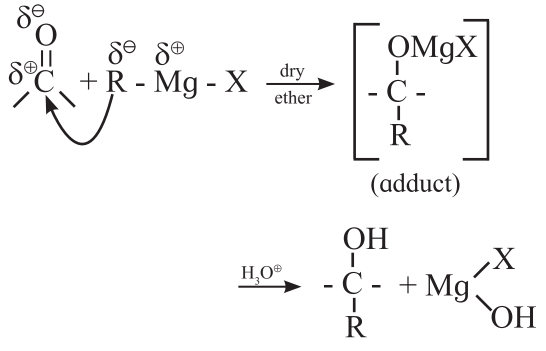
$$R-COOH + R'OH \xrightleftharpoons{H^{\oplus}} R-COOR' + H_2O$$

$$RCOOR' + 2H_2 \xrightarrow[\Delta]{Ni/Pd} R-CH_2OH + R'OH$$

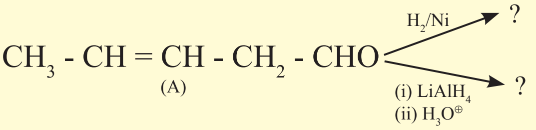
Remember...

The advantage of $LiAlH_4$ over H_2/Ni is that it does not reduce the isolated olefinic bond and hence it can reduce unsaturated aldehyde and ketones to unsaturated alcohols.

e. By addition of Grignard reagent to aldeheydes and ketones : Grignard reagent reacts with aldehyde or ketone to form an adduct which on hydrolysis with dilute acid gives the corresponding alcohols.



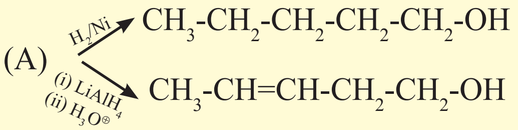
Problem 11.2 : Predict the products for the following reaction.



$$\underset{(A)}{CH_3-CH=CH-CH_2-CHO} \xrightarrow{H_2/Ni} ?$$

$$\underset{(A)}{CH_3-CH=CH-CH_2-CHO} \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} ?$$

Solution : The substrate (A) contains an isolated $>C=C<$ and an aldehyde group. H_2/Ni can reduce both these functional groups while $LiAlH_4$ can reduce only -CHO of the two, Hence



$$(A) \xrightarrow{H_2/Ni} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$$

$$(A) \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}OH$$

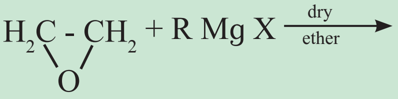
This reaction is useful in synthesis of a variety of alcohols (see Table 11.4).

Table 11.4 Preparation of alcohols by Grignard reagent

Aldehyde/ ketone	Grignard reagent	Final product	Type of alcohol
H - CHO (formaldehyde)	R - Mg Br	$R-CH_2OH$	1^0
R' - CHO (aldehyde)	R - Mg Br	$R-\underset{R'}{CH}-OH$	2^0
R' - CO - R" (ketone)	R - Mg Br	$R-\overset{R''}{\underset{R'}{C}}-OH$	3^0

Do you know ?

Epoxide reacts with Girgnard reagent followed by acidic hydolysis to give primary alcohols

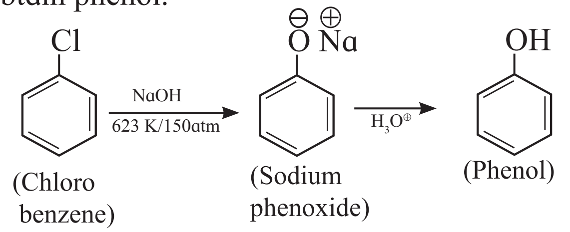


$$H_2C-CH_2\ (\text{bridged by } O) + R\,Mg\,X \xrightarrow[ether]{dry}$$

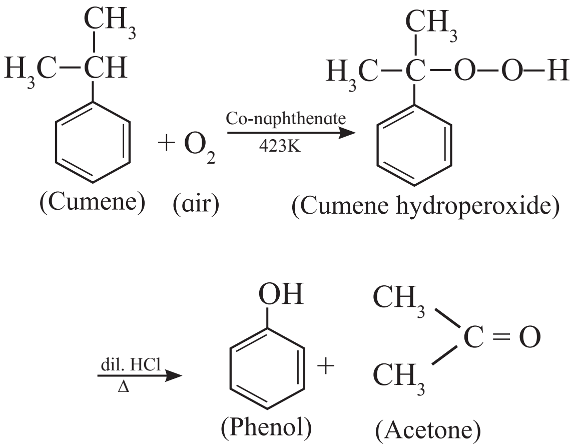
$$[R-CH_2-CH_2-OMgX] \xrightarrow{H_3O^{\oplus}} R\text{-}CH_2CH_2\text{-}OH + Mg\begin{matrix}X\\OH\end{matrix}$$

11.4.2 Preparation of phenol :

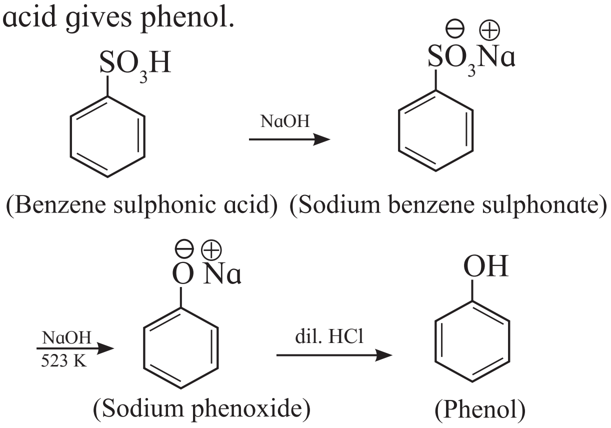
a. From chlorobenzene (Dow Process) : Chlorobenzene is fused with NaOH at high temperature and pressure (623K and 150atm) followed by treatment with dilute HCl to obtain phenol.



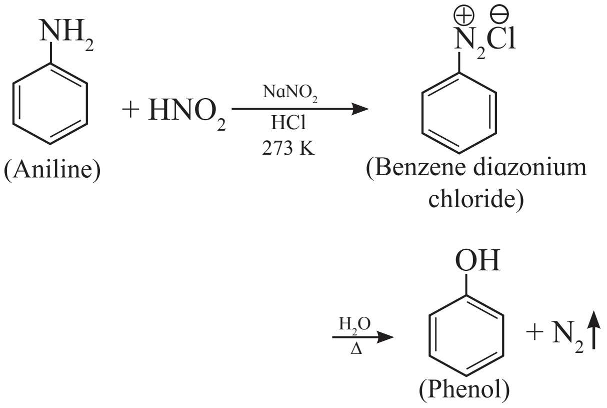
b. From Cumene : This is the commercial method of preparation of phenol. Cumene (isopropylbenzene) on air oxidation in presence of Co-naphthenate gives cumene hydroperoxide, which on decomposition with dilute acid gives phenol with acetone as a valuable by product.



c. From benzene sulfonic acid : Benzene sulfonic acid on neutralization by NaOH gives sodium benzene sulfonate, which on fusion with solid NaOH at 573 K gives sodium phenoxide, followed by reaction with dilute acid gives phenol.

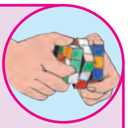


d. From aniline : Aniline is treated with nitrous acid [$NaNO_2$ + HCl] at low temparature to obtain benzene diazonium chloride, which on hydrolysis gives phenol (Also refer to chapter 13 for this reaction).



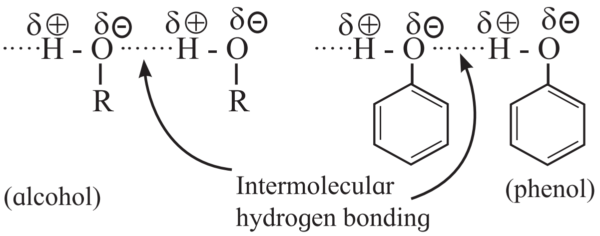
11.4.3 Physical Properties of alcohols and phenols

Try this...



Arrange O-H, C-H and N-H bonds in increasing order of their bond polarity.

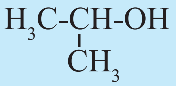
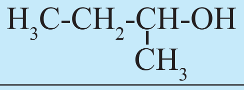
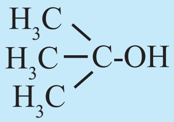
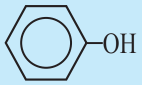
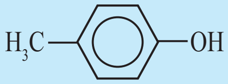
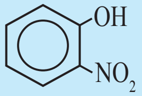
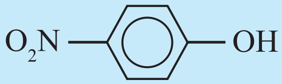
a. Nature of intermolecular forces : Alcohols and phenols are very polar molecules due to presence of -OH groups. The polar -OH groups are held together by the strong intermolecular forces, namely hydrogen bonding.



b. Physical State : Lower alcohols are colourless, toxic liquids having characterstic alcoholic odour. Pure phenol is colourless, toxic, low melting solid having characterstic carbolic or phenolic odour.

c. Boiling Points : The boiling points of alcohols and phenols increase with increase in their molecular mass (Table 11.5).

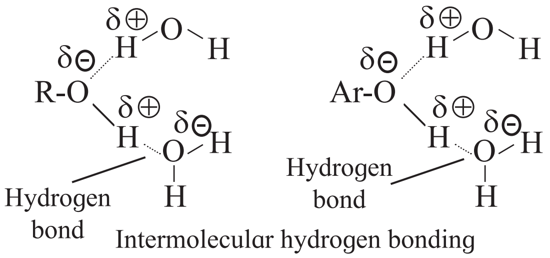
Table 11.5 M.P/B.P and solubilities of some alcohols and phenols

Name	Formula	M.P. (^{0}C)	B.P. (^{0}C)	Solubility (g/100g H_2O)
Methyl alcohol	$H_3C\text{-}OH$	-97	65	0.793
Ethyl alcohol	$H_3C\text{-}CH_2\text{-}OH$	-115	78	0.789
n-Propyl alcohol	$H_3C\text{-}CH_2\text{-}CH_2\text{-}OH$	-126	97	0.804
Isopropyl alcohol	 $H_3C\text{-}\underset{CH_3}{\underset{\mid}{C}}H\text{-}OH$	-86	83	0.789
n-Butyl alcohol	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	-90	118	0.810
Isobutyl alcohol	 $H_3C\text{-}\underset{CH_3}{\underset{\mid}{C}}H\text{-}CH_2\text{-}OH$	-108	108	0.802
sec-Butyl alcohol	 $H_3C\text{-}CH_2\text{-}\underset{CH_3}{\underset{\mid}{C}}H\text{-}OH$	-114	99.5	0.806
tert-Butyl alcohol	 $(H_3C)_3C\text{-}OH$	25.5	83	0.789
Phenol		41	182	9.3
p-Cresol		35	202	2.3
o-Nitrophenol		45	217	0.2
p-Nitrophenol		114	-	1.7

Problem 11.3 : The boiling point of n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol and tert-butyl alcohol are 118^{0}C, 108^0 C. 99^{0}C and 82^{0}C respectively. Explain.

Solution : As branching increases intermolecular van der Waal's force become weaker and the boiling point decreases. Therefore n-butyl alcohol has highest boiling point 118^{0}C and tert-butyl alcohol has lowest boiling point 83^{0}C. Isobutyl alcohol is a primary alcohol and hence its boiling points is higher than that of sec-butyl alcohol.

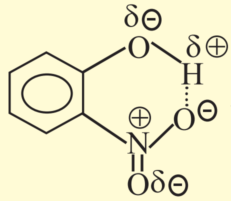
d. Solubility : Phenols and lower alcohols (having upto three carbons) show appreciable solubility in water due to their ability to form intermolecular hydrogen bonding with water molecule (See Table 11.5).



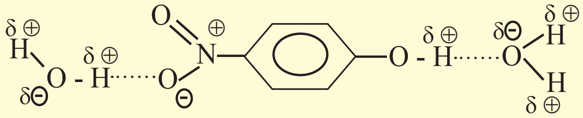
Intermolecular hydrogen bonding of R-OH and Ar-OH with water

Problem 11.4 : The solubility of o-nitrophenol and p-nitrophenol is 0.2 g and 1.7 g/100 g of H_2O respectively Explain the difference.

Solution :



(intramolecular hydrogen bonding in o-nitrophenol)



(intermolecular hydrogen bonding in p-nitrophenol and water)

p-Nitrophenol has strong intermolecular hydrogen bonding with solvent water. On the other hand, o-nitrophenol has strong intramolecular hydrogen bonding and therefore the intermolecular attraction towards solvent water is weak. The stronger the intermolecular attraction between solute and solvent higher is the solubility. Hence p-nitrophenol has higher solubility in water than that of o-nitrophenol.

11.4.4 Chemical properties of Alcohols and Phenols

a. Laboratory tests of alcohols and phenols :

i. Litmus test : Water soluble alcohols and phenols can be tested with litmus paper. Aqueous solution of alcohols is neutral to litmus (neither blue nor red litmus change colour). Aqueous solutions of phenols turn blue litmus red. Thus, phenols have acidic character.

ii. Reaction with bases :

- Acid strength of phenols being very low, phenols cannot react with $NaHCO_3$ but react with NaOH.

$$Ar\text{ - }OH + NaHCO_3(aq) \longrightarrow \text{No reaction}$$

Phenols dissolve in aqueous NaOH by forming water soluble sodium phenoxide and are reprecipitated/regenerated on acidification with HCl.

$$Ar\text{ - }OH + NaOH(aq) \longrightarrow Ar\text{-}O^{\ominus}Na^{\oplus}(aq) + H_2O(l)$$

$$Ar\text{ - }O^{\ominus}Na^{\oplus}(aq) + HCl(aq) \longrightarrow Ar\text{ - }OH\downarrow + NaCl(aq)$$

Do you know ?

Sodium bicarbonate, sodium hydroxide, sodium metal are increasingly strong bases. Weak and strong acids can be distinguished from each other qulitatively by testing their reactivity towards bases of different strengths. A weak acid does not react with a weak base, it requires a stronger base instead. Hence phenols react with NaOH but not with $NaHCO_3$. A strong acid shows high reactivity towards weak as well as strong base. For example : HCl is a strong acid. Its reacts with both $NaHCO_3$ and NaOH as shown below:

$$HCl(aq)+NaHCO_3(aq) \longrightarrow H_2O(l)+ NaCl(aq)+ CO_2\uparrow$$

$$HCl(aq)+NaOH(aq)\longrightarrow NaCl(aq)+H_2O(l)$$

- Alcohols show no acidic character in aqueous solution, thus, alcohols do not react with either aqueous $NaHCO_3$ or aqueous NaOH. Very weak acidic character of alcohol is revealed in the reaction with active metal. When alcohols are treated with very strong base like alkali metal Na or K they react to give sodium or potassium alkoxide with liberation of hydrogen gas.

$$2R\text{ - }OH + 2Na \longrightarrow 2R\text{-}O^{\ominus}Na^{\oplus} + H_2\uparrow$$

Liberation of H_2 gas is used to detect the presence of alcoholic -OH group in a molecule.

iii. Characteristic test for phenols : Phenols reacts with neutral ferric chloride solution to give deep (purple/violet/green) colouration of ferric phenoxide.

$$3Ar\text{ - }OH + \underset{\text{(neutral)}}{FeCl_3} \longrightarrow \underset{\text{(deep colour)}}{(Ar\text{ -}O)_3\!-\!Fe} + 3HCl$$

iv. Distinguishing test for alcohols (Lucas test) : Primary, secondary and tertiary alcohols can be distinguished from each other in the laboratory using Lucas reagent (conc. HCl and $ZnCl_2$). The reaction involved is :

$$R - OH \xrightarrow[ZnCl_2]{HCl} R - Cl$$

Alcohols are soluble in Lucas reagent but the product alkyl chloride is not. Hence, the clear solution becomes turbid when product starts forming. Tertiary alcohols reacts fast and the reagent turns turbid instantaneously. Secondary alcohols turn the reagent turbid slowly. Primary alcohols turn the reagent turbid only on heating.

b. Reactions due to breaking of O -H bond.

i. Acidic character of alcohols and phenols :

From the laboratory tests it is understood that in aqueous medium phenols show weak acidic character while alcohols are neutral. It is clear, therefore, that the reactivity of alcohols and phenols towards ionization of O-H bond in them is different. The reason behind this difference lies in the extent of stabilization of their respective conjugate bases by electronic effects as shown below.

- Ionization of alcohols is represented by the following equilibrium

$$\underset{\text{(alcohol)}}{R - OH} + H_2O \rightleftharpoons \underset{\text{(alkoxide)}}{R \rightarrow O^{\ominus}} + H_3O^{\oplus}$$

Electron donating inductive effect (+I effect) of alkyl group destabilizes the alkoxide ion (the conjugate base of alcohol). As a result alcohol does not ionize much in water, and behaves like neutral compound in aqueous medium.

- Ionization of phenol is represented by the equilibrium shown in Fig. 11.1.

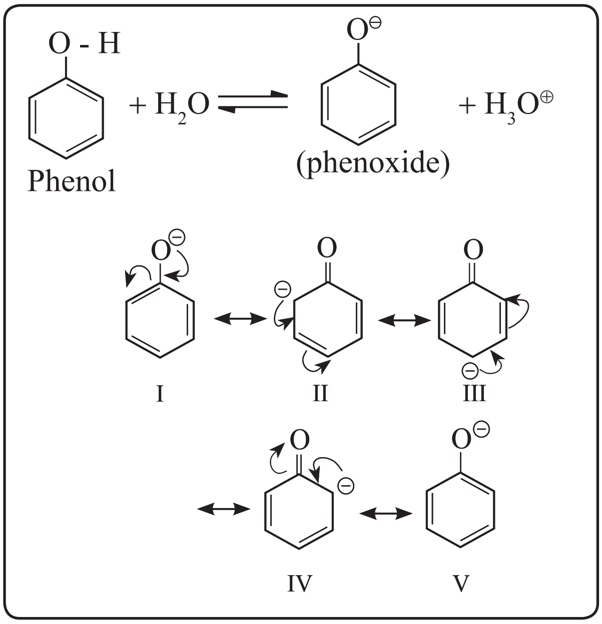


Fig. 11.1 Ionization of phenol and resonance stabilization phenoxide ion

Phenoxide ion, the conjugate base of phenol, is resonance stabilized by delocalization of the negative charge. Therefore phenol ionizes in aqueous medium to a moderate extent, and thereby shows a weak acidic character.

Problem 11.5 : Arrange the following compounds in decreasing order of acid strength and justify.

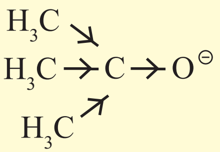
i. CH_3-CH_2-OH ii. $(CH_3)_3C$-OH

iii. C_6H_5-OH iv. p-NO_2-C_6H_4-OH

Solution : Compounds (iii) and (iv) are phenols and therefore are more acidic than the alcohols (i) and (ii). The acidic strenghts of compounds depend upon stabilization of the corresponding conjugate bases. Hence let us compare electronic effects in the conjugate bases of these compounds :

Alcohols :

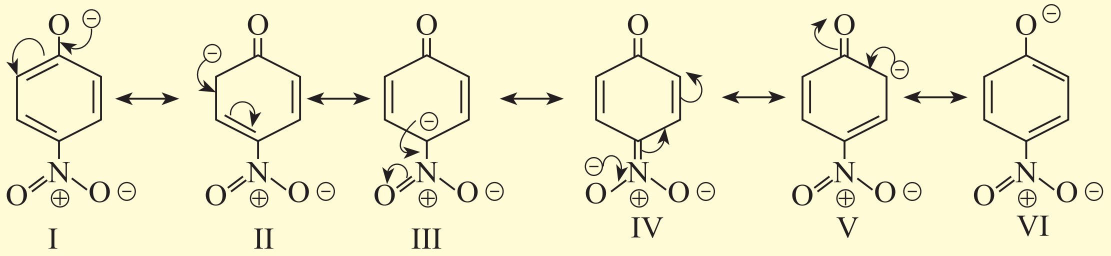
$CH_3 \rightarrow CH_2 \rightarrow O^{\ominus}$ (Conjugate base of (i)) and



$$H_3C \rightarrow \overset{H_3C \searrow}{\underset{H_3C \nearrow}{C}} \rightarrow O^{\ominus}$$

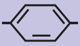
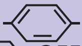
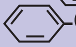
(Conjugate base of (ii))

The conjugate base of the alcohol (i) is destabilized by +I effect of one alkyl group, where as conjugate base of the alcohol (ii) is destabilized by +I effect of three alkyl groups. Hence (ii) is weaker acid than (i)



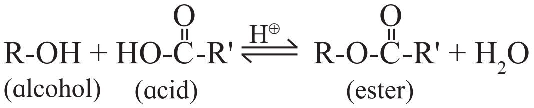
Phenols : The conjugate base of p-nitrophenol (iv) is better resonance stabilized due to six resonance structures compared to the five resonance structures of conjugate base of phenol (iii) (see Fig. 11.1). The resonance structure VI has -ve charge on only electronegative oxygens. Hence the phenol (iv) is stronger acid than (iii). Thus the decreasing order of acid strength is (iv) > (iii) > (i) > (ii)

Use your brain power

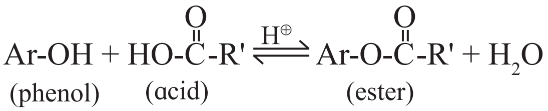
What are the electronic effects exerted by $-OCH_3$ and -Cl ? predict the acid strength of H_3C-O--OH and Cl --OH relative to parent phenol -OH .

ii. Esterification : Alcohols and phenols form esters by reaction with carboxylic acid, acid halides and acid anhydrides. The reaction between alcohol or phenol with a carboxylic acid to form an ester is called **esterification**.

Esterification of alcohol or phenol is carried out in the presence of concentrated sulphuric acid. The reaction is reversible and can be shifted in the forward direction by removing water as soon as it is formed.

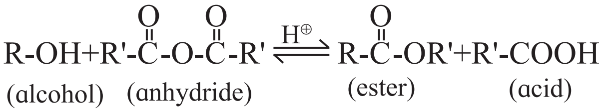


$$\underset{\text{(alcohol)}}{\text{R-OH}} + \underset{\text{(acid)}}{\text{HO-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} \overset{\text{H}^{\oplus}}{\rightleftharpoons} \underset{\text{(ester)}}{\text{R-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} + \text{H}_2\text{O}$$

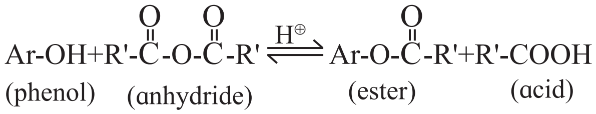


$$\underset{\text{(phenol)}}{\text{Ar-OH}} + \underset{\text{(acid)}}{\text{HO-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} \overset{\text{H}^{\oplus}}{\rightleftharpoons} \underset{\text{(ester)}}{\text{Ar-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} + \text{H}_2\text{O}$$

Alcohols and phenols react with acid anhydrides in presence of acid catalyst to form ester.

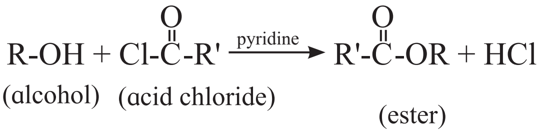


$$\underset{\text{(alcohol)}}{\text{R-OH}} + \underset{\text{(anhydride)}}{\text{R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} \overset{\text{H}^{\oplus}}{\rightleftharpoons} \underset{\text{(ester)}}{\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OR'}} + \underset{\text{(acid)}}{\text{R'-COOH}}$$



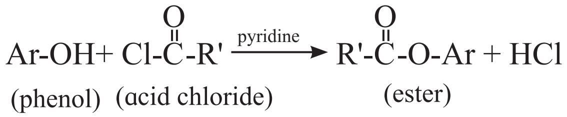
$$\underset{\text{(phenol)}}{\text{Ar-OH}} + \underset{\text{(anhydride)}}{\text{R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} \overset{\text{H}^{\oplus}}{\rightleftharpoons} \underset{\text{(ester)}}{\text{Ar-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'}} + \underset{\text{(acid)}}{\text{R'-COOH}}$$

The reaction of alcohol and phenols with acid chloride is carried out in the presence of pyridine (base), which neutralizes HCl.



$$\text{R-OH} + \text{Cl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'} \xrightarrow{\text{pyridine}} \text{R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OR} + \text{HCl}$$

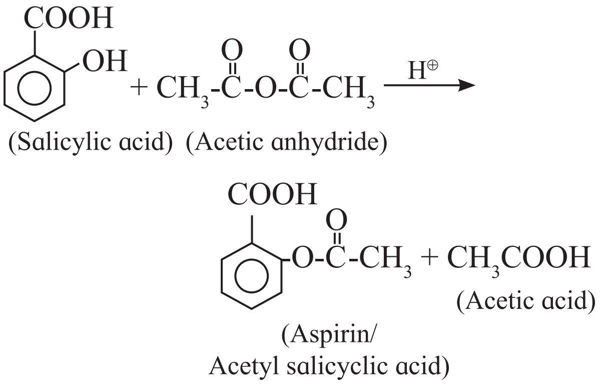
(alcohol) (acid chloride) (ester)



$$\text{Ar-OH} + \text{Cl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'} \xrightarrow{\text{pyridine}} \text{R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-Ar} + \text{HCl}$$

(phenol) (acid chloride) (ester)

Acetyl derivatives : The CH_3-CO- group is called **acetyl group**. The acetate esters of alcohols or phenols are also called 'acetyl derivatives' of alcohols or phenols repectively. The number of alcoholic or phenolic -OH groups in the given compound can be deduced from the number of acetyl groups introduced in it as a result of acetylation. Aspirin, a well known generic medicine, is an acetyl derivative of salicylic acid formed by its acetylation using acetic anhydride.



c. Reaction due to breaking of C-O bond in alcohols :

i. Reaction with hydrogen halides : Alcohols reacts with hydrogen halides to form alkylhalides (refer to Chapter 10 section 10.3.1) In general, tertiary alcohols react rapidly with hydrogen halides; secondary alcohols react somewhat slower; and primary alcohols, even more slowly. The order of reactivity of hydrogen halides is

$$\text{HI} > \text{HBr} > \text{HCl}$$

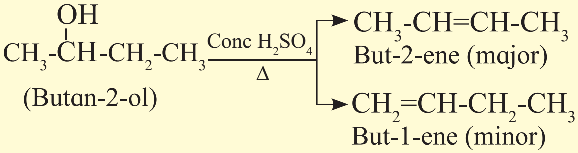
HCl reacts only in the presence of anhydrous $ZnCl_2$. No catalyst is required in the case of HBr and HI.

ii. Reaction with phosphorous halide : Alcohols react with phosphorous pentahalide (PX_5) and phosphorous trihalide (PX_3) to form alkyl halides. (refer to Chapter 10 section 10.3.1).

iii. Dehydration of alcohols to alkenes : Alcohol when treated with concerntrated sulphuric acid or phosphoric acid or alumina undergoes dehydration to form alkene and water. (refer to Std. XI Chemistry Textbook section 15.2) The reaction gives more substituted alkene as the major product, in accordance with **Saytzeff rule**.

Problem 11.6 : Write the reaction showing major and minor products formed on heating butan-2-ol with concentrated sulfuric acid.

Solution : In the reaction described butan-2-ol undergoes dehydration to give but-2-ene (major) and but-1-ene (minor) in accordance with Saytzeff rule.



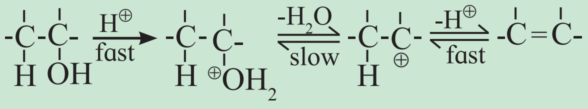
$$CH_3\text{-}\overset{\overset{OH}{|}}{C}H\text{-}CH_2\text{-}CH_3 \xrightarrow[\Delta]{\text{Conc } H_2SO_4} \begin{cases} CH_3\text{-}CH{=}CH\text{-}CH_3 & \text{But-2-ene (major)} \\ CH_2{=}CH\text{-}CH_2\text{-}CH_3 & \text{But-1-ene (minor)} \end{cases}$$

(Butan-2-ol)

Do you know ?

According to the common accepted mechanism dehydration involves following three steps.

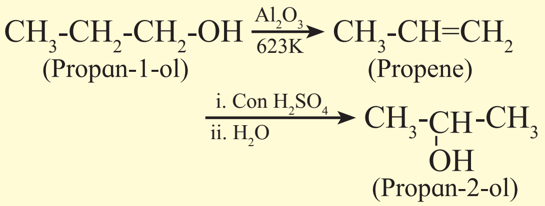
1. Formation of protonated alcohols R-$\overset{\oplus}{O}H_2$
2. Its slow dissociation into carbocation
3. Fast removal of hydrogen ion to form alkene.



(Alcohol) (Protonated alcohol) (Carbocation) (Alkene)

Problem 11.7 : Write and explain reactions to convert propan-1-ol into propan-2-ol ?

Solution : The dehydration of propane-1-ol to propene is the first step. Markownikoff hydration of propene is the second step to get the product propan-2-ol. This is brought about by reaction with concerntrated H_2SO_4 followed by hydrolysis.



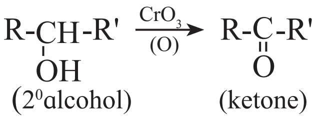
$$\underset{\text{(Propan-1-ol)}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}OH} \xrightarrow[623K]{Al_2O_3} \underset{\text{(Propene)}}{CH_3\text{-}CH{=}CH_2} \xrightarrow[\text{ii. } H_2O]{\text{i. Con } H_2SO_4} \underset{\text{(Propan-2-ol)}}{CH_3\text{-}\underset{OH}{CH}\text{-}CH_3}$$

iv. Oxidation of alcohols :

Can you recall ?

What are the various definitions of oxidation ?

On reaction with oxidising agent primary and secondary alcohols undergo dehydrogenation to form carbonyl compounds, namely aldehydes and ketones respectively Seondary alcohol on oxidation with chromic anhydride (CrO_3) forms ketone.

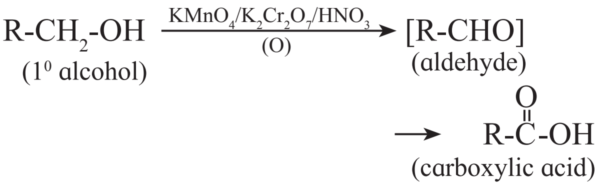


$$\underset{(2^0\text{alcohol})}{R\text{-}\underset{OH}{CH}\text{-}R'} \xrightarrow[(O)]{CrO_3} \underset{\text{(ketone)}}{R\text{-}\underset{O}{\underset{\|}{C}}\text{-}R'}$$

Primary alcohol on oxidation with CrO_3 forms aldehyde. However, a better reagent to bring about this oxidation is PCC (pyridinium chlorochromate).

$$\underset{(1^0\text{ alcohol})}{R\text{-}CH_2\text{-}OH} \xrightarrow[(O)]{PCC} \underset{\text{(aldehyde)}}{R\text{-}CHO}$$

When common oxidizing agents like nitric acid, potassium permanganate or potassium dichromate are used to oxidise primary alcohol, the oxidation does not stop at aldehyde stage, but the aldehyde formed is further oxidized to carboxylic acid containing the same number of carbon atoms.

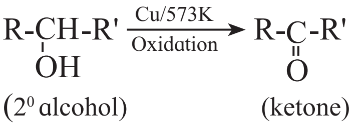


$$\underset{(1^0\text{ alcohol})}{R\text{-}CH_2\text{-}OH} \xrightarrow[(O)]{KMnO_4/K_2Cr_2O_7/HNO_3} \underset{\text{(aldehyde)}}{[R\text{-}CHO]} \longrightarrow \underset{\text{(carboxylic acid)}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH}$$

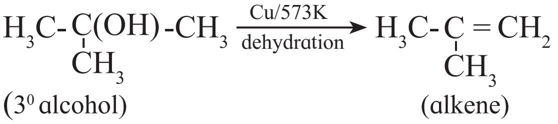
Tertiary alcohols are difficult to oxidise. On oxidation with strong oxidising agents at high temperature tertiary alcohol undergoes breaking of C-C bonds and gives a mixture of carboxylic acids containing less number of carbon atoms than the starting 3° alcohol.

Heating with Cu : When vapours of various types of alcohols are passed over hot copper the following reactions are observed.

$$\underset{(1^0\text{ alcohol})}{R\text{-}CH_2\text{-}OH} \xrightarrow[\text{Oxidation}]{Cu/573K} \underset{\text{(aldehyde)}}{R\text{-}CHO}$$



$$\underset{(2^0\text{ alcohol})}{R\text{-}\underset{OH}{CH}\text{-}R'} \xrightarrow[\text{Oxidation}]{Cu/573K} \underset{\text{(ketone)}}{R\text{-}\underset{O}{\underset{\|}{C}}\text{-}R'}$$



$$\underset{(3^0\text{ alcohol})}{H_3C\text{-}\underset{CH_3}{C}(OH)\text{-}CH_3} \xrightarrow[\text{dehydration}]{Cu/573K} \underset{\text{(alkene)}}{H_3C\text{-}\underset{CH_3}{C}{=}CH_2}$$

Problem 11.8 : An organic compound gives hydrogen on reaction with sodium metal. It forms an aldehyde having molecular formula C_2H_4O on oxidation with pyridinium chlorochromate Name the compounds and give equations of these reactions.

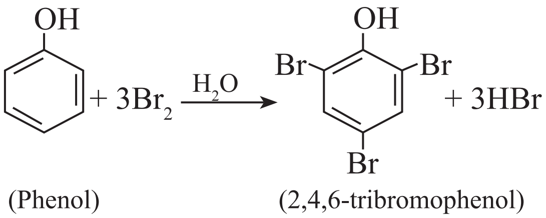
Solution : The given molecular formula C_2H_4O of aldehyde is written as CH_3 -CHO. Hence the formula of alcohol from which this is obtained by oxidation must be $CH_3\text{-}CH_2\text{-}OH$. The two reactions can, therefore, be represented as follows.

$$\underset{\text{(Ethyl alcohol)}}{2CH_3\text{-}CH_2\text{-}OH} \xrightarrow{2Na} \underset{\text{(Sodium ethoxide)}}{2CH_3\text{-}CH_2O^{\ominus}Na^{\oplus}} + H_2\uparrow$$

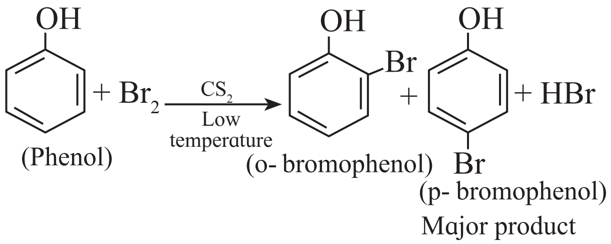
$$\underset{\text{(Ethyl alcohol)}}{CH_3\text{-}CH_2\text{-}OH} \xrightarrow[PCC]{[O]} \underset{\text{(Acetaldehyde)}}{CH_3\text{-}CHO} + H_2O$$

d. Reactions of phenols : Phenol undergoes electrophilic substitution reactions more readily as compared to benzene. The -OH group in phenol is ring activating and an ortho-/para-directing group.

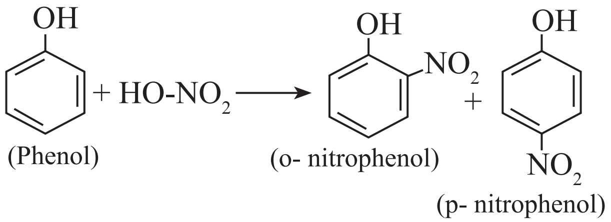
i. Halogentaion of phenol: Phenol reacts with aqueous solution of bromine to give 2,4,6 -tribromophenol (chlorine reacts in the same way.)



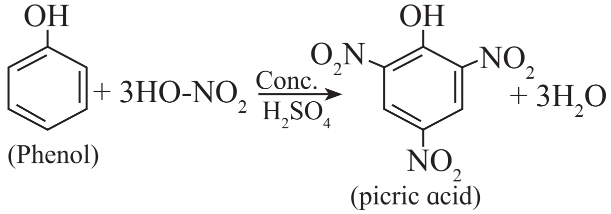
If the reaction is carried out in a solvent of lower polarity than water, such as $CHCl_3$, CCl_4 or CS_2, a mixture of ortho- and para-bromophenol is formed.



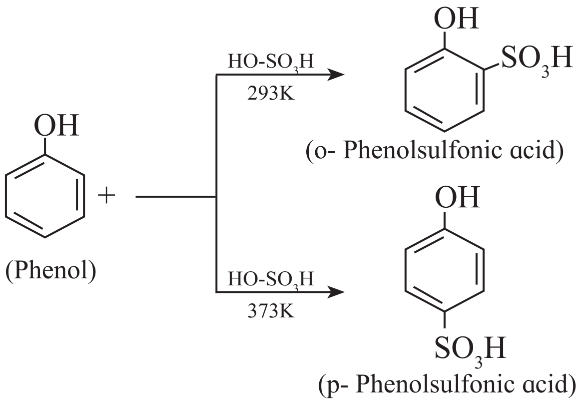
ii. Nitration of phenol : Phenol reacts with dilute nitric acid at low temperature to give mixture of ortho- and para-nitrophenol.



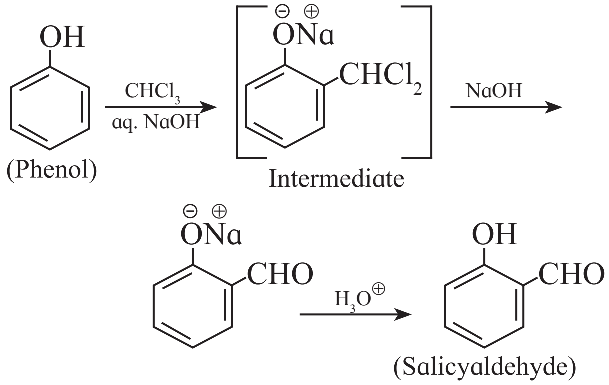
Phenol reacts with concerntrated nitric acid to form 2, 4, 6-trinitrophenol (picric acid)



iii. Sulfonation of phenol : Phenol reacts with concerntrated sulfuric acid at room temperature to give o-phenolsulfonic acid and at 373K, p-phenol sulfonic acid

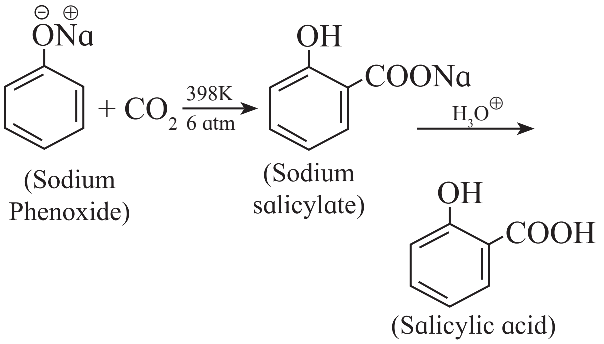


iv. Reimer-Tiemann Reaction : When phenol is treated with chloroform in aqueous sodium hydroxide solution followed by hydrolysis with acid, salicylaldehyde is formed. This reaction is known as Reimer-Tiemann reaction.



If carbon tetrachloride is used in place of chloroform, salcylic acid is formed.

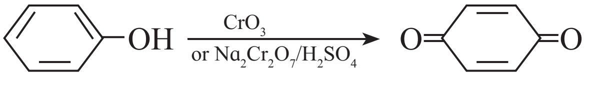
v. Kolbe reaction : The treatment of sodium phenoxide with carbondioxide at 398 K under pressure of 6 atm followed by acid- hydrolysis, salicylic acid (o-hydroxybenzoic acid) is formed. This reaction is known as Kolbe's reaction



Do you know ?

Sodium phenoxide is more reactive than phenol towards electrophilic substitution. Hence it is able to react with a weak electrophile like CO_2 at high temperature and pressure in Kolbe reaction.

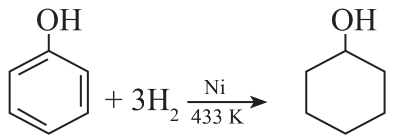
vi. Oxidation of phenol : Phenol on oxidation with chromic anhydride or sodium dichromate in presence of H_2SO_4 gives p-benzoquinone.



(Phenol) (p-Benzoquinone)

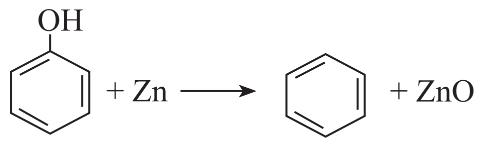
Phenol oxidizes slowly giving a dark coloured mixture in presence of air.

vii. Catalytic hydrogenation of phenol: Phenol on catalytic hydrogenation gives cyclohexanol. In this reaction a mixture of vapours of phenol and hydrogen is passed over nickel catalyst at 433 K.



(Phenol) (Cyclohexanol)

viii. Reduction of phenol : Phenol is reduced to benezene on heating with zinc dust.



(Phenol) (Benzene)

11.5 Ethers

11.5.1 Preaparation of ethers

a. Dehydration of alcohols : When alcohol is heated with dehydrating agent like concentrated H_2SO_4 or H_3PO_4 two products, either an ether or an alkene, can form depending upon the temperature. For example : dehydration of ethanol by H_2SO_4 gives ethoxyethane at 413 K, while ethene is formed at 443 K.

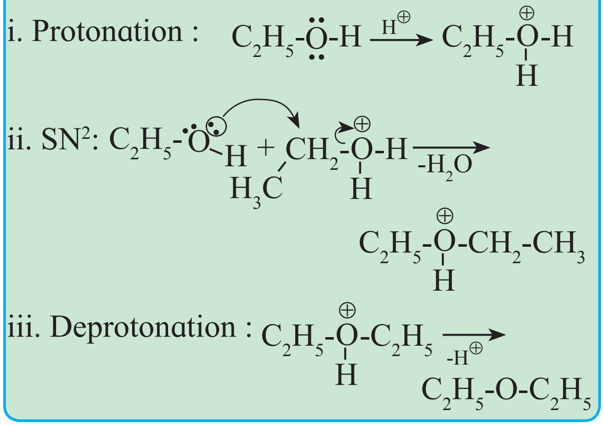
$$\underset{\text{(ethanol)}}{2C_2H_5OH} \xrightarrow[-H_2O]{H_2SO_4/413K} \underset{\text{(Ethoxyethane)}}{C_2H_5\text{-}O\text{-}C_2H_5}$$

$$\underset{\text{(ethanol)}}{C_2H_5OH} \xrightarrow[-H_2O]{H_2SO_4/443K} \underset{\text{(ethene)}}{CH_2{=}CH_2}$$

Symmetrical ethers can be obtained from primary alcohols by this method. Use of higher temperature or 2°/3° alcohols gives alkene as the major product.

Do you know ?

Dehydration of alcohols to form ether is a SN^2 reaction. Protonated alcohol species undergoes a backside attack by second molecule of alcohol in a slow step. Subsequent fast deprotonation results in formation of ether.



i. Protonation : $C_2H_5\text{-}\ddot{\underset{..}{O}}\text{-}H \xrightarrow{H^{\oplus}} C_2H_5\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}H$

ii. SN^2: $C_2H_5\text{-}\ddot{O}\text{-}H + \underset{H_3C}{CH_2}\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}H \xrightarrow[-H_2O]{} C_2H_5\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_2\text{-}CH_3$

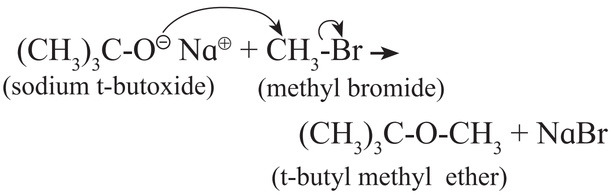
iii. Deprotonation : $C_2H_5\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}C_2H_5 \xrightarrow[-H^{\oplus}]{} C_2H_5\text{-}O\text{-}C_2H_5$

b. Williamson Synthesis : Simple as well as mixed ethers can be prepared in laboratory by Williamson Synthesis. In this method alkyl halide is treated with sodium alkoxide or sodium phenoxide to give dialkyl ethers or alkyl aryl ethers.

$$R\text{-}X + Na^{\oplus}\ O^{\ominus}\text{-}R \longrightarrow R\text{-}O\text{-}R + NaX$$

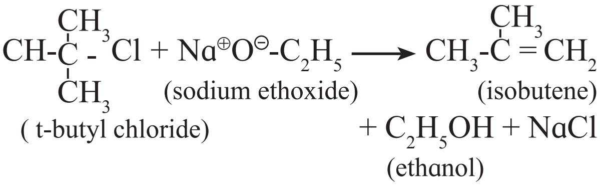
$$R\text{-}X + Na^{\oplus}\ O^{\ominus}\text{-}Ar \longrightarrow R\text{-}O\text{-}Ar + NaX$$

This reaction follows S_N2 mechanism. Ether is formed as a result of backside attack by alkoxide/ phenoxide ion (a nucleophile) on alkyl halide. The alkyl halide used in this reaction must be primary. For example : t-butyl methyl ether can be synthesised by reaction of methyl bromide with sodium t-butoxide.



$$\underset{\text{(sodium t-butoxide)}}{(CH_3)_3C\text{-}O^{\ominus}\ Na^{\oplus}} + \underset{\text{(methyl bromide)}}{CH_3\text{-}Br} \rightarrow \underset{\text{(t-butyl methyl ether)}}{(CH_3)_3C\text{-}O\text{-}CH_3} + NaBr$$

If secondary or tertiary alkyl halides are used, the reaction leads mainly to alkene formation (elimination reaction). For example :

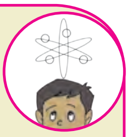


$$CH-\underset{CH_3}{\overset{CH_3}{C}}-Cl + Na^{\oplus}O^{\ominus}-C_2H_5 \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + C_2H_5OH + NaCl$$

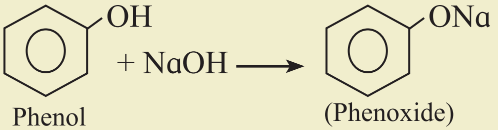
(t-butyl chloride) (sodium ethoxide) (isobutene) (ethanol)

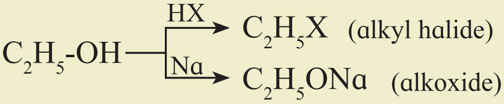
Aryl halides do not give Williamson's synthesis.

Can you think ?



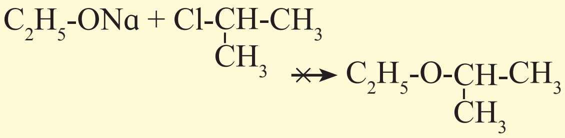
Williamson synthesis is effectively a method of preparation of ethers from two hydroxy compounds. The two substrates of Williamson synthesis, namely the nucleophile and alkyl hadlides are obtained from hydroxy compounds as shown below.





$$C_2H_5-OH \begin{cases} \xrightarrow{HX} C_2H_5X \text{ (alkyl halide)} \\ \xrightarrow{Na} C_2H_5ONa \text{ (alkoxide)} \end{cases}$$

Problem 11.9 : Ethyl isopropyl ether does not form on reaction of sodium ethoxide and isopropyl chloride.

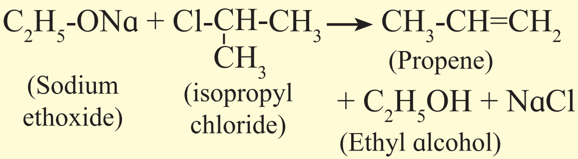


$$C_2H_5-ONa + Cl-\underset{CH_3}{CH}-CH_3 \not\longrightarrow C_2H_5-O-\underset{CH_3}{CH}-CH_3$$

i. What would be the main product of this reaction ?

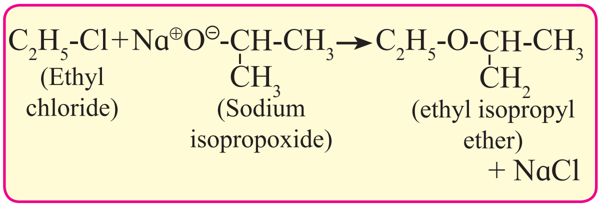
ii. Write another reaction suitable for the preparation of ethyl isopropyl ether.

Solution : i. Isopropyl chloride is a secondary chloride. On treating with sodium ethoxide it gives elimination reaction to form propene as the main product .



$$\underset{\text{(Sodium ethoxide)}}{C_2H_5-ONa} + \underset{\text{(isopropyl chloride)}}{Cl-\underset{CH_3}{CH}-CH_3} \longrightarrow \underset{\text{(Propene)}}{CH_3-CH=CH_2} + \underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + NaCl$$

ii. Ethyl isopropyl ether can be prepared as follows using ethyl chloride (1^0chloride) as as substrate.



$$\underset{\text{(Ethyl chloride)}}{C_2H_5-Cl} + \underset{\text{(Sodium isopropoxide)}}{Na^{\oplus}O^{\ominus}-\underset{CH_3}{CH}-CH_3} \longrightarrow \underset{\text{(ethyl isopropyl ether)}}{C_2H_5-O-\underset{CH_2}{CH}-CH_3} + NaCl$$

11.5.2 Physical properties :

a. Physical states and boiling points

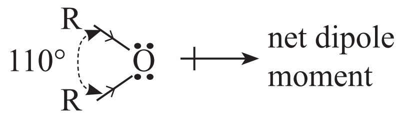
i. Dimethyl ether and ethyl methyl ether are gases. Other ethers are colourless liquids with pleasant odour.

ii. Lower ethers are highly volatile and highly inflammable substances.

iii. Boiling points of ethers show gradual increase with the increase in molecular mass.

Ether	B.P. / K
CH_3-O-CH_3	248
C_2H_5-O-CH_3	284
C_2H_5-O-C_2H_5	308

b. Polarity and solubility : Since $-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$ bond angle is 110° and not 180°, the bond dipole moments of the two C-O bonds donot cancel each other; therefore ethers posses a small net dipole moment (For example, dipole moment of diethyl ether is 1.18 D)

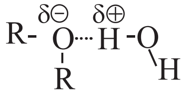


Weak polarity of ethers does not affect their boiling points, which are about the same as those of alkanes having comparable molecular mass. (see table 11.6).

Table 11.6 Comparative boiling points of alkane, ether and alcohol

Name	n-Heptane	Methyl n-pentyl ether	n-Hexyl alcohol
Molecular mass	100	102	102
Boiling point / K	371	373	430

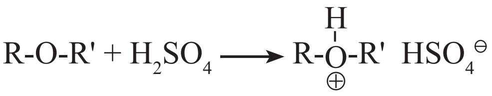
The intermolecular hydrogen bonding that holds alcohol molecules together strongly, is not present in ethers and alkanes. However, solubility/miscibility of ethers in water is similar to that of alcohols of comparable molecular mass. This is because ethers can form hydrogen bonds with water through the ethereal oxygen.



For example diethyl ether and n-butyl alcohol have respective miscibilities of 7.5 and 9g per 100 g of water.

11.5.3 Chemical properties of ethers :

a. Laboratory test for ethers : Ethers are neutral compounds in aqueous medium. Ethers do not react with bases, cold dilute acids, reducing agents, oxidizing agents and active metals. However, ethers dissolve in cold concerntrated H_2SO_4 due to formation of oxonium salts.

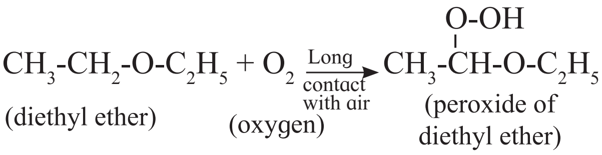


$$R\text{-}O\text{-}R' + H_2SO_4 \longrightarrow R\text{-}\underset{\oplus}{\overset{H}{O}}\text{-}R' \ \ HSO_4^\ominus$$

This property distinguishes ethers from hydrocarbons.

b. Reaction involving alkyl group of ether :

i. Formation of peroxide : Ethers combine with atmospheric oxygen to form peroxide.



$$\underset{\text{(diethyl ether)}}{CH_3\text{-}CH_2\text{-}O\text{-}C_2H_5} + \underset{\text{(oxygen)}}{O_2} \xrightarrow[\text{with air}]{\text{Long contact}} \underset{\text{(peroxide of diethyl ether)}}{CH_3\text{-}\overset{O\text{-}OH}{CH}\text{-}O\text{-}C_2H_5}$$

All ethers which have been exposed to the atmosphere contain peroxide. This is very undesirable reaction. Peroxides are hazardous because they decompose violently at high temperature.

c. Reaction involving C-O bond

i. Reaction with hot dilute sulphuric acid (Hydrolysis) : Ethers when heated with dilute sulfuric acid undergo hydrolysis to give alcohols/phenols.

$$R\text{-}O\text{-}R + H\text{-}O\text{-}H \xrightarrow[\Delta]{H_3O^\oplus} 2R\text{-}OH$$

$$R\text{-}O\text{-}R' + H\text{-}O\text{-}H \xrightarrow[\Delta]{H^\oplus} R\text{-}OH + R'\text{-}OH$$

$$Ar\text{-}O\text{-}R + H\text{-}O\text{-}H \xrightarrow[\Delta]{H^\oplus} Ar\text{-}OH + R\text{-}OH$$

ii. Reaction with PCl_5 : Ethers react with PCl_5 to give alkyl chlorides

$$R\text{-}O\text{-}R' + PCl_5 \xrightarrow{\Delta} R\text{-}Cl + R'\text{-}Cl + POCl_3$$

iii. Reaction with hot concentrated acid : Alkyl ethers react with hot and concentrated HI and HBr to give an alcohol and an alkyl halide.

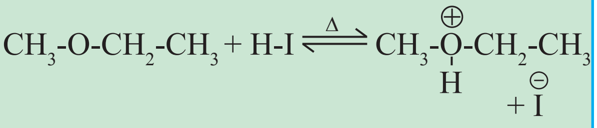
$$R\text{-}O\text{-}R + HX \longrightarrow R\text{-}X + R\text{-}OH \xrightarrow{HX} R\text{-}X$$

$$R\text{-}OH \xrightarrow{HX} R\text{-}X + H_2O$$

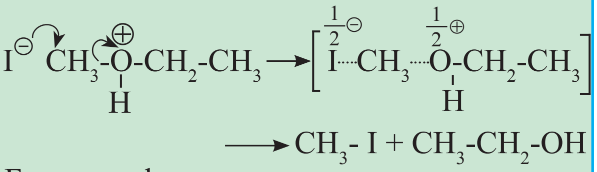
The order of reactivity of HX is HI>HBr>HCl

Do you know ?

Mechanism of first stage : Reaction of ether with hot concentrated HI involves formation of oxonium ion by protonation in the first step and subsequent nucleophilic substitution reaction brought about by the powerful nucleophile $I^\ominus$. The least substituted carbon in oxoinium ion is attacked by $I^\ominus$ following SN^2 mechanism.



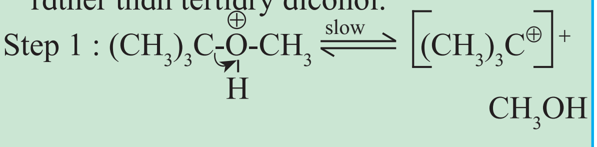
$$CH_3\text{-}O\text{-}CH_2\text{-}CH_3 + H\text{-}I \overset{\Delta}{\rightleftharpoons} CH_3\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_2\text{-}CH_3 + I^\ominus$$



$$I^\ominus \ CH_3\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_2\text{-}CH_3 \longrightarrow \left[\overset{\frac{1}{2}\ominus}{I}\cdots CH_3\cdots\underset{H}{\overset{\frac{1}{2}\oplus}{O}}\text{-}CH_2\text{-}CH_3\right] \longrightarrow CH_3\text{-}I + CH_3\text{-}CH_2\text{-}OH$$

For example :

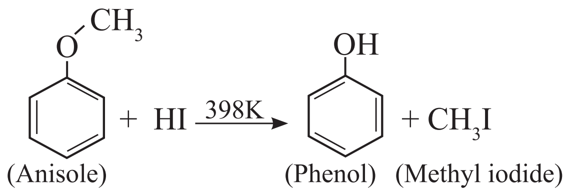
- Use of excess HI converts the alcohol into alkyl iodide.
- In case of ether having one tertiary alkyl group the reaction with hot HI follows SN^1 mechanism, and tertiary iodide is formed rather than tertiary alcohol.



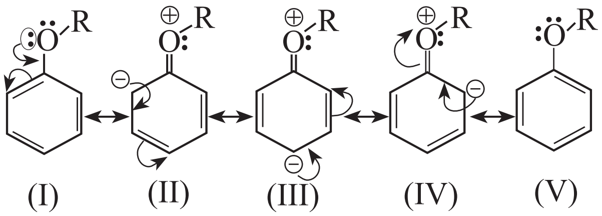
$$\text{Step 1 : } (CH_3)_3C\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_3 \overset{\text{slow}}{\rightleftharpoons} \left[(CH_3)_3C^\oplus\right] + CH_3OH$$

$$\text{Step 2 : } (CH_3)_3C^\oplus + I^\ominus \xrightarrow[\text{fast}]{} (CH_3)_3C\text{-}I$$

Aryl alkyl ethers have stronger and shorter bond between oxygen and the aromatic ring. Hence an aryl alkyl ether undergoes cleavage of oxygen - alkyl bond and yields a phenol and an alkyl halide on reaction with HI.

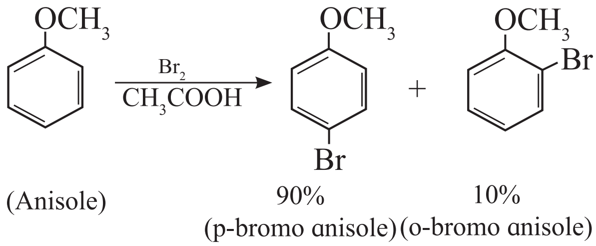


d. Electrophilic substitution in aromatic ethers : The alkoxy group in aromatic ether is a ring activating and ortho-, para-directing group toward electrophilic aromatic substitution. This is evident from the resonance structures:

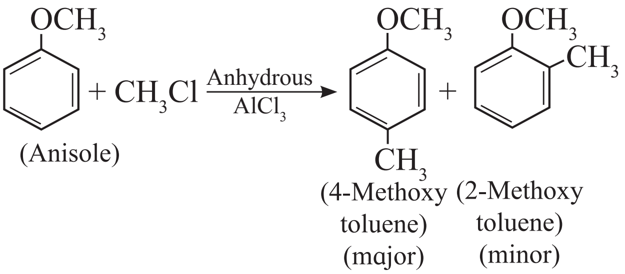


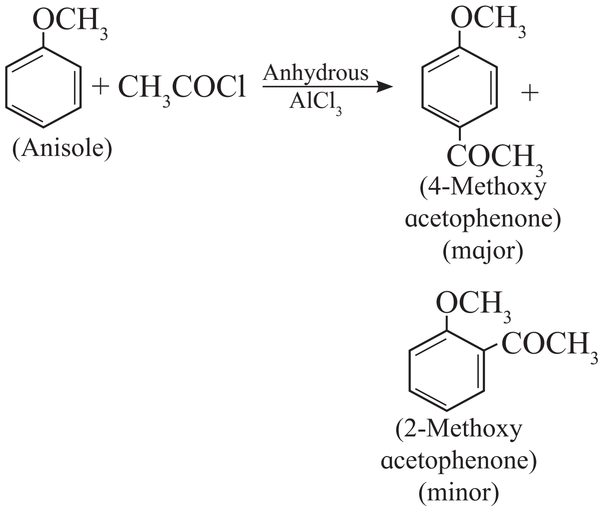
+R Effect of -$\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$R group results in increased electron density at the para- and two ortho-positions (see resonance structures II, III and IV).

i. Halogenation : Anisole undergoes bromination with bromine in acetic acid even in the absence of ferric bromide catalyst. It is due to activation of benzene ring by the methoxy group.

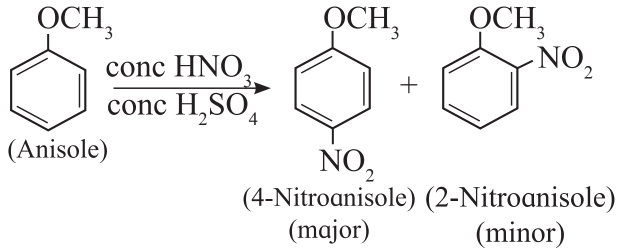


ii. Friedel Crafts reaction : Anisole reacts with alkyl halide and acyl chloride in presence of anhydrous $AlCl_3$ (Lewis acid) as catalyst.





iii. Nitration : Anisole reacts with concentrated nitric acid in presence of concentrated sulfuric acid (Nitrating mixture) to give a mixture of o-nitro anisole and p-nitro anisole.



11.6 Uses of alcohols, phenols and ethers

Alcohols :

1. Methyl alcohol is used as a solvent for paints and varnishes.
2. Ethyl alcohol is used as antifreeze agent in automobile radiators. It is also used as solvent.

Ethers :

1. Earlier diethyl ether was used as a general anaesthetic in surgical operations.
2. Diethyl ether is used as a solvent for Grignard reagents, fats, waxes, oil, etc.

Phenols :

1. Phenol is used in preparation of phenol formaldehyde resin For example : bakelite.
2. Phenols are used as antiseptic in common products like air freshners, deodarants, mouthwash, calamine lotions, floor cleaners, etc.

Exercises

1. Choose the correct option.

i. Which of the following represents the increasing order of boiling points of (1), (2) and (3)?

(1) CH_3-CH_2-CH_2-CH_2-OH

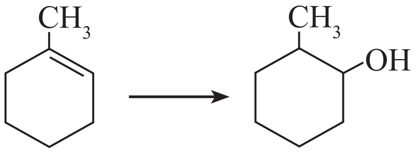
(2) $(CH_3)_2CHOCH_3$

(3) $(CH_3)_3COH$

A. (1) < (2) < (3) B. (2) < (1) < (3)

C. (3) < (2) < (1) D. (2) < (3) < (1)

ii. Which is the best reagent for carrying out following conversion ?



A. $LiAlH_4$ B. Conc. H_2SO_4, H_2O

C. H_2/Pd D. B_2H_6, H_2O_2-NaOH

iii. Which of the following substrate will give ionic organic product on reaction ?

A. CH_3-CH_2-OH + Na

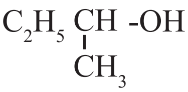
B. CH_3-CH_2-OH + $SOCl_2$

C. CH_3-CH_2-OH + PCl_5

D. CH_3-CH_2-OH + H_2SO_4

iv. Which is the most resistant alcohol towards oxidation reaction among the follwoing ?

A. CH_3-CH_2-OH B. $(CH_3)_2$CH-OH

C. $(CH_3)_3$C-OH D. 
$C_2H_5\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-OH}$

v. Resorcinol on distillation with zinc dust gives

A. Cyclohexane B. Benzene

C. Toluene D. Benzene-1, 3-diol

vi. Anisole on heating with concerntrated HI gives

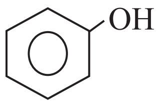
A. Iodobenzene

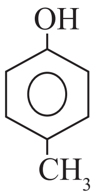
B. Phenol + Methanol

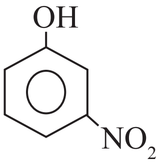
C. Phenol + Iodomethane

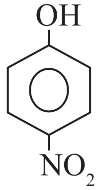
D. Iodobenzene + methanol

vii. Which of the following is the least acidic compound ?

A. 

B. 

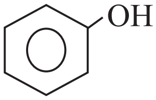
C. 

D. 

viii. The compound incapable of hydrogen bonding with water is ......

A. CH_3-CH_2-O-CH_3

B. CH_3-CH_2-CH_2-CH_3

C. 

D. CH_3-CH_2-CH_2-OH

ix. Ethers are kept in air tight brown bottles because

A. Ethers absorb moisture

B. Ethers evaporate readily

C. Ethers oxidise to explosive peroxide

D. Ethers are inert

x. Ethers reacts with cold and concentrated H_2SO_4 to form

A. oxonium salt B. alkene

C. alkoxides D. alcohols

2. Answer in one sentence/ word.

i. Hydroboration-oxidation of propene gives.....

ii. Write the IUPAC name of alcohol having molecular formula $C_4H_{10}O$ which is resistant towards oxidation.

iii. Write structure of optically active alcohol having molecular formula $C_4H_{10}O$

iv. Write name of the electrophile used in Kolbe's Reaction.

3. Answer in brief.

i. Explain why phenol is more acidic than ethyl alcohol.

ii. Explain why p-nitrophenol is a stronger acid than phenol.

iii. Write two points of difference between properties of phenol and ethyl alcohol.

iv. Give the reagents and conditions necessary to prepare phenol from

a. Chlorobenzene

b. Benzene sulfonic acid.

v. Give the equations of the reactions for the preparation of phenol from isopropyl benezene.

vi. Give a simple chemcial test to distinguish between ethanol and ethyl bromide.

4. An ether (A), $C_5H_{12}O$, when heated with excess of hot HI produce two alkyl halides which on hydrolysis form compound (B)and (C), oxidation of (B) gave and acid (D), whereas oxidation of (C) gave a ketone (E). Deduce the structural formula of (A), (B), (C), (D) and (E).

5. Write structural formulae for

a. 3-Methoxyhexane

b. Methyl vinyl ether

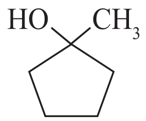
c. 1-Ethylcyclohexanol

d. Pentane-1,4-diol

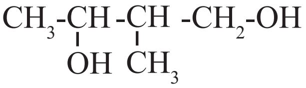
e. Cyclohex-2-en-1-ol

6. Write IUPAC names of the following

i.

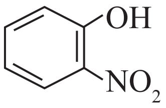


ii.

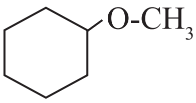


$$CH_3\text{-}\underset{OH}{CH}\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}OH$$

iii.



iv.



Activity :

- **Collect information about production of ethanol as byproduct in sugar industry and its importance in fuel economy.**
- **Collect information about phenols used as antiseptics and polyphenols having antioxidant activity.**