UNIT 18

ALCOHOLS, PHENOLS AND ETHERS

Learning Outcomes:

After carefully studying this unit and working the exercise, students will be able to.

- Explain nomenclature, structure and acidity of alcohols as exemplified by ethanol.
- Describe the preparation of alcohols by reduction of aldehydes, ketones, carboxylic acids and esters.
- Explain reactivity of alcohols.
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidative cleavage of 1, 2 –diols.
- Discuss thiols (RSH).
- Explain the nomenclature, structure and acidity of phenols.
- Describe the preparation of phenol from benzene sulphonic acid, chlorobenzene, acidic oxidation of cumene and hydrolysis of diazonium salts.
- Discuss the reactivity of phenol and their chemistry by electrophilic aromatic substitution, reaction with sodium metal and oxidation.
- Differentiate between alcohol and phenol.
- Describe isomerism in alcohols and phenols.
- Identify ethers from their formula.

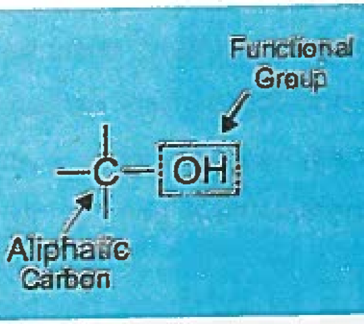
18.1 ALCOHOLS

Introduction:

Alcohols, phenols and ethers are derivatives of water. In alcohol one H of H_2O has been replaced by an alkyl group. In phenol one H is replaced by an aromatic ring, whereas in ether both H have been replaced by two alkyl groups.

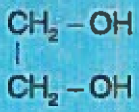
$R-OH$	$Ar-OH$	$R-\ddot{\underset{\cdot\cdot}{O}}-R$
Alchol	Phenol	Ether

Alcohols are organic compounds, in which a hydroxyl group $(-OH)$ is attached to an aliphatic carbon atom. Hydroxyl group is the functional group of alcohols. The general formula of alcohols is $R-OH$ or $C_nH_{2n+1}OH$ e.g methyl alcohol (CH_3OH)



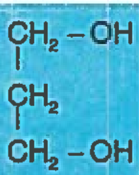
Alcohols may be monohydric, dihydric, trihydric or polyhydric, depending upon the number of $-OH$ groups in a molecule

CH_3-CH_2-OH ,



$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array}$$

,



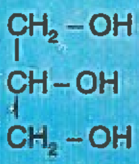
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2\\ |\\ CH_2-OH\end{array}$$

Ethy alcohol
(Ethanol)
Monohydric alcohol

Ethylene glycol
(1,2-Ethandiol)
OR
Ethan, 1,2-diol

Trimethylene glycol
(1,3-propanediol)
OR
Propa, 1,3-diol

Dihydric alcohol



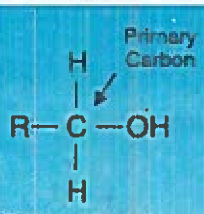
$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array}$$

Glycerol
(1,2,3-Propanetriol) OR Propa,1,2,3,-triol
Trihydric alcohol

<u>1996</u>-IUPAC system

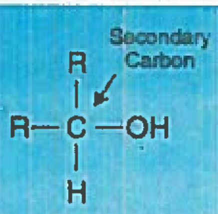
Dihydric alcohols (diols) are usually called glycols because of their sweet taste. (Greek glycys= Sweet).

- Monohydric alcohols may be primary, secondary or tertiary. When the hydroxyl group is attached to the primary carbon atom, it is classified as primary alcohol but when the hydroxyl group is attached to the secondary or tertiary carbon atom, the alcohol is accordingly classified as secondary or tertiary alcohol.



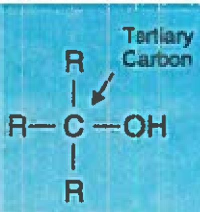
$$\begin{array}{c}H\\ |\\ R-C-OH\\ |\\ H\end{array}$$

Primary alcohol



$$\begin{array}{c}R\\ |\\ R-C-OH\\ |\\ H\end{array}$$

Secondary alcohol



$$\begin{array}{c}R\\ |\\ R-C-OH\\ |\\ R\end{array}$$

Tertiary alcohol

18. 1.1 Nomenclature

Alcohols are named by the following two systems.

a. Common System. b. IUPAC System.

a. Common System:

In this system, alcohols $(R-OH)$ are named "Alkyl Alcohols". That is alkyl group (R) of the alcohol is named first, which is followed by the word alcohol. For example,

CH_3-OH

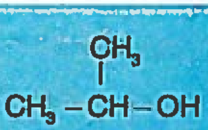
Methyl alcohol

CH_3-CH_2-OH

Ethyl alcohol

$CH_3-CH_2-CH_2-OH$

n –Propyl alcohol



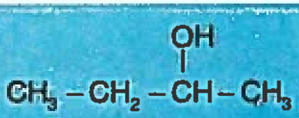
$CH_3-\overset{\overset{CH_3}{|}}{C}H-OH$

Isopropyl alcohol

For higher members in the series, it becomes necessary to indicate, whether a particular alcohol is primary (pri.), secondary (sec.) or tertiary (ter.) For example,

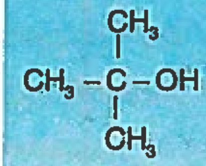
$CH_3-CH_2-CH_2-CH_2-OH,$

n –Butyl alcohol



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

sec –Butyl alcohol



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

ter –Butyl alcohol

b. IUPAC System:

In this system alcohols are named as "alkanols". That is, the final "e" of the corresponding alkane is replaced by "-ol".

The IUPAC rules are:

1. Select the longest continuous carbon chain containing the –OH group.
2. Name this chain as "alkanol". That is, drop the ending "e" of the corresponding alkane and add "ol" as suffix. This will serve as the parent name or stem name of the alcohol.
3. Number the chain from one end or the other, so as to give the carbon carrying the –OH group, the lowest possible number.
4. Mention the position of the hydroxyl group by putting its number before the parent name or before the "-ol".
5. Indicate the positions of the other substituents (if any) using the numbers of the carbon atoms, to which they are attached.
6. The substituents, along with their positions, are named in alphabetical order before the parent name.
7. If the number of carbon atoms carrying the hydroxyl group is the same from either side, then number the chain from the end which is heavily substituted.
8. In case of dihydric, trihydric and polyhydric alcohols, the prefix di, tri, tetra etc is used before "–ol", alongwith the numbers of the carbon atoms to which these hydroxyl groups are attached.
9. If more than one hydroxyl groups are attached to the same carbon atom, the number of that carbon atom is repeated.

The following examples will illustrate the above rules.

1. CH_3-OH

Methanol

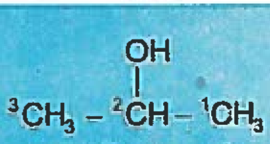
2. CH_3-CH_2-OH

Ethanol

3. ${}^3CH_3-{}^2CH_2-{}^1CH_2-OH$

1 –Propanol

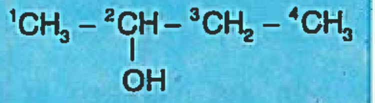
4.



$${}^3CH_3-{}^2\overset{\overset{OH}{|}}{C}H-{}^1CH_3$$

2 –Propanol
Prop-2-ol

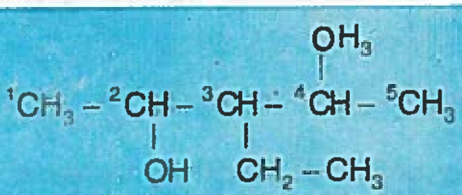
5.



$${}^1CH_3-{}^2\underset{\underset{OH}{|}}{C}H-{}^3CH_2-{}^4CH_3$$

2 –Butanol (or But-2- ol)

6.

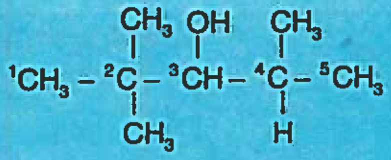


$${}^1CH_3-{}^2\underset{\underset{OH}{|}}{C}H-{}^3\underset{\underset{CH_2-CH_3}{|}}{C}H-{}^4\overset{\overset{OH_3}{|}}{C}H-{}^5CH_3$$

3 –Ethyl -4 –methyl -2 –pentanol

(or 3 –Ethyl -4 –methyl–pent -2–ol)

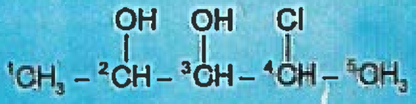
7.



$${}^1CH_3-{}^2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-{}^3\overset{\overset{OH}{|}}{C}H-{}^4\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-{}^5CH_3$$

2, 2, 4 –Trimethyl pent -3 -ol.

8.

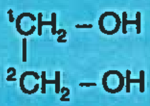


$${}^1CH_3-{}^2\overset{\overset{OH}{|}}{C}H-{}^3\overset{\overset{OH}{|}}{C}H-{}^4\overset{\overset{Cl}{|}}{C}H-{}^5CH_3$$

4 –Chloropenta -2,3-diol.

or (4-chloro-2,3-pentadiol)

9.

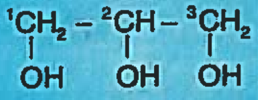


$$\begin{array}{l}{}^1CH_2-OH\\ |\\ {}^2CH_2-OH\end{array}$$

Ethane -1,2 –diol

or (1,2-Ethanediol)

10.



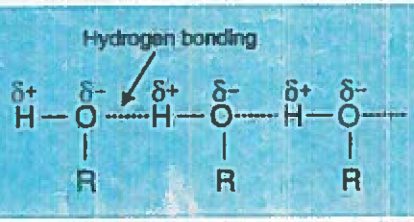
$${}^1\underset{\underset{OH}{|}}{CH_2}-{}^2\underset{\underset{OH}{|}}{C}H-{}^3\underset{\underset{OH}{|}}{CH_2}$$

Propa -1,2,3 –triol

or (1,2,3-Propan triol)

18.1.2 Physical Properties

Lower alcohols are colourless, toxic liquids. They have characteristic sweet smell. The boiling points of alcohols are much higher than those of corresponding alkanes. It is due to hydrogen bonding among the alcohol molecules.



Boiling points of alcohols increase regularly with the increase in the number of carbon atoms.

Table 18.1 Boiling point of some alcohols.

Name	Structure and Name	Boiling Points (°C)
Methanol	CH_3-OH	64.5
Ethanol	CH_3-CH_2-OH	78.3
1 –Propanol	$CH_3-CH_2-CH_2-OH$	97.0
1 –Protanol	$CH_3-CH_2-CH_2-CH_2-OH$	118.0
1 –Pentanol	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	138.0

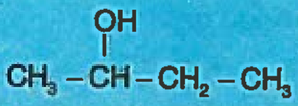
However, among the isomeric alcohols, as the branching increases, the boiling points decrease.

For Example:

$CH_3-CH_2-CH_2-CH_2-OH$

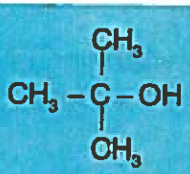
1 –Butanol OR (But, 1-ol)

(BP 118°C)



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

2 –Butanol
OR (But, 2-ol)
(BP 99°C)



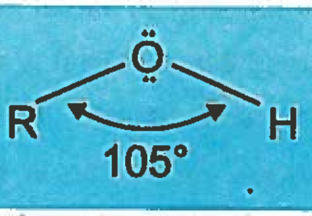
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

2–Methyl-2–Propanol
(2-Methyl Prop,2-ol)
(BP 83°C)

Lower alcohols (C_1-C_3) are completely soluble in water in any proportion. However the solubility of higher alcohols in water falls rapidly.

18. 1.3 Structure of Alcohols

Alcohol are alkyl derivatives of water molecules. Water molecule has an angular structure with H–O–H bond angle slightly smaller than tetrahedral angle (109.5°). Alcohols molecule have a similar geometry where R–O–H angle is 105°.



18. 1.4 Acidity of Alcohols

Alcohols are acidic in nature. It is because the O–H bond in alcohols is polar due to difference in electronegativities of the two atoms.

$$R-\overset{\delta-}{O}-\overset{\delta+}{H}$$

This allows the release of hydrogen atom as proton (H^+). Due to this acidic behaviour, alcohols react with sodium or potassium to form alkoxide with the liberation of hydrogen gas.

$$\underset{\text{Alcohol}}{2ROH} + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RO^-Na^+} + H_2\uparrow$$

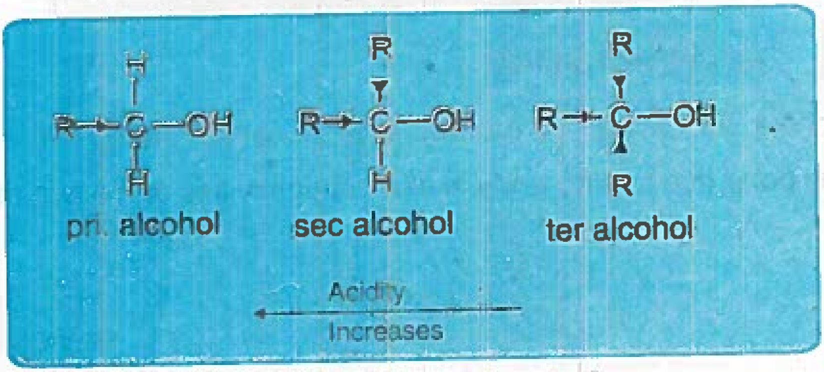
$$\underset{\text{Ethanol}}{2CH_3CH_2OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{CH_3CH_2ONa} + H_2\uparrow$$

However, alcohols are very weakly acidic with Ka value 10^{-16} to 10^{-18}

$$\underset{\text{Water}}{H-OH} \longrightarrow H^+ + OH^- \ (Ka = 1\times10^{-14})$$

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow RO^- + H^+ \ (Ka = 1\times10^{-16} - 1\times10^{-18})$$

The alkyl group in alcohols releases electrons (electron donating group) towards the oxygen atom, increasing its partial negative charge and hence the release of proton becomes difficult. That is why the alcohols are less acidic than water. Tertiary alcohols are less acidic than secondary alcohols and secondary alcohols are less acidic than primary alcohols.



It is to be noted that alcohols are not acidic enough to react with aqueous NaOH or KOH.

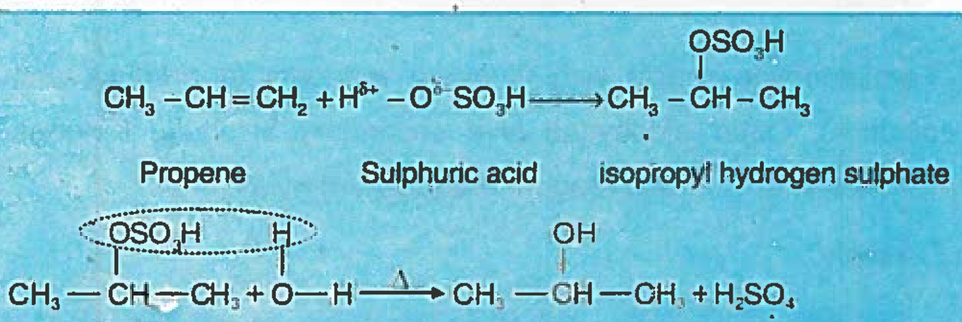
$$R-OH + NaOH \longrightarrow \text{No Reaction}$$

18. 1.5 Preparations of Alcohols

Alcohols can be prepared by the following methods.

18.1.5.1 Hydration of Alkenes:

Alkenes react with cold concentrated sulphuric acid to produce alkyl hydrogen sulphates, which on hydrolysis yield alcohols. Unsymmetrical alkenes follow the Markovnikov's rule.



$$CH_3-CH=CH_2 + H^{\delta+}-O^{\delta-}SO_3H \longrightarrow CH_3-\overset{\overset{\large OSO_3H}{|}}{C}H-CH_3$$

Propene Sulphuric acid isopropyl hydrogen sulphate

$$CH_3-\overset{\overset{\large OSO_3H}{|}}{C}H-CH_3 + \overset{\overset{\large H}{|}}{O}-H \xrightarrow{\Delta} CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_3 + H_2SO_4$$

Isopropyl alcohol
(2-Propanol) OR (Prop, 2-ol)

18.1.5.2 Hydrolysis of Alkyl halides:

Alcohols can be prepared by the hydrolysis of alkyl halides by means of water or an aqueous alkali.

$$CH_3I + KOH \xrightarrow[H_2O]{\Delta} CH_3-OH + KI$$

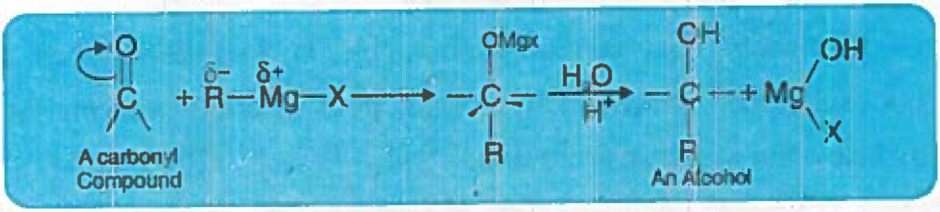
Methyl iodide Methyl alcohol

$$CH_3-CH_2-Br + KOH \xrightarrow[H_2O]{\Delta} CH_3-CH_2-OH + KBr$$

Ethyl bromide Ethyl alcohol

18.1.5.3 Reaction of RMgX with Aldehydes and Ketones (Grignard Synthesis):

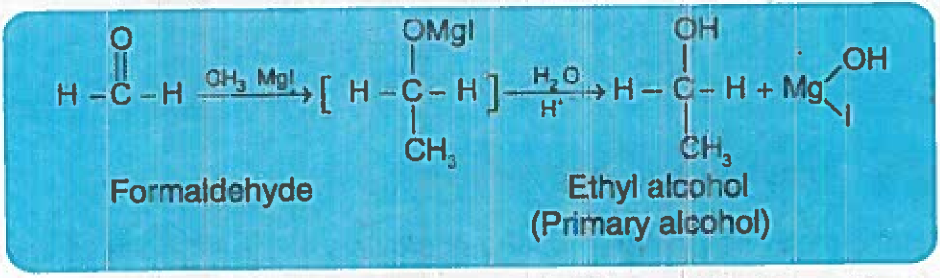
Grignard reagent $(R-Mg-X)$ adds to the carbon –Oxygen double bond $(-\overset{\overset{O}{\|}}{C}-)$ of the carbonyl compound to form an addition compound which on acid hydrolysis gives alcohol.



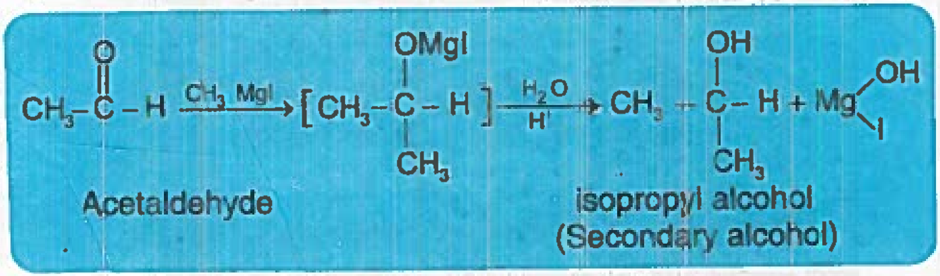
$$>C=O + \overset{\delta-}{R}-\overset{\delta+}{Mg}-X \longrightarrow -\overset{\overset{OMgX}{|}}{\underset{\underset{R}{|}}{C}}- \xrightarrow[H^+]{H_2O} -\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}- + Mg\begin{matrix}OH\\X\end{matrix}$$

Formaldehyde reacts with Grignard reagents to produce primary alcohols. Other aldehydes give secondary alcohols. Ketones on reaction with Grignard reagent produce tertiary alcohols.

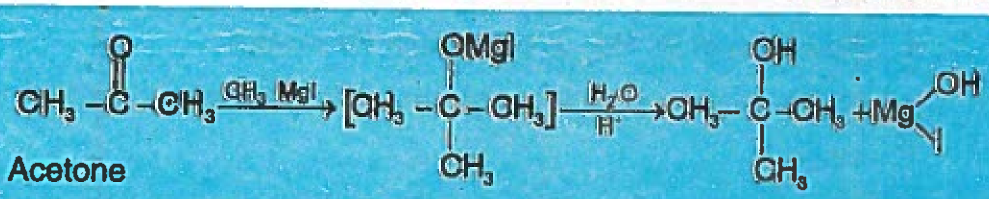
For Example:



$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{CH_3MgI} \left[H-\overset{\overset{OMgI}{|}}{\underset{\underset{CH_3}{|}}{C}}-H\right] \xrightarrow[H^+]{H_2O} H-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H + Mg\begin{matrix}OH\\I\end{matrix}$$



$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{CH_3MgI} \left[CH_3-\overset{\overset{OMgI}{|}}{\underset{\underset{CH_3}{|}}{C}}-H\right] \xrightarrow[H^+]{H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H + Mg\begin{matrix}OH\\I\end{matrix}$$



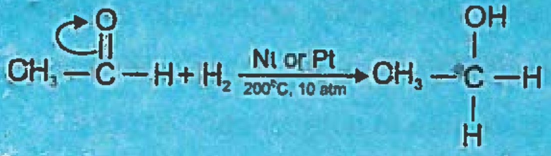
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3MgI} [CH_3-\underset{CH_3}{\overset{OMgI}{C}}-CH_3] \xrightarrow[H^+]{H_2O} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3 + Mg\begin{smallmatrix}OH\\I\end{smallmatrix}$$

Acetone

2-Methyl-2-Propanol
(Tertiary alcohol)

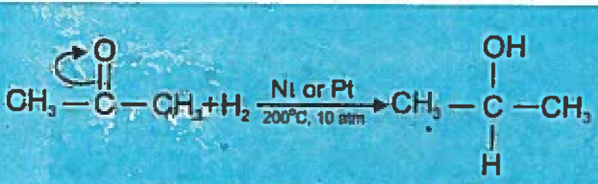
18.1.5.4 Reduction of Aldehydes and ketones:

Carbonyl compounds can easily be reduced to alcohols under different conditions. Aldehydes produce primary alcohols while ketones produce secondary alcohols. Reduction (Hydrogenation) is carried out in the presence of metal catalyst such as Ni, Pt or Pd at elevated temperatures (200°C) and pressure (10 atmosphere)



$$CH_3-\overset{\overset{O}{\|}}{C}-H+H_2 \xrightarrow[200^\circ C,\ 10\ atm]{Ni\ or\ Pt} CH_3-\underset{H}{\overset{OH}{C}}-H$$

Ethanol
(A Primary alcohol)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+H_2 \xrightarrow[200^\circ C,\ 10\ atm]{Ni\ or\ Pt} CH_3-\underset{H}{\overset{OH}{C}}-CH_3$$

2-Propanol
(A Secondary alcohol)

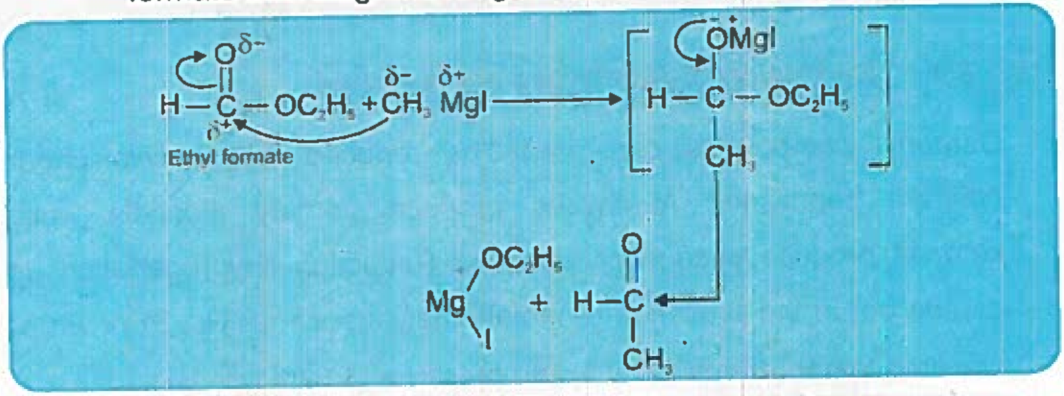
18.1.5.5 Reaction of R –Mg –X with Esters:

Formate esters on reaction with Grignard reagent produce secondary alcohols while other esters form tertiary alcohols.

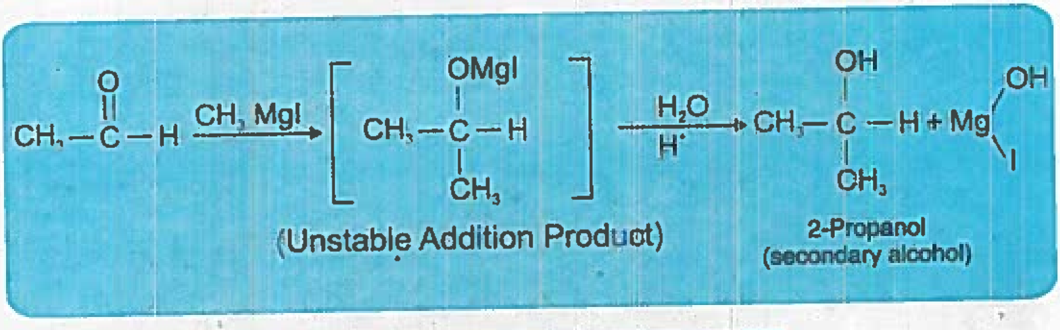
a. Reaction of R- Mg –X with Ethyl Formate:

In this case, a secondary alcohol is formed which involves two steps.

Step 1: An aldehyde is first formed by the reaction of ethyl formate with Grignard reagent.



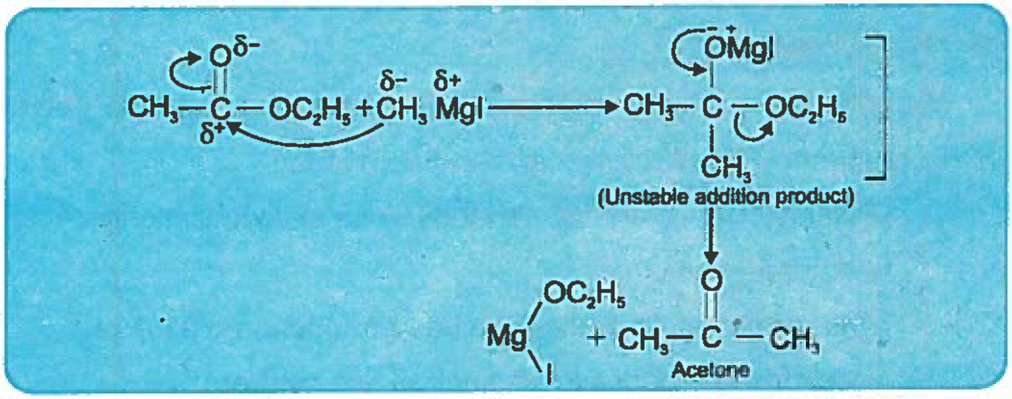
Step 2: The aldehyde then reacts with another molecule of the Grignard reagent to form an unstable addition product which on hydrolysis gives rise to a secondary alcohol.



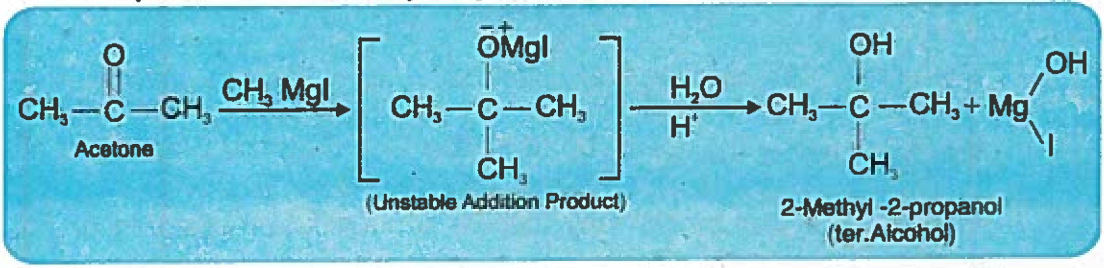
b. Reaction of R –Mg –X with Ethyl Acetate:

In this case a tertiary alcohol is formed which also involves two steps.

Step 1: A ketone is first formed by the reaction of ethyl acetate with Grignard reagent.

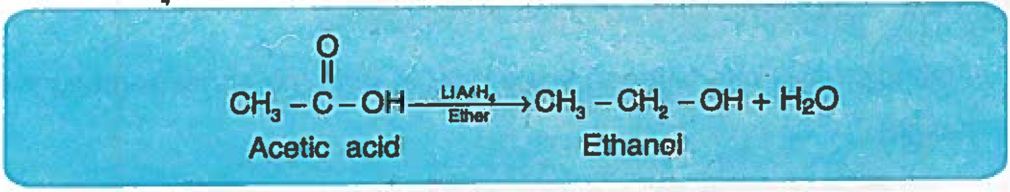


Step 2: The Ketone (in this case the acetone) then reacts with another Grignard reagent molecule to give an unstable addition product which on hydrolysis forms a tertiary alcohol.

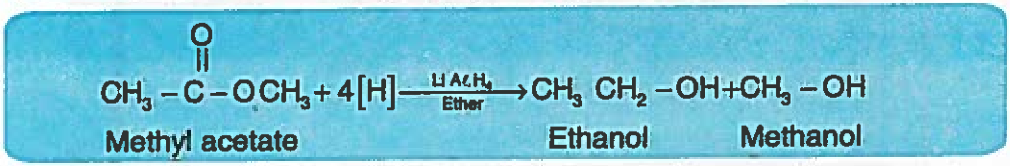


18.1.5.6 Reduction of Carboxylic Acids and Esters:

Both carboxylic acids and esters can be reduced to Primary alcohols with $LiA\ell H_4$.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\text{Ether}]{LiA\ell H_4} CH_3-CH_2-OH + H_2O$$



$$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3+4[H] \xrightarrow[\text{Ether}]{LiA\ell H_4} CH_3\ CH_2-OH+CH_3-OH$$

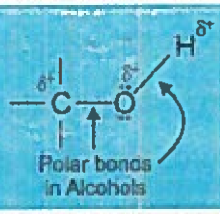
Carboxylic acids cannot be reduced with H_2/Ni or $Na+C_2H_5-OH$.

18. 1.6 Reactivity:

Alcohols are reactive compounds. They readily react with polar or ionic reagents. This reactivity can be attributed to:

i. Polarity of C – O and O – H bonds since oxygen is highly electronegative.

ii. The oxygen atom of alcohols has two unshared pairs of electrons and hence is an electron rich centre.



Polar bonds in Alcohols

Generally, the reactions of alcohols $(-\overset{|}{\underset{|}{C}}-\ddot{\underset{\cdot\cdot}{O}}-H)$ involve the fission of either the O – H bond or the C – O bond. Cleavages of either of the two bonds may involve a substitution reaction or an elimination reaction.

18. 1.7 Reactions of Alcohols:

18.1.7.1 Reaction with Halogen acids (HX):

Alcohols react with halogen acids (HX) to form the corresponding alkyl halides.

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

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}+HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3-CH_2-Br}+H_2O$$

The order of reactivity of different hydrogen halides with a particular alcohol is:

$$HI > HBr > HCl$$

HCl reacts only in the presence of a catalyst (anhydrous $ZnCl_2$), while HBr and HI require no catalyst. The order of reactivity of various alcohols with a particular hydrogen halide is:

Tertiary alcohol > Secondary alcohol> Primary alcohol.

Lucas Test: This test is used to distinguish between primary, secondary and tertiary alcohols. In this test alcohols are treated with a solution of HCl and $ZnCl_2$ (Lucas reagent) to form alkyl halides $(R-X)$, $ZnCl_2$ acts as a catalyst.

$$\underset{\text{Alcohol}}{R-OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{Alkyl halides}}{R-Cl} + H_2O$$

The three types of alcohols undergo this reaction at different rates. Tertiary alcohols react with Lucas reagent immediately. Secondary alcohols react some what slower. Primary alcohols react even more slowly.

18.1.7.2 Reaction with thionyl Chloride ($SOCl_2$) and Phosphorous Trihalides (PX_3):

Alcohols react with thionyl chloride $(SOCl_2)$ to form alkyl chlorides.

$$\underset{\text{Ethyl Alcohol}}{CH_3CH_2-OH} + SOCl_2 \longrightarrow \underset{\text{Ethyl Chloride}}{CH_3-CH_2-Cl} + SO_2 + HCl$$

Phosphorous Trihalides (PX_3) also form alkyl halides with alcohols.

$$3CH_3-CH_2-OH+PBr_3 \longrightarrow 3CH_3-CH_2-Br+H_3PO_3$$

Ethyl alcohol Ethyl bromide

$$3CH_3-OH+PI_3 \longrightarrow 3CH_3-I + H_3PO_3$$

Methyl alcohol Methyl iodide

18.1.7.3 Dehydration:

Alcohols, when treated with concentrated sulphuric acid at 170°C undergo dehydration to form alkenes. In case of ethyl alcohol, ethylene is formed.

$$CH_3-CH_2-OH \xrightarrow[170^\circ C]{Conc\ H_2SO_4} CH_2=CH_2+H_2O$$

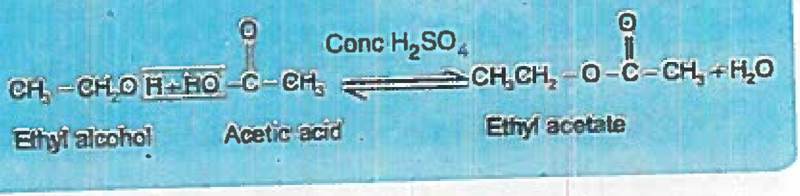
Ethyl alchol Ethylene

The order of rate of dehydration of different alcohols is

tertiary alcohols> secondary alcohols> Primary alcohols.

18.1.7.4 Reaction With Carboxylic Acids (Esterification):

Alcohols react with carboxylic acids to form esters. Concentrated H_2SO_4 is used as catalyst.



$$CH_3-CH_2O\boxed{H+HO}-\overset{O}{\overset{\|}{C}}-CH_3 \underset{}{\overset{Conc\ H_2SO_4}{\rightleftharpoons}} CH_3CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3+H_2O$$

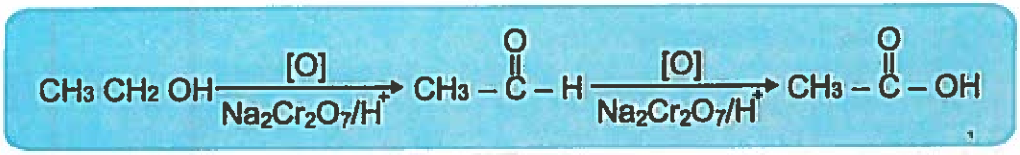
Ethyl alcohol Acetic acid Ethyl acetate

The reaction is reversible. The equilibrium can be shifted in the forward direction by removing water as soon as it is formed.

18.1.7.5 Oxidation:

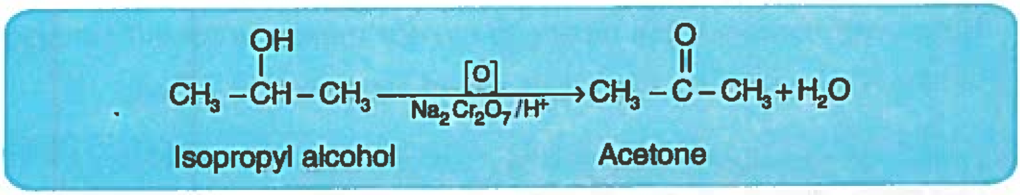
Using strong oxidizing conditions such as "$Na_2Cr_2O_7 + H_2SO_4$" or "$KMnO_4 + H_2SO_4$", alcohols can be oxidized to carbonyl compounds, and finally to acids.

Primary alcohols are first oxidized to aldehydes and then to acids.



$$CH_3CH_2OH \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{\overset{O}{\parallel}}{C}-H \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{\overset{O}{\parallel}}{C}-OH$$

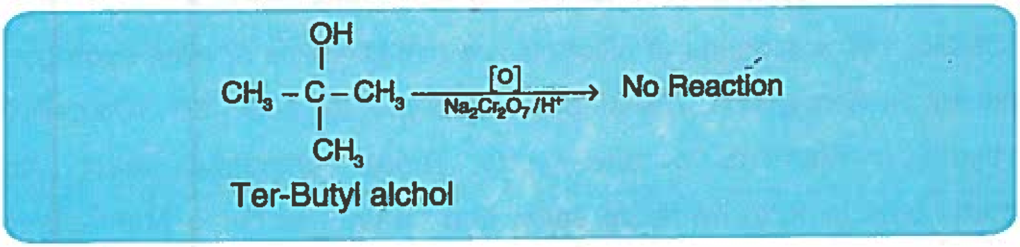
Secondary alcohols are first oxidized to corresponding ketones, whose further oxidation to carboxylic acids needs even more drastic conditions.



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3+H_2O$$

Isopropyl alcohol Acetone

Tertiary alcohols are stable to oxidation under normal conditions.

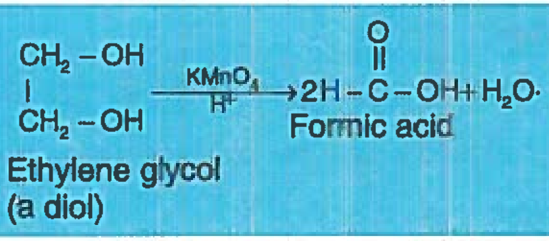


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} \text{No Reaction}$$

Ter-Butyl alchol

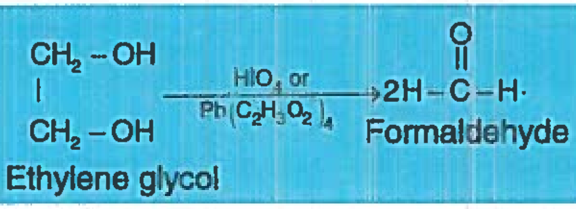
18.1.7.6 Cleavage of 1, 2 diols (Glycols):

1, 2 –diols (glycols), for example, ethylene glycol when treated with acidic $KMnO_4$ or $K_2Cr_2O_7$, results in the formation of formic acid by cleavage of $C-C$ bond.



$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[H^+]{KMnO_4} 2H-\overset{\overset{\large O}{\|}}{C}-OH + H_2O$$

But when treated with periodic acid or lead tetra acetate, ethylene glycol gives formaldehyde.



$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[Pb(C_2H_3O_2)_4]{HIO_4 \text{ or}} 2H-\overset{\overset{\large O}{\|}}{C}-H$$

18. 1.8 The Sulphur Analogues (Thiols, RSH):

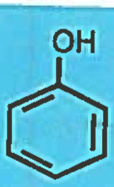
Both oxygen and sulphur belong to the same group VI of the periodic table. Thus, there are sulphur analogies of alcohols and ethers.

$R-OH$	$R-SH$	$R-O-R$	$R-S-R$
Alcohol	Thiol	Ether	Thioether

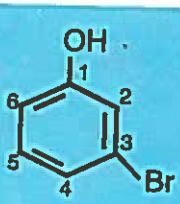
The Sulphur analogues of alcohols are called Thiols or alkyl hydrogen sulphides or Mercaptans. The functional group of thiols is $-SH$. It is called sulphydryl or Marcapto or thiol group. These compounds react with mercuric ions to form insoluble salts, and hence the name Mercaptans (Latin, mercurium captans = mercury catching). Methanthiol (CH_3SH) is a gas. Ethanthiol (C_2H_5SH) and higher members are colourless, volatile liquids at STP. Lower members have strong repulsive odours. For example, methanthiol and ethanthiol are added to natural gas in minute amounts to make gas leakage detectable by smell. Thiols have lower boiling points than the corresponding alcohols, due to lack of hydrogen bonding. They are insoluble in water but soluble in ethanol and ether.

18.2 Phenols

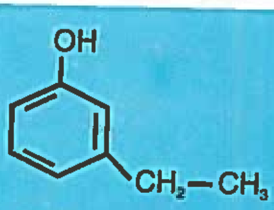
Introduction: Phenols are organic compounds in which –OH group is attached directly to an aromatic ring. Just like alcohols, they may also be monohydric, dihydric or polyhydric, depending upon the number of –OH groups attached per molecule. The word "phenol" is also used as the name of a specific compound "hydroxyl benzene". Some examples are.



Phenol



m - Bromophenol

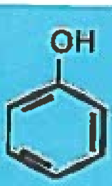


m - Ethylphenol

18. 2.1 Nomenclature:

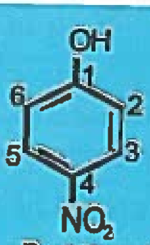
Phenols are usually named as derivatives of the parent phenol (C_6H_5OH).

Examples are:

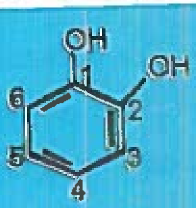


Phenol

m-Bromophenol
(3- Bromophenol)

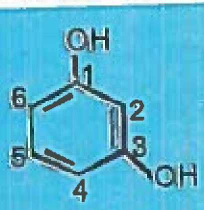


p - Nitrophenol
(4 - Nitrophenol)



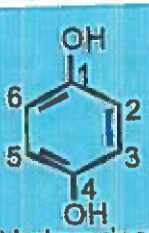
Catechol

(1,2-dihydroxy benzene)



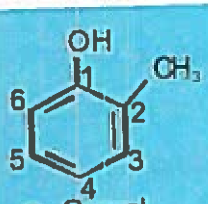
Resorcinol

(1,3-dihydroxy benzene)

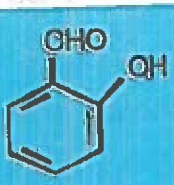


Hydroquinone

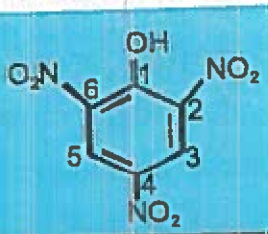
(1,4-dihydroxy benzene)



o - Cresol
(o - Methyl phenol)



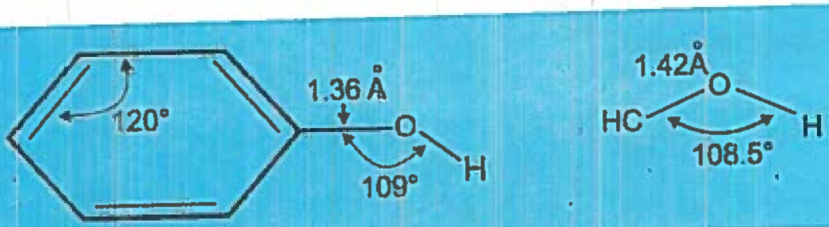
Salicylaldehyde
(o-Hydroxybenzaldehyde)



Picric acid
(2, 4, 6-Trinitrophenol)

18. 2.2 Structure of phenol:

In phenol molecule hydroxyl group (–OH) is attached to a benzene ring. The molecule is planar, with a C–O–H bond angle of 109°, almost the same as tetrahedral angle and not much different from the 108.5° C–O–H angle of methanol.



In phenol the six carbon atoms are sp^2 hybridized forming a hexagonal ring with internal angles of 120°. Since the bonds formed by sp^2 hybridized carbon, are shorter than those formed by sp^3 hybridized carbon, therefore the C–O bond length is slightly less than the C–O bond length in methanol.

18. 2.3 Physcisl Properties:

1. Phenols are colourless liquids or low melting crystalline solids at room temperature and pressure.
2. They have a characteristic odour.
3. The vapours of phenol itself is highly toxic.
4. The boiling points of phenols are slightly higher than the aliphatic alcohols of comparable molecular weights, due to the presence of stronger hydrogen bonding in phenols than in alcohols.
5. Due to stronger hydrogen bonding, phenols are more soluble in water than alcohols of comparable molecular mass. Above 65°C both phenols and water are miscible in all proportions.
6. The liquid phenol, containing 5% of water is known as carbolic acid and is used as disinfectant and germicide.

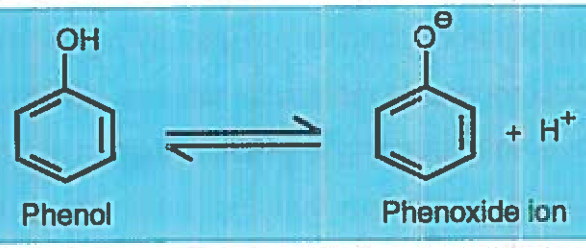
18. 2.4 Acidity of Phenols:

Phenols are much more acidic than alcohols but are less acidic than carboxylic acids or even water and carbonic acid. This is clear from the pKa values of these compounds.

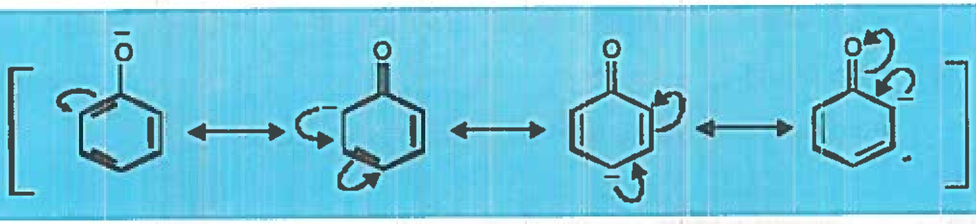
Table 18.2 ka & pka values of some compounds.

Compound	Formula	ka (approx)	pka
Phenol	Ar – OH	10^{-10}	10
Alcohols	R – OH	$10^{-16} - 10^{-18}$	16 – 18
Carboxylic acids	R – COOH	10^{-5}	5
Water	H – OH	10^{-7}	7

The acidic nature of phenols, as compared to alcohols, can be attributed to the formation of stable phenoxide ions after loss of proton.

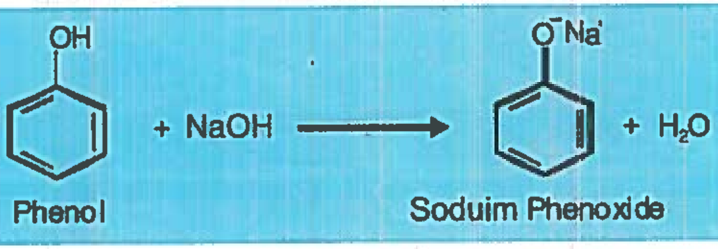


The phenoxide ion, thus formed is resonance stabilized.



The negative charge spreads throughout the benzene ring and is thereby dispersed. This delocalization of the charge accounts for the stability of the phenoxide ion.

Being acidic, phenol reacts with NaOH or Na metal to form salt.

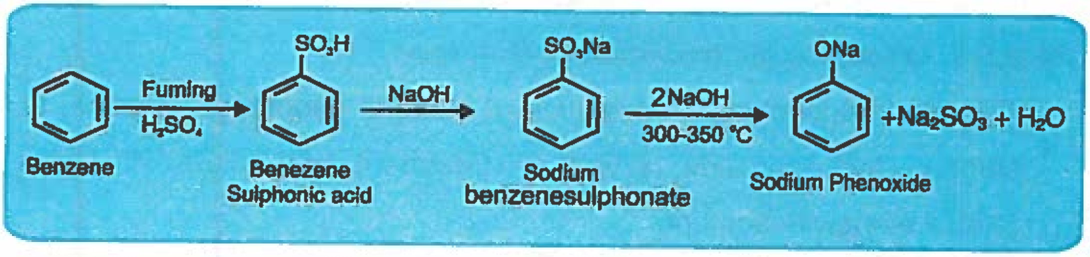


18. 2.5 Preparation of Phenols:

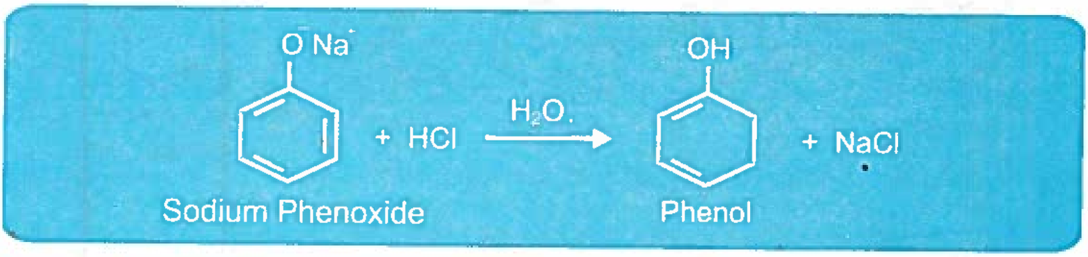
Phenols can be prepared by the following methods.

18.2.5.1 From Benzene Sulphonic Acid:

This method involves the fusion of sodium–benzene sulphonate with solid NaOH at 300 – 350°C.

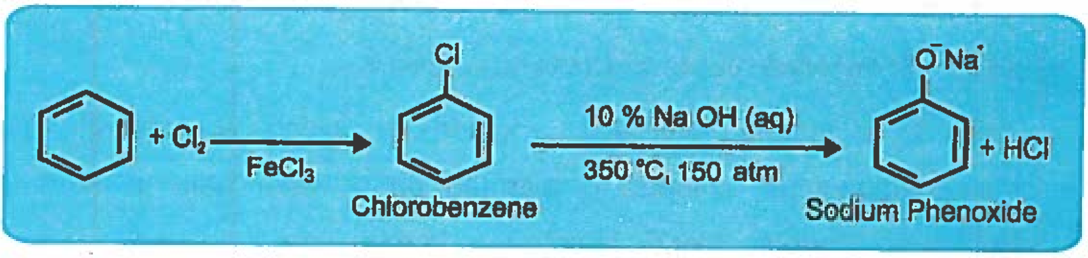


The resultant sodium phenoxide is then treated with dilute $HC\ell$ to form phenol.

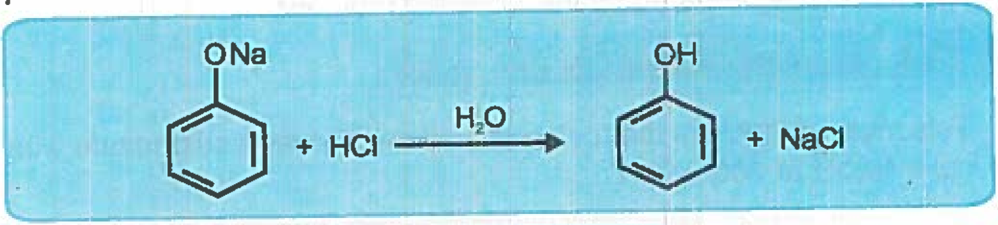


18.2.5.2 From Chlorobenzene:(Dow Process):

In this method, chlorobenzene is hydrolysed with aqueous NaOH at high temperature and pressure. This process was developed by Dow Chemical Company of USA in 1928.

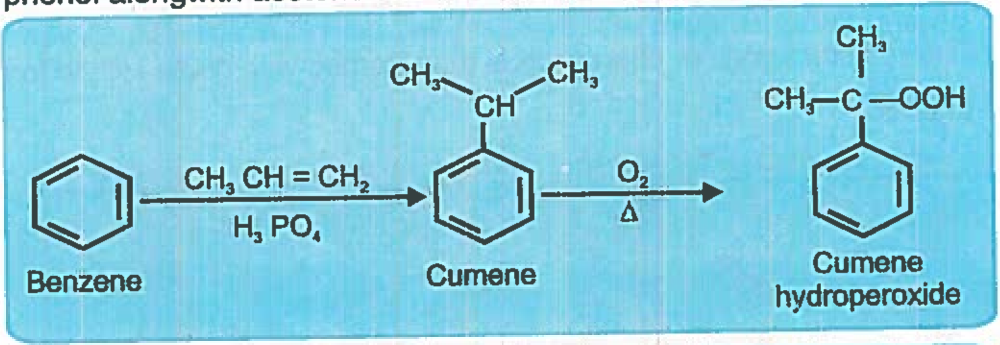


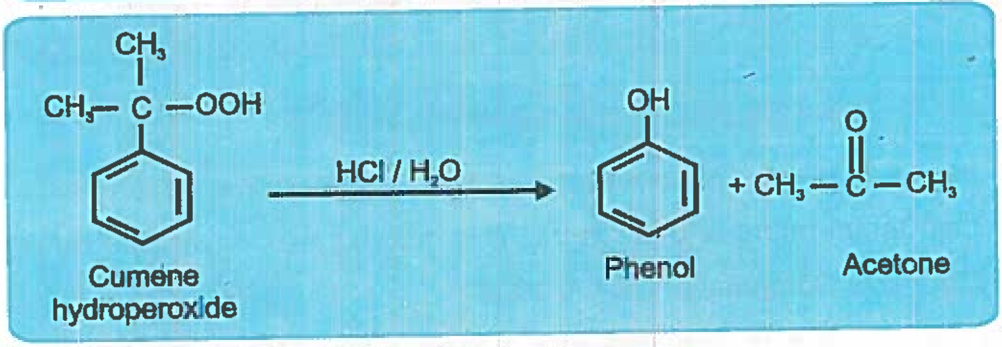
The resultant sodium phenoxide is then treated with dilute HCl to form phenol.



18.2.5.3 From Acidic oxidation of Cumene:

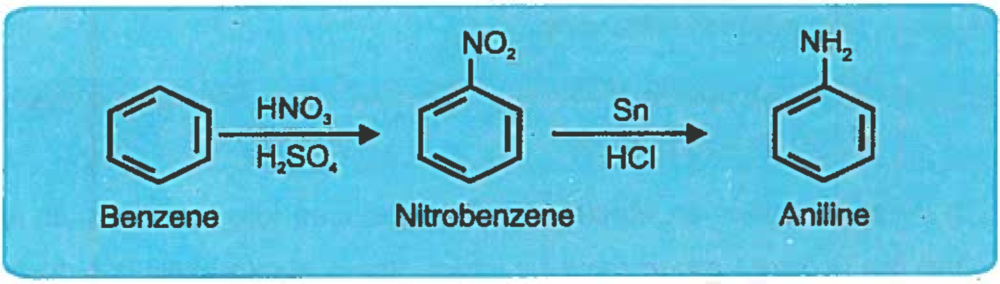
This method involves air oxidation of cumene (isopropyl benzene) to cumene hydroperoxide, which on treatment with dilute HCl forms phenol alongwith acetone.

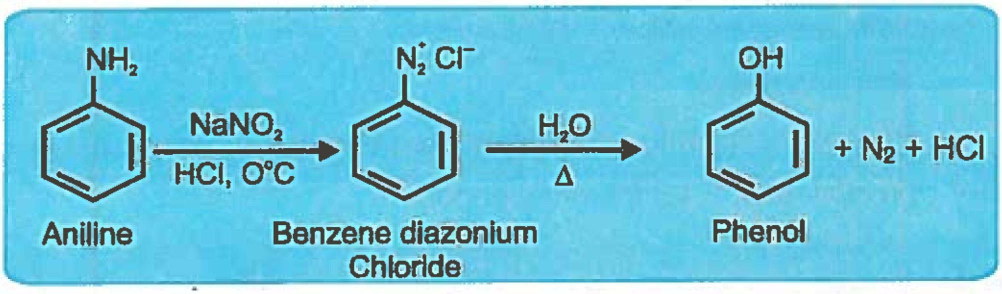




18.2.5.4 From Hydrolysis of Diazonium Salts:

This is a simple laboratory method in which a solution of benzenediazonium chloride is warmed on a water bath at 50°C. Benzenediazonium chloride is prepared from aniline.





Phenol is recovered by steam distillation and extracted with diethyl ether.

18. 2.6 Reactivity of Phenol:

Generally phenols exhibit two types of reactions. (1) reactions due to hydroxyl group and (2) reactions due to the aromatic ring.

In the first type of reactions, usually the $O-H$ bond is broken to form salts, ethers, esters etc. In the second type of reactions, the benzene ring of phenol undergoes electrophilic substitution reactions which are characteristic of most of the aromatic compounds.

The presence of hydroxyl group on the benzene ring in phenol increases electron density of the ring at ortho and para positions by giving its electron pair to the ring and hence increases the reactivity of the ring relative to benzene itself, for electrophillic substitution reactions.

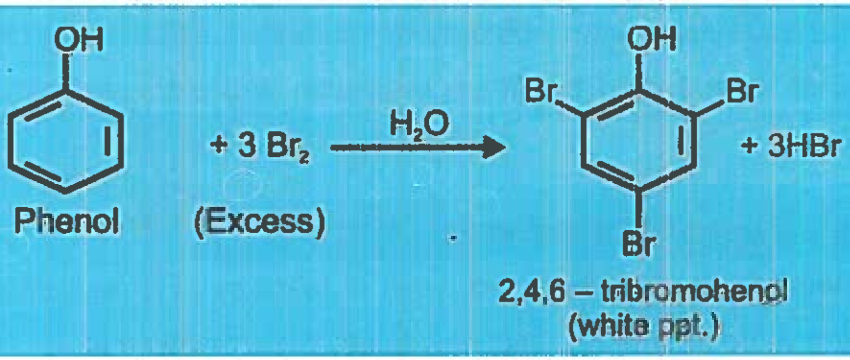
18. 2.7 Reactions of Phenols:

18.2.7.1 Electrophilic Aromatic Substitutions: (Reactions due to Benzene ring)

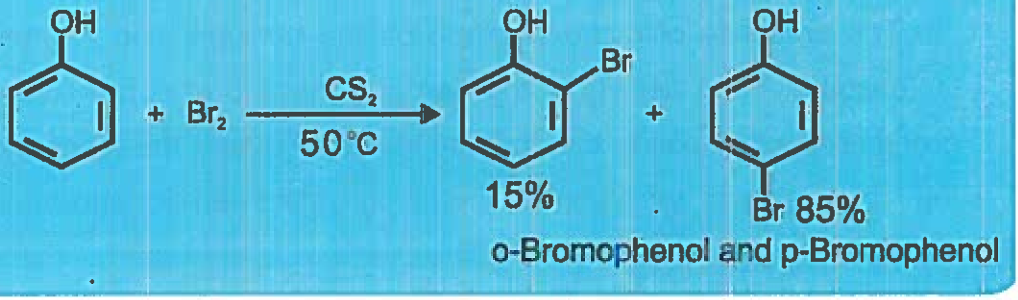
In these reactions an electrophile is introduced into the aromatic ring and the hydroxyl group remains intact. Some electrophilic substitution reactions are given below.

i. ***Halogenations:***

Phenol reacts with bromine water (aqueous bromine) to give a precipitate of 2,4,6 tribromophenol.

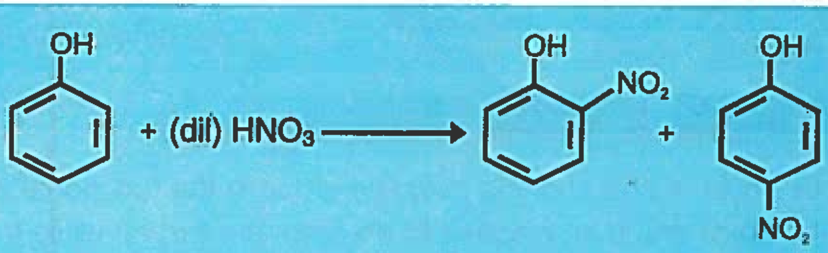


Chlorine reacts in the same way. In the presence of a non–polar solvent like CCl_4 or CS_2, a mixture of ortho and para–bromophenols is formed.



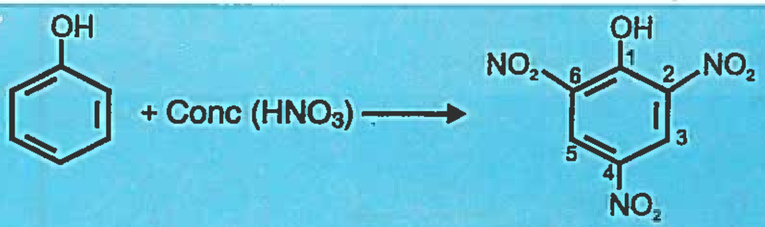
ii. *Nitration*:

With dilute HNO_3, phenol reacts to form ortho and para nitrophenol.



o- and p- Nitrophenol

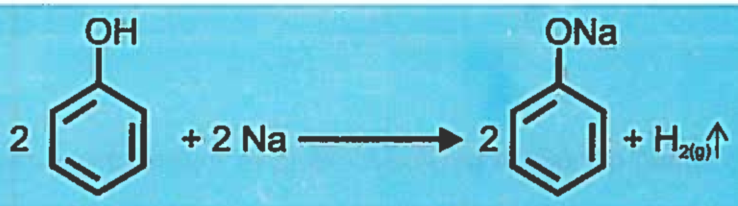
With concentrated HNO_3, picric acid (2,4,6 –trinitrophenol) is formed.



Picric acid
(2,4,6 –Trinitrophenol)

18.2.7.2 Reaction with Sodium Metal:

Phenol, being acidic in nature, reacts with sodium metal to form salt with the release of H_2 gas

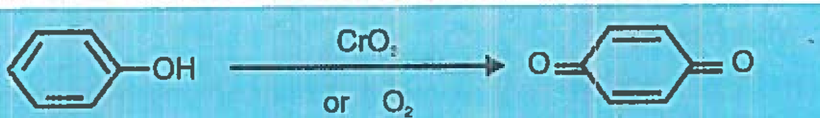


Phenol

Soduim Phenoxide

18.2.7.3 Oxidation:

Phenol undergoes oxidation with air or chromic acid to form p–benzoquinone.



p – Benzoquinone

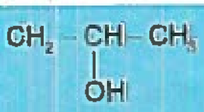
18.2.8 Difference Between Alcohol and Phenol:

In both alcohols and phenols hydroxyl group is the functional group. In phenols hydroxyl group is attached to an aromatic carbon while in alcohol the hydroxyl group is attached to carbon atom other than aromatic carbon.

For Example,

CH_3-OH
Methy alcohol

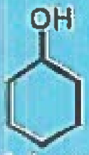
CH_3-CH_2-OH
Ethyl alcohol



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

2-Propanol

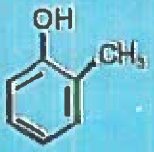
Cyclopentanol



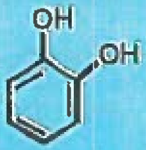
Cyclohexanol

are alcohols; and

Phenol



Cresol

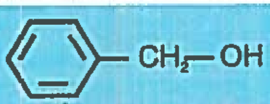


Catechol

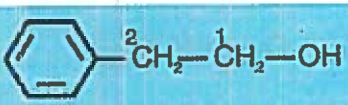
are phenols

Compounds which contain a hydroxyl group in a side chain attached to an aromatic ring are not phenols. They are called aromatic alcohols.

For example:



Benzyl alcohol
(an alcohol)



2 – Phenyl ethanol)
(an alcohol)

Society, Technology and Science

The common home disinfectant is chlorine bleach (a 5% solution of sodium hypochlorite), which is effective against most common pathogens, such as tuberculosis , hepatitis B and C, fungi etc.

The negative effect of disinfectant is that it is caustic to the skin, lungs, and eyes (especially at higher concentrations), it degrades in the presence of organic substances, it has a strong odor and extreme caution must be taken not to combine it with ammonia or any acid (such as vinegar), as this can cause noxious gases to be formed.

To use chlorine bleach effectively, the surface of item to be disinfected must be clean. In the bathroom special caution must be taken to wipe up urine first, before applying chlorine, to avoid reaction with the ammonia in urine, causing toxic gaseous by-products. Extreme caution must be taken to avoid contact with eyes and mucous membranes. Protective goggles and good ventilation are mandatory when applying concentrated bleach.

All disinfectants kill bacteria (called bactericidal). Some also kill fungi (fungicidal), bacterial spores (sporicidal) and/or viruses (virucidal).

The term biocide is a broad term for a substance that kills, inactivates or otherwise controls living organisms. It includes antiseptics and disinfectants, which combat micro-organisms, and also includes pesticides.

Antiseptics are antimicrobial substances that are applied to living tissue/skin to reduce the possibility of infection, sepsis, or putrefaction. Antiseptics are generally distinguished from antibiotics by the latter's ability to be transported through the lymphatic system to destroy bacteria within the body, and from disinfectants, which destroy microorganisms found on non-living objects.

The first person to demonstrate ether's use as anesthetic was Dr. Morton in 1846.

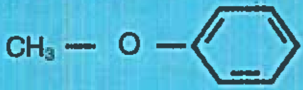
18.3 ETHERS:

Introduction:

Ethers are a class of compounds in which the oxygen atom is linked to two alkyl groups or two aryl groups or one alkyl and one aryl group. They can be represented by the general formula $R-O-R'$ where R and R' may be the same or different. Thus the functional group of ethers is $C-O-C$. Examples of ethers are:

CH_3-O-CH_3,
Dimethyl ether
(Methyl ether)

$CH_3-CH_2-O-CH_2-CH_3$
Diethyl ether
(Ethyl ether)



Methyl Phenyl ether

18. 3.1 Nomenclature:

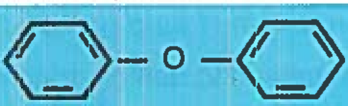
(A) Common System:

The two alkyl or aryl groups that are attached to the oxygen atom are named in alphabetical order and the word ether is added. If the two groups are the same, the prefix "di" is used.

For example:

$CH_3-CH_2-O-CH_2-CH_3$
Diethyl ether

$CH_3-O-C_2H_5$, $CH_3-O-C_6H_5$
Ethyl methyl ether Methyl phenyl ether



Diphenyl ether or
(Phenyl ether)

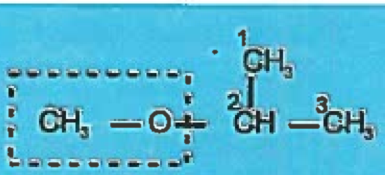
(B) IUPAC System:

In this system, ethers are generally named as alkoxy derivatives of hydrocarbons. The larger alkyl group is taken for parent name and the smaller alkyl group along with oxygen atom is named as alkoxy before the parent name.

For example:

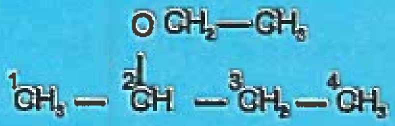
$\boxed{CH_3-O}-CH_2-CH_3$

Methoxyethane



$\boxed{CH_3-O}-\overset{\overset{1}{CH_3}}{\overset{|}{\overset{2}{C}H}}-\overset{3}{C}H_3$

2-Methoxy propane



$\overset{1}{C}H_3-\overset{\overset{O\,CH_2-CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$

2-Ethyoxy butane

18. 3.2 Preparation:

Ethers can be prepared by the following methods.

1. ***Dehydration of alcohols*:**

Symmetrical ethers (ethers with identical groups) are prepared by heating an excess of alcohol with concentrated H_2SO_4 at 140°C.

$$C_2H_5-OH+HO-C_2H_5 \xrightarrow[140°C]{H_2SO_4} C_2H_5-O-C_2H_5+H_2O$$

Ethanol Diethylether

The reaction conditions (Temp. = 140°C) must be well controlled otherwise at temperature higher than this the formation of alkenes is favoured.

2. *Williamson's Synthesis:*

In this methods, sodium alkoxide is treated with an alkyl halide.

$$ROH + Na \rightarrow \underset{\text{Soduim alkoxide}}{RONa} + H_2$$

$$\underset{\text{Sodium methoxide}}{CH_3-O^-Na^+} + \underset{\text{Bromoethane}}{C_2H_5-Br} \rightarrow \underset{\text{Ethyl methylether}}{CH_3-O-C_2H_5} + NaBr$$

18. 3.3 Physical Properties:

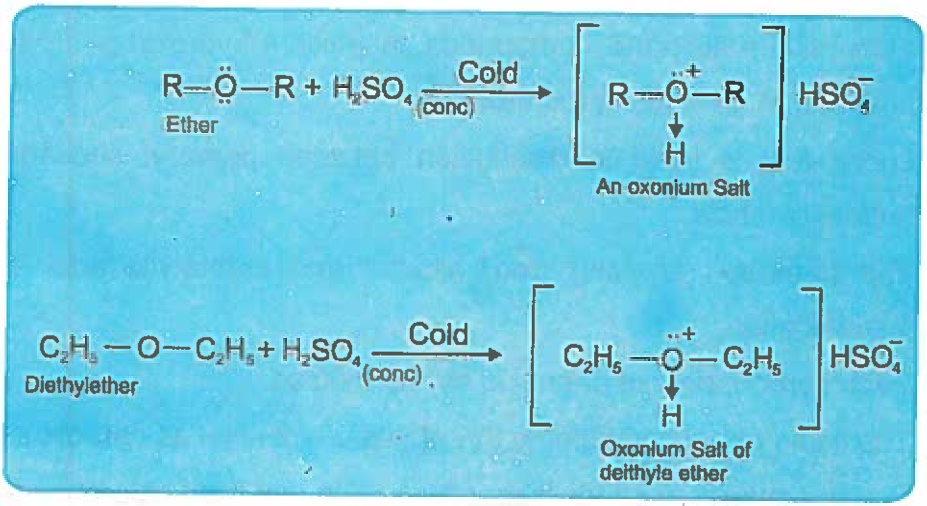
1. Dimethyl ether and ethyl methyl ether are gases at STP, while others are colourless volatile liquids with pleasant odours.
2. Ethers are highly inflammable.
3. They have much lower boiling points than those of alcohols of comparable molecular weights.
4. Low molecular weight ethers are soluble in water as they form hydrogen bonding with water.
5. Ethers are generally less denser than water.
6. They are readily soluble in organic solvents.

18. 3.4 Chemical Reactivity:

Ethers are quite stable compounds. They do not react with bases, active metals, oxidising agents and reducing agents. They are also stable to dilute acids. However, they form oxonium salts with strong concentrated acids.

1. Formation of Oxonium Salts:

Ethers react with cold concentrated HCl or H_2SO_4 to form oxonium salts. Ethers donate a pair of electrons to hydrogen ion to form these salts.



$$R-\ddot{\underset{\cdot\cdot}{O}}-R + H_2SO_{4\,(conc)} \xrightarrow{Cold} \left[R-\overset{\cdot\cdot +}{\underset{\substack{\downarrow\\ H}}{O}}-R \right] HSO_4^-$$

Ether

An oxonium Salt

$$C_2H_5-O-C_2H_5 + H_2SO_{4\,(conc)} \xrightarrow{Cold} \left[C_2H_5-\overset{\cdot\cdot +}{\underset{\substack{\downarrow\\ H}}{O}}-C_2H_5 \right] HSO_4^-$$

Diethylether

Oxonium Salt of deithyla ether

2. Reaction with halogen acids (HX):

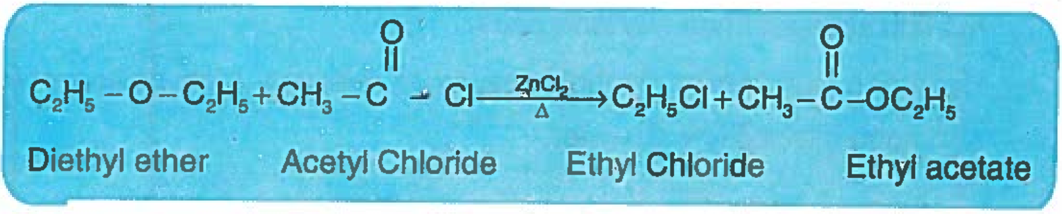
Ethers react with hot concentrated HI or HBr to form an alcohol and alkyl halide.

$$C_2H_5-O-C_2H_5 + HI \xrightarrow{\Delta} C_2H_5OH + C_2H_5-I$$

Ethyl iodide

3. Reaction with Acetyl Chloride:

Ethers react with acetyl chloride in the presence of anhydrous $ZnCl_2$, on heating, to form alkyl chloride and ethyl acetate.



$$C_2H_5-O-C_2H_5 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[\Delta]{ZnCl_2} C_2H_5Cl + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5$$

Diethyl ether Acetyl Chloride Ethyl Chloride Ethyl acetate

Key Points:

- Alcohols are aliphatic compounds, in which a hydroxyl group (–OH) is attached to aliphatic carbon atom.
- Lucas test is used to distinguish between primary, secondary and tertiary alcohols.
- The formation of ester from alcohol and carboxylic acid is called 'esterification'.
- Each carbon atom in phenol is sp^2 hybridized.
- The liquid phenol containing 5% of water is known as carbolic acid.
- Dow process is used for preparation of phenol from chlorobenzene and aquous NaOH at high pressure and temperature.
- Ethers are class of compounds in which, with oxygen atom two alkyl groups, two aryl groups or one alkyl and one aryl group are attached.
- General formula of ether is R–O–R.
- Ethers react with cold conc.HCl or H_2SO_4 to form oxomium salt.
- In Williamson's synthesis, sodium alkoxide is treated with an alkyl halide to produce ether.
- In case of alcohols, phenols and ether oxygen atom undergoes sp^3 hybridization and has two lone pairs.
- Hydrogen bonding in alcohols results in relatively high boiling points and good miscibility with water.

Exercise

Q1. Choose the correct option.

1. The reaction of alcohol with sodium produces

   (a) Ethane (b) Ethene (c) Alkoxide (d) Aldehyde

2. Oxidation of secondary alcohol gives

   (a) Organic acid (b) Ether
   (b) Aldehyde (d) Ketone

3. The compound 'x' when heated with dry silver oxide forms an ether identify 'x'

   (a) Alcohol (b) Phenol (c) Alkyl halide (d) Ether

4. Phenol on hydrogenation with H_2 in presence of Ni catalyst gives

   (a) Benzene (b) Toluene
   (c) Cyclohexanol (d) Aldehyde

5. Diethyl ether is prepared by passing vapours of ethanol over a catalyst under high pressure and temperature. The catalyst is

   (a) S_iO_2 (b) CuO (c) Ag_2O (d) Al_2O_3

6. Denatured alcohal is known as

   (a) Absolute alcohal (b) Wood spirit
   (b) Methylated spirit (d) Rectified spirit

7. A compound "x" is formed when the vapours of phenol are passed over red hot zinc dust. The compound "x" is called

   (a) Toluene (b) xylene (c) Benzene (d) Benzol

8. Ethoxyethane react with Con.H_2SO_4 to give

   (a) Oxonium ion (b) Oxoanion
   (c) Alkyl free radical (d) Zwitter ion

9. The secondary alcohols undergo nucleophilic substituion reaction by

   (a) SN^1 (b) SN^2

   (c) Both SN^1 and SN^2 (d) Neither SN^1 and SN^2

10. The appearance of cloudiness in the Lucas test for alcohol is due to formation of:

    (a) Alkyle chloride (b) Acid chlorides

    (c) Aldehydes (d) Ketones

Q II. Short questions:

1. What is the functional group of alcohols?
2. Indicate some physical properties of alcohol.
3. What is Lucas test?
4. Why phenol is more acidic than alcohols?
5. What is meant by primary, secondary and tertiary alcohols?
6. Why alcohol is easily protonated unlike phenol?
7. Differentiate between alcohol and phenol.
8. Enlist the physical properties of ether.

Q III. Long questions:

1. (a) Describe the method for preparation of diethyl ether from alcohol and sodium methoxide.

   (b) Write two chemical reactions of diethyl ether.

2. (a) What are phenols? Give method of preparation of phenol.

   (b) Discuss the acidic behaviour of phenol.

3. Give detail description of chemical properties of phenol.

4. Discuss the structure of alcohol.

5. (a) How alcohol can be prepared from Grignard reagents.

   (b) Mention the reaction for the formation of following compound from an alcohol.

   (a) Ethene (b) Ethlyacetate

   (c) Acetone (d) Formaldehyde