11

Organic Compounds with Functional Group Containing Oxygen (Part-1)

11.1 ALCOHOL

The hydroxy derivatives of alkanes are known as alcohols. These are obtained by replacement of one or more hydrogen atoms of alkanes by corresponding number of hydroxy groups.

$$\underset{\text{alkane}}{R-H} \xrightarrow[+OH]{-H} \underset{\text{alcohol}}{ROH}$$

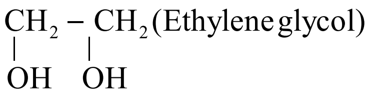
Alcohols with one, two, three or more hydroxyl group are termed mono, di, tri or polyhydric alcohols, respectively. Only one hydroxyl group should be linked with one carbon atom (C). If more than one hydroxyl groups are linked with one carbon atom then compound is unstable.

Example.

(i) Monohydric Alcohol

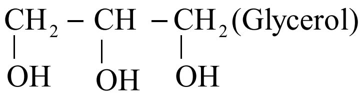
$$\underset{\text{methyl alcohol}}{CH_3OH}\ ,\underset{\text{ethyl alcohol}}{CH_3CH_2OH}$$

(ii) Dihydric Alcohol



$$\underset{OH}{\underset{|}{CH_2}} - \underset{OH}{\underset{|}{CH_2}}\text{(Ethylene glycol)}$$

(iii) Trihydric Alcohol



$$\underset{OH}{\underset{|}{CH_2}} - \underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH_2}}\text{(Glycerol)}$$

In this chapter, we shall discuss only monohydric alcohols. The general formula of monohydric alcohol is $C_nH_{2n+1}OH$. It is also written as R-OH, where R is any alkyl group.

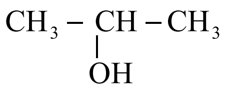
Monohydric alcohols are further classified into three types : primary alcohol (1°), secondary (2°) alcohol and tertiary (3°) alcohol. If OH group in monohydric alcohol is attached with primary (1°) carbon atom then it is termed primary (1°) alcohol.

Example

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} \qquad \underset{\text{propyl alcohol}}{CH_3-CH_2-CH_2-OH}$$

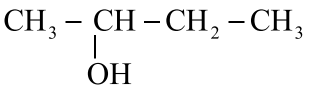
If –OH group in monohydric alcohol is attached with secondary (2°) carbon atom then it is termed secondary (2°) alcohol.

Example-



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

isopropyl alcohol

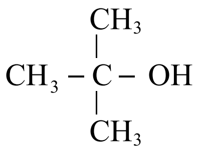


$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$$

2–butanol

If –OH group in monohydic alcohol is attached with tertiary (3°) carbon atom then it is termed as tertiary (3°) alcohol. Primary carbon atom is that which is attached to one carbon, secondary carbon atom is that which is attached to two carbons, and tertiary carbon atom is that which is attached to three carbons.

Example-



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

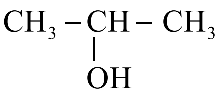
tertiary butyl alcohol

Thus, it is evident from the above examples that the characteristic or functional groups of primary, secondary and tertiary alcohols are $-CH_2OH$, $\rangle CH-OH$ and $-\overset{|}{\underset{|}{C}}-OH$, respectively.

11.1.1 Nomenclature

Here, we discuss two different systems for nomenclature.

(i) **Common System :** In the common system, monohydric alcohols are called alkyl alcohols. The general formula of monohydric alcohols is ROH i.e. –OH group is attached with alkyl group. So, their names are derived by adding the word *alcohol* to the name of the alkyl group present in the molecule. For Example –

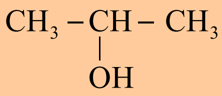
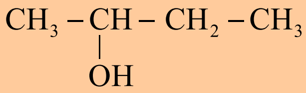
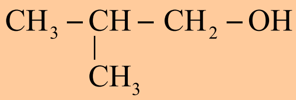
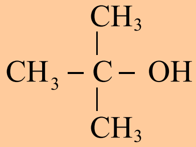
(a)	$CH_3–OH$	methyl alcohol
(b)	$CH_3–CH_2–OH$	ethyl alcohol
(c)	 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_3$	isopropyl alcohol

(ii) **IUPAC System :** In this system of nomenclature, alcohols are called *alkanols*. The longest chain containing the OH group is selectd as the parent chain. This chain is numbered in such a way that the carbon atom carrying the OH group gets the smallest number.

The name of an alcohol is derived by replacing the final 'e' from the name of the corresponding alkane by the suffix-'ol'.

"If more than one –OH groups are present in carbonic compounds, then mono-, di-, tri-, tetra- is used before *suffix-ol*. The position of the –OH group is then indicated by suitable numbers. **Example**– IUPAC name of $OH–CH_2–CH_2–OH$ is "ethane-1, 2-diol."

Monohydric alcohols are given below–

Compound	General Name	IUPAC Name
CH_3-O-H	methyl alcohol	methanol
CH_3-CH_2-OH	ethyl alcohol	ethanol
$CH_3-CH_2-CH_2-OH$	n-propyl alcohol	propan-1-ol
 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_3$	isopropyl alcohol	propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	n–butyl alcohol	butan-1-ol
 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_3$	sec-butyl alcohol	butan-2-ol
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-OH$	isobutyl alcohol	2-methyl propan-1-ol
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-OH$	ter-butyl alcohol	2-methyl propan-2-ol

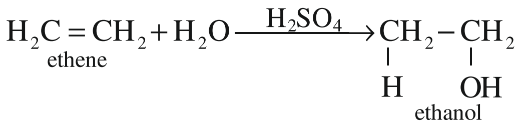
11.1.2 Synthesis Methods of Alcohols

The following methods are used for the preparation of alcohols.

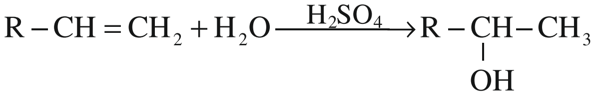
(1) By Alkenes–

By Catalytic Hydration of Alkenes

Alcohols are produced by the reaction of alkenes with water in the presence of dilute acid catalyst (H_2SO_4, H_3PO_4). In case of unsymmetrical alkenes, the addition takes place in accordance with the Markovnikov's rule. Methanol can not be produced by this method as the first member of alkene series has two carbon atoms.



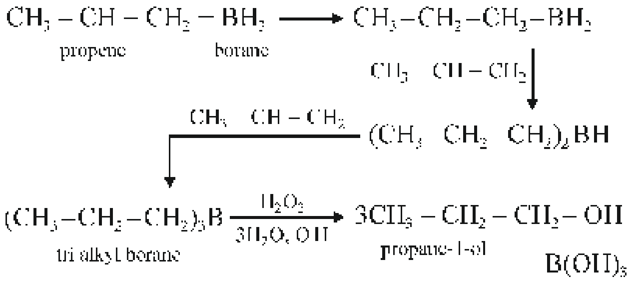
$$\underset{\text{ethene}}{H_2C=CH_2}+H_2O\xrightarrow{H_2SO_4}\underset{\text{ethanol}}{\underset{H}{CH_2}-\underset{OH}{CH_2}}$$



$$R-CH=CH_2+H_2O\xrightarrow{H_2SO_4}R-\underset{OH}{CH}-CH_3$$

(ii) By Hydroboration-oxidation of Alkenes–

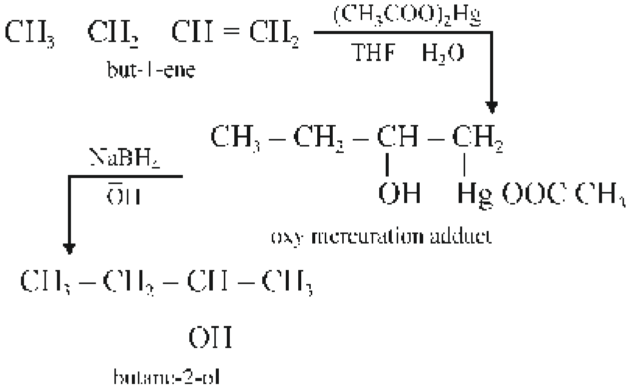
Alcohols react with diborane (B_2H_6) to form trialkyl borane. Subsequent oxidation of tri alkyl borane by hydrogen peroxide (H_2O_2) in presence of aqueous sodium hydroxide (NaOH) give alcohols. In this complete reaction, addition of water to alkene takes place in accordance with the anti-Markovnikov's rule.



Addition of borane upon double bond of alkene takes place in such a manner that boron atom will attach to sp^2 hybridized carbon atom having more hydrogen atoms. A good yield is obtained by this reaction.

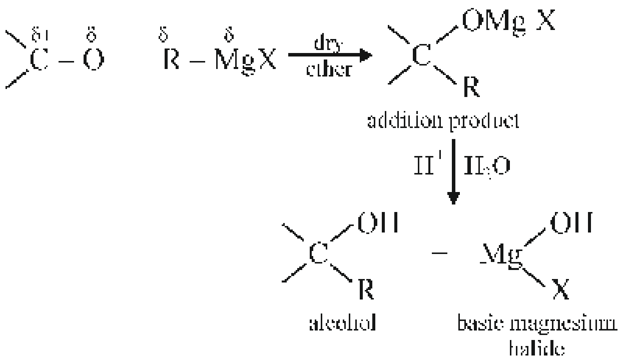
(iii) By Oxymercuration-reduction of alkenes-

Alkenes react with mercuric acetate $(CH_3COO)_2$ Hg to form adducts which upon reduction with $NaBH_4$ (sodium borohydride) in basic medium give alcohols.



(2) By Grignard Reagents–

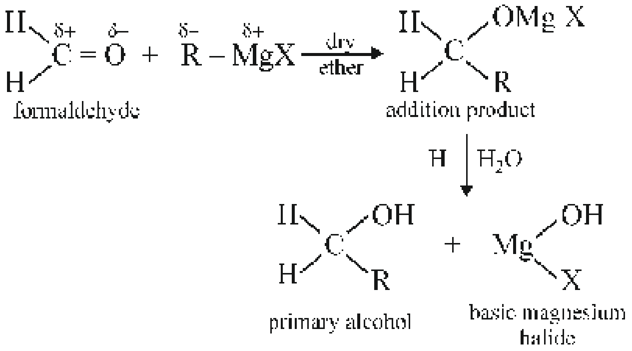
Grignard reagnts react with aldehydes, ketones and esters to form addition products which upon decomposition with dil. HCl or dil. H_2SO_4 give alcohols.



(I) Preparation of Primary Alcohols

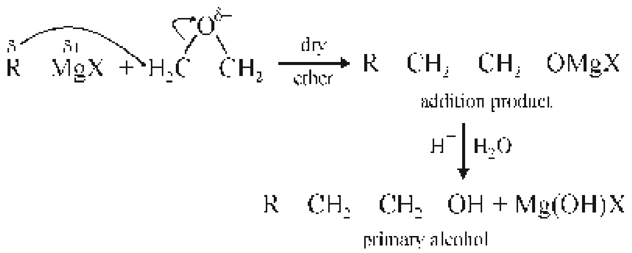
(i) Reaction with formaldehyde–

When Grignard reagents (GR) reacts with formaldehyde it give primary alcohols.



(ii) Reaction with ethylene oxide or oxirane–

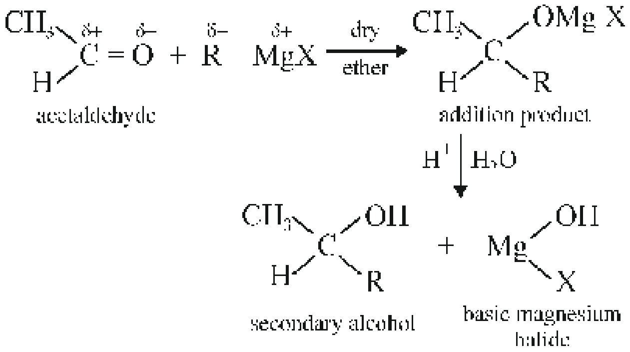
Grignard reagents react with oxirane to form addition product which upon acid hydrolysis give primary alcohols.



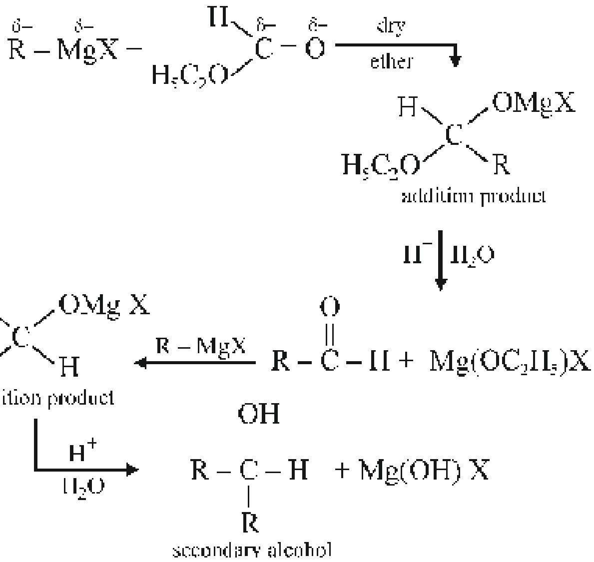
(II) Preparation of Secondary Alcohols :

(i) Reaction with aldehydes other than formaldehyde

Grignard reagents react with aldehydes other than form aldehyde to give secondary alcohols.

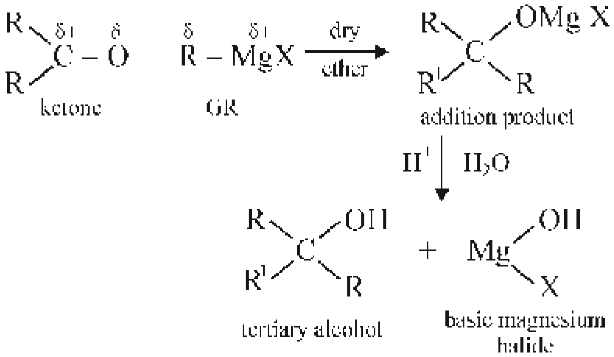


(ii) Secondary alcohols can also be prepared by the reaction of Grignard reagent with esters of formic acid. In this reaction one mole ester react with two moles of Grignard reagent.

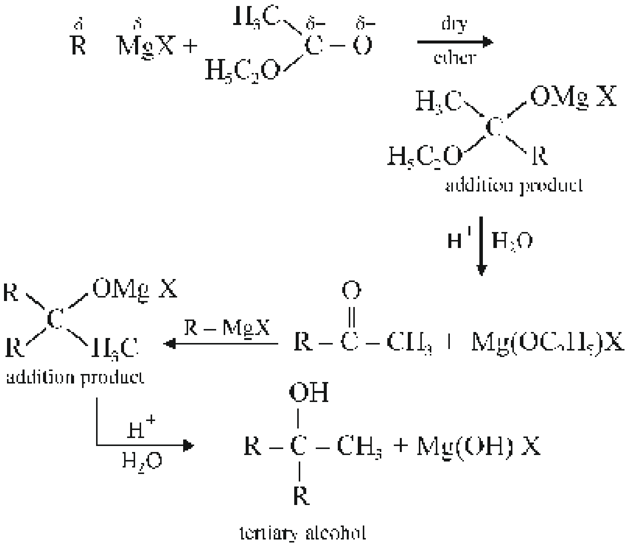


(III) Preparation of Tertiary Alcohols

(i) Grignard reagent reacts with ketone to form tertiary alcohols.



(ii) **Reaction with esters of acid other than esters of formic acid :** Grignard reagents react with esters of acid other than esters of formic acid to form addition product which upon acid hydrolysis give tertiary alcohol. In this complete reaction, two moles of Grignard reagents are used.



(3) By Reduction of aldehyde and Ketone :

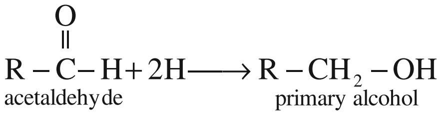
Primary alcohols are prepared by reduction of aldehydes and secondary alcohols are prepared by reduction of ketones. The commonly used reducing agents are-

(i) Catalytic hydrogenation in inert solvent in the presence of Pt or Pd.

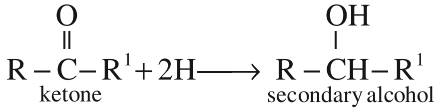
(ii) Na-Hg (sodium amalgum) and water (H_2O)

(iii) Lithium aluminium hydride ($LiAlH_4$) or Sodium borohydride ($NaBH_4$)

(iv) Bouveault - Blanc reduction with sodium (Na) and ethanol.



$$\underset{\text{acetaldehyde}}{R-\overset{\overset{O}{||}}{C}-H}+2H\longrightarrow \underset{\text{primary alcohol}}{R-CH_2-OH}$$



$$\underset{\text{ketone}}{R-\overset{\overset{O}{||}}{C}-R^1}+2H\longrightarrow \underset{\text{secondary alcohol}}{R-\overset{\overset{OH}{|}}{C}H-R^1}$$

(4) By reduction of corboxylic acid and esters:

Corboxylic acid give primary alcohols by reduction with $LiAlH_4$

$$R-COOH\xrightarrow{LiAlH_4}R-CH_2-OH+H_2O$$

Primary alcohols are also prepared by catalytic hydrogenation of esters.

$$R-COOR^1+4H\xrightarrow{\text{catalyst}} R-CH_2-OH+R^1-OH$$

(5) From Haloalkanes :

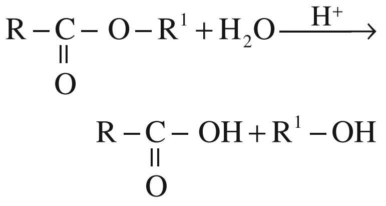
Alkanols are produced when haloalkanes are reacted with aqueous NaOH/KOH or moist silver oxide (Ag_2O). The reactivity order of haloalkanes is 3° >2° > 1° i.e. tertiary alkyl halides are most reactive.

$$\underset{\text{ethyl Iodide}}{CH_3-CH_2-I}+\text{aqueous NaOH}\longrightarrow \underset{\text{ethanol}}{CH_2-CH_2-OH}+NaI$$

$$CH_3-CH_2-Br+Ag_2O\,(\text{moist})\longrightarrow C_2H_5-OH+AgBr$$

(6) By Hydrolysis of Esters :

Alcohols and carboxylic acids are generally prepared by hydrolysis of esters in the presence of aqueous alkalies.

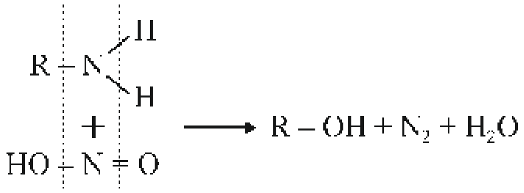


$$R-\underset{\underset{O}{\|}}{C}-O-R^1+H_2O\xrightarrow{H^+} R-\underset{\underset{O}{\|}}{C}-OH+R^1-OH$$

(7) From Aliphatic Primary Amines :

Aliphatic primary amines on treatment with nitrous acid (HNO_2) give alkanols. Methyl amines give methoxy methane (i.e. an ether) not methanol

In this reaction, nitrous acid is obtained by the raction between $NaNO_2$ and HCl.



$$R-NH_2+HO-N=O\longrightarrow R-OH+N_2+H_2O$$

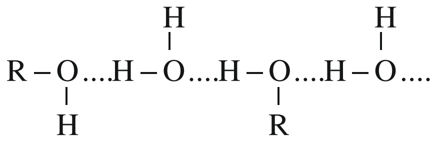
11.1.3 Physical Properties

(i) Alcohols are neutral molecules.

(ii) Alcohols having carbon numbers from C_1-C_{11} are volatile liquid with characteristic sharp smell. C_{12} and members having more than 12 carbon atoms are wax like solids.

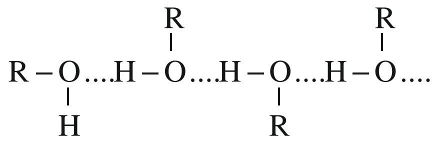
(iii) Alcohols have hypnotic or narcotic nature. Ethanol relaxes the central nervous system and cause unconsciousness. The use of methanol in small amount can cause blindness. Cursed alcohol (tertiary) is used as hypnotic and tranquilizer due to its more hypnotic effect.

(iv) **Solubility :** The lower members of alcohols are highly soluble in water. These are soluble in water due to their ability to form hydrogen bonds with it. As the size of the alkyl groups in alcohols increases, solubility in water decreases. In isomeric alcohols, solubility increases as the number of branches increases. The surface area of non-polar hydrocarbon part decreases as the number of branches increases and hence solubility in water increases.



$$R-\underset{H}{\underset{|}{O}}\ldots\overset{H}{\overset{|}{H-O}}\ldots H-\underset{R}{\underset{|}{O}}\ldots\overset{H}{\overset{|}{H-O}}\ldots$$

(v) **boiling point :** Generally alcohols have higher boiling points as compared to hydrocarbons, ether and haloalkanes of similar molecular masses. In alcohols, as th numbers of carbon atoms increases, van der waals force increases and therefore boiling point increases. As the branches increases, surface area of alcohol molecule decreases, therefore, van der waals force decreases and boiling point decreases. In alcohol (lower members) molecules intermolecular hydrogen bonding is also present, which increases their boiling points. As the carbon chain in alcohols increases, H-bonding decreases.



$$R-\underset{H}{\underset{|}{O}}\ldots\overset{R}{\overset{|}{H-O}}\ldots H-\underset{R}{\underset{|}{O}}\ldots\overset{R}{\overset{|}{H-O}}\ldots$$

11.1.4 Chemical Properties

Chemical reactions of alcohols can be divided into four types – R-CH_2-O-H

(A) Due to cleavage of O ¦ H bond.

(B) Due to cleavage of C ¦ O bond.

(C) Reactions involving both the alkyl and hydroxy groups.

(D) Reactions due to presence of lone pair of electrons on oxygen atom of hydroxy group.

(A) Due to cleavage of O ¦ H bond of hydroxy group

The case of cleavage of the O–H bond in alcohols follows the sequence :

$$\text{primary alcohols} > \text{secondary alcohols} > \text{tertiary alcohols}$$

(i) Reaction with active metals–acidic nature:

Alcohols react with alkali metals-like Na, K, Mg, Al, Zn, etc. to form metal alkoxides with the evolution of hydrogen gas.

$$2\,R-OH + 2Na \longrightarrow 2R-ONa + H_2\uparrow$$

$$\underset{\text{methanol}}{2\,CH_3-OH} + 2Na \longrightarrow \underset{\text{sodium methoxide}}{2CH_3-ONa} + H_2\uparrow$$

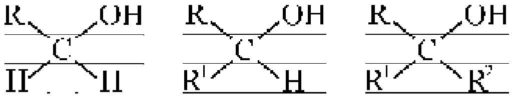
The above reaction suggests that alcohols behave as acids. The acidic character of alcohols is due to the electronegative oxygen atom which withdraws electrons of the O–H bond towards itself. As a result, the O–H bond becomes weak and splits off a proton. However, alcohols are weak acids ($K_a = 1\times10^{-16} - 10^{-18}$) even weaker than water ($Kw = 1 \times 10^{-14}$).

In alcohols, O – H group is attached with alkyl group. Alkyl group show electron releasing inductive effect (+I effect). This effect shifts electrons of C–O bond towards oxygen atom. Due to this, electron density increases around the oxygen atom and therefore polarity of O–H bond decreases.

As a result, the electrons of the O–H bond are not sufficiently attracted towards the oxygen atom and hence the release of a proton becomes difficult. In nut shell, we can say that the electron releasing inductive effect (+I effect) of the alkyl group makes the alcohols weaker acid than water.

Comparison of acidic character of primary, secondary and tertiary alcohols –

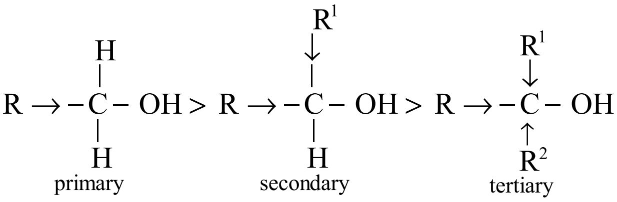
In primary alcohols, only one alkyl group is attached to the carbon atom having the –OH group. In secondary alcohols two alkyl groups are attached and in tertiary alcohol three alkyl groups are attached to the carbon atom having –OH group.



Alkyl group shows electron releasing effct (+I effect) and this effect is maximum in tertiary alcohols. As a result, release of proton is most difficult in tertiary alcohol due to minimum polarity of O–H bond.

Thus the acidic strenght of alcohols follow the order:

$$\text{primary alcohols} > \text{secondary alcohols} > \text{tertiary alcohols}$$



$$\underset{\text{primary}}{R\rightarrow-\overset{H}{\underset{H}{C}}-OH} > \underset{\text{secondary}}{R\rightarrow-\overset{R^1\downarrow}{\underset{H}{C}}-OH} > \underset{\text{tertiary}}{R\rightarrow-\overset{R^1\downarrow}{\underset{\uparrow R^2}{C}}-OH}$$

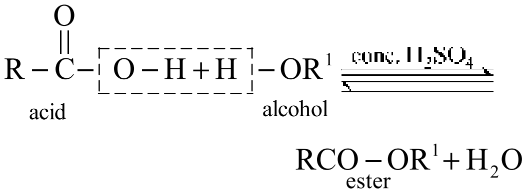
(ii) Reaction with metal hydride :

Alcohols react with metal hydride to form metal alkoxides with the evolution of H_2 gas.

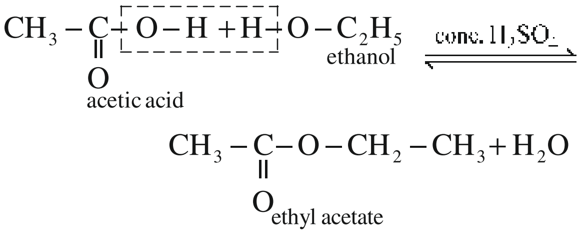
$$R-OH + NaH \longrightarrow R-ONa + H_2$$

(iii) Reaction with carboxylic acid-Esterification :

Alcohols react with carboxylic acids, in presence of conc. H_2SO_4 or dry HCl gas, to form esters



$$\underset{\text{acid}}{R-\overset{O}{\overset{\|}{C}}-O-H} + \underset{\text{alcohol}}{H-OR^1} \xrightleftharpoons{\text{conc. }H_2SO_4} \underset{\text{ester}}{RCO-OR^1} + H_2O$$



$$\underset{\text{acetic acid}}{CH_3-\underset{\underset{O}{\|}}{C}-\boxed{O-H+H}-O-\underset{\text{ethanol}}{C_2H_5}} \xrightleftharpoons{\text{conc. } H_2SO_4} \underset{\text{ethyl acetate}}{CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3}+H_2O$$

This reaction is called esterification. This reaction is reversible and slow.

As the size of alkyl group in carboxylic acid and alcohols increases, the rate of esterification reaction decreases. Thus, the order of reactivity in alcohols and carboxylic acid follows the sequence :

$$CH_3OH > CH_3CH_2OH > (CH_3)_2\ CHOH > (CH_3)_3\ COH$$

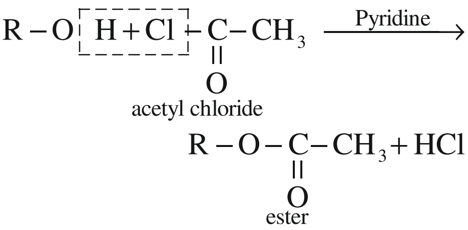
$$HCOOH > CH_3COOH > (CH_3)_2\ CHCOOH > (CH_3)_3\ C\text{-}COOH$$

(iv) Acetylation :

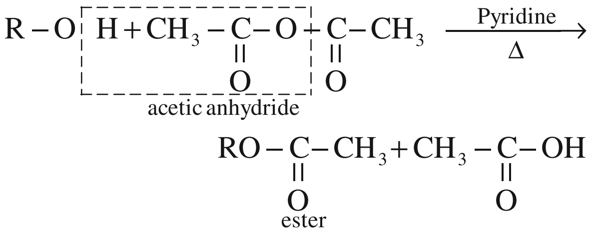
When alcohols are treated with acid chlorides or anhydrides, the H–atom of the –OH group is replaced by th acyl (RCO–) group to form esters. This reaction is called acylation.

$$\underset{\text{acid choloride}}{R-CO-}\boxed{Cl+H}\underset{\text{alcohol}}{-O-R^1} \longrightarrow \underset{\text{ester}}{R\ CO-O-R^1}+HCl$$

If the acid halide and anhydride used are acetyl chloride (CH_3COCl) and acetic anhydride ($(CH_3CO)_2O$), respectively, the reaction is usually termed as acetylation because acetyl group ($CH_3CO–$) is attached here.



$$R-O\boxed{H+Cl}\underset{\text{acetyl chloride}}{-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow{\text{Pyridine}} \underset{\text{ester}}{R-O-\underset{\underset{O}{\|}}{C}-CH_3}+HCl$$



$$R-O\boxed{H+CH_3-\underset{\underset{O}{\|}}{C}-O}\underset{\text{acetic anhydride}}{-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow[\Delta]{\text{Pyridine}} \underset{\text{ester}}{RO-\underset{\underset{O}{\|}}{C}-CH_3}+CH_3-\underset{\underset{O}{\|}}{C}-OH$$

The acetylation of alcohols is carried out in presence of a base such as pyridine, dimethyl aniline. Base removes acid which formed during the reaction and thus reaction proceeds further.

(v) Reaction with Grignard Reagents

Active hydrogen atom is present in alcohols. It react with Grignard reagents to form alkanes.

$$\underset{\text{alcohol}}{R-O-}\boxed{H+R^1}\underset{\substack{\text{Grignard}\\\text{reagent}}}{-MgX} \longrightarrow \underset{\text{alkane}}{R^1-H}+Mg\begin{smallmatrix}X\\OR\end{smallmatrix}$$

(B) Reactions due to cleavage of C – O bond in alkanols :

Alcohols undergo a number of reactions involving the cleavage of C – O bond. In these reactions, the order of reactivity of different alcohols follows the sequence:

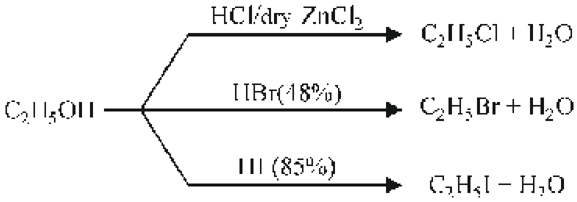
$$\begin{matrix}\text{tertiary}\\\text{alcohols}\end{matrix} > \begin{matrix}\text{secondary}\\\text{alcohols}\end{matrix} > \begin{matrix}\text{primary}\\\text{alcohols}\end{matrix}$$

(i) Reaction with halogen acids:

Alcohols react with halogen acids to form haloalkanes (alkyl halides) and water. The order of reactivity of the halogen acids is

$$HI > HBr > HCl$$

$$R-\boxed{O-H+H}-X \longrightarrow R-X+H_2O$$



(ii) Reaction with Phosphorous tri halides :

Phosphorous tri halides [PCl_3, $PBr_2(P+Br_2)$, $PI_3(P+I_2)$] react with alcohols to form the corresponding haloalkanes or alkylhalides. Phosphorous tri halides can be prepared by the reaction of phosphorous and hologens.

$$2P + 3X_2 \longrightarrow 2PX_3$$

$$3R\text{-}OH + PX_3 \longrightarrow 3R\text{-}X + H_3PO_3$$

$$\underset{\text{methanol}}{3CH_3OH}+PBr_3 \xrightarrow[(P+Br_2)]{} 3\underset{\substack{\text{Bromo}\\\text{methane}}}{CH_3Br}+\underset{\substack{\text{phosphorous}\\\text{acid}}}{H_3PO_3}$$

(iii) Reaction with Phosphorous Penta Chloride (PCl_5):

Alcohols react with phosphorous penta chloride (PCl_5) to form chloroalkane.

$$R-O-H+PCl_5 \longrightarrow \underset{\text{chloroalkane}}{R-Cl} + \underset{\text{phosphorous oxychloride}}{POCl_3} + HCl$$

(iv) Reaction with Thionyl Chloride :

Alcohols react with thionyl chloride to form chloro alkanes or alkyl chlorides. This reaction is carried out in the presence of Pyridine. This is the best method for synthesis of chloroalkanes. In this reaction, separation of by products (SO_2 + HCl) is very easy as these are gases.

$$R-OH+SOCl_2 \xrightarrow{\text{pyridine}} R-Cl+ \rightarrow SO_2\uparrow + HCl\uparrow$$

(v) Reaction with ammonia:

Alcohols react with ammonia in the presence of dry $ZnCl_2$ at 573K temperature to form alkylamines.

$$R-O-H+H-NH_2 \xrightarrow[573\,K]{\text{dry } ZnCl_2} R-NH_2+H_2O$$

(vi) Reduction:

In the presence of red phosphorous (red P) and HI, alkanols reduced to form alkanes.

$$R-OH+2HI \xrightarrow{\text{red P}} R-H+I_2+H_2O$$

(C) Reactions involving both alkyl group and hydroxy group:

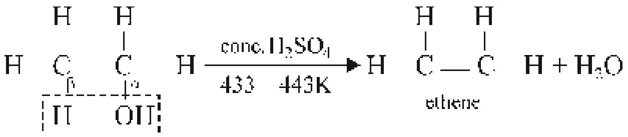
(i) Reaction with Conc. H_2SO_4 (Dehydration reaction):

When an alcohol is heated with conc. H_2SO_4 at different temperatures, different products are obtained.

At 413K, in presence of excess of alcohol, ether is formed.

$$2CH_3\,CH_2OH \xrightarrow[413\,K]{\text{conc. } H_2SO_4} \underset{\text{diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3}+H_2O$$

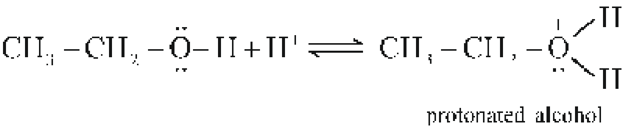
In the presence of excess of conc. H_2SO_4, alcohols loses a molecule of water at 433-443 K to give alkenes. This reaction is known as **dehydration of alcohols**.



$$H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \xrightarrow[433-443K]{\text{conc. } H_2SO_4} \underset{\text{ethene}}{H-\overset{H}{C}=\overset{H}{C}-H} + H_2O$$

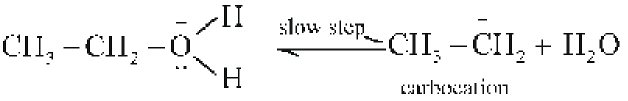
Mechanism :

Step 1 : Due to presence of two lone pairs of electrons on oxygen, alcohols act as weak bases. Therefore they react with strong mineral acids (e.g. conc. H_2SO_4)



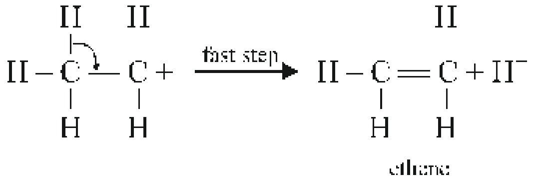
$$CH_3-CH_2-\ddot{\underset{..}{O}}-H+H^+ \rightleftharpoons \underset{\text{protonated alcohol}}{CH_3-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix}}$$

Step 2 : The protonated alcohol eliminates a molecule of water to form carbocation. This step is slow and hence is the rate determining.



$$CH_3-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix} \xrightleftharpoons{\text{slow step}} \underset{\text{carbocation}}{CH_3-\overset{+}{C}H_2} + H_2O$$

Step 3 : In this last step, carbocation readily loses a proton to form alkene.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{\overset{+}{C}}} \xrightarrow{\text{fast step}} \underset{\text{ethene}}{H-\underset{H}{C}=\underset{H}{\overset{H}{C}}} + H^+$$

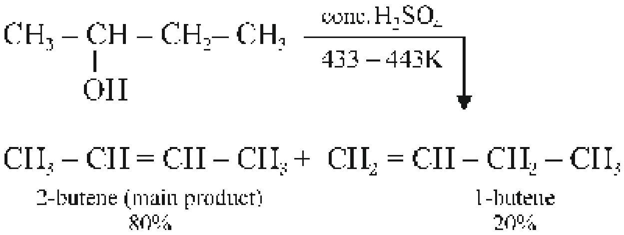
The ease of dehydration of alcohols follows the order.

$$\begin{matrix}\text{tertiary}\\\text{alcohols}\end{matrix} > \begin{matrix}\text{secondary}\\\text{alcohols}\end{matrix} > \begin{matrix}\text{primary}\\\text{alcohols}\end{matrix}$$

In this reaction carbocation is formed and since tertiary corbocation is most stable so tertiary alcohols easily undergo dehydration reaction.

The stability order of primary, secondary and tertiary carbocations follows the sequence 3°>2°>1°.

When more than one alkene products ar possible then the favoured (main) prodcut is usually more substituted alkenes i.e. alkene having more substituents on its double bond.



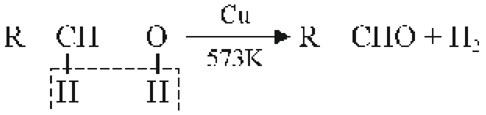
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[433-443K]{conc.\ H_2SO_4} \underset{\substack{\text{2-butene (main product)}\\ 80\%}}{CH_3-CH=CH-CH_3} + \underset{\substack{\text{1-butene}\\ 20\%}}{CH_2=CH-CH_2-CH_3}$$

This is in accordance with Saytzeff rule. In this reaction the carbocation undrgoes rearrangement to form more stable carbocation and the final product is formed by this rearranged carbocation.

(ii) Dehydrogenation :

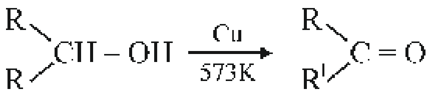
Alcohols giv diffrent products when their vapours are passed over heated copper at 573K.

Primary alcohols give alkanals.

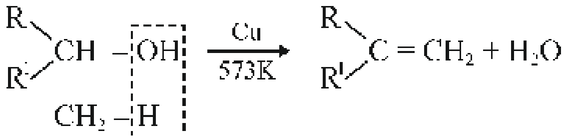


$$R-\underset{H}{\underset{|}{CH}}-\underset{H}{\underset{|}{O}} \xrightarrow[573K]{Cu} R-CHO+H_2$$

Secondary alcohols also undergo dehydrogenation to give alkanones.



When the vapour of tertiary alcohols are passed over heated copper it undergo dehydration rather than dehydrogenation to form alkenes.



(iii) Oxidation :

Primary, secondary and tertiary alcohols give different products on oxidation. For oxidation, variety of reagents such as neutral, acidic or alkaline $KMnO_4$, acidified $K_2Cr_2O_7$ or dil HNO_3 are used.

(a) Oxidation of Primary alcohols:

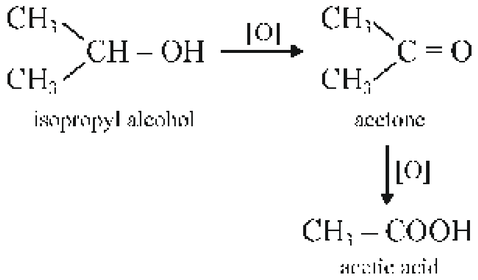
On oxidation, primary alcohols first give an aldehyde which on further oxidation giv carboxylic acid. The number of carbon atoms in aldehydes and alkanoic acid are same as in th original alcohol.

$$R-CH_2-OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} RCOOH$$

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow{[O]} \underset{\text{acetaldehyde}}{CH_3-CHO} \xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3COOH}$$

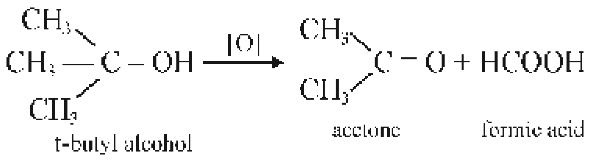
(b) Oxidation of Secondary alcohol:

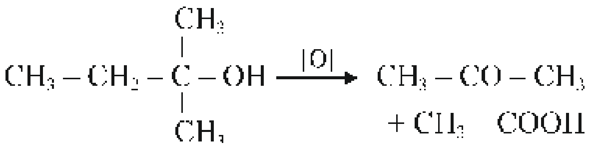
Secondary alcohols are oxidised to ketones, which have the same number of carbon atom as in the original alcohol. However, ketones resist furthr oxidation but when they are treated with oxidizing agent for longer time, they form carboxylic acids containing lesser number of carbon atoms.



(c) Oxidation of tertiary alcohols :

Tertiary alcohols are resistant to oxidation in neutral or alkaline medium but in acidic medium, mixture of ketone and alkanoic acids is obtained. In products, number of carbon atoms are less than original alcohol.

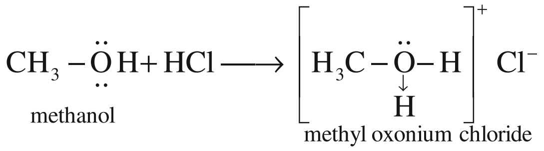




$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH \xrightarrow{[O]} CH_3-CO-CH_3 + CH_3\ \ COOH$$

(IV) Reactions due to presence of lone pair electrons on oxygen atom of hydroxy group:

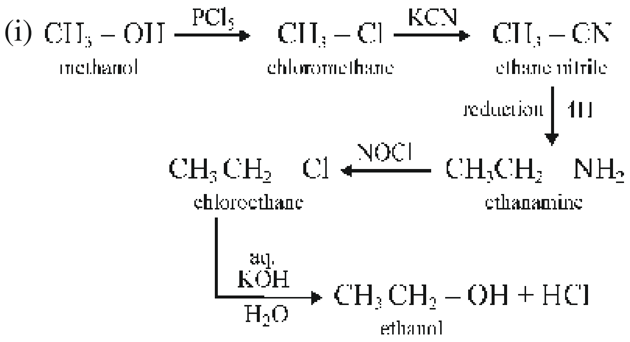
Alcohols behave as lewis base due to presence of two lone pairs on oxygen atom of hydroxy group and form oxonium salts with mineral acids.

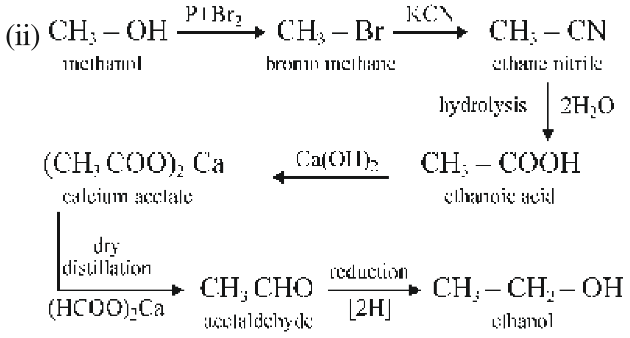


$$CH_3-\ddot{\underset{\cdot\cdot}{O}}H + HCl \longrightarrow \left[H_3C-\underset{\underset{H}{\downarrow}}{\ddot{O}}-H\right]^+ Cl^-$$

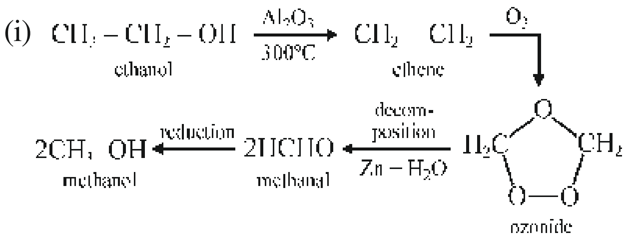
methanol — methyl oxonium chloride

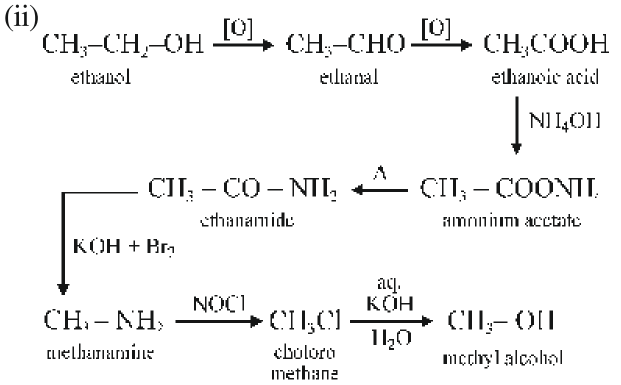
Ascent of carbon chain in alcohols





Descent of carbon chain in alcohols-





Distinction between primary, secondary and tertiary alcohols.

Primary, secondary and tertiary alcohols can be distinguished by the following methods:

(1) Lucas Test-

Equimolar mixture of anhydrous $ZnCl_2$ and concentrated HCl is called Lucas reagent. Primary, secondary and tertiary alcohols react with Lucas reagent at different rates to form respective chloride. White turbidity is appeared due to formation of insoluble alkyl chloride in th reaction mixture.

(i) Tertiary alcohols immediately react with Lucas reagent and produces turbidity.

$$\underset{\text{tertiary alcohols}}{R_3-OH} \xrightarrow[\text{dry } ZnCl_2]{\text{conc. HCl +}} \underset{\text{insoluble chloride}}{R_3C-Cl} + H_2O$$

(ii) Secondary alcohols do not react immediately with Lucas reagent. Turbidity is produced within five minutes.

$$\underset{\text{secondary alcohols}}{R_2-CH-OH} \xrightarrow[\text{dry } ZnCl_2]{\text{conc. HCl +}} \underset{\text{insoensle chloride}}{R_2CH-Cl+H_2O}$$

(iii) Primary alcohols do not rect at room temperature and do not produce turbidity.

$$\underset{\text{primary alcohol}}{R-CH_2-OH} \xrightarrow[\text{dry } ZnCl_2]{\text{conc. HCl}} \begin{matrix}\text{no reaction}\\ \text{(at room temp.)}\end{matrix}$$

(2) Victor Meyer Method:

Following steps are involved in this method.

(i) The given alcohol is treated with phosphorous and iodine ($P+I_2$) to form alkyl iodide.

(ii) The alkyl iodide then treated with silver nitrite ($AgNO_2$) to form nitroalkane.

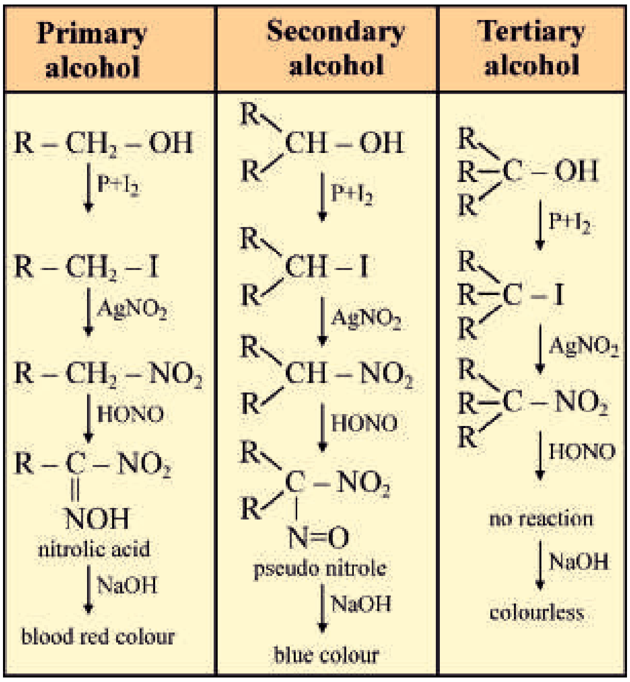
(iii) Raction of nitroalkane with nitrous acid ($NaNO_2$ + HCl).

(iv) The resulting solution is made alkaline by addition of NaOH or KOH.

→ Formation of blood red colour indicates the presence of primary alcohols.

→ formation of blue colour indicates the presence of secondary alcohols.

→ If solution remains colourless, then it indicates the presence of tertiary alcohols.



(3) Esterification:

Esterification reaction is used to distinguish primary, secondary and tertiary alcohols. In esterification reaction, alcohols react with carboxylic acid in the presenc of acid catalyst to form ester.

Order of ease of various alcohols towards estrification follows the sequence-

$$\text{primary alcohols} \rangle \text{secondary alcohols} \rangle \text{tertiary alcohols}$$

(4) Oxidation Method:

Primary, secondary and tertiary alohols react with oxidising agents to form different products. Hence, this method is used to distinguish between them. This method is already described in chemical properties of alkanols involving both the alkyl group and hydroxy group.

(5) Dehydrogenation:

When vapour of alcohols are passed on red hot copper at 573K, dehydrogenation of primary and secondary alcohols take place to form aldehydes and ketones, respectively. Whereas, tertiary alcohols form alkenes in these conditions. The chemical equation of the reaction is already described in chemical properties of alkanols involving both the alkyl group and hydroxy group.

11.1.5 Some Commercially Important Alcohols:

(I) Methanol : Chemical formula of methanol is CH_3OH. It is also known as wood spirit because it was originally prepared by destructive distillation of wood.

Commercially, methanol is produced by catalytic hydrogenation of carbon monoxid at high temperature and pressure. Mixture of carbon monoxid and hydrogen are passed over oxide of catalyst (Copper, Zinc and Chromium) at 573K temperature and 200 atm pressure, as a result, methanol is formed.

$$CO + 2H_2 \xrightarrow[573K,\ 200\ atm]{CuO-ZnO-Cr_2O_3} \underset{\text{methanol}}{CH_3OH}$$

For commercial production of methanol, CO and H_2 are obtained from water gas or by partial oxidation of methane.

Properties:

Methanol is a colourless liquid and its boiling point is 337.5K. It is soluble or miscible in water. Its relative density is 0.795. It is poisonous liquid and when taken internally it causes blindness or even death when taken in excess.

Methanol gives most of the general reactions of alcohols.

Uses:

1. As a solvent for paints, varnishes and celluloide.
2. In the formation of formaldehyde.
3. For denaturing of ethanol.
4. As an antifreeze for automobile radiators.
5. In the formation of organic compounds for example - Iodomethane.

(II) Ethanol : Its chemical formula is C_2H_5OH. It is main constituent of alcoholic beverage. It is also known as grain alcohol because it can be prepared from starchy grains. Commercially, it can be manufactured by fermentation of molasses or starchy substances.

A process in which complex organic substance break down into simple molecules by nitrogen containing complex organic compounds (Enzyme) is known as fermentation. It is an exothermic reaction. In this reaction, CO_2 gas is released and it appears as boiling of solution hence it is known as fermentation.

(i) Formation of Ethanol from molasses: After separation of sugar crystals from the juice of sugarcane or Beet, the red-brown coloured mother liquid is left behind, it is known as molasses. It is a mixtur of sugar, glucose and fructose. Glucose is obtaind from molosses in the following steps:

(a) Dilution : Molasses is diluted with water. In one volume molesses, five volume of water is added.

(b) Addition of Acid and Ammonium Salt : dil. H_2SO_4 is addd to the diluted aqueous solution of molasses to adjust the pH of solution in between 4-5 so that undesirabl bacteria does not grow. A small quantity of ammonium sulphate or ammonium phosphate is addd which acts as a food for the yeast cells.

(c) Addition of Yeast : Above solution is taken in a wooden container and yeast is added. Then the solution is allowed to stand for some days at 298K-303K temperature. The invertase enzyme present in yeast convert the sugar into glucose and fructose.

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} 2\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Other enzyme Zymase present in yeast converts glucose and fructose into ethanol and CO_2 gas evolve.

The solution thus obtained by fermentation contains 10-15% ethanol. This solution is known as wash.

(d) Distillation of wash : Distillation of wash is carried out in a special apparatus called Coffey's still and 90% ethanol is obtained by it. Ethanol thus obtained is again subjected to fractional distillation. The collected distillate at 351.2K temperature contain 95.5% ethanol which is known as rectified spirit.

(ii) Formation of ethanol from starchy materials: Starch is present in edable materials like wheat, barley, maize, rice, potatoes etc. Ethanol is obtaind from these starchy materials in the following steps:

(a) Saccharification : To convert starch into maltose:

Formation of maltose sugar from starch occurs in following steps:

Formation of mash → Formation of malt → Mash+ Malt (maltose solution)

Small pieces of starchy materials like barley, wheat, maize, rice, patatoes, etc. are heated with the help of steam under high pressure and temperature. Due to this, starch forms milky slurry with water known as mash.

Diastase enzyme is present in barley. Germinated barley contain high amount of diastase. To germinate berley it is spreaded in a dark room at 288K temperature. Barley germinate in two-three days and this is known as malt. A germinated barley is grinded with water and then filtered. Filtered liquid is called malt extract. It cantain high amount of diastase enzyme.

Mash and malt extract both are mixed at temperature 323-333K. Diastase enzyme present in malt extract, hydrolyses starch which is present in mash and convert it into maltose. This solution of maltose is known as wort.

$$2\underset{\text{starch}}{(C_6H_{10}O_5)n} + nH_2O \xrightarrow{\text{diastase}} n\underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

(b) Conversion of maltose into Glucose: Yeast is added in wort (maltose solution) and temperature of solution is kept at 303K approximately. Maltase enzyme present in yeast hydrolyses maltose into glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltose}} 2\underset{\text{gulcose}}{C_6H_{12}O_6}$$

(c) Conversion of Glucose into Ethanol: Zymase enzyme present in yeast converts glucose into ethanol.

$$\underset{\text{gulcose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{C_2H_5OH} + 2CO_2$$

The solution obtained after fermentation contains 10-15% ethanol which is known as wash.

(d) Distillation : Distillation of wash is carried out in Coffey's still and approximate 90-95% pure ethanol is obtained.

Properties :

It is a colourless, volatile liquid. It has characteristic pleasant odour. Its boiling point is 351.25K. It is soluble in water. It gives all general reactions of alcohols.

Absulute alcohol : 100% pure ethanol is known as absolute alcohol.

Rectified alcohol : Mixture of ethanol (95.5%) and water (4.5%) which distillate at constant temperature 351.2K, is known as rectified alcohol.

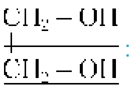
Power alcohol : Absolute ethyl alcohol is mixed in petrol with ether and benzenc. can be used as motor fuel. Alcohol thus used is called power alcohol.

Denatured alcohol : To make rectifid alcohol unfit for drinking purpose, methanol, dyes or base like pyridine is added in it. It is called denatured alcohol also called methylated spirit.

II. Ethanol (C_2H_5OH) :

1. As a solvent for paints, varnishes, etc.
2. For the preparation of organic compounds like-ester, ether, chloral, chloroform, iodoform, etc.
3. In the manufacture of medicines. For example-formation of tincture.
4. In the form of antiseptic and dehydrating agent.
5. In the form of alcoholic beverages.
6. In the manufacture of transparent soap. colour, polish, perfumes, etc.

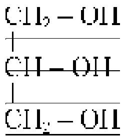
III. Ethylene Glycol



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

1. In the manufacture of Terylene
2. In the form of preservative
3. In the form of lubricant.

IV. Glycerol or glycerine



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

1. In the manufacture of drugs like boroglycerine, glycerophosphoric acid, etc.
2. Due to its hygroscopic nature, it is used in cosmetics like shaving soap, toothpaste, cream and lipstick, etc.
3. In the manufacture of plastics and synthetic fibres.
4. In the form of lubricant.
5. As an antifreeze in automobile radiators.

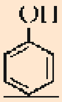
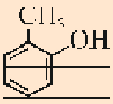
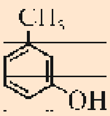
11.2 Phenol:

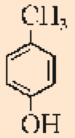
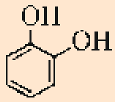
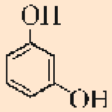
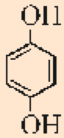
Hydroxy derivative of aromatic hydrocarbons in which hydroxy group is directly attached to the carbon atom of the benzene ring are known as phenols. They are also known as carbolic acid. It was first isolated in the early nineteenth century from coaltar.

11.2.1 Nomenclature :

The common name of aromatic compounds in which –OH group is attached to benzene ring is Phenol.

This name (phenol) is also accepted in IUPAC nomenclature. If other substituents are present on ring with -OH group then main functional group is given 1-position and numbering is done in such a way that substituents get lowest number.

Structural formula	General Name	IUPAC Name
1. 	Phenol	Phenol
2. 	o-cresol	2-methyl phenol
3. 	m-cresol	3-methyl phenol

4.		p-cresol	4-methyl phenol
5.		catechol	benzene-1, 2-diol
6.		resorcinol	benzene-1, 3-diol
7.		quinol/ hydroquinone	benzene-1,4-diol

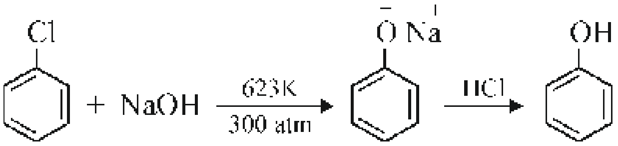
11.2.2 Synthesis Methods of Phenol

1. Laboratory Methods :

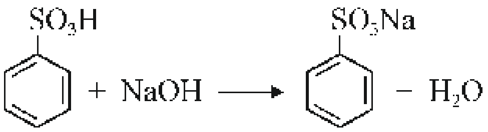
(i) From Benzene diazonium Salt : On boiling an aqueous solution of benzene diazonium salt gives phenol.

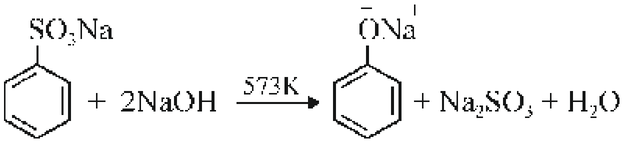
$$C_6H_5\overset{+}{N_2}\overset{-}{Cl} + HOH \xrightarrow{\text{boiling}} C_6H_5-OH + N_2 + HCl$$

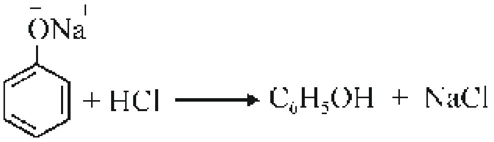
(ii) From Haloarenes : Sodium phenoxide is formed when chlorobenzene is heated or fused with NaOH at 623K temperature and 320 atmospheric pressure. By acidification of this sodium phenoxide gives phenol.



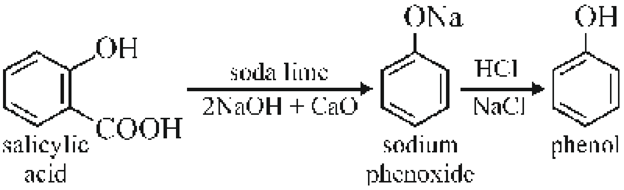
(iii) From benzenesulphonic Acid : Benzene sulphonic acid is obtained by sulphonation of benzene with olium. sodium phenoxide is formed, when it is heated with sodium hydroxide. Acidification of this sodium salt gives phenol.



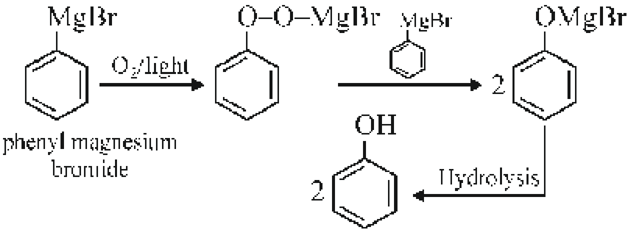




(iv) From Salicylic Acid : On heating with soda lime, salicylic acid forms sodium phenoxide. Which on acidic hydrolysis gives phenol.

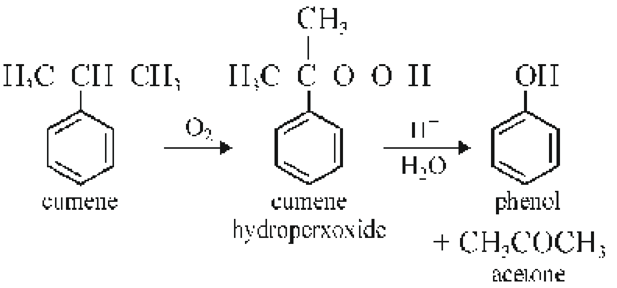


(v) From Grignard Reagent : Phenyl magnisium bromide reacts with O_2 in the presence of light. The product thus obtained gives phenol on hydrolysis..



2. Commercial Preparation :

(i) From Cumene : Phenol is prepared commercially from cumene. Isopropyl benzene is known as cumene. Cumene is oxidized to hydroperoxide in the presence of air. On reaction with dil. acid it is converted into phenol and acetone. In this reaction, acetone is obtained as by product, which is an important reagent for industrial purpose.

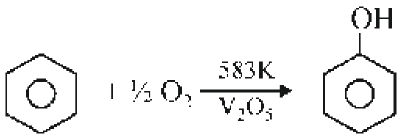


(ii) **From Coaltar :** Middle oil fraction is obtained by fractional distillation of coaltar. It contains mainly phenol and naphthalene. When this fraction react with NaOH, sodium phenoxide forms, which upon decomposition gives phenol.

$$\underset{\text{middle oil fraction}}{C_6H_5OH} + NaOH \longrightarrow C_6H_5ONa$$

$$\underset{\text{sodium phenoxide}}{2C_6H_5ONa} + CO_2 + H_2O \longrightarrow 2C_6H_5OH + Na_2CO_3$$

(iii) **By Oxidation of Benzene :** It is a modern method for the preparation of phenol. When mixture of benzene and air are passed over hot vanadium pentaoxide (V_2O_5) at 583K, benzene forms phenol.



(iv) **Rasching's Process :** In this process, first chlorobenzene is prepared from benzene, and then this chlorobenzene reacts with red hot silica and steam to give phenol.

$$\underset{\text{benzene}}{C_6H_6} + HCl + \tfrac{1}{2}O_2 \xrightarrow[523K]{CuCl_2/FeCl_3} C_6H_5Cl + H_2O$$

$$\underset{\text{chlorobenzene}}{C_6H_5Cl} + H_2O \xrightarrow[723K]{SiO_2} C_6H_5OH + HCl$$

(v) **Dow's Process :** Chlorobenzene prepared from Rasching's process is hydrolysed with sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3) in the presence of $CuCl_2$ under 300 atmospheric pressure and 623K temperature.

$$C_6H_5Cl + NaOH \xrightarrow[\text{300 atmospheric pressure}]{CuCl_2,\,623K} C_6H_5OH + NaCl$$

$$C_6H_5Cl + Na_2CO_3 + H_2O \xrightarrow[\text{300 atm. pressure}]{CuCl_2,\,623K} C_6H_5OH + NaCl + NaHCO_3$$

11.2.3 Physical properties

(i) It is colourless crystalline solid with characteristic odour.

(ii) Its melting point is 314K and boiling point is 455K.

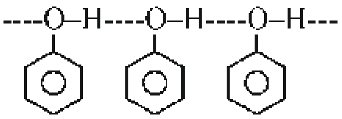
(iii) It is sparingly soluble in water. Its solubility in water is due to formation of hydrogen bond with molecules of water.

(iv) It is soluble in ether and ethanol.

(v) In the presence of air, is oxidized to pink colour liquid due to the formation of para-benzoquinone.

(vi) It is used as antiseptic and pesticide.

The –OH roup in phenols is involved in intermolecular hydrogen bonding. Due to this, its boiling points are higher than other classes of compounds of comparable molecular masses, namely, hydrocarbons, ethers, haloalkanes and holoarens.



11.2.4 Chemical properties of phenol :

The chemical properties of phenol are divided into three types-

(A) Reactions of phenolic (–OH) group.

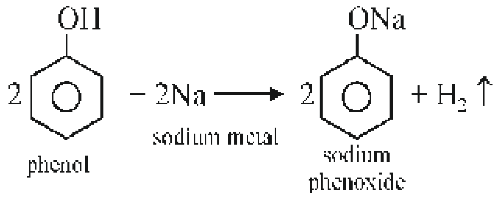
(B) Reactions of benzene ring.

(C) Condensation reactions.

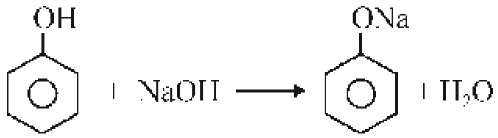
(A) **Reactions of Phenolic (-OH) group :** Phenol behaves as a weak acid.

(1) **Acidic Nature :**

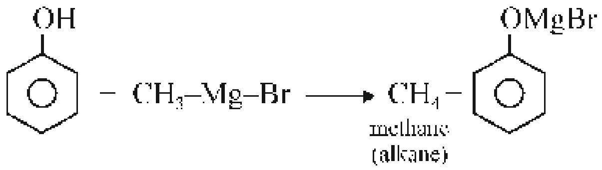
(i) Phenol reacts with active metals like sodium, Potasium and Aluminium to form phenoxide and hydrogen gas.



(ii) Phenol reacts with aqueous sodium hydroxide to form sodium phenoxide.

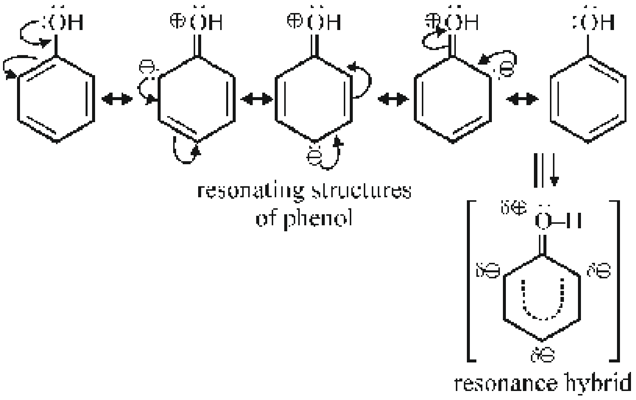


(iii) Phenol reacts with Grignard reagent to form alkane. In which H atom of –OH group is substituted.

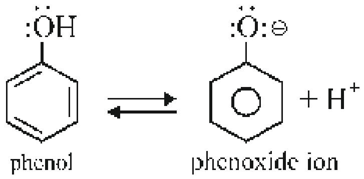


Reactions of phenol with metals, sodium hydroxide and Grignard reagent represents its acidic nature the acidic nature of phenol is due to following reasons :

(a) In phenol, lone pair of electrons present on oxygen of –OH group, are in conjugation with π electrons of ring. Hence due to resonance effect, lone pair on oxygen (O) are displaced towards benzene ring. In this way oxygen of -OH group gets positively charged.

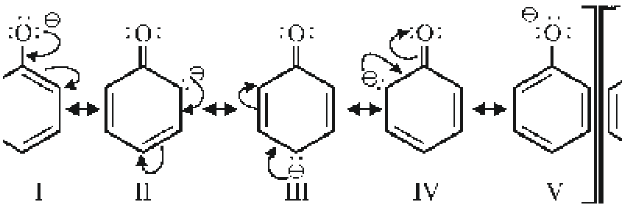


(b) In phenol, the -OH group is directly attached to the sp^2 hybridized carbon atom. sp^2 hybridized carbon has electron withdrawing nature. Due to its high electronegativity, electron density on oxygen atom decreases. Hence polarity of O–H bond increases and release of proton becomes easy.



(c) Phenoxide ion is formed by ionisation of phenol. Phenoxide ion shows resonance and it is more stable than resonating structures of phenol because in resonating strucutres of phenoxide ion, only negative charge in delocalised and there is no charge separation. Whereas in phenol, separation of charge takes place. Structure having charge separation are less stable than those which do not have charge separation.

As phenoxide ion is more stable than phenol, it facilitiate the ionisation of –OH group of phenol and phenol shows acidic charactor.



Effect of Substituents on acidic character of Phenol :

(a) Presence of electron withdrawing group :

Acidic strength of phenol increases when electron withdrawing group like nitro group is present on benzene ring. The effect of these groups is more when they are present at ortho and para positions because delocalization of negative charge is more effective in phenoxide ion.

(b) Presence of electron releasing group :

Acidic strength of phenol decreses when eleectron releasing group like alkyl group is present on benzene ring because these groups do not favour the formation of phenoxide ion.

Greater the value of Ka (and lesser the value of pKa), stronger will be the acid. Comparison of acidity of phenol and substituted phenol with the pKa values can be done in following way.

Name of compound	Formula	pKa Value
o-cresol	o-CH_3-C_6H_4-OH	10.2
m-cresol	m-CH_3-C_6H_4-OH	10.1
p-cresol	p-CH_3-C_6H_4-OH	10.2
phenol	C_6H_5-OH	10.0
o-nitrophenol	o-NO_2-C_6H_4-OH	7.2
m-nitrophenol	m-O_2N-C_6H_4-OH	8.3
p-nitrophenol	p-O_2N-C_6H_4-OH	7.1

Comparison of acidity of Phenol and Alcohol:

Phenols show acidic nature but alcohols are almost neutral in nature. In alcohols, -OH group is attached with sp^3 hybridized carbon. Electronegativity of sp^3 hybridized carbon is less so it cannot increases the polarity of O–H bond and proton (H^+) cannot be released easily. Besides this, in alcohols –OH group is attached with alkyl group. It has electron releasing (+I) effect. As a result, polarity of –OH group does not increase as much high that it can release H^+. Also, on releasing H^+ ion, alcohols form alkoxide ions. This alkoxide ion is not stable because there is no resononce effect present in it which provide stability to it.

$$\text{R-O-H} \longrightarrow \text{R-O}^- + H^+$$

Due to above reasons acidity of alcohols is negligible. In comparison to alcohol, water is a strong proton donor.

Comparison of acidity of Phenol and Carboxylic acid:

Acidity of phenol is very less in comparison to carboxylic acid.

(1) Carboxylic acid decompose weak base like sodium bicarbonate and CO_2 gas evolve with effervescence. But phenol doest not decompose $NaHCO_3$ because it is a weak acid and CO_2 gas does not evolve. This reaction is used to distinguish between phenol and carboxylic acid.

Phenol reacts with strong base like NaOH to form salt.

(2) **With Zinc :** Phenol gives benzene when heated with Zn dust.

$$\underset{\text{phenol}}{C_6H_5OH} + Zn \longrightarrow \underset{\text{benzene}}{C_6H_6} + ZnO$$

(3) **With Ammonia :** Phenol react with ammonia in the presence of anhydrous $ZnCl_2$ at 573K temperature to give aniline.

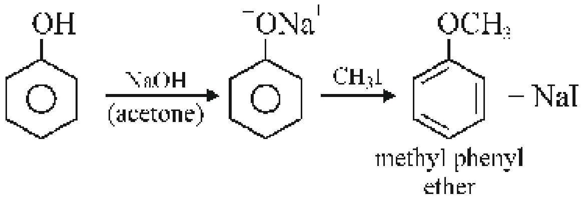
$$C_6H_5-OH + NH_3 \xrightarrow[573K]{ZnCl_2} C_6H_5-NH_2 + H_2O$$

(4) **Reaction with Phosphorous Pentachloride :** Phenol reacts with PCl_5 to form chlorobenzene and phosphorous oxychloride. If phenol is taken in excess then it reacts with $POCl_3$ to give triphenyl phosphate as final product.

$$C_6H_5-OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \longrightarrow \underset{\text{triphenyl phosphate}}{(C_6H_5)_3PO_4} + 3HCl$$

(5) **Etheration :** Phenol reacts with sodium hydroxide in acetone to form sodium phenoxide which reacts with alkyl halide to give alkyl phenol ether.



Methylation of Phenol can also be done by diazomethane.

$$C_6H_5-OH + CH_2N_2 \rightarrow C_6H_5-O-CH_3 + N_2$$

(6) **Esterification :** Phenol reacts with carboxylic acid, acid chloride and acid anhydride to give ester. Reaction with carboxylic acid and acid anhydride is carried out in the presence of concentrated sulphuric acid. This reaction is reversible therefore water is removed instantly (formed as a product). Reaction of phenol with acid chloride is carried out in the presence of base (like : pyridine).

Base neutralizes the HCl formed during reaction and shift the equilibrium towards right.

$$C_6H_5-OH + R^1-COOH \overset{H^+}{\rightleftharpoons} C_6H_5OCOR^1 + H_2O$$

$$C_6H_5-OH + (R^1CO)_2O \overset{H}{\rightleftharpoons} C_6H_5OCOR^1 + R^1COOH$$

$C_6H_5-OH + R^1COCl \xrightarrow{pyridine} C_6H_5OCOR^1 + HCl$

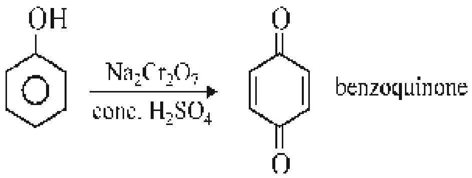
Introduction of acetyl group (CH_3CO-) into phenol is known as acetylation.

(7) Benzoylation : Phenol reacts with benzoyl chloride to give phenol benzoate.

$C_6H_5-O\boxed{H-Cl}OCC_6H_5 \longrightarrow C_6H_5OOCC_6H_5$

phenyl benzoate

(8) Oxidation : Phenol is oxidised by chromyl chloride (CrO_2Cl_2) to give benzoquinone.

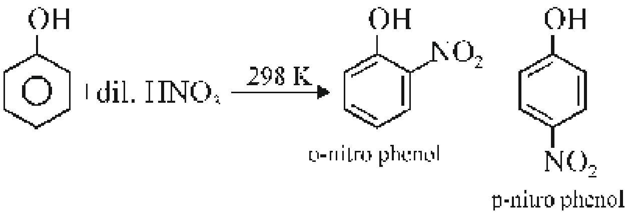


In the presence of air, phenol get oxidised slowly and form quinone.

(B) Reactions of Benzene Ring :

Due to presence of bnzene ring, phenol undergose electrophilic substitution reactions. The –OH group attached to benzene ring is ortho and para directing group therefore electrophilic substitution occurs at ortho and/or para positions.

(1) Nitration : Nitration of phenol with dilute nitric acid at low temperature (298K) give ortho-nitrophenol and para-nitrophenol.

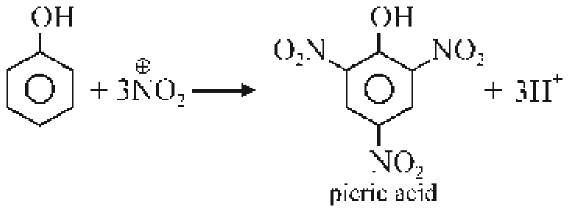


In this reaction, $\overset{\oplus}{NO_2}$ attacks on the ring, is an electrophile which can be formed as follows-

$$HNO_3 + HNO_3 \longrightarrow \overset{\oplus}{NO_2} + \overset{\ominus}{NO_3} + H_2O$$

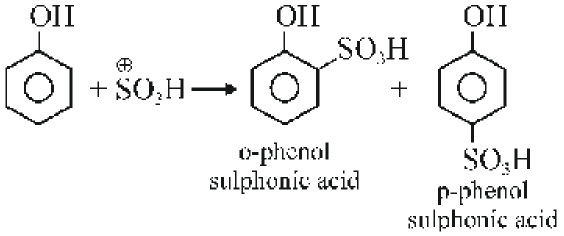
When nitration is carried out with a mixture of concentrated nitri acid and concentrated sulphuric acid, 2, 4, 6-trinitro phenol forms which is also known as Picric acid. Due to the presene of three electron withdrawing groups on ring it behaves as a strong acid.

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{\oplus}{NO_2} - 2H\overset{\ominus}{SO_4} + \overset{\oplus}{H_3O}$$



(2) Sulphonation : Phenol reacts with concentrated sulphuric aid to give ortho- and para-phenol sulphonic acid. In the reaction, electrophile attacks on the ring can be formed as follows :

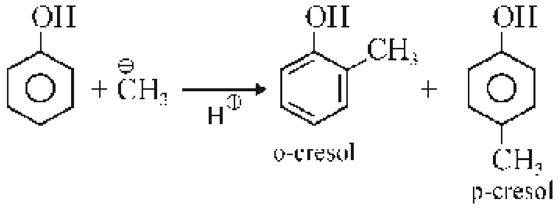
$$H_2SO_4 + H_2SO_4 \longrightarrow HSO_4^- + \overset{\oplus}{HSO_3} + H_2O$$



(3) Friedel-Craft reaction :

(i) Alkylation : Phenol reacts with alkyl halides in the presence of anhydrous aluminium chloride ($AlCl_3$) to form o– and p– alkyl derivatives.

$$CH_3Cl + AlCl_3 \longrightarrow \overset{\oplus}{CH_3} + \overset{\ominus}{AlCl_4}$$

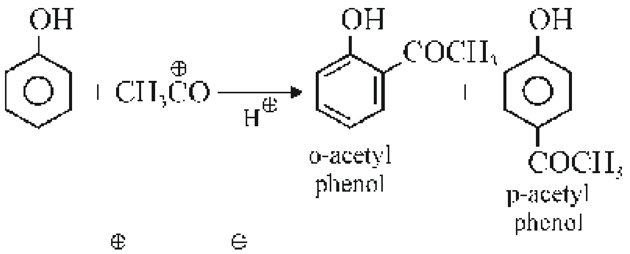


$$\overset{\oplus}{H} + \overset{\ominus}{AlCl_4} \longrightarrow HCl + AlCl_3$$

(ii) Acylation : Phenol reats with acetyl chloride in the presene of anhydrous $AlCl_3$ to form o- and p-acetyl derivatives.

$$CH_3COCl + AlCl_3 \longrightarrow CH_3\overset{\oplus}{C}O + \overset{\ominus}{AlCl_4}$$

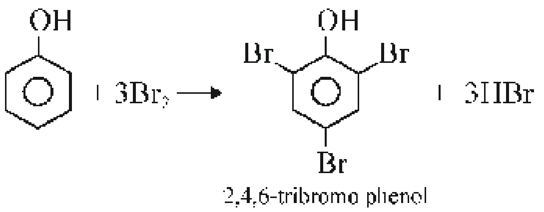
acetyl chloride



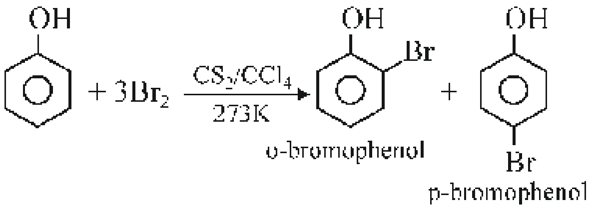
$$\overset{\oplus}{H} + Al\overset{\ominus}{Cl_4} \longrightarrow AlCl_3 + HCl$$

(4) Bromination : Phenol reacts with bromine in different experimental conditions to form different products.

(i) Phenol reacts with excess of bromine water to form white precipitate of 2, 4, 6 - tribromo phenol.

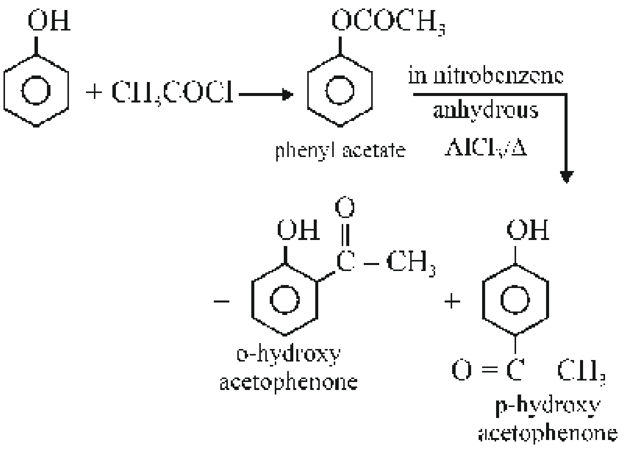


(ii) Phenol reacts with bromine in presene of CS_2 or CCl_4 solvents at 273K temperature to give mono substituted produts.



(5) Fries rearrangement : Phenol reacts with acetyl chloride to form phenyl esters. When phenyl esters are heated with nitrobenzen in the presence of anhydrous $AlCl_3$, acyl group $(-\underset{\underset{O}{\|}}{C}-R)$ rearranged to ortho- and para- positions of phenolic group.

At 333K or below this temperature, para subsituted and at 433K or above this temperature, ortho substituted products are formed as a main product.

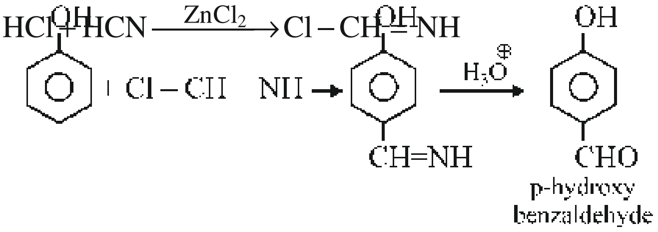


(6) Formylation : In benzene ring of phenol, –CHO group can be substituted by following reactions:

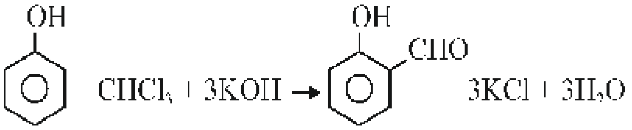
(i) Gattermann Reaction : Reaction of phenol is carried out with the mixture of HCN and HCl in the presence of catalyst $ZnCl_2$. Aldimine is formed as intermediate. On hydrolysis of aldimine, p-hydroxy benzaldehyde is formed.

(aldimine)

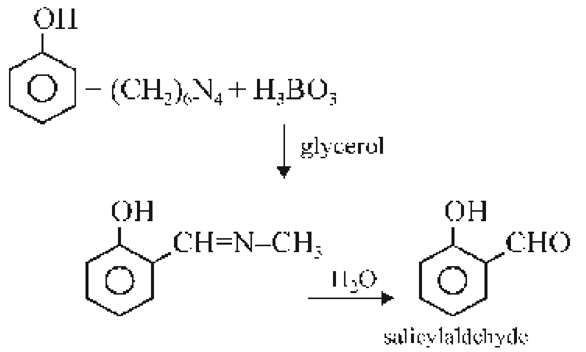
$HCl + HCN \xrightarrow{ZnCl_2} Cl-CH=NH$



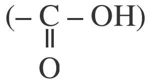
(ii) Reimer-Tiemann Reaction : When phenol reacts with chloroform in the presence of bases [NaOH/KOH], –CHO group gets introduced in the ring at ortho position to the phenol group and salicylal dehyde is formed.



(iii) Duff Reaction : When phenol is heated with hexamethylene tetramine $[(CH_2)_6N_4]$ and boric acid (H_3BO_3) in the presene of glycerol, salicylaldehyde is formed.



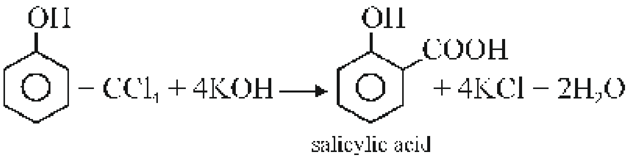
(7) Carboxylation : In benzene ring of phenol carboxylic acid group



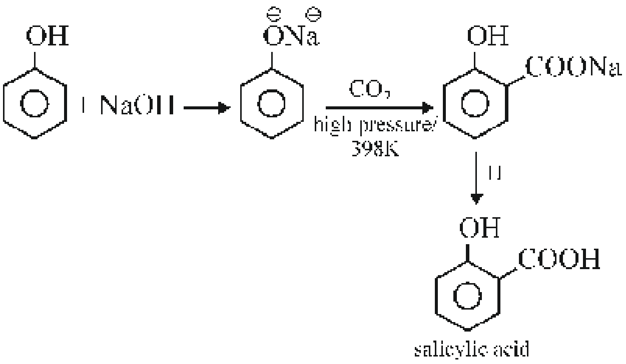
$(-\underset{\underset{O}{\|}}{C}-OH)$

can be introduced by following methods.

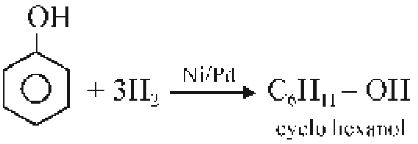
(i) Reimer-Tiemann Reaction : Phenol reacts with carbon tetrachloride in alkaline solution (NaOH/KOH) to form salicylic acid.



(ii) Kolbe's Reaction or Kolbe-Schmidt Reaction: Reaction of phenol with NaOH form sodium phenoxide. Sodium phenoxide is heated with CO_2 at high pressure and 398K temperature to form sodium salicylate. On acidifiation this gives salicylic acid as a major product.

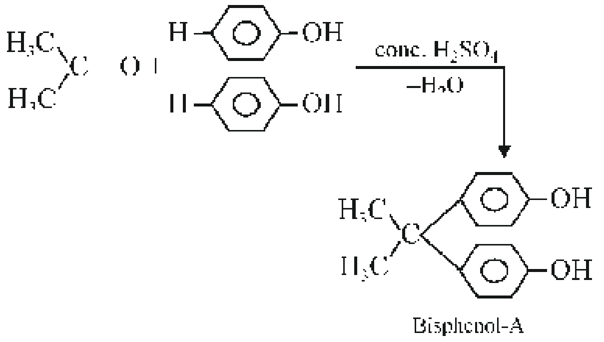


(8) Hydrogenation : Phenol gets hydrogenated by hydrogen (H_2) in the presence of nickel or palladium and cylohexanol is formed.

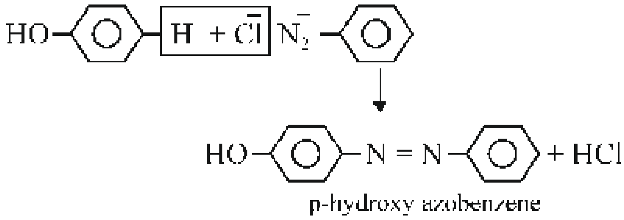


(C) Condensation Reactions :

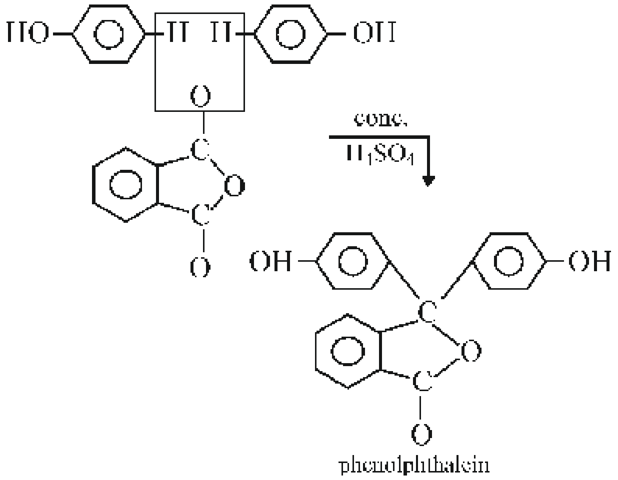
(i) Reaction with acetone : Phenol reacts with acetone in the presence of concentrated HCl to gives Bis-Phenol-A.



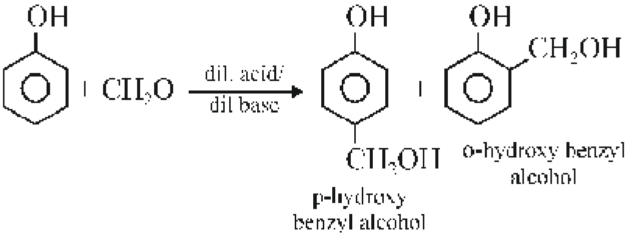
(ii) Reaction with benzene diazonium salt : Phenol couples with benzene diazonium salt at para position to form p-hydroxyazobenzene.



(iii) Reaction with Phthalic anhydride : Phenol reacts with phthalic anhydride in the presence of concentrated H_2SO_4 to form phenolphthalein.

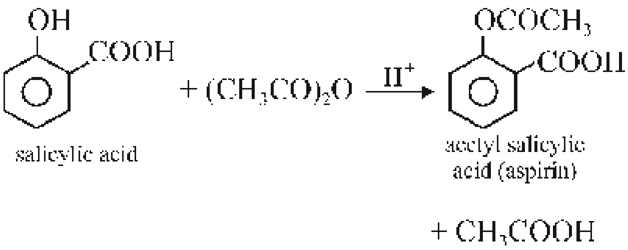


(iv) Reaction with formaldehyde (Lederer Manasse Reaction): Phenol forms para hydroxy benzyl alcohol by condensation reaction with formaldehyde in presence of dilute HCl or dil base, which further condenses to form high molecular weight polymer called 'Bakelite' and ortho-hydroxy benzyl alcohol forms in less amount.



11.2.5 Applications of Phenol :

1. In the formation of Bakelite polymer (Plastic).
2. In the preparation of picric acid.
3. In the formation of carbolic soap.
4. In the formation of phenolphthalein indicator.
5. In the formation of medicines like-Aspirin, Salol, salicylic acid.
6. In the formation of many pesticides.



11.3 Ether

Those organic compounds in which both the valency of bivalent oxygen atom are satisfied by alkyl groups are called ethers or alkoxy alkane. Aryl groups can also be present in place of alkyl group. Its general formula is R-O-R^1, where R and R^1 = alkyl/aryl group, R and R^1 may be same or different. If R and R^1 are same in ether then it is called simple ether. But if R and R^1 are different then it is called mixed ether.

For example :

Simple Ether : General formula R-O-R^1 (R = R^1)

(i) CH_3-O-CH_3
dimethyl ether
(methoxy methane)

(ii) $C_2H_5-O-C_2H_5$
diethyl ether
(ethoxy ethane)

(iii) $C_6H_5-O-C_6H_5$
diphenyl ether

Mixed ether : general formula $R-O-R^1 (R \# R^1)$

(i) $CH_3OC_2H_5$
ethyl methyl ether
(methoxy ethane)

(ii) $CH_3CH_2OCH_2CH_2CH_3$
ethyl propyl ether
(ethoxy propane)

(iii) $C_6H_5-O-CH_3$
methyl phenyl ether
(Anisol)

Ether can be considered as derivatives of water if in place of two hydrogen atoms, alkyl groups are placed.

Ethers are also called anhydrides of alcohol. On elimination of one molecule of water from two molecules of alcohol, ether is obtained.

Their general formula is $C_nH_{2n+2}O$. Where value of n is always greater than one.

$$R-O-\boxed{H+H-O}-R^1 \longrightarrow R-O-R^1+H_2O$$

11.3.1 Nomenclature :

(i) Common system : In common system of nomenclature the names of two alkyl groups linked to oxygen are written alphabetically followed by suffix ether.

(ii) IUPAC system : In IUPAC system ethers are named as alkoxy alkanes. Ethers are considered as organic compounds obtained by replacing a hydrogen atom of an alkane (R-H) by alkoxy group (-OR). In ether, out of two alkyl groups, the group which contains lesser number of carbon atoms forms the part of alkoxy group and alkly group which contain higher number of carbon atoms is considered as parent alkane.

	Molecular formula	Structure	Common Name	IUPAC Name
(i)	C_2H_6O	CH_3-O-CH_3	dimethyl ether	methoxy methane
(ii)	C_3H_8O	CH_3-O-CH_2-CH_3	ethyl methyl ether	methoxy ethane
(iii)	$C_4H_{10}O$	CH_3-O-CH_2-CH_2-CH_3	methyl propyl ether	methoxy propane
		$CH_3-O-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	isopropyl methyl ether	2-methoxy propane
		CH_3-CH_2-O-CH_2-CH_3	diethyl ether	ethoxy ethane
(iv)	C_7H_8O	C_6H_5-O-CH_3	methyl phenyl ether	methoxy benzene

11.3.2 Synthesis Methods of Ether

(1) Laboratory Method : In this method, diethyl ether is synthesised by **Williamson continuous etheration** process.

The reaction of ethanol is carried out with excess of concentrated sulphuric acid at 413K temperature.

$$\underset{\text{ethyl alcohol}}{C_2H_5\,OH} + \underset{\text{sulphuric acid}}{H_2SO_4} \xrightarrow{373\text{ K}} \underset{\text{ethyl hydrogen sulphate}}{CH_3CH_2HSO_4} + H_2O$$

$$CH_3\,CH_2HSO_4 + H\,O\,CH_2\,CH_3 \xrightarrow{413\text{ K}} \underset{\text{ethoxy ethane}}{CH_3CH_2O\,CH_2CH_3} + H_2SO_4$$

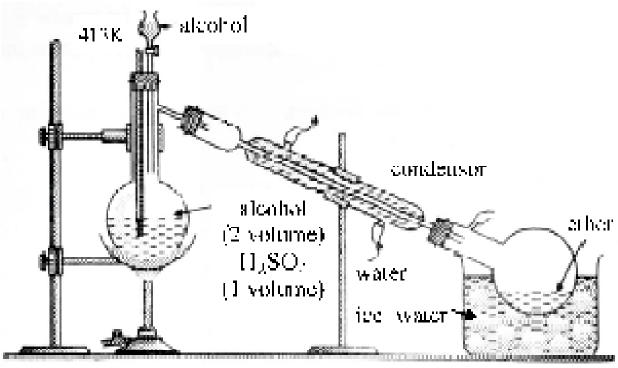


Fig. 11.1 : Formation of ethoxyethane (ether)

Method : According to figure 11.1 ethyl alcohol is taken in distillation flask (2 volume), to this concentrated H_2SO_4 (1 volume) is added slowly. Flask is heated on sand bath at 413K temperature, diethyl ether start forming which is collected in a receiver kept in ice. By the addition of ethanol with the help of dropping funnel, in distillation flask, ether is prepared continuously.

Purifiation : Diethyl ether obtained by this method contains impurities of ethanol, water and sulphur dioxide. Impure ether is taken in a separating funnel and then stirred with dil NaOH due to which impurities of sulphur dioxide is removed. Lower layer of NaOH solution is removed and ether is stirred with water and concentrated solution of $CaCl_2$, respectively. By this impurity of ethanol is removed. Surface of ether is again dried with fused $CaCl_2$ and pure ether is obtained on fractional distillation at 306-308K temperature.

By the above method it is known that during reaction, H_2SO_4 is also formed with ether as product. Hence, initial amount of concentrated H_2SO_4 should be enough to convert ethanol into ether and reaction should continuously go on. But this does not happen due to following reasons :-

(i) When ether forms from ethanol, water comes out and it dilutes the concentrated H_2SO_4.

(ii) Some part of concentrated H_2SO_4 is used in the oxidation of alcohol and H_2SO_4 itself reduced to sulphur dioxide.

Hence, during whole process, sulphuric acid should be replaced.

(2) Industrial Method : Concentrated H_2SO_4 is taken in ether still shown in fig. 11.2, to this ethanol is added drop by drop and mixture is heated by passing steam through coils. Temperature is maintained at 413K. The vapour mixture which comes out from ether still is a mixture of ethanol vapour, ehter vapour and acid fumes. This is passed through the bottom of a chamber. In this chamber, dil NaOH solution falls down from above. Here acid fumes are separated out from vapour mixture. Remaining vapour mixture is passed through fractional coloumn, here ethanol and water are condensed out and due to low boiling temperature of ether, it is collected in the upper part of the column. This is then received in a receiver after condensation.

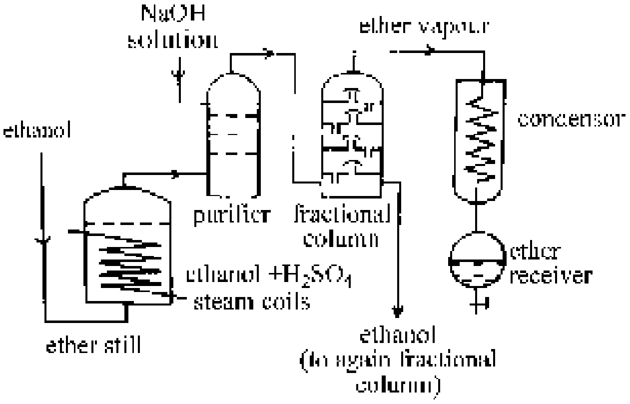


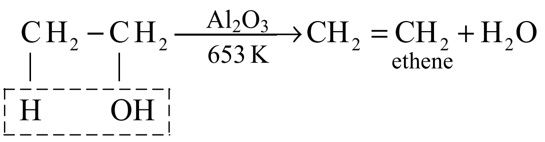
Fig. 11.2 : Industrial method of ether manufacturing

(3) Other methods :

(i) When vapour of ethanol is passed over alumina or aluminium phosphate catalyst at 523K temperature, ether is obtained.

$$CH_3CH_2-O-H+HO-CH_2CH_3 \xrightarrow[523K]{Al_2O_3} CH_3CH_2-O-CH_2CH_3+H_2O$$

Vapours of this ether are dried by the help of fused $CaCl_2$. If temperature of reaction increases to about 653K then ethene is formed in place of ether.



$$\underset{\boxed{H\qquad\quad OH}}{CH_2-CH_2} \xrightarrow[653\,K]{Al_2O_3} \underset{\text{ethene}}{CH_2=CH_2}+H_2O$$

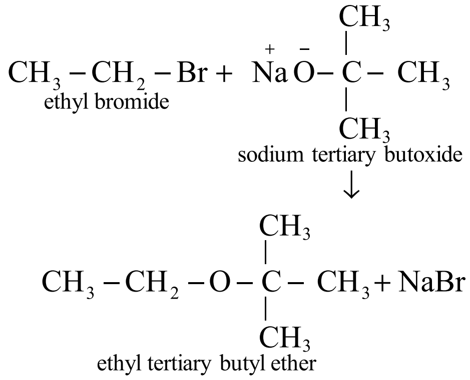
(ii) **Williamson synthesis–** Ether is formed when alkyl halide is treated with sodium or potassium alkoxide. It is a nucleophilic substitution reaction. This method can be used to prepare simple and mixed both types of ether.

$$R-X+\overset{+}{N}a\overset{-}{O}R^1 \longrightarrow R\text{-}O\text{-}R^1+NaX$$

$$CH_3-CH_2-I+Na-O-CH_2CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3+NaI$$

Note :- for the synthesis of mixed ether, suitable reagent should be chosen. For preparing mixed ether, primary alkyl halide and secondary or tertiary alkyl group containing alkoxide should be taken because secondary and tertiary alkyl halides undergo elimination reaction in the presence of strong base and form alkene as major product.

For example : (i) To prepare ethyl ter-butyl ether, reaction of ethyl bromide should be carried out with sodium tertiary butoxide.

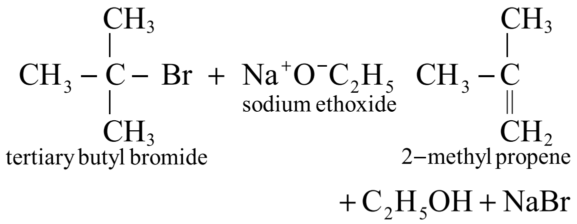


$$\underset{\text{ethyl bromide}}{CH_3-CH_2-Br}+\underset{\text{sodium tertiary butoxide}}{\overset{+}{Na}\overset{-}{O}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3}$$

$$\downarrow$$

$$\underset{\text{ethyl tertiary butyl ether}}{CH_3-CH_2-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3}+NaBr$$

(ii) However, if tertiary butyl bromide and sodium ethoxide is used then in the presence of strong base (sodium ethoxide), tertiary butyl bromide undergoes elimination reaction to form 2-methyl propene.



$$\underset{\text{tertiary butyl bromide}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br}+\underset{\text{sodium ethoxide}}{Na^+O^-C_2H_5}\ \ \underset{\text{2-methyl propene}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle \| \atop CH_2}{C}}}+C_2H_5OH+NaBr$$

(iii) On heating ethyl halide with dry silver oxide

$$CH_3-CH_2-\boxed{I+Ag}-O-\boxed{Ag+I}-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3+2AgI$$

11.3.3 Physical properties of diethyl ether

(i) It is a colorless liquid with sweet or pleasant smell.

(ii) It is highly volatile and inflammable liquid.

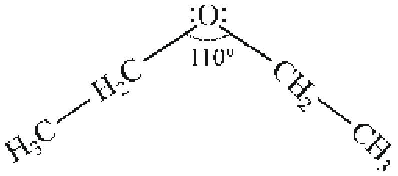
(iii) It is lighter than water and insoluble in it.

(iv) It is completely miscible in organic solvents like alcohols, benzene etc.

(v) It is used as anaesthetic as its vapour cause uncoonceousness.

(vi) Its boiling point is 307.6K

(vii) Structure of diethyl ether : Oxygen atom of ether molecule is sp^3 hybridised and two hybrid orbitals of O-atom are used to form σ-bond with two ethyl groups. The remaing two sp^3 hybrid orbitals contain a lone pair of electrons. In this way two bond pair and two lone pair surround the O-atom in tetrahedral form but C-O-C bond angle is 110° instead of 109° 28'. This is due to the repulsion between alkyl groups. As the size of the alkyl group increases, bond angle increases due to greater repulsive interactions.



Thus ethers have angular structure and its dipole moment is 1.3D.

11.3.4 Chemical properties of diethylether

Ethoxy ethane $CH_3-CH_2-O-CH_2-CH_3$ performs the following four types of reactions :

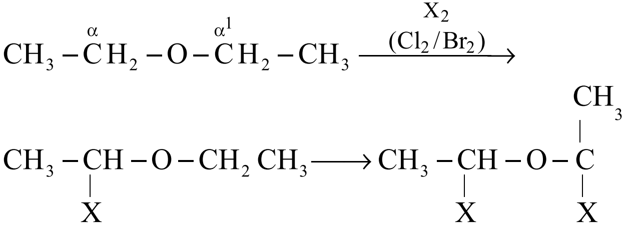
1. Substitution reactions of ethyl group.
2. Reaction due to presence of lone pairs of electrons on oxygen atom of functional group ether.
3. Reactions involving clevage of C–O bond
4. Other reactions.

1. Substitution reactions of ethyl group

Halogenation :

When diethyl ether is heated with chloine or bromine, hydrogen atom present on α-carbon atom of diethyl ether gets substituted by hologen atom.

(i) Halogenation in dark:



$$CH_3-\overset{\alpha}{C}H_2-O-\overset{\alpha^1}{C}H_2-CH_3 \xrightarrow{\overset{X_2}{(Cl_2/Br_2)}}$$

$$CH_3-\underset{X}{CH}-O-CH_2CH_3 \longrightarrow CH_3-\underset{X}{CH}-O-\underset{X}{\overset{CH_3}{C}}$$

α, α^1–dihaloether

(ii) Halogenation in presence of sunlight: Ethoxy ether ether reacts with chlorine in presence of sunlight to form perchloro ethoxy ethane.

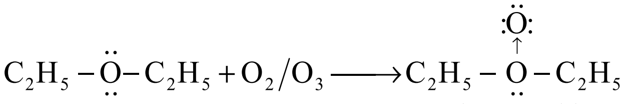
$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{sunlight}]{10Cl_2}$$

$$CCl_3-CCl_2-O-CCl_2-CCl_3+10HCl$$

perchloro diethyl ether

2. Reaction due to presence of lone pairs of electrons on oxygen atom of functional group ether

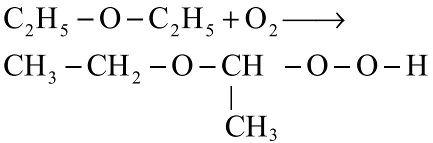
(i) Formation of peroxides : Ether reacts with oxygen or ozone present in air to form peroxides.



$$C_2H_5-\underset{..}{\overset{..}{O}}-C_2H_5+O_2/O_3 \longrightarrow C_2H_5-\underset{..}{\overset{:\ddot{O}:\ \uparrow}{O}}-C_2H_5$$

ether peroxide

If ether is left for long time in air then it is self oxidised to form 1-ethoxy ethyl hydro peroxides, which is explosive in nature.



$$C_2H_5-O-C_2H_5+O_2 \longrightarrow$$

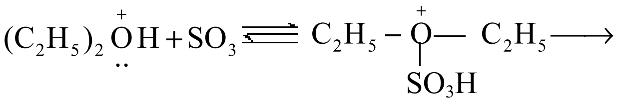
$$CH_3-CH_2-O-\underset{CH_3}{\underset{|}{CH}}-O-O-H$$

ethoxy ethyl hydroperoxide

(ii) Formation of oxonium salt : Ether acts as bronsted lowry base with inorganic acid and forms oxonium salts. **For example-** when diethyl ether is heated with concentrated sulphuri acid firstly oxonium salt forms which finally converts into ethyl hydrogen sulphate.

$$(C_2H_5)_2-\ddot{O}:+H_2SO_4\longrightarrow(C_2H_5)_2\underset{+}{\ddot{O}}H+HS\bar{O}_4$$

$$2H_2SO_4\rightleftharpoons SO_3+HSO_4^-+H_3O^+$$

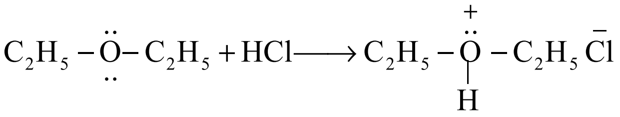


$$(C_2H_5)_2\overset{+}{\underset{\cdot\cdot}{O}}H+SO_3\rightleftharpoons C_2H_5-\underset{SO_3H}{\overset{+}{O}}-C_2H_5\longrightarrow$$

$$\overset{+}{C}_2H_5+C_2H_5HSO_4$$

$$\overset{+}{C}_2H_5+HSO_4^-\longrightarrow\underset{\text{ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

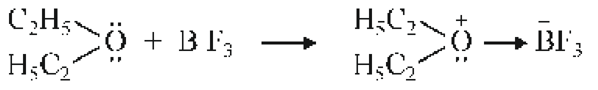
(b) With HCl gase also, diethyl ether forms oxonium salts.



$$C_2H_5-\underset{\cdot\cdot}{\ddot{O}}-C_2H_5+HCl\longrightarrow C_2H_5-\underset{H}{\overset{+}{\ddot{O}}}-C_2H_5\,\bar{Cl}$$

diethyl oxonium chloride

Ether acts as lewis base with electron deficient compounds and form oxonium salts.



boron trifluoride etherate

3. Reactions involving clevage of C-O bond–

(i) Reaction with hydrogen halides (HX)– Alkyl halides and alcohol are formed when ether react with hydrogen halides.

$$C_2H_5OC_2H_5+HX\longrightarrow C_2H_5\text{–}OH+C_2H_5\text{–}X$$

$$C_2H_5\text{–}O\text{–}C_2H_5+HI\longrightarrow C_2H_5\text{–}OH+C_2H_5\text{–}I$$

When hydrogen halides are taken in excess, alkyl halides and water are formed as end products.

$$R\text{–}O\text{–}R+HX\longrightarrow RX+R\text{–}O\text{–}H$$

$$R\text{–}OH+HX\longrightarrow RX+H_2O$$

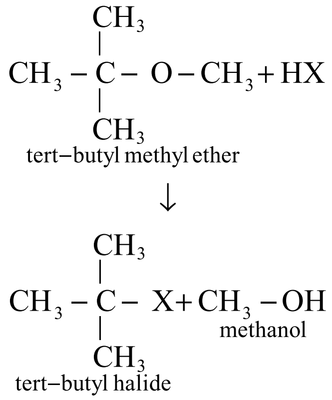
The order of reactivity of hydrogen halides is–

HI > HBr > HCl

Zeisel Method : For quantitative analysis of methoxy group, reaction of methyl ether with HI is used. This method is known as Zeisel method.

When reaction of mixed ether is carried out with hydrogen halides then different products are obtained according to the nature of alkyl group (primary/ secondary/tertiary).

In mixed ether if one alkyl group is primary and second group is tertiary then alcohol is formed by primary group and halides are formed by tertiary alkyl group and reaction goes through S_N1 mechanism.

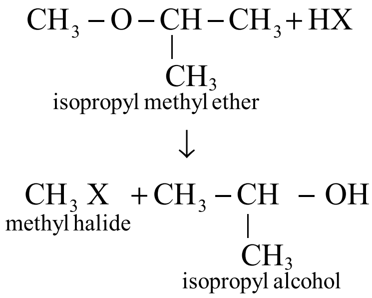


$$\underset{\text{tert–butyl methyl ether}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3}+HX$$

$$\downarrow$$

$$\underset{\text{tert–butyl halide}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X}+\underset{\text{methanol}}{CH_3-OH}$$

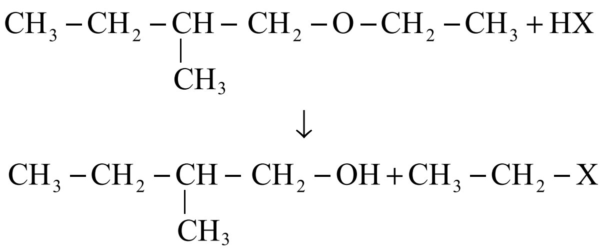
If in mixed ether, alkyl groups are primary and secondary, then primary or small alkyl group form halides and reaction goes by S_N2 mechanism.



$$\underset{\text{isopropyl methyl ether}}{CH_3-O-\underset{CH_3}{CH}-CH_3}+HX$$

$$\downarrow$$

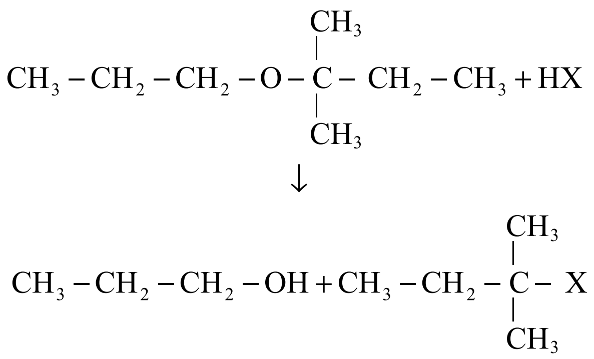
$$\underset{\text{methyl halide}}{CH_3X}+\underset{\text{isopropyl alcohol}}{CH_3-\underset{CH_3}{CH}-OH}$$



$$CH_3-CH_2-\underset{CH_3}{CH}-CH_2-O-CH_2-CH_3+HX$$

$$\downarrow$$

$$CH_3-CH_2-\underset{CH_3}{CH}-CH_2-OH+CH_3-CH_2-X$$



$$CH_3-CH_2-CH_2-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3+HX$$

$$\downarrow$$

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

(ii) Hydrolysis : Ethanol is formed when ether is heated with dil H_2SO_4 at high pressure.

$$C_2H_5-O-C_2H_5\xrightarrow[\text{high pressure}]{\text{dil. }H_2SO_4}2C_2H_5-OH$$

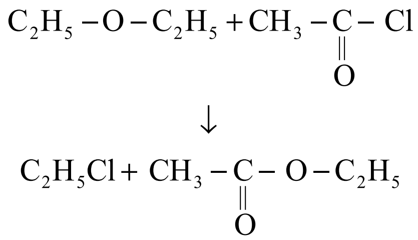
(iii) Reduction : When reduction of diethyl ether is carried out in liquid ammonia with Na, alkane and alkanol are formed.

$$CH_3-CH_2-O-CH_2-CH_3+2H\xrightarrow[Na]{\text{liquid }NH_3}\underset{\text{ethane}}{CH_3-CH_3}+\underset{\text{ethanol}}{CH_3-CH_2-OH}$$

When heated with red phosphours and HI, ethane is formed

$$C_2H_5-OC_2H_5+4H\xrightarrow[\Delta]{HI/P}2C_2H_6+H_2O$$

(iv) With acetyl chloride : Ether reacts with acetyl chloride in presence of anhydrous $ZnCl_2$ to form ethyl acetate and ethyl chloride.



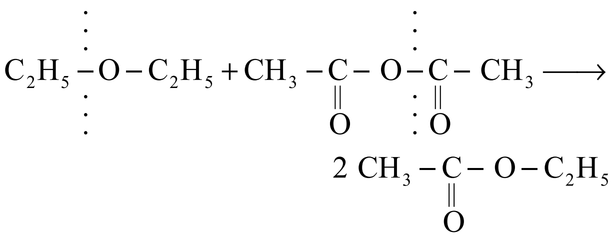
$$C_2H_5-O-C_2H_5+CH_3-\underset{\underset{O}{\|}}{C}-Cl$$

$$\downarrow$$

$$C_2H_5Cl+CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5$$

ethyl acetate

(v) Reaction with acetic anhydride : Ether heated with acetic anhydride in presence of anhydrous $ZnCl_2$ to form ethyl acetate.



$$C_2H_5-O-C_2H_5+CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3\longrightarrow$$

$$2\,CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5$$

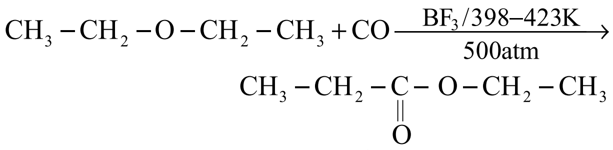
ethyl acetate

4. Other Reactions :

(i) Dehydration : When vapours of diethyl ether are passed over alumina at 653K temperature, water molecule eliminates and ethene is formed.

$$CH_3-CH_2-O-CH_2-CH_3\xrightarrow[653\,K]{Al_2O_3}2CH_2=CH_2+H_2O$$

(ii) With carbon monoxide : Ether forms esters, with CO in presence of catalyst BF_3 and water at 500 atm. pressure and 398-423K temperature.



$$CH_3-CH_2-O-CH_2-CH_3+CO\xrightarrow[500atm]{BF_3/398\text{–}423K}CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3$$

ethyl propionate

(iii) Combustion : In air, diethyl ether burns with flame and form water and carbon dioxide.

$$C_2H_5-O-C_2H_5+6O_2\longrightarrow 4CO_2+5H_2O$$

11.3.5 Applications of Ether

(1) As a solvent in organic reactions (like-in formation of Grignard reagent and in Wurtz reaction.)

(2) In the form of anaesthetic in hospitals.

(3) used as coolant when mixed with CO_2. Temperature of this mixture is about 193K.

(4) The mixture of alcohol and ether is used as a substitute of petrol under the trade name "natalite".

(5) It is used in the production of smokeless powders and perfumaries.

important points

(1) Hydroxy derivatives of alkanes are known as alcohols.

(2) Alcohols can be prepared by the following methods:

1. By alkene
2. By Grignard reagent
3. By reduction of carboxylic acid and ester
4. By haloalkane
5. By hydrolysis of ester
6. By aliphatic primary amine

(3) Due to intermolecular hydrogen bonds, alcohols with low molecular weight are soluble in water and as the molecular weight increases, solubility decreases.

(4) Chemical reactions of alcohols can be divided into four parts.

(i) Due to the cleavage of O-H bond of hydroxyl group.

(ii) Due to the cleavage of C-O bond of alkanal.

(iii) Reactions involving alkyl and hydroxyl group.

(iv) Due to the presence of lone pair of electrons on oxygen atom of hydroxyl group.

(5) Compounds in which hydroxyl group is directly attached to benzene ring are known as phenols.

(6) Phenol is colourless liquid with characteristic smell. When it comes in contact with air it gets oxidized and form para-benzoquinone, due to which it becomes pink colour. It is sparingly soluble in water.

(7) Chemical reactions of phenol are divided into three classes :

1. Of phenolic group
2. Of benzene ring
3. Condensation reactions

(8) Ethers are colourless liquids with pleasant (sweet) smell. They are soluble in water.

EXERCISE QUESTIONS

Multiple Choice Questions

(1) Which of the following is not obtained in any condition by the reaction of ethanol and concentrated H_2SO_4?

(a) CH_3CHO
(b) $CH_3CH_2HSO_4$
(C) C_2H_4
(D) $CH_3CH_2OCH_2OCH_2CH_3$

(2) General formula of alcohol is:

(a) $C_{n+1}H_{2n+2}O$ (b) $C_nH_{2n+1}O$
(c) $C_{n+1}H_{2n}O$ (d) $C_{n+2}H_nO$

(3) R-MgX + HCHO $\longrightarrow$ [P], here, [P] is

(a) RCH_2OH (B) CH_3COCH_3
(C) CH_3 OH (D) R-C-R

(4) Final product obtained by the reaction between alcohol and phosphorus pentachloride is:

(a) chloro alkene
(b) dichloro alkene
(c) chloro alkane
(d) dichloro alkane

(5) Which of the following phenol is strongest acidic.

(a) o-nitro phenol (b) m-nitro phenol
(c) p-nitro phenol (d) p-chloro phenol

(6) victor Meyer test is not given by :

(a) C_2H_5OH
(b) CH_3CHO
(c) $(CH_3)_2CHOH$
(d) $CH_3CH_2CH_2OH$

(7) Which one is the strongest acid?

(a) Phenol
(b) m-chlorophenol
(c) benzyl alcohol
(d) cyclohexanol.

(8) When salicylic acid is heated with sodalime, the product is:

(a) methyl alcohol

(b) ether

(c) ethyl alcohol

(d) acetaldehyde

(9) Phenol + Chloroform + Base → Main product, the main product is:

(a) salicylaldehyde

(b) alkane

(c) alcohol

(d) phenol

Very Short Answer Questions

1. Write the general formula of alcohol.
2. Write the IUPAC name of ethyl alcohol.
3. Write the name of the product formed when Grignard reagent reacts with formaladehyde.
4. Write the order of acidity for primary, secondary any tertiary alcohols.
5. Write Fries rearrangement.
6. What happens when phenol is kept open in air?
7. What is the effect of electron withdrawing group on acidity of phenol?
8. Write the general formula of ether.

Short Answer Type Questions

9. Explain hydroboration oxidation reaction .
10. Write method for the preparation of primary alcohol from Grignard reagent.
11. Alcohols are soluble in water whereas ethyl ether is not . Explain.
12. Describe one commercial method for the preparation of phenol.
13. Phenols show less acidity in comparison to carboxylic acids. Explain.
14. Write short notes on the followings:

    (i) Gattermann reaction

    (ii) Reimer-Tiemann reaction

    (iii) Duff reaction

(15) Explain the halogenation reaction of diethyl ether.

Long Answer Questions

(16) What does alcohol form by reaction with following.

(i) PCl_3 (ii) $SOCl_2$?

(17) What does Phenol from by reaction with following:

(i) HCN and HCl

(ii) In presence of NaOH or KOH?

(18) Write the substitution reactions of diethyl ether.

Answers (Multiple Choice Questions)

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