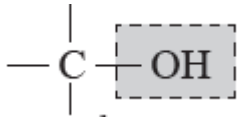
ALCOHOLS, PHENOLS AND ETHERS

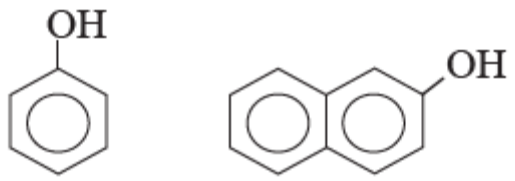
-- SUSHMA DESHMUKH

ALCOHOLS

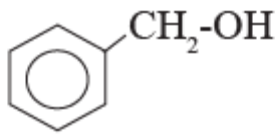
- Alcohols are organic compounds whose molecule contain hydroxyl group(-OH) attached to a saturated carbon atom.



- There are two types of aromatic hydroxyl compounds. Phenols and Aromatic alcohols.
- Phenols-- -OH group attached to carbon atom of benzene ring.
- Aromatic alcohols-- -OH group is present in the side chain of aromatic ring.



Phenols



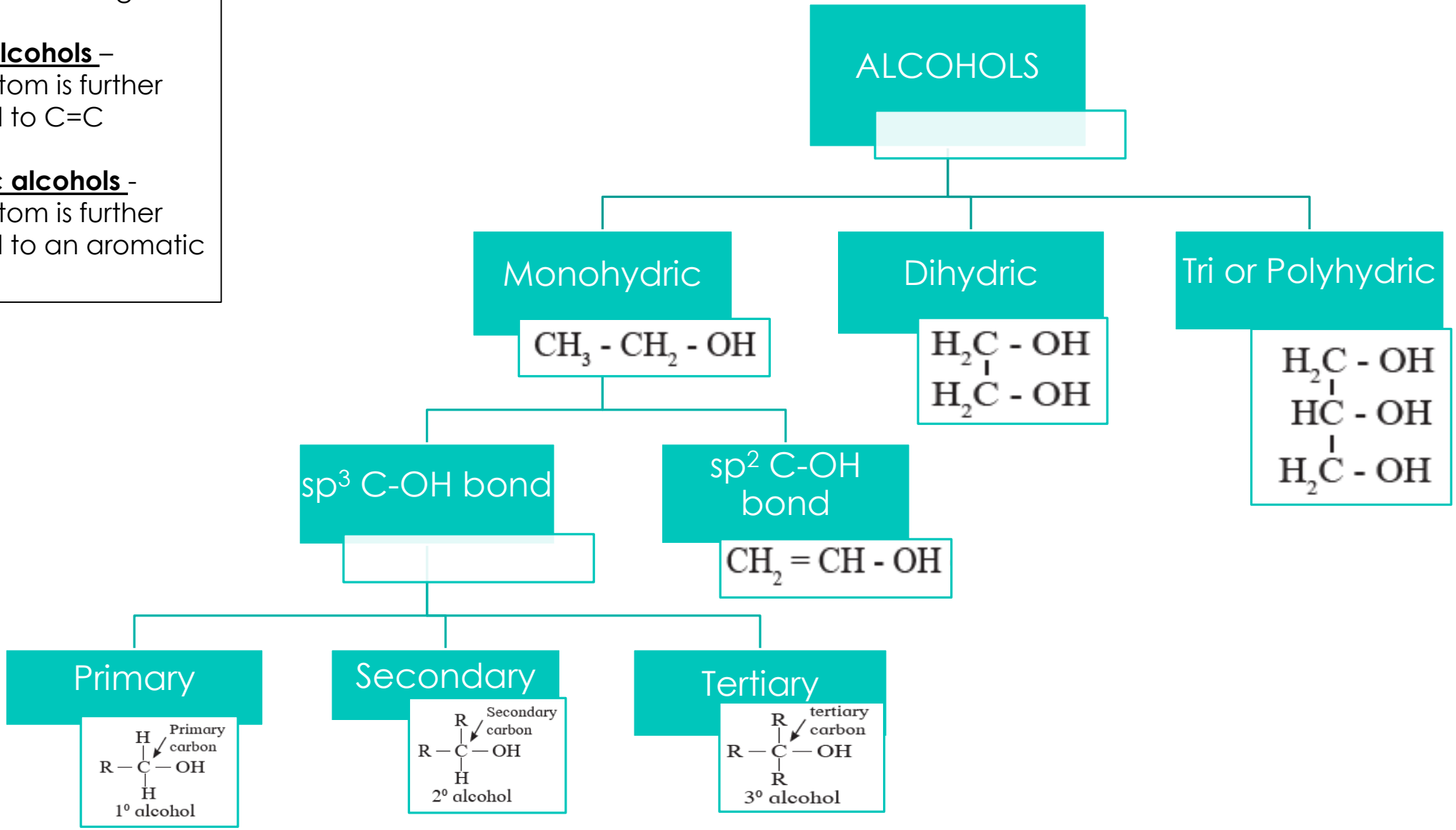
Aromatic alcohol

CLASSIFICATION OF ALCOHOLS

sp^3 C-OH bond linkages can be :-

- **Allylic alcohols** –
- sp^3 C atom is further bonded to C=C

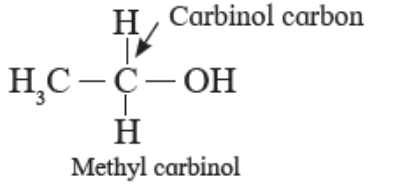
- **Benzylic alcohols** -
- sp^3 C atom is further bonded to an aromatic ring



Nomenclature of Alcohols---

Common/trivial system—There are named as Alkyl Alcohol

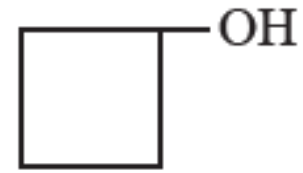
Carbinol system—They are considered as derivative of methyl alcohol which is called carbinol.



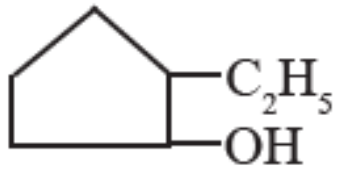
Methyl carbinol

IUPAC system—They are named as alkanols.The ending ‘e’ from parent alkane , alkene , alkyne is replaced by the suffix ‘ol’.

Cyclic alcohols are named by using prefix cyclo to the parent alkane.



Cyclobutanol



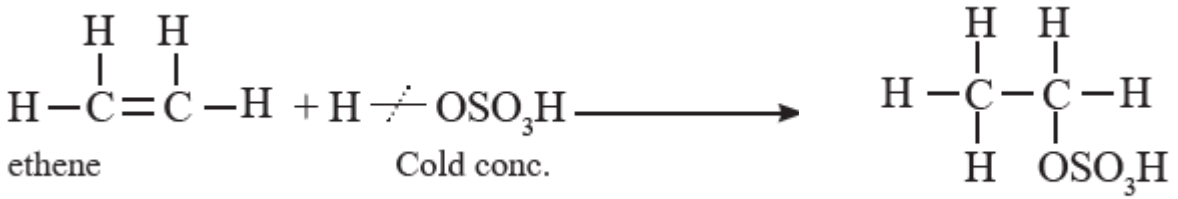
2- Ethylcyclopentanol

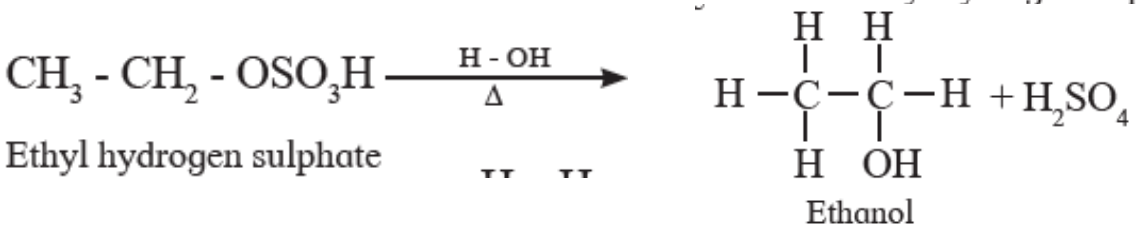
Structural formula	Common/ Trivial Name	IUPAC Name
$H_3C\text{-}OH$	Methyl alcohol	Methanol
$H_3C\text{-}CH_2\text{-}OH$	Ethyl alcohol	Ethanol
$H_3C\text{-}CH_2\text{-}CH_2\text{-}OH$	n -Propyl alcohol	Propan -1-ol
$H_3C\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\text{-}OH$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

Preparation of alcohols

- From alkyl halide—By hydrolysis with aqueous alkali or moist silver oxide.

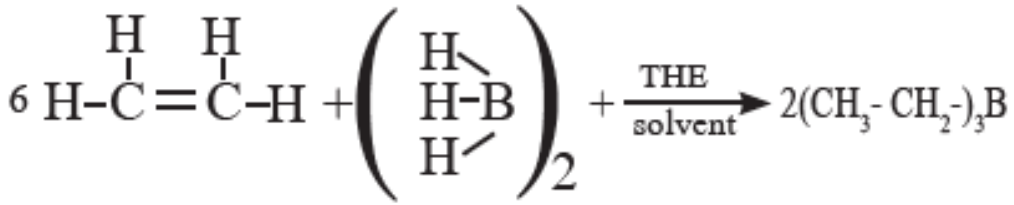
- By acid catalysed hydration of alkens—Alkene reacts with sulphuric acid to produce alkyl hydrogensulfate,which on hydrolysis gives alcohol.



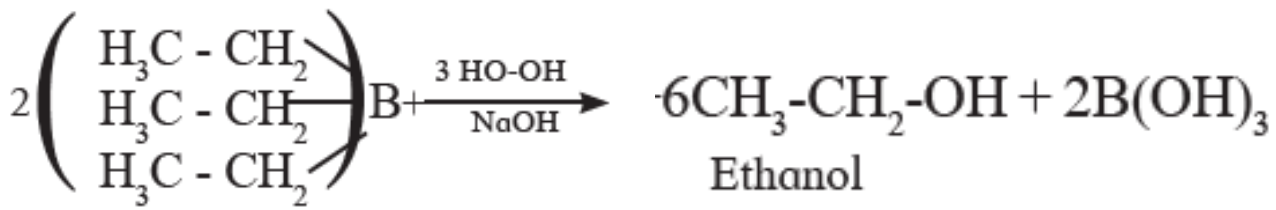


Hydroboration—Oxidation of alkenes----

Alkene undergoes addition reaction with diborane to give to trialkylborane which on oxidation with Hydrogen peroxide in alkaline medium gives alcohol.



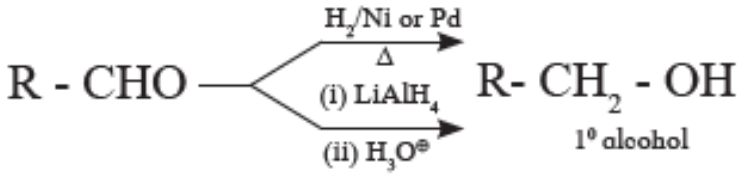
Ethene Diborane

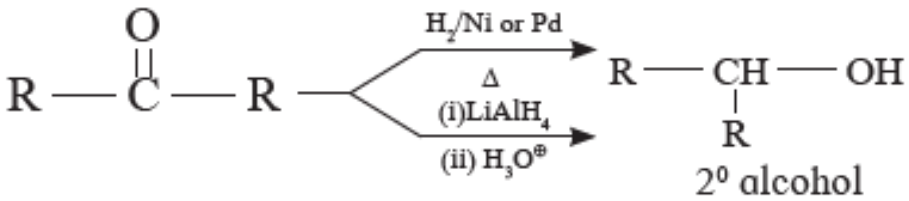


Triethylborane Ethanol

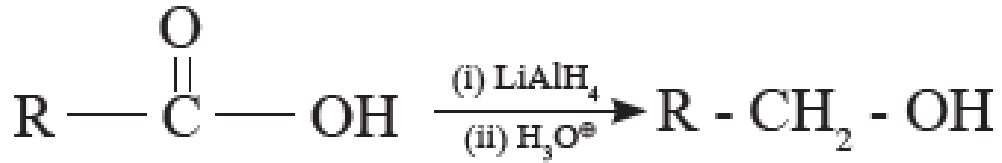
i. By reduction of aldehydes and ketones :

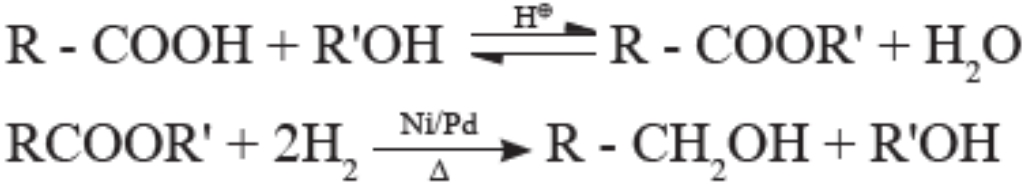
Aldehydes on reduction by H_2/Ni or $LiAlH_4$ give primary alcohols (1^0). Similarly ketones on reduction with H_2/Ni or $LiAlH_4$ give secondary alcohols (2^0).





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





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

(adduct)

Chemical Properties of Alcohols

a. Laboratory tests

i. Litmus test : Aqueous solution of alcohols is neutral to litmus.

ii. Reaction with bases : Alcohols show no acidic character.It do not react with aq NaHCO or aq NaOH When alcohols treated with alkali metals like Na or K they React to give sodium or potassium alkoxide with liberation of hydrogen gas

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

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

i. Acidic character of alcohols

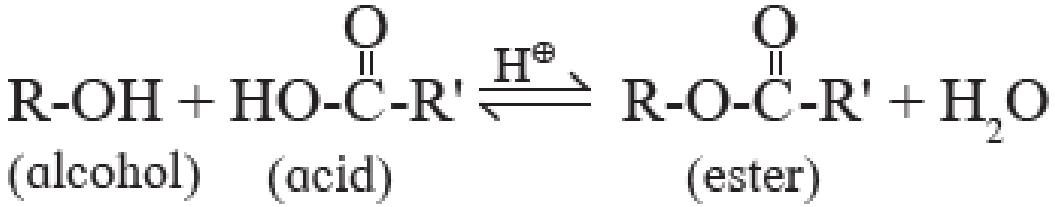
Ionization of alcohols is represented by the following equilibrium

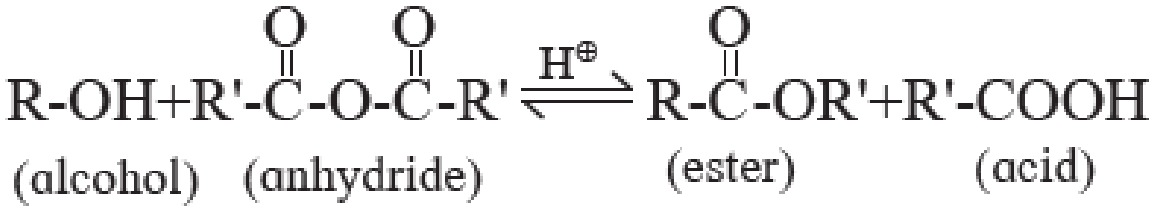
$$\underset{\text{(alcohol)}}{R - OH} + H_2O \rightleftharpoons \underset{\text{(alkoxide)}}{R{\rightarrow}O^{\ominus}} + H_3O^{\oplus}$$

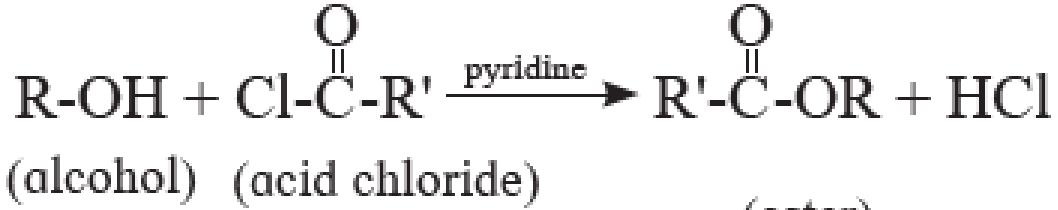
Electron donating inductive effect (+I effect) of alkyl group destabilizes the alkoxide ion (the conjugate base of alcohol). As a result alcohol does not ionize much in water, and behaves like neutral compound in aqueous medium.

ii. Esterification :

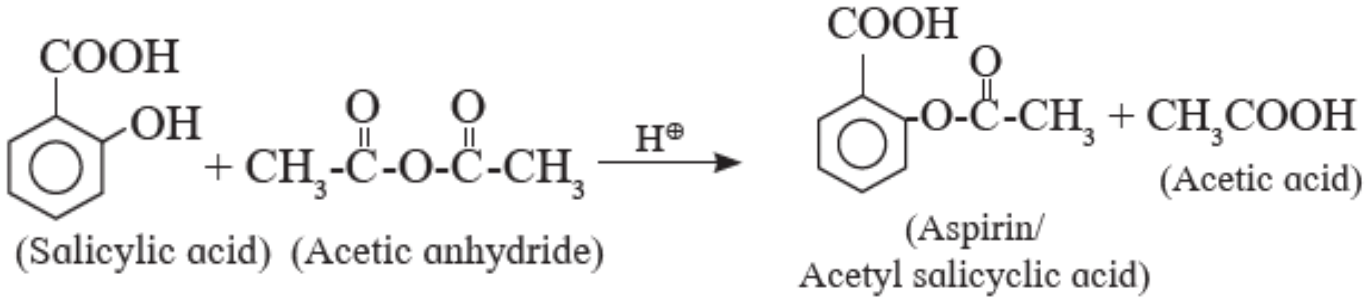
Alcohols by reaction with carboxylic acid, acid halides and acid anhydrides
Forms esters in presence of concentrated sulphuric acid .







Aspirin, a well known generic medicine, is an acetyl derivative of salicylic acid formed by its acetylation using acetic anhydride.



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

i. Reaction with hydrogen halides : Alcohols reacts with hydrogen halides to form alkylhalides (

$$R - OH + HX \xrightarrow[\text{condition}]{\text{suitable}} R - X + H_2O$$

(Alcohol) (Alkyl halide)

$$R - OH + HCl \xrightarrow[ZnCl_2]{\text{anhydrous}} R - Cl + H_2O$$

$$R - OH + HBr \xrightarrow[\text{heat}]{NaBr, H_2SO_4} R - Br + H_2O$$

$$R - OH + HI \xrightarrow{NaI/H_3PO_4} R - I + H_2O$$

ii. Reaction with phosphorous halide :

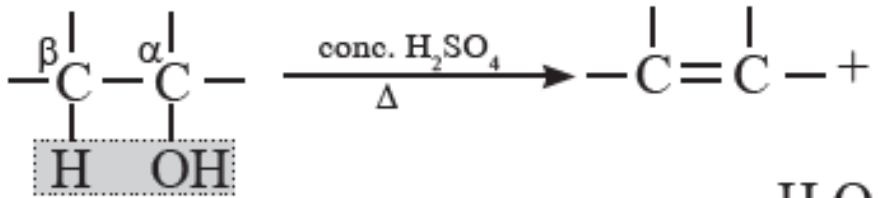
Alcohols react with phosphorous pentahalide (PX_5) and phosphorous trihalide (PX_3) to form alkyl halides.

$$3R - OH + PX_3 \longrightarrow 3R - X + H_3PO_3$$

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

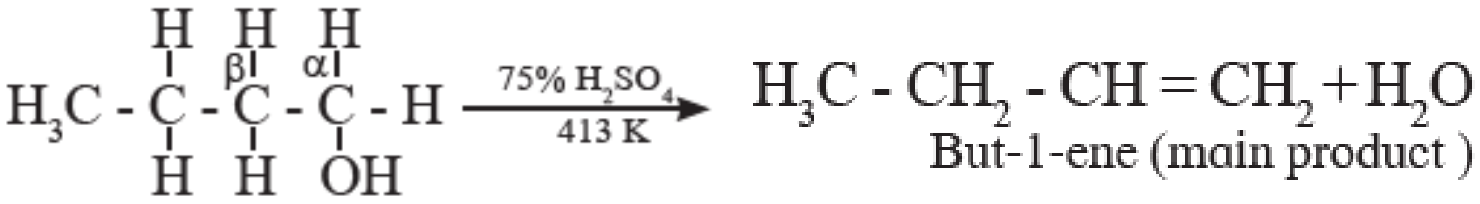
iii. Dehydration of alcohols to alkenes :

Alcohol when treated with concerntrated sulphuric acid or phosphoric acid or alumina undergoes dehydration to form alkene and water.

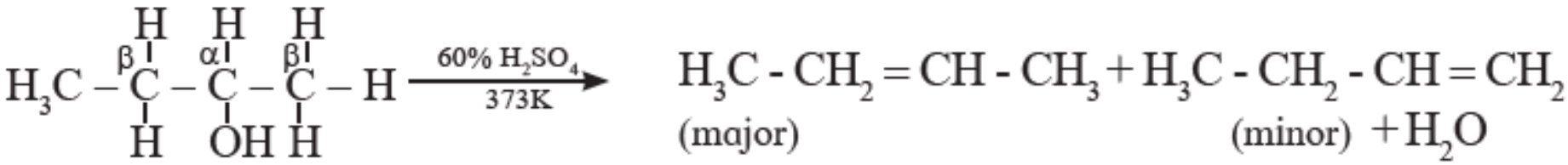


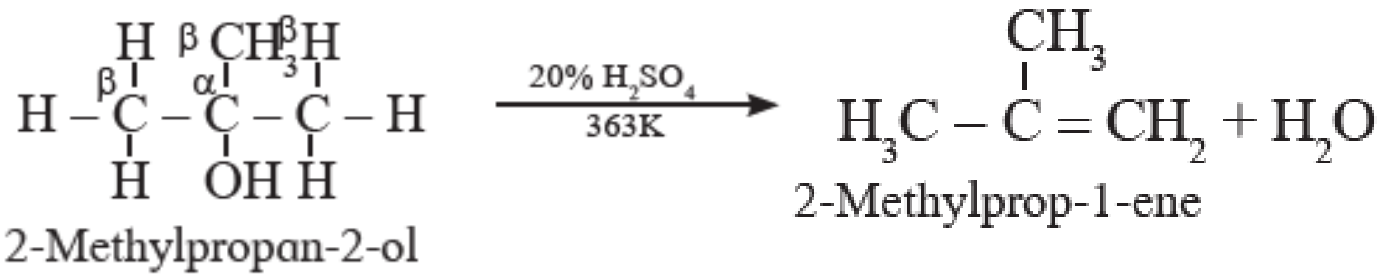
Alcohol Alkene

The ease of dehydration of alcohols is in the order $3^0 > 2^0 > 1^0$



But-1-ene (main product)



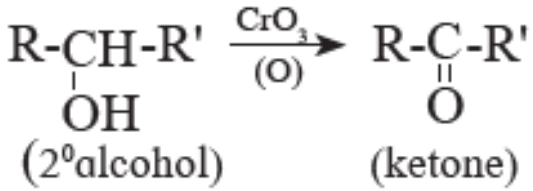


2-Methylpropan-2-ol

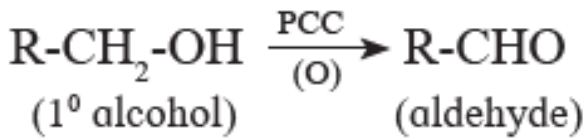
2-Methylprop-1-ene

iv. Oxidation of alcohols :

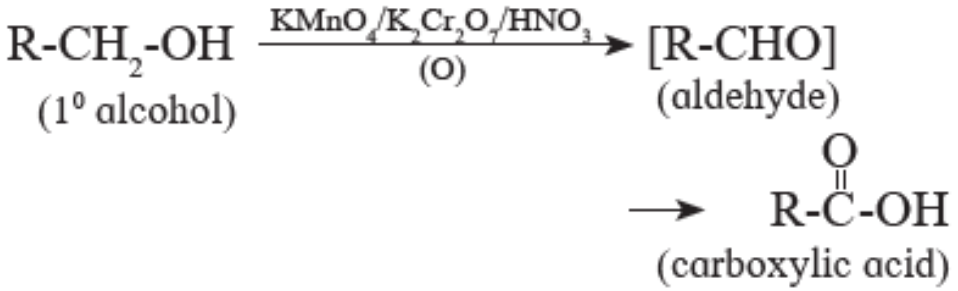
On reaction with oxidising agent primary and secondary alcohols undergo dehydrogenation to form carbonyl compounds, namely aldehydes and ketones respectively Seondary alcohol on oxidation with chromic anhydride (CrO_3) forms ketone.



(2⁰alcohol) (ketone)



(1⁰ alcohol) (aldehyde)



(1⁰ alcohol) (aldehyde) (carboxylic acid)

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

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

PCC (pyridiniun chlorochromate).

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

$$R\text{-}CH_2\text{-}OH \xrightarrow[\text{Oxidation}]{Cu/573K} R\text{-}CHO$$

(1^0 alcohol) (aldehyde)

$$R\text{-}\underset{\underset{OH}{|}}{CH}\text{-}R' \xrightarrow[\text{Oxidation}]{Cu/573K} R\text{-}\underset{\underset{O}{||}}{C}\text{-}R'$$

(2^0 alcohol) (ketone)

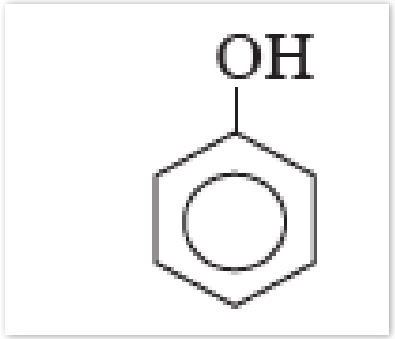
$$H_3C\text{-}\underset{\underset{CH_3}{|}}{C}(OH)\text{-}CH_3 \xrightarrow[\text{dehydration}]{Cu/573K} H_3C\text{-}\underset{\underset{CH_3}{|}}{C}=CH_2$$

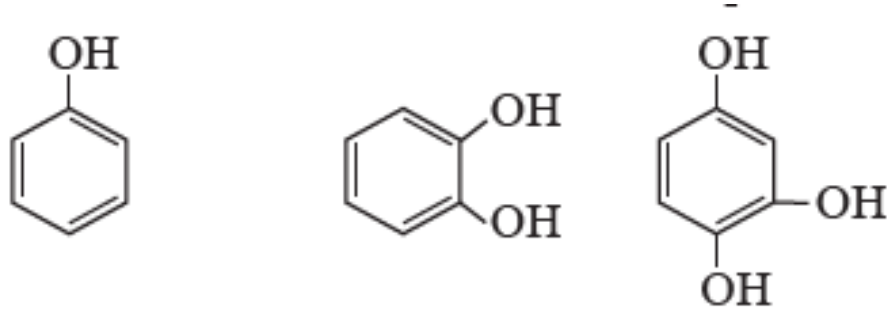
(3^0 alcohol) (alkene)

Alcohols :

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

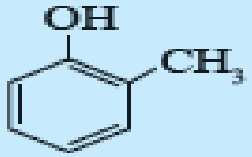
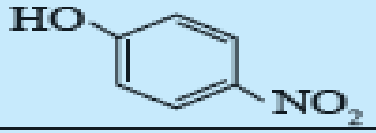
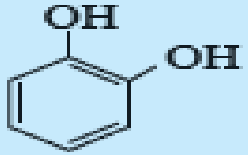
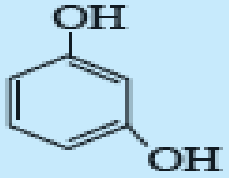
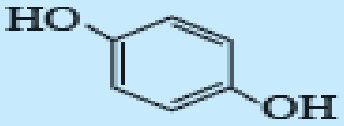
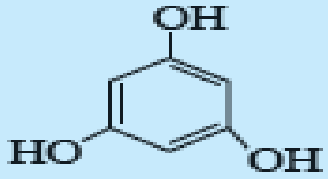
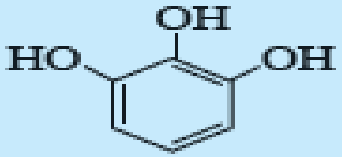
PHENOLS





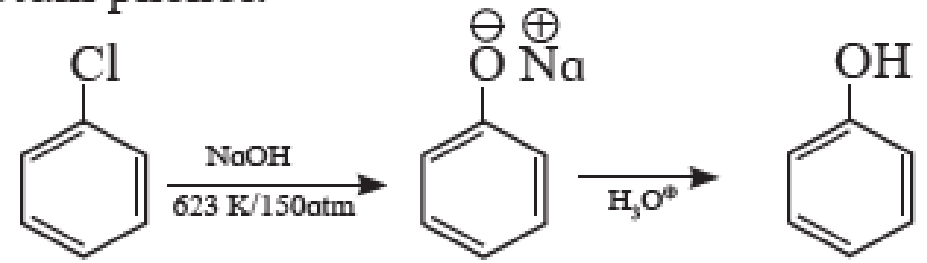
Monohydric alcohols/phenols | **Dihydric alcohols/ phenols** | **Trihydric alcohols/phenols**

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

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

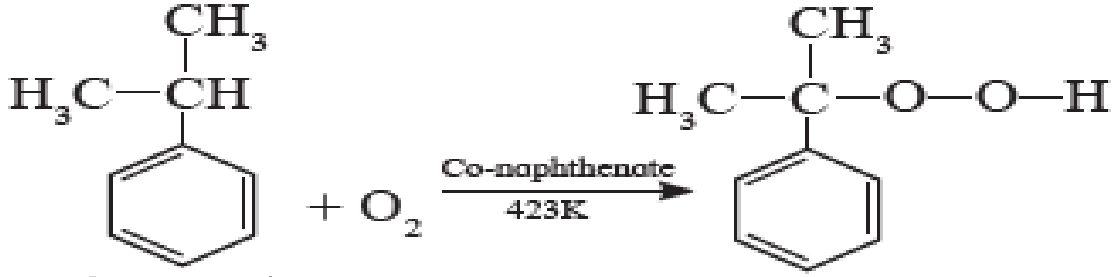
Preparation Of Phenols

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

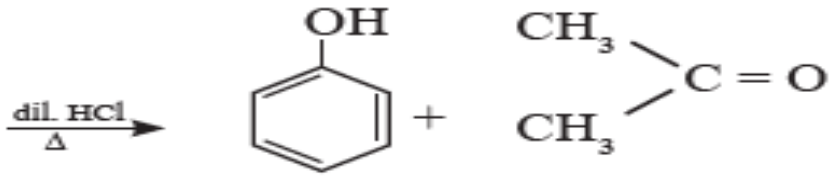


(Chloro benzene) (Sodium phenoxide) (Phenol)

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

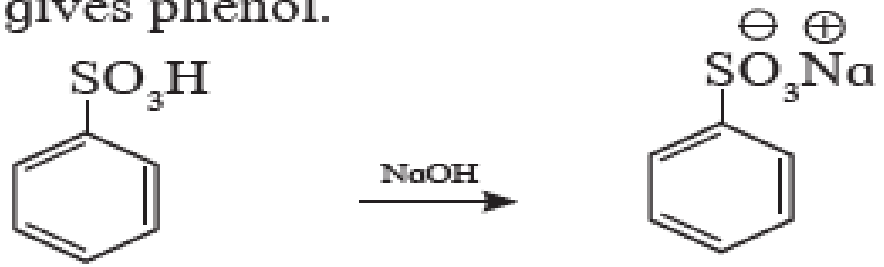


(Cumene) (air) (Cumene hydroperoxide)

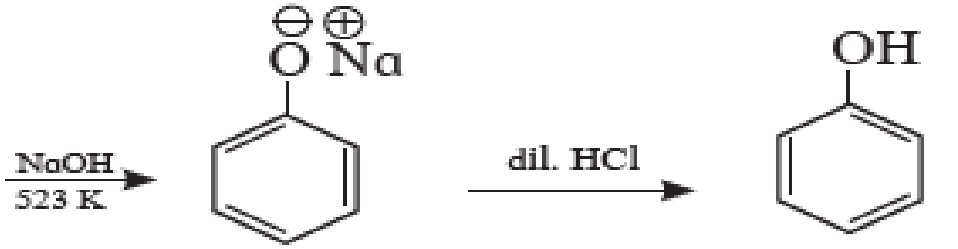


(Phenol) (Acetone)

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

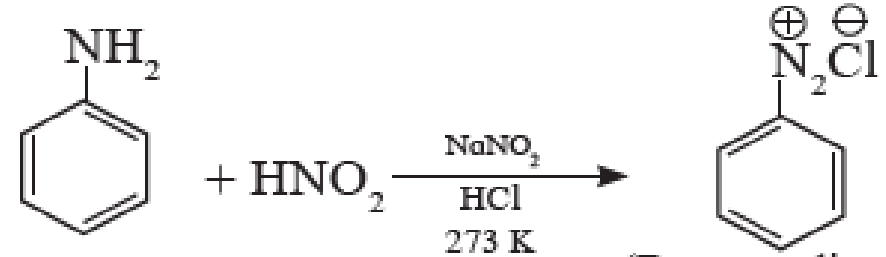


(Benzene sulphonic acid) (Sodium benzene sulphonate)

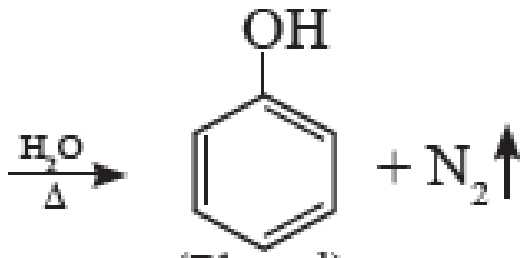


(Sodium phenoxide) (Phenol)

d. From aniline : Aniline is treated with nitrous acid [$NaNO_2$ + HCl] at low temparature to obtain benzene diazonium chloride, which on hydrolysis gives phenol



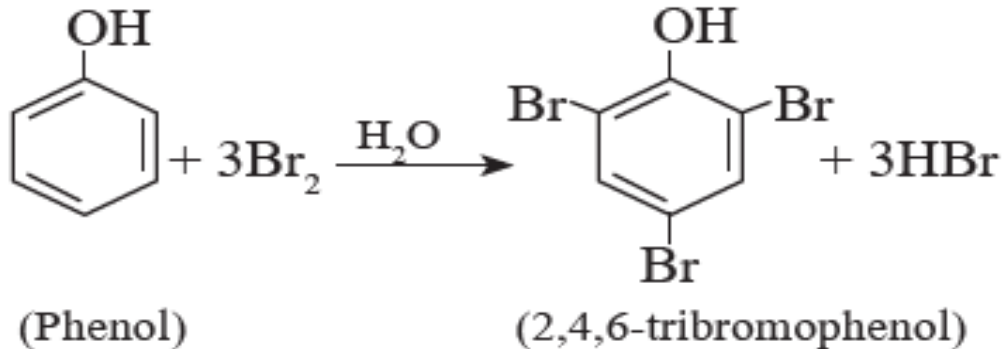
(Aniline) (Benzene diazonium chloride)



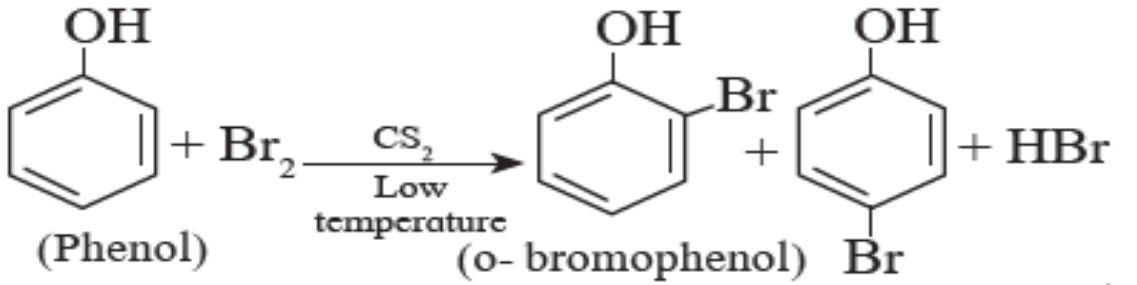
(Phenol)

Reactions of Phenols

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



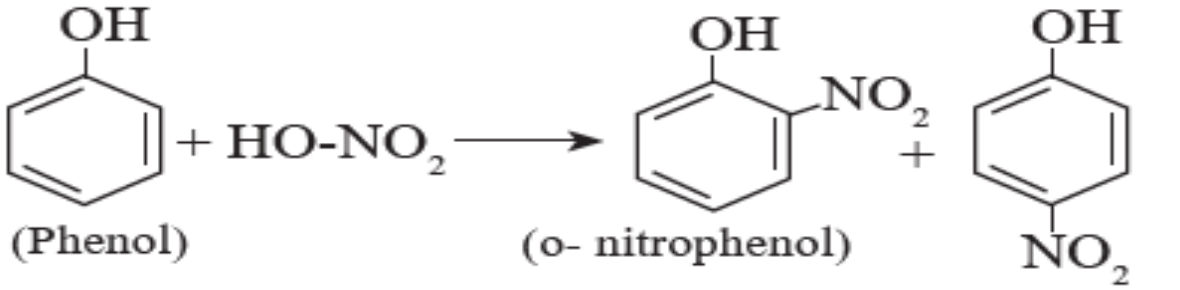
(Phenol) (2,4,6-tribromophenol)



(Phenol) (o- bromophenol) (p- bromophenol)

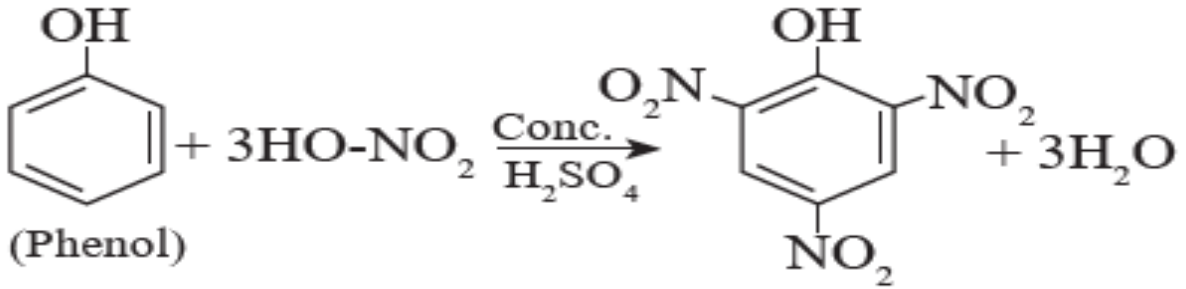
Major product

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



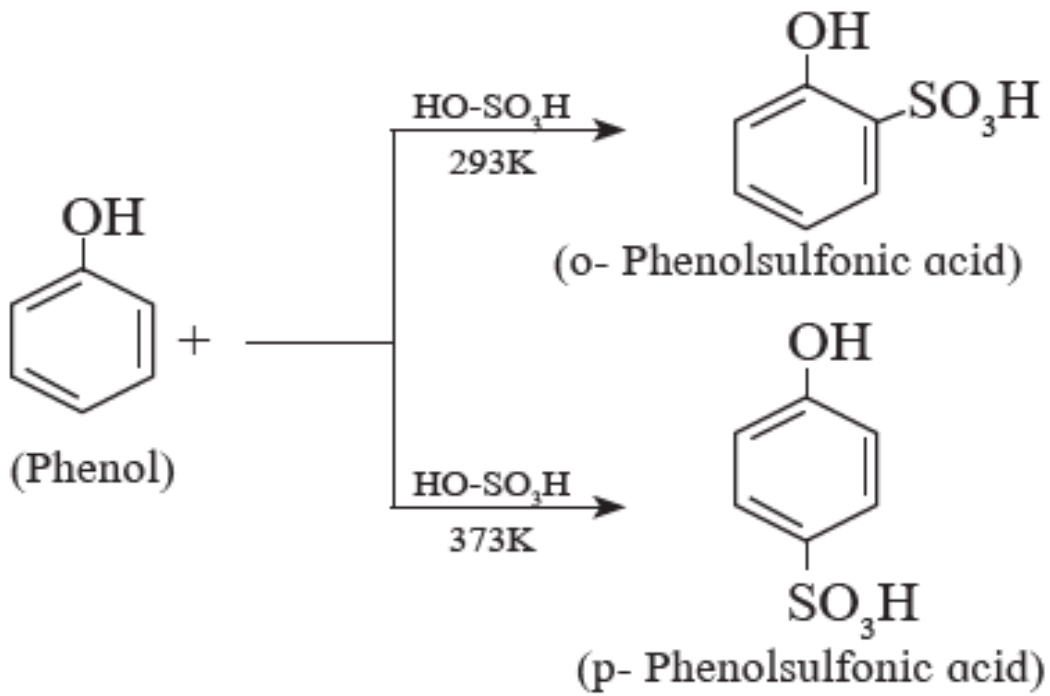
(Phenol) (o- nitrophenol) (p- nitrophenol)

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

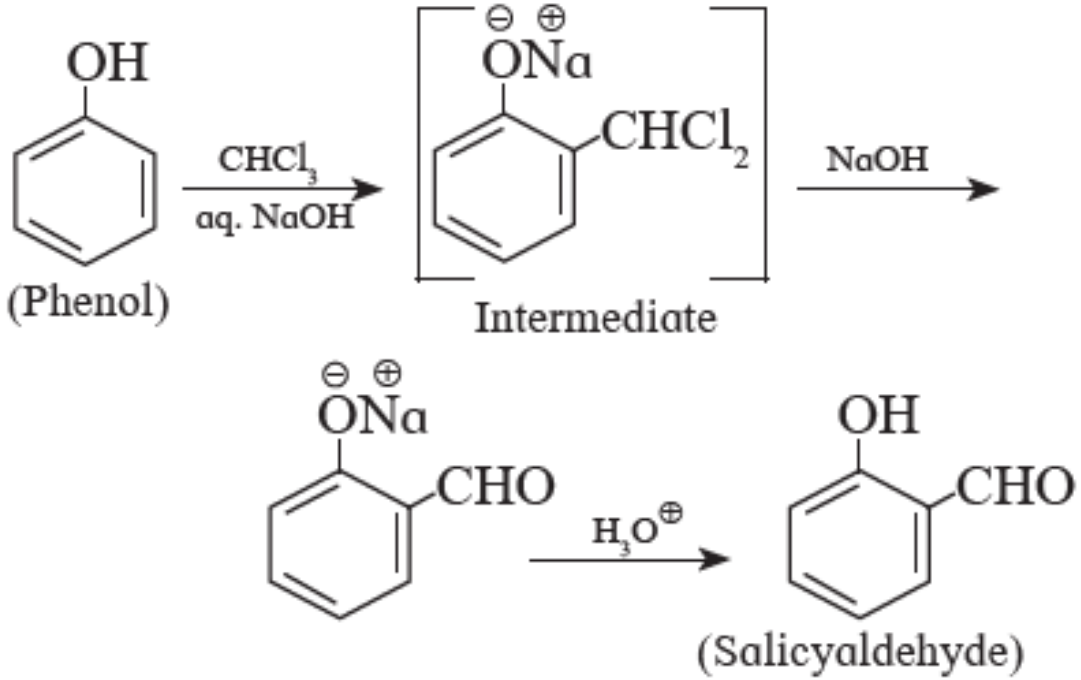


(Phenol) (picric acid)

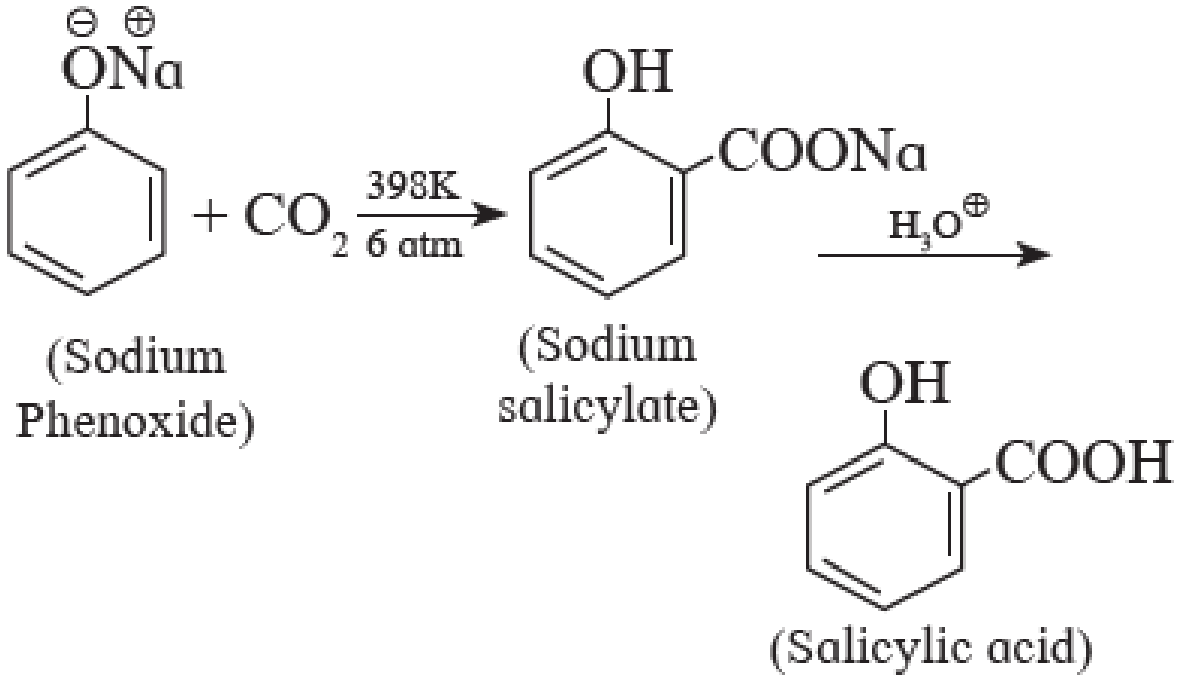
iii. Sulfonation of phenol : Phenol reacts with concerntrated sulfuric acid at room temperature to give o-phenolsulfonic acid and at 373K, p-phenol sulfonic acid



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

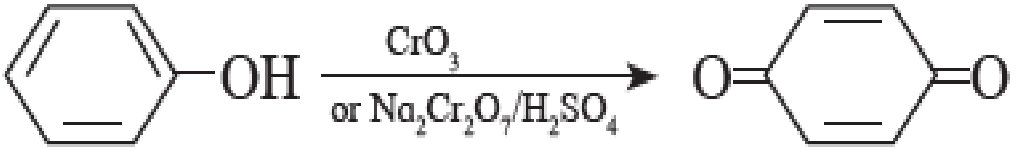


v. Kolbe reaction : The treatment of sodium phenoxide with carbondioxide at 398 K under pressure of 6 atm followed by acid- hydrolysis, salicylic acid (o-hydroxybenzoic acid) is formed. This reaction is known as Kolbe's reaction



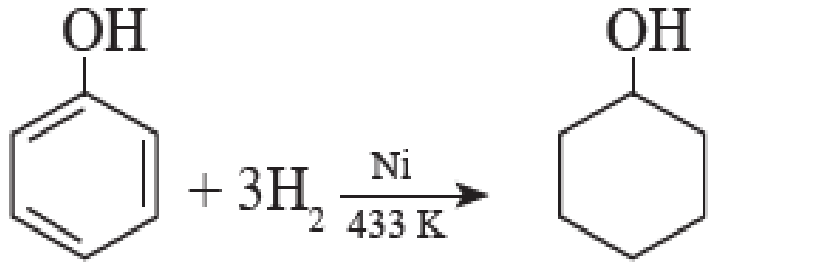
(Sodium Phenoxide) (Sodium salicylate) (Salicylic acid)

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



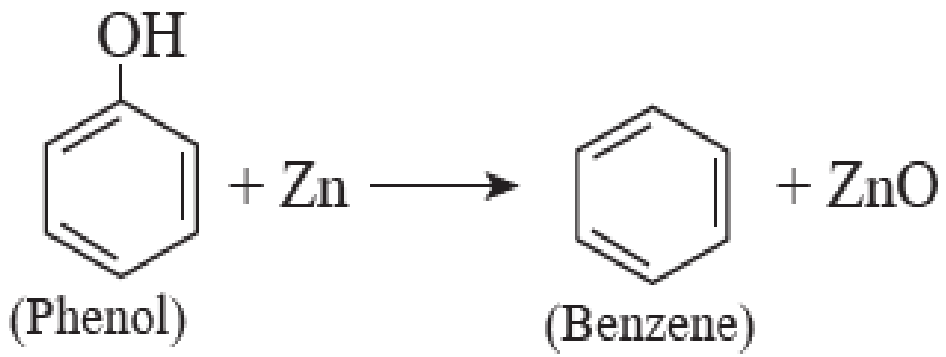
(Phenol) (p-Benzoquinone)

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

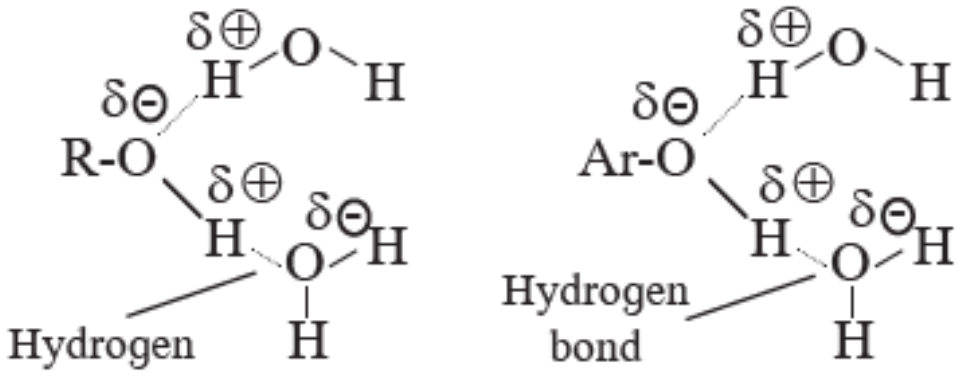


(Phenol) (Cyclohexanol)

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



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



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

Uses of phenols

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

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

$$3Ar - OH + FeCl_3 \longrightarrow (Ar - O)_3 - Fe + 3HCl$$

(neutral) (deep colour)

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

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

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

ETHERS

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

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

Classification of Ethers :

symmetrical ethers (simple ethers)

two alkyl/ aryl groups bonded to oxygen atom are same $R - O - R/Ar - O - Ar$

$CH_3 - O - CH_3$

unsymmetrical ethers (mixed ethers)

two alkyl/ aryl groups bonded to oxygen atom are different

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

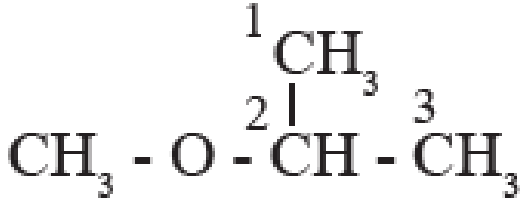
$CH_3 - O - C_2H_5$, $C_6H_5 - O - CH_3$

Nomenclature of Ethers :

common system ethers are named by writing names of the alkyl groups attached to the oxygen atom in alphabetical order and word ether is added. If two alkyl groups are same, prefix di- is used. .

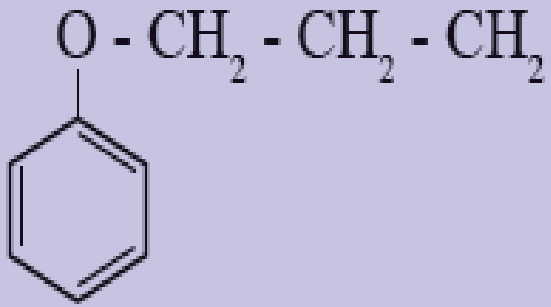
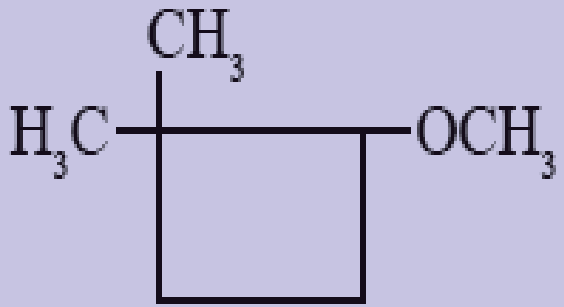
IUPAC system ethers are named as **alkoxyalkanes**

The larger alkyl group is considered to be the parent alkane. The name of the smaller alkane is prefixed by the name of alkoxy group and its locant. For example :



2-Methoxypropane

Some alkoxy group	
CH_3-CH_2O-	Ethoxy
CH_3-CH_2-CH_2-O-	n-Propoxy
CH_3-CH(-CH_3)-O-	Isopropoxy

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

Preparation Of Ethers

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

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

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

b. Williamson Synthesis :

alkyl halide is treated with sodium alkoxide or sodium phenoxide to give dialkyl ethers or alkyl aryl ethers.

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

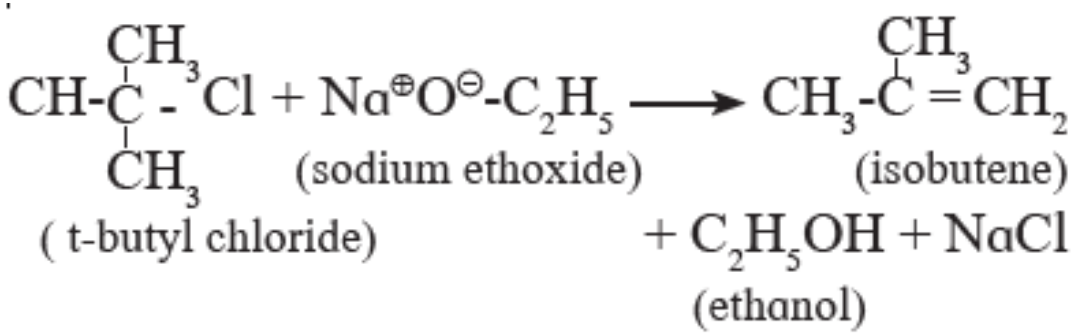
$$R\text{-}X + Na^{\oplus}\, O^{\ominus}\text{-}Ar \longrightarrow R\text{-}O\text{-}Ar + NaX$$

This reaction follows S_N2 mechanism. Ether is formed as a result of backside attack by alkoxide/ phenoxide ion (a nucleophile) on alkyl halide.

For example : t-butyl methyl ether can be synthesised by reaction methyl bromide with sodium t-butoxide.

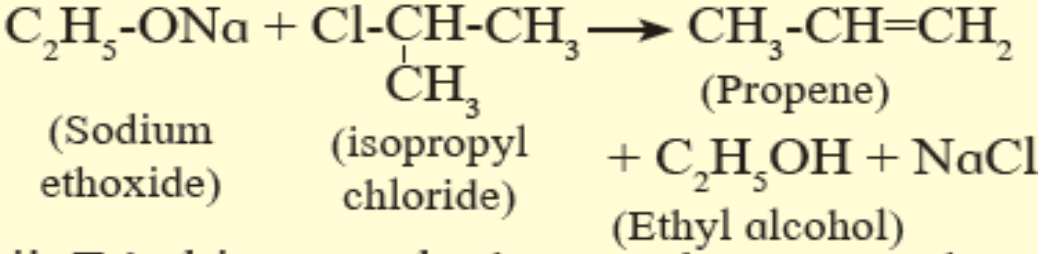
$$\underset{\text{(sodium t-butoxide)}}{(CH_3)_3C\text{-}O^{\ominus}\, Na^{\oplus}} + \underset{\text{(methyl bromide)}}{CH_3\text{-}Br} \rightarrow \underset{\text{(t-butyl methyl ether)}}{(CH_3)_3C\text{-}O\text{-}CH_3} + NaBr$$

If secondary or tertiary alkyl halides are used, the reaction leads mainly to alkene formation

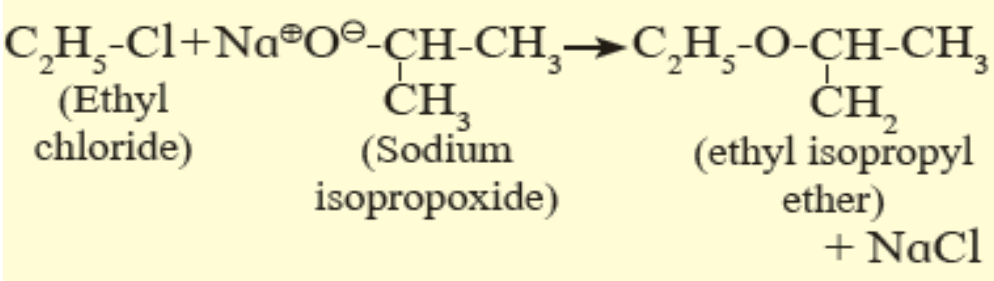


Problem 11.9 : Ethyl isopropyl ether does not form on reaction of sodium ethoxide and isopropyl chloride.

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



ii. Ethyl isopropyl ether can be prepared as follows using ethyl chloride (1⁰chloride) as as substrate.

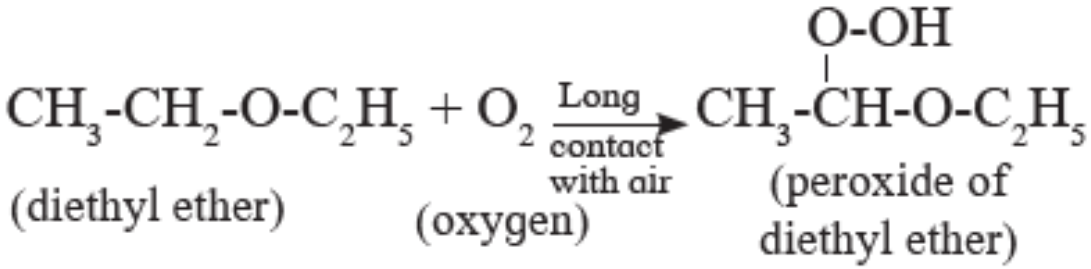


Reactions of Ethers

a. Laboratory test for ethers : Ethers are neutral compounds in aqueous medium.

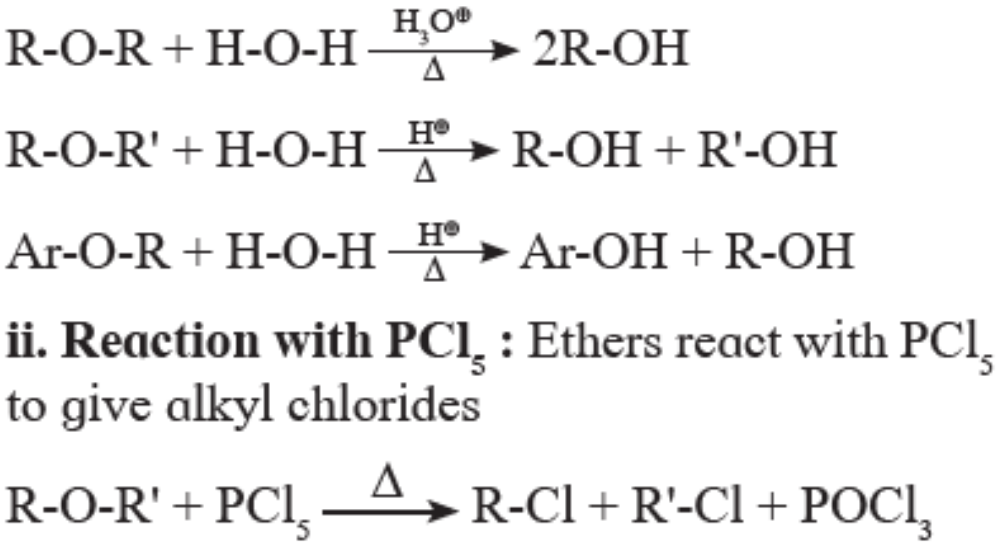
b. Reaction involving alkyl group of ether :

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



c. Reaction involving C-O bond

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



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

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

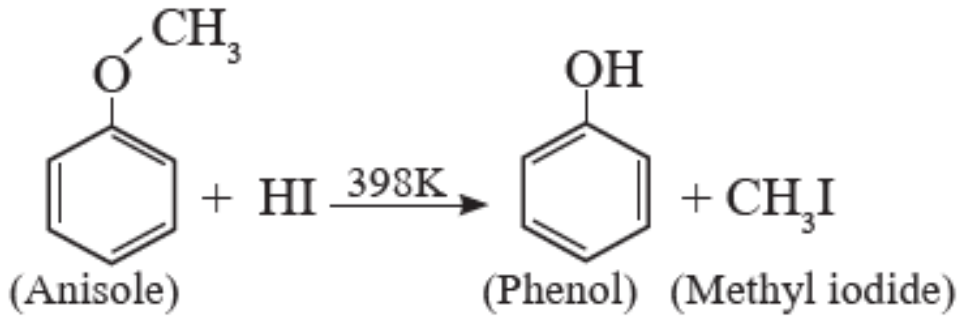
$$R\text{-}O\text{-}R' + PCl_5 \xrightarrow{\Delta} R\text{-}Cl + R'\text{-}Cl + POCl_3$$

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

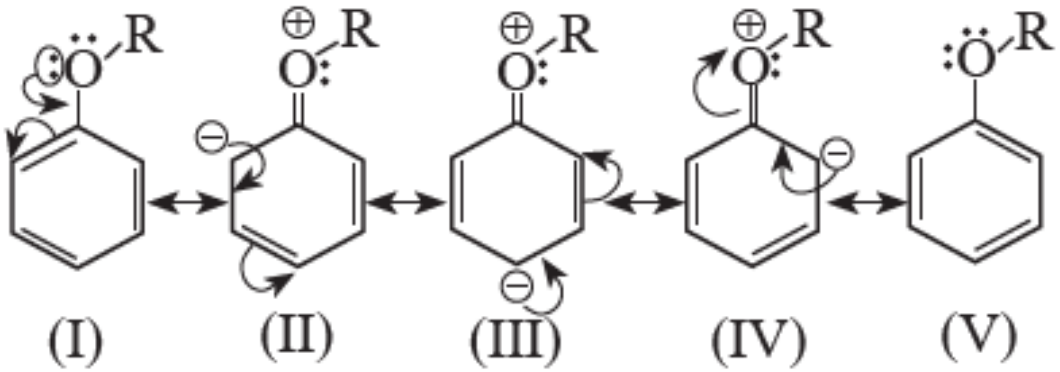
$$R\text{-}O\text{-}R + HX \longrightarrow R\text{-}X + R\text{-}OH \xrightarrow{HX} R\text{-}X$$

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

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

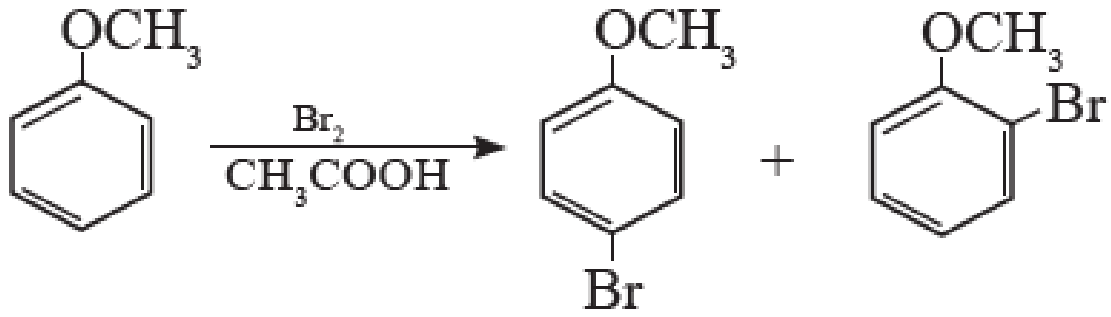


d. Electrophilic substitution in aromatic ethers : The alkoxy group in aromatic ether is a ring activating and ortho-, para-directing group toward electrophilic aromatic substitution. This is evident from the resonance structures:



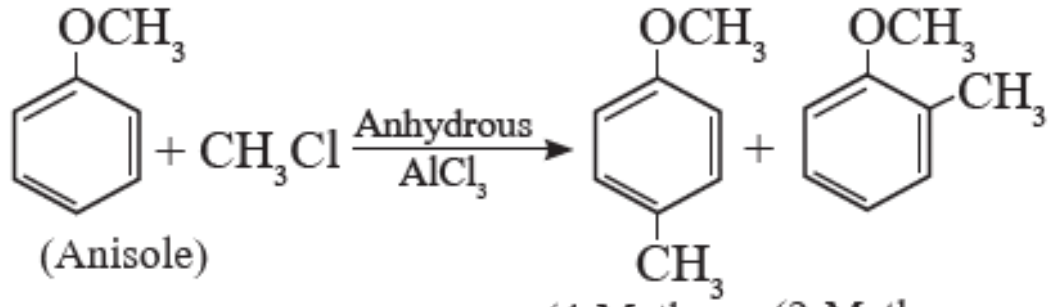
+R Effect of -$\ddot{O}$R group results in increased electron density at the para- and two ortho-positions (see resonance structures II, III and IV).

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

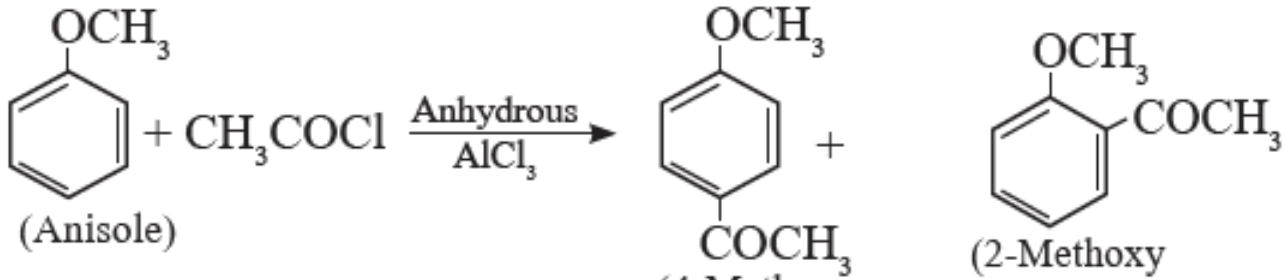


(Anisole) 90% (p-bromo anisole) 10% (o-bromo anisole)

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

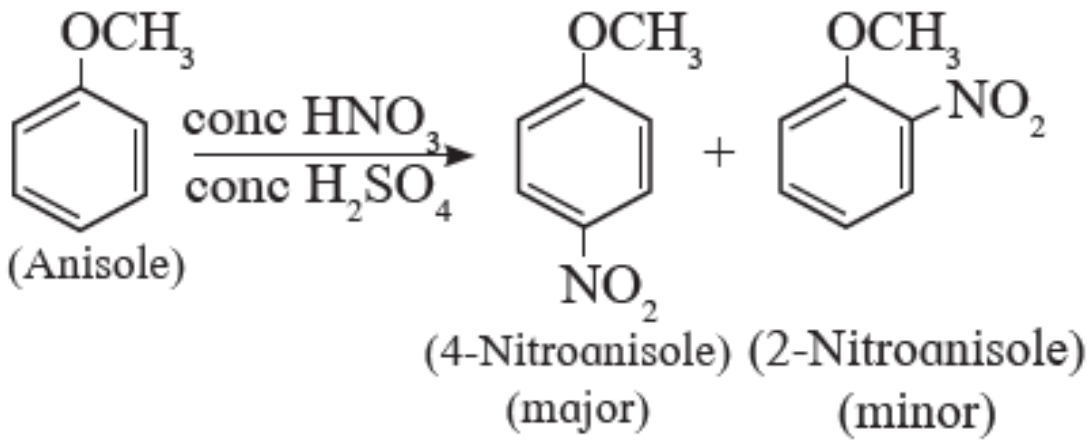


(Anisole) (4-Methoxy toluene) (major) (2-Methoxy toluene) (minor)



(Anisole) (4-Methoxy acetophenone) (major) (2-Methoxy acetophenone) (minor)

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



Uses of ethers

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