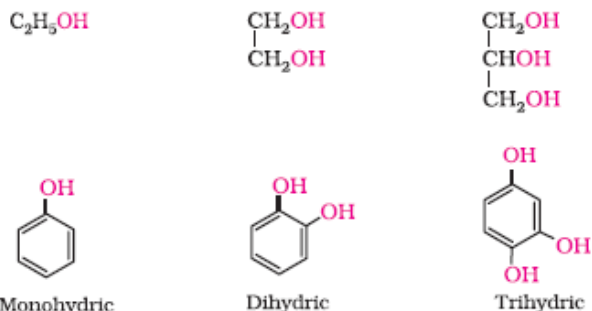
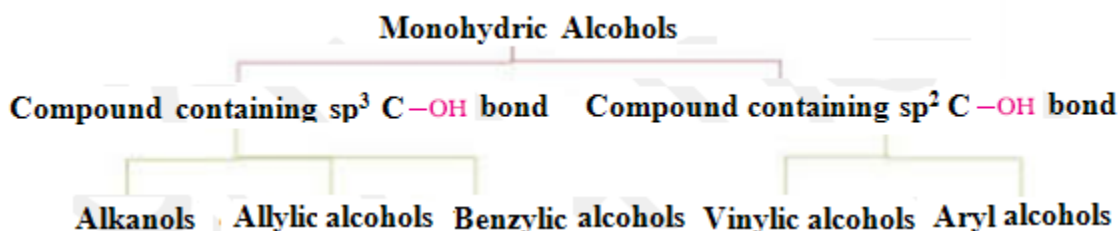


Chapter 11: Alcohol, Phenol and Ethers

1. Classification: On the basis of number of –OH group it can be classified as mono, di and poly hydric (tri, tetra etc), for example



Classification of Monohydric alcohol: It further categorized according to hybridization of carbon atom like as

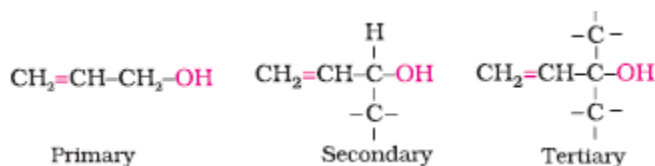


i) Compound containing sp^3 C-OH bond: -OH group is bonded with sp^3 hybridized carbon. This class includes-

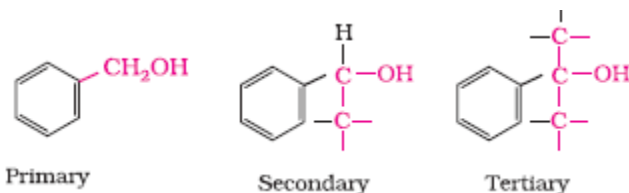
a) Alkanols:



b) Allylic alcohols:



c) Benzylic alcohols:

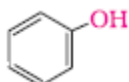


ii) Compound containing sp^2 C-OH bond:

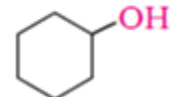
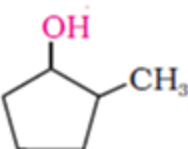
a) Vinylic alcohols:



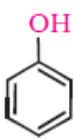
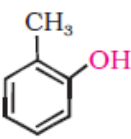
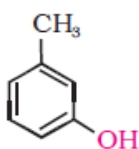
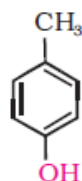
b) Aryl alcohols:



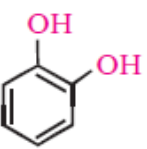
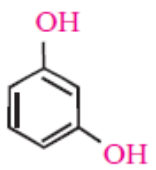
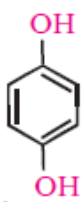
2. Common and IUPAC name of Alcohols:

Compound	Common name	IUPAC name
$\text{CH}_3 - \text{OH}$	Methyl alcohol	Methanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	<i>n</i> -Propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array}$	Isopropyl alcohol	Propan-2-ol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	<i>n</i> -Butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{OH} \end{array}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Glycerol	Propane -1, 2, 3-triol
	—	Cyclohexanol
	—	2-Methylcyclopentanol

3. Common and IUPAC name of Phenols:

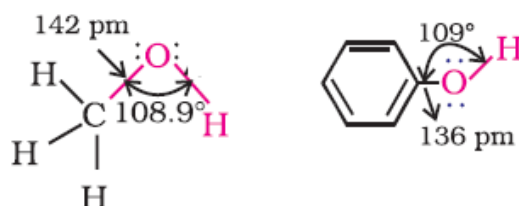
				
Common name	Phenol	<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

4. Dihydroxy derivatives of Benzene:

			
Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

5. Structure of alcohol and phenol: In alcohols, carbon atom of R (-CH₃) and oxygen atom of -OH group are sp³ hybridised. The C-OH bond angle is slightly less than tetrahedral angle (109.28°) due to repulsions b/w lone pairs of electrons of oxygen atom. The C-O and O-H bonds are polar because of high electronegativity of oxygen atom.

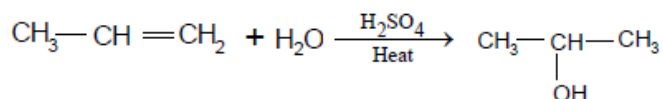
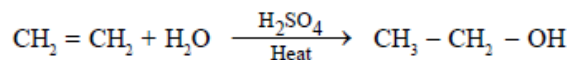
In phenols, the -OH group is attached to Sp² hybridised carbon and thus, the C - O bond acquires a partial double bond character.



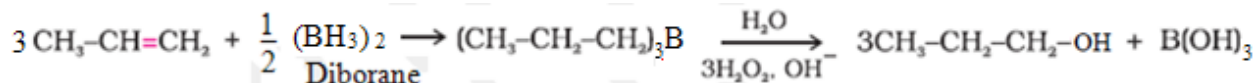
6. Preparation of Alcohols:

1) From Alkenes:

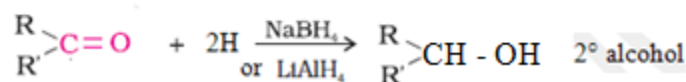
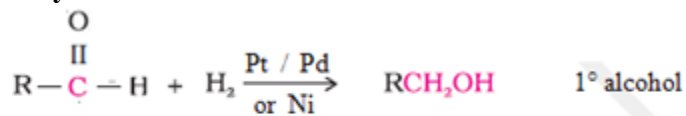
(i) **By acid catalysed hydration:** Alkenes react with water to form alcohols with presence of few drop of concentrated sulphuric acid. This is electrophilic addition which is carried out as Markonikov rules.



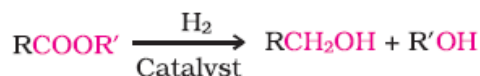
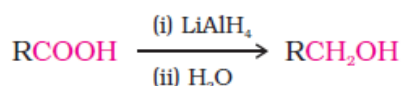
(ii) **By hydroboration -oxidation:** Addition occurs as anti-Markonikov rules.



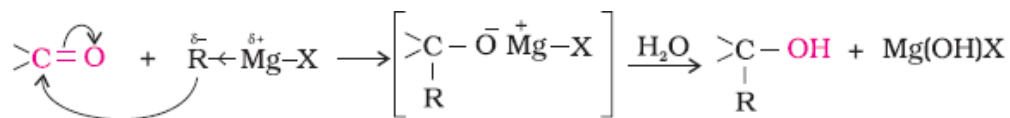
2) By reduction of aldehyde and ketones:



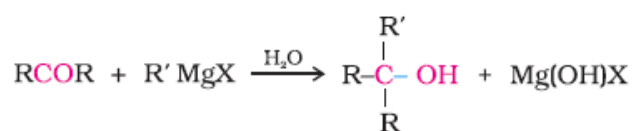
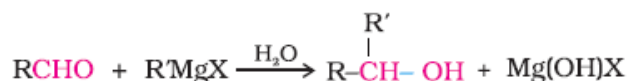
3) By reduction of carboxylic acid and esters:



4) **From Grignard reagents:** First step of reaction is nucleophilic addition to form an intermediate.

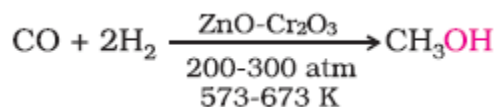


By using different aldehyde and ketones, it gives primary, secondary and tertiary alcohols like as

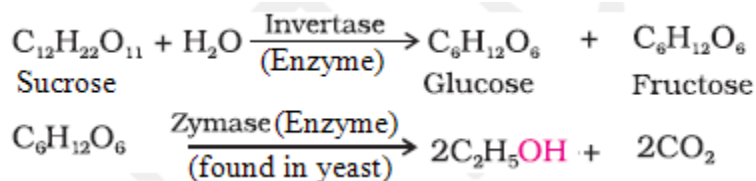


7. Some commercially important alcohols:

1) **Methyl alcohol (Wood spirit):** It is obtained by destructive distillation of wood. It is highly poisonous, drinking of methanol causes blindness. Commercially it is produced by catalytic hydrogenation of CO at high temperature and pressure.



2) **Ethyl alcohol (Grain alcohol):** 100% ethyl alcohol is called absolute alcohol. It is commercially obtained by fermentation.

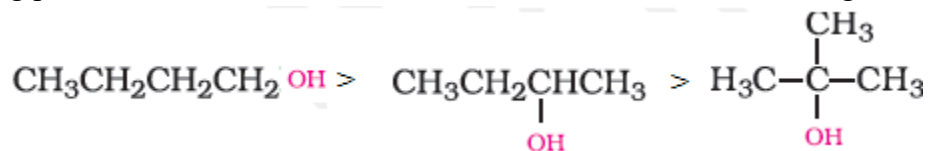


8. Physical Properties of Alcohols:

1) Boiling Point:

i) Alcohols have higher boiling points as compared to those of comparable molecular masses of alkanes, Haloalkanes or ethers. This is b/c in alcohols intermolecular hydrogen bonding exists.

ii) The boiling points of isomeric alcohols decreases with increase in branching-



2) Solubility: The first three members are completely miscible in water due to their ability to form hydrogen bond with water molecules. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but they are soluble in organic solvent like benzene, ether etc.

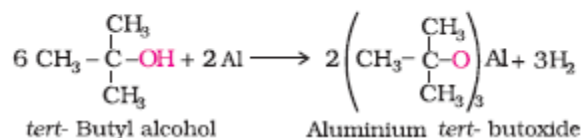
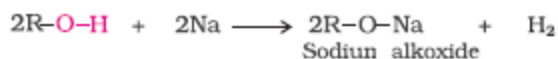
9. Chemical Properties of Alcohols: The reactions of alcohols can be classified into two types-

1) Reactions involving cleavage of oxygen-hydrogen bond (R-CH₂-O----H)

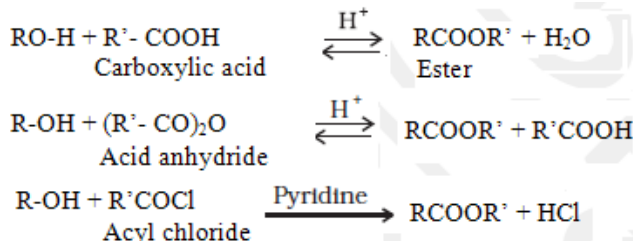
2) Reactions involving cleavage of carbon-oxygen bond (R-CH₂....OH)

1) Reactions involving cleavage of oxygen-hydrogen bond (R-CH₂-O-----H): In that type of bond cleavage, an alcohol reacts as nucleophile.

i) Reaction with metals:

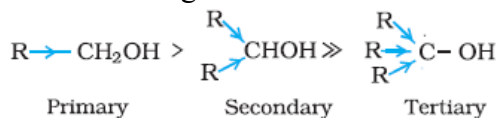


ii) Esterification: Below initial two reactions is reversible so conc H₂SO₄ is used to remove water while in last reaction pyridine is used to neutralize HCl which is formed during the reaction.



Acidity of alcohols and Phenol:

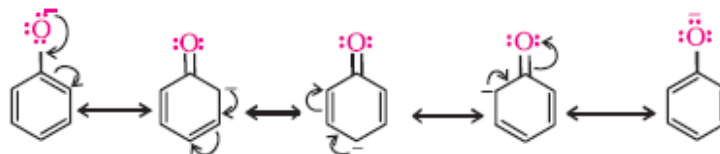
- The above reactions show that alcohols are acidic in nature. The acidic character of alcohols is due to the polar nature of O-H bond. An electron releasing group (alkyl group) increases the electron density on oxygen which decreases the polarity of O-H bond. This decreases the acid strength of alcohol. So the acid strength orders of alcohols are as following-



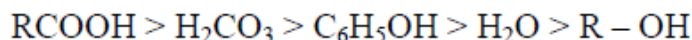
- Alcohols are weaker acids than water due to +I group (alkyl group) present in alcohols, which decreases the polarity of -O-H bond.

+I effect group ↑ polarity of -O-H bond ↓ Acidity of alcohol or Phenol ↓

- Phenol is more acidic than water and alcohols due to stabilisation of phenoxide ion through resonance.



So the order of acidity is

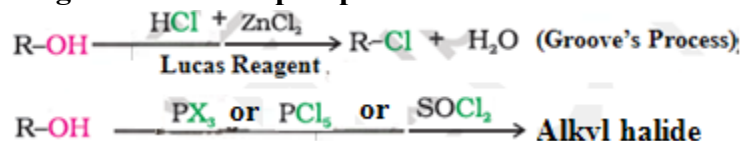


- Presence of electron withdrawing group (-I effect group like $-\text{NO}_2$) increases the acidity of phenol by stabilising phenoxide ion while presence of electron releasing group (+I effect group like $-\text{CH}_3$) decreases the acidity of phenol by destabilising phenoxide ion. Thus increasing acidic strength is
o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4, 6-trinitrophenol (picric acid)

2) Reactions involving cleavage of carbon-oxygen bond ($\text{R-CH}_2\text{---OH}$): In such type of reaction the order of reactivity of alcohols are



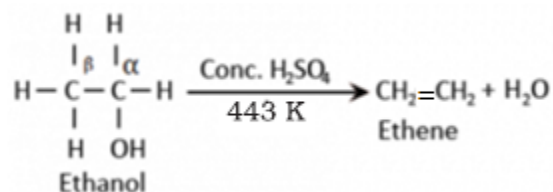
i) Reaction with hydrogen halides and phosphorus halides:



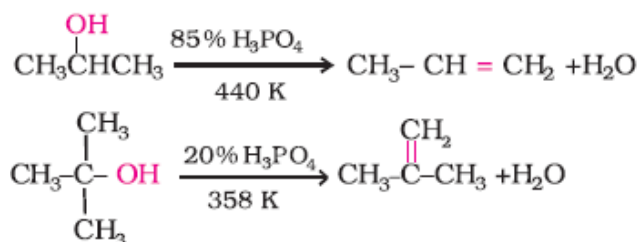
Note: Lucas test is applicable for distinction b/w primary, secondary and tertiary alcohol. Alcohols are soluble in Lucas reagent while their halides are insoluble and produce turbidity in solution.

In case of tertiary alcohol, it easily formed their halide so turbidity appears immediately. If turbidity appears within five minutes, secondary alcohol is indicated. If turbidity appears only upon heating, primary alcohol is indicated

ii) Dehydration:

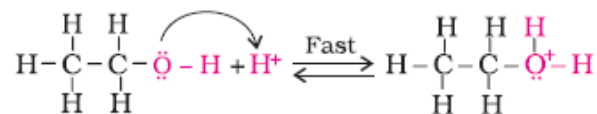


Secondary and tertiary alcohols are dehydrated under milder condition like as

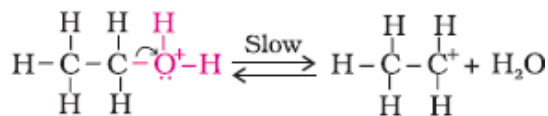


Mechanism:

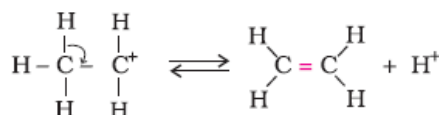
Step 1: Formation of protonated alcohol:



Step 2: Formation of carbocation: It is rate determining step of reaction.

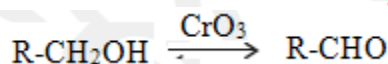
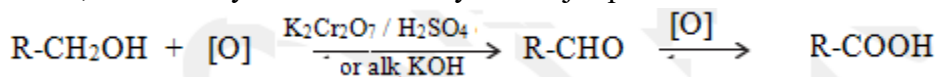


Step 3: Formation of ethene by elimination of proton.

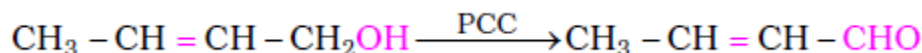


iii) Oxidation:

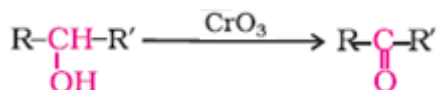
- Primary alcohols can be oxidised to aldehyde or further to carboxylic acids. In aqueous media, the carboxylic acid is usually the major product.



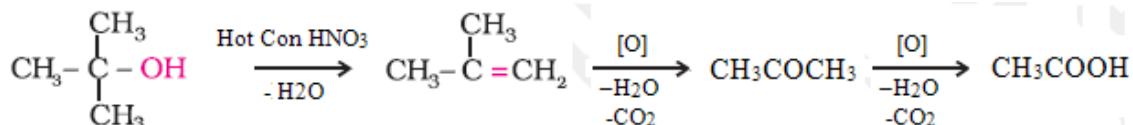
- Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl is used to stop the oxidation at the intermediate aldehyde.



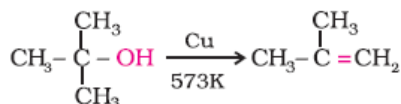
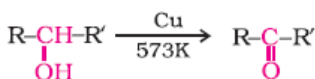
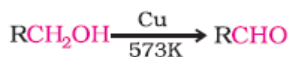
- Secondary alcohols can be oxidised to ketones but no further:



- Tertiary alcohols cannot be oxidised due to non availability of alpha hydrogen. If oxidation is carried out under strong conditions then they undergo oxidation with the cleavage of C-C bond and form lesser carbon number carboxylic acids.



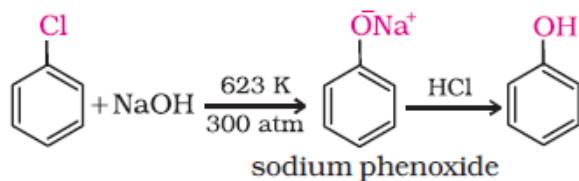
iv) Dehydrogenation: 1° and 2° alcohol formed aldehyde & ketone but 3° alcohol produced alkene.



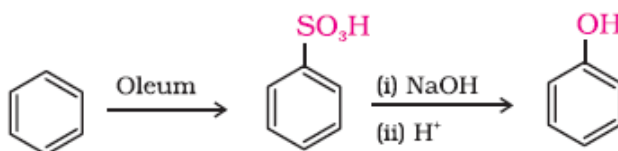
Phenol (Carbolic Acid)

1. Preparation of Phenol:

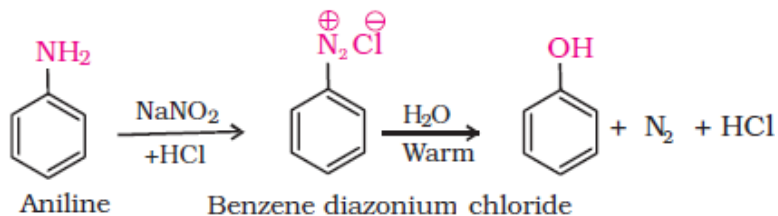
1) From Aryl halides (Dow Process):



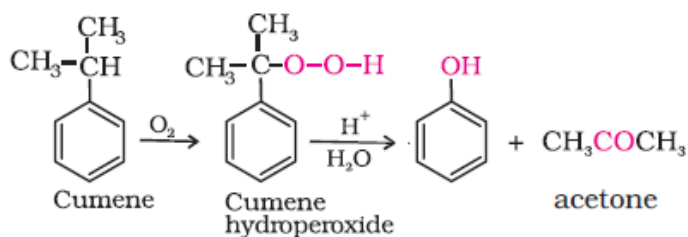
2) From Benzene sulphonic acid:



3) From Diazonium salt:



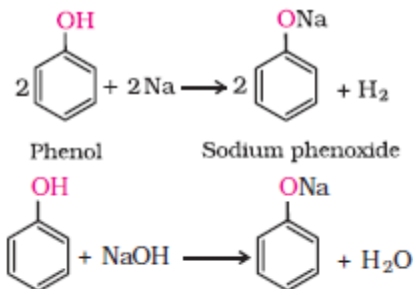
4) From Cumene (Isopropyl benzene):



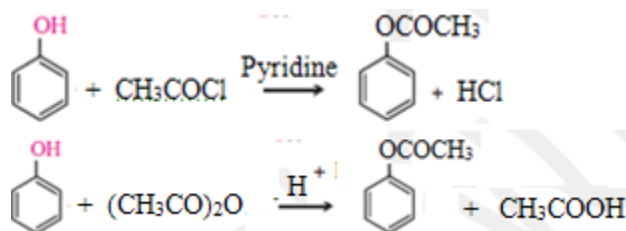
2. Physical Properties: Same as alcohols.

3. Chemical Properties:

1) Acidity of Phenol: Reaction with metal and NaOH show that phenol is acidic in nature.



2) Esterification:

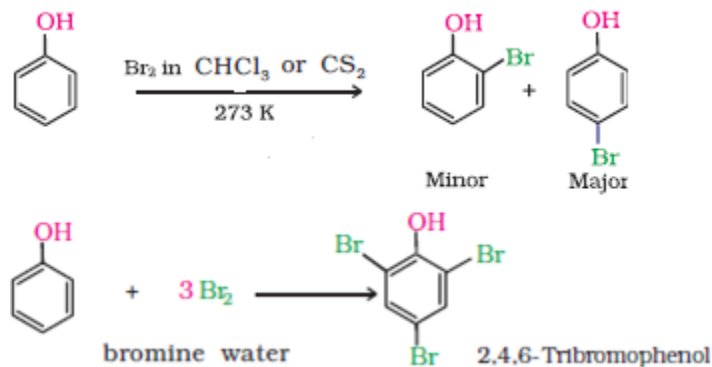


3) Electrophilic substitution reactions of Phenol: The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions.

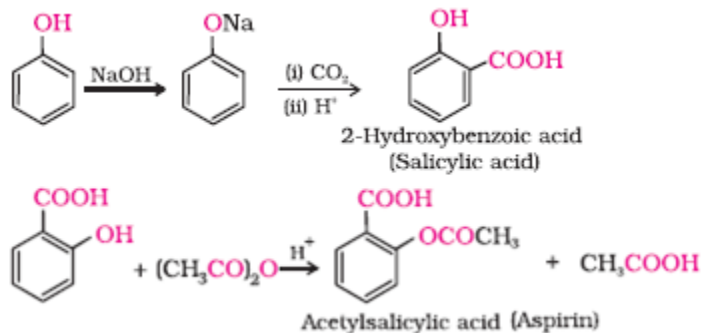
i) Nitration:



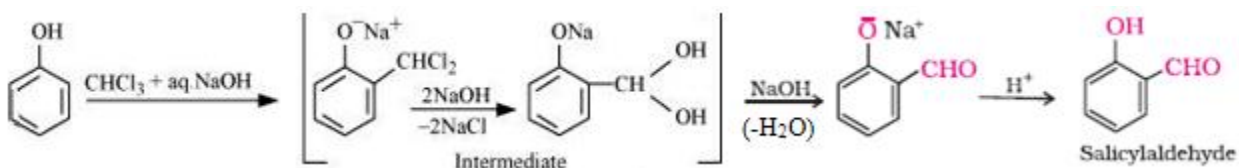
ii) Halogenation:



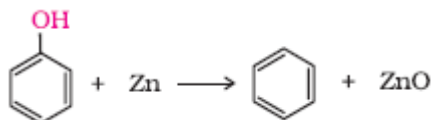
iii) Kolbe's reaction: Sodium phenoxide is more reactive than phenol towards electrophile substitution reaction. Here CO_2 act as weak electrophile.



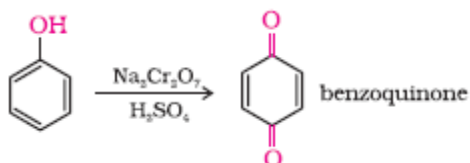
iv) **Reimer-Tiemann reaction:** This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene. Similarly with carbon tetrachloride and alkali, o- and p-hydroxybenzoic acid are obtained.



4) **Reaction with zinc dust:**



5) **Oxidation:**



Ethers

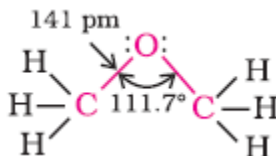
1. Introduction: These are represented by the general formula R–O–R', where R may be alkyl or aryl groups. These are the functional isomers of alcohols and exhibit chain isomerism & metamerism.

The group R and R' may either be same or different, so according to that ethers are two types- Simple or symmetrical ether CH₃-O-CH₃ and Mixed or unsymmetrical ether CH₃-O-C₂H₅

2. Common and IUPAC name of some Ethers:

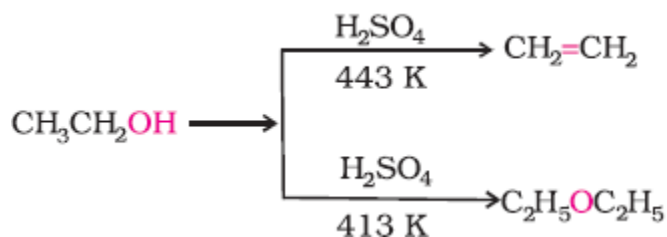
Compound	Common name	IUPAC name
CH ₃ OCH ₃	Dimethyl ether	Methoxymethane
CH ₃ OCH ₂ CH ₂ CH ₃	Methyl n-propyl ether	1-Methoxypropane
C ₆ H ₅ OCH ₃	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
C ₆ H ₅ OCH ₂ CH ₃	Ethylphenyl ether (Phenetole)	Ethoxybenzene
C ₆ H ₅ O(CH ₂) ₆ -CH ₃	Heptylphenyl ether	1-Phenoxyheptane
CH ₃ O-CH(CH ₃)-CH ₃	Methyl isopropyl ether	2-Methoxypropane
C ₆ H ₅ -O-CH ₂ -CH ₂ -CH(CH ₃)-CH ₃	Phenylisopentyl ether	3- Methylbutoxybenzene
CH ₃ -O-CH ₂ -CH ₂ -OCH ₃	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

3. Structure of Ether: The hybridisation of oxygen atom in ethers is sp^3 (tetrahedral) and its shape is V-shape. The bond angle is slightly greater (111.7°) than the tetrahedral angle due to the repulsive interaction b/w two bulky alkyl (-R) groups. The C-O bond length is 141 pm which is almost same as in alcohol (142 pm).

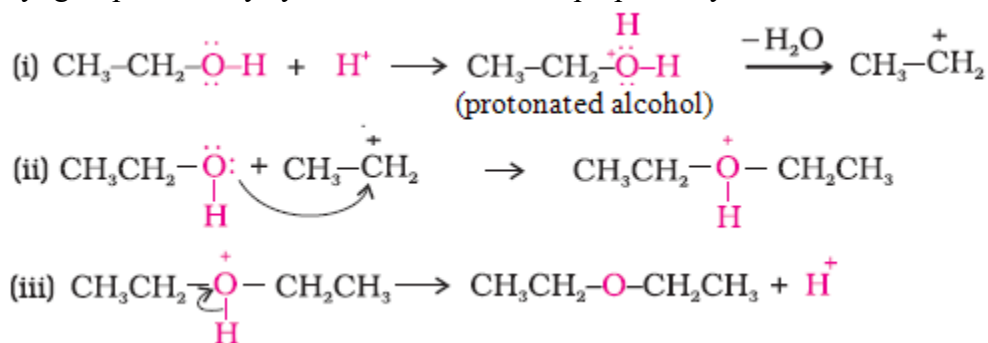


4. Preparation of Ethers:

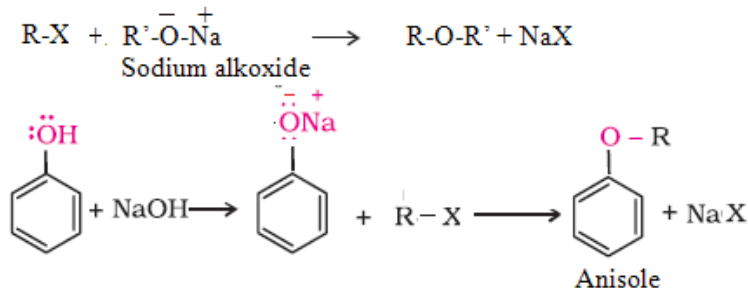
1) By dehydration of alcohols:



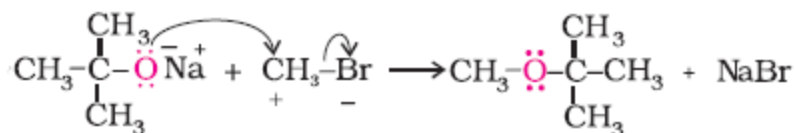
Mechanism: It is nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol. This method is suitable for the preparation of ethers having primary alkyl groups and only symmetric ether can be prepared by this method.



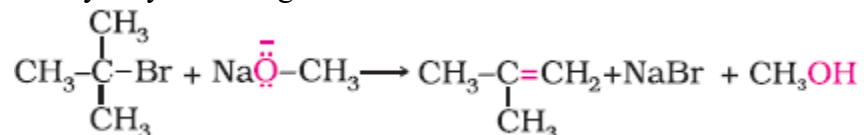
2) Williamson synthesis: Only **primary alkyl halides** when react with sodium alkoxide (strong base) give ether while tertiary alkyl halides give alkene due to steric hindrance.



Secondary and tertiary Ethers also prepared by this method. The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide.



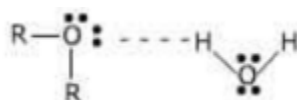
Secondary and tertiary alkyl halides give alkene due to steric hindrance.



5. Physical Properties of Ethers:

Boiling points: Ethers have much lower boiling points as compared to isomeric alcohols. This is because alcohol molecules are associated by hydrogen bonds while ether molecules are not.

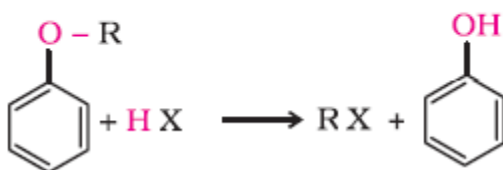
Solubility: Ethers containing up to 3 carbon atoms are soluble in water, due to their hydrogen bond formation with water molecules.



The solubility decreases with increase in the number of carbon atoms. The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone etc.

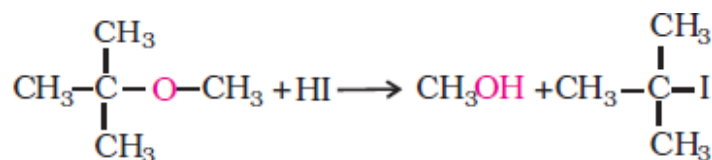
6. Chemical Reactions of Ether

1) Reaction with HX: Ethers are least reactive functional group. During reaction with HX, the cleavage of C-O bond carried out in extreme conditions and formed a primary halide (or smaller and less complex alkyl halide) by $\text{S}_{\text{N}}2$ mechanism.

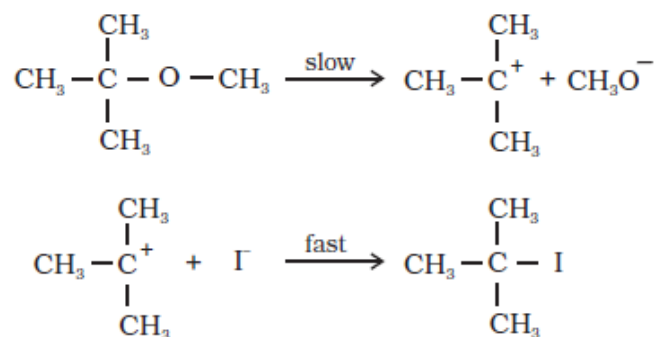


The order of reactivity of hydrogen halides is as follows $\text{HI} > \text{HBr} > \text{HCl}$

In ethers if one of the alkyl groups is a tertiary group, then it formed tertiary halide by $\text{S}_{\text{N}}1$ mechanism.

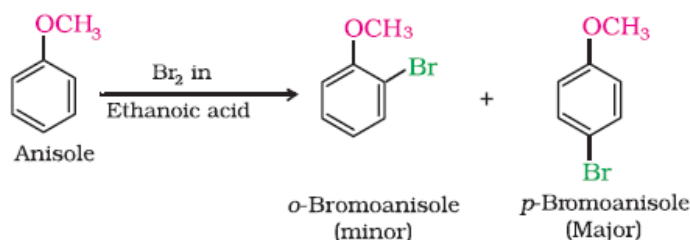


Mechanism:

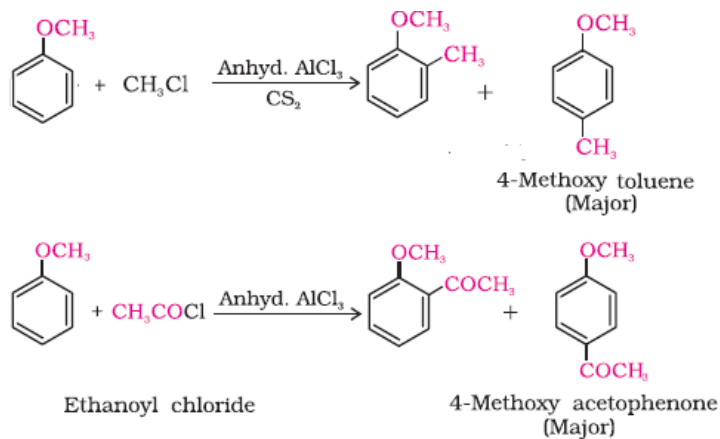


2) **Electrophilic substitution reactions:** -OR is ortho, para directing group and activate the aromatic ring towards electrophilic substitution reaction.

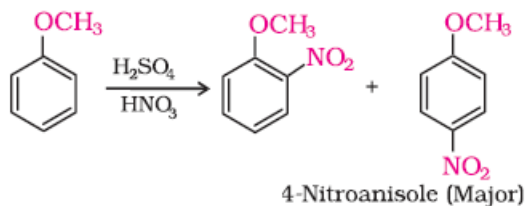
i) Halogenation:



ii) Friedel crafts reaction:



iii) Nitration:



7. Uses of Ethers:

- 1) Dimethyl ether is used as refrigerant and as a solvent at low temperature.
- 2) Diethyl Ether is used as anesthesia in surgery.