

Alcohols

Formula IUPAC Name Suffix Prefix

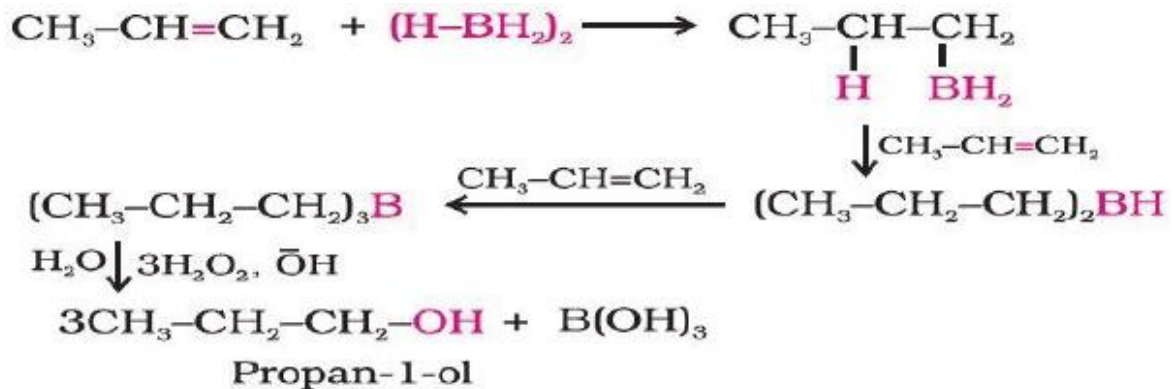
Formula	IUPAC Name	Suffix	Prefix
R - OH	Alkanol	-ol	Hydroxy

Common and IUPAC names of a few alcohols: Alkan+ol

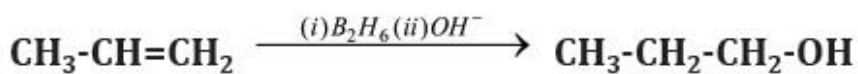
Compound	Common name	IUPAC name
CH ₃ -OH	Methyl alcohol	Methanol
CH ₃ -CH ₂ -CH ₂ -OH	<i>n</i> -Propyl alcohol	Propan-1-ol
CH ₃ -CH(OH)-CH ₃	Isopropyl alcohol	Propan-2-ol
CH ₃ -CH ₂ -CH ₂ -CH ₂ -OH	<i>n</i> -Butyl alcohol	Butan-1-ol
CH ₃ -CH(OH)-CH ₂ -CH ₃	<i>sec</i> -Butyl alcohol	Butan-2-ol
CH ₃ -CH(CH ₃)-CH ₂ -OH	Isobutyl alcohol	2-Methylpropan-1-ol
CH ₃ -C(CH ₃) ₂ -OH	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
HO-H ₂ C-CH ₂ -OH	Ethylene glycol	Ethane-1,2-diol
CH ₂ (OH)-CH(OH)-CH ₂ (OH)	Glycerol	Propane -1, 2, 3-triol

Preparation of Alcohols & Phenols:

1. Hydroboration –Oxidation reaction: Diborane reacts with alkenes to form trialkylboranes which are oxidized to alcohols on reaction with hydrogen peroxide in presence of alkali. *The alcohol obtained corresponds to anti- Markownikov's addition of water on alkenes.*



i.e.



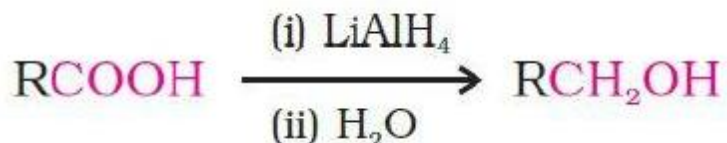
2. Hydration of Alkene:



3. Reduction of aldehydes and ketones (Reducing agents: H₂/Pd or Pt, NaBH₄ or LiAlH₄)



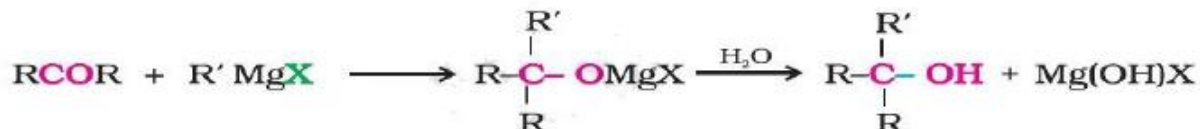
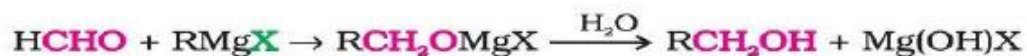
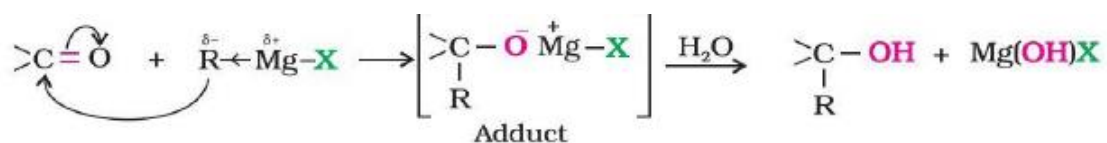
4. Reduction of carboxylic acids:



5. Reaction of Grignard reagents with aldehydes and ketones.

Mechanism for the addition Grignard reagent on carbonyl compounds.

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



Physical Properties of Alcohols:

1. Boiling Points

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces).

In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

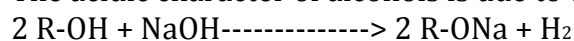
2. Solubility: Solubility of alcohols and phenols in water is due to their ability to form

hydrogen bonds with water molecules.

Chemical Properties of Alcohols:

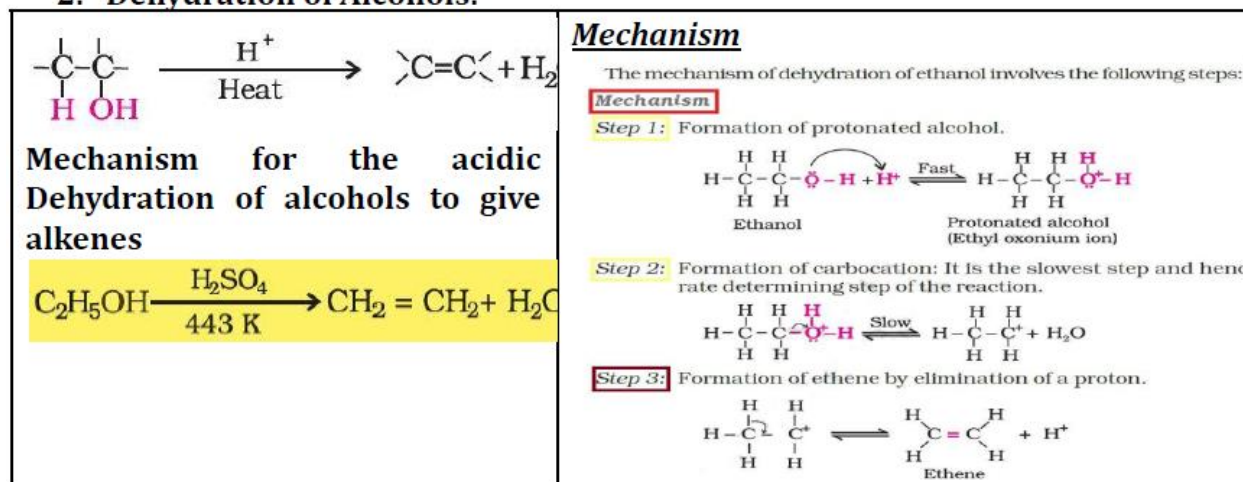
1. Reaction with metals:

The acidic character of alcohols is due to the polar nature of O-H bond.



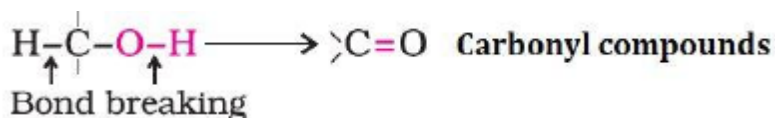
Order of acidic strength of alcohols: $1^\circ > 2^\circ > 3^\circ$

2. Dehydration of Alcohols:

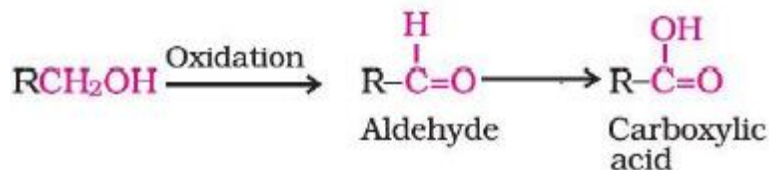


3. Oxidation of Alcohols

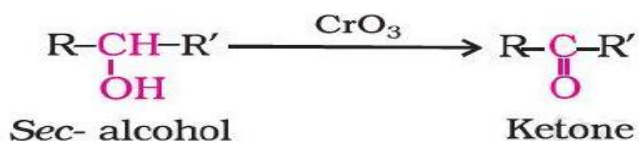
- **Primary alcohol to carboxylic acid.** [Strong oxidising agents such as acidified



- **Primary alcohol to Aldehyde.** [oxidising agents CrO_3 in anhydrous medium. pyridinium chlorochromate (PCC)]



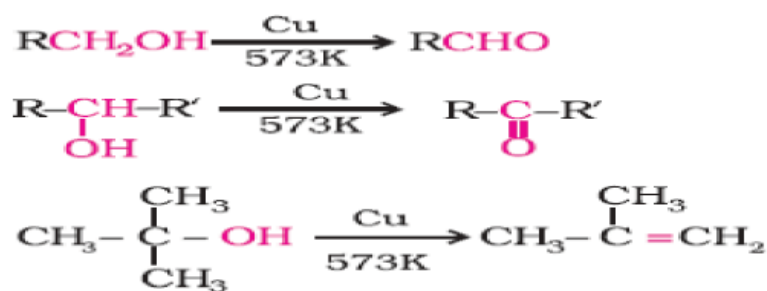
- **Secondary alcohols to ketones** [chromic anhydride (CrO_3).]



- Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents (KMnO_4) and elevated temperatures, cleavage of various C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

4. Dehydrogenation [loss of dihydrogen from an alcohol molecule]:

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.



Chemical tests Based Questions (with suitable examples)

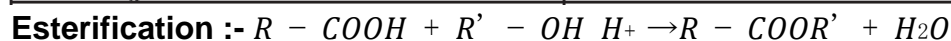
1. Lucas test

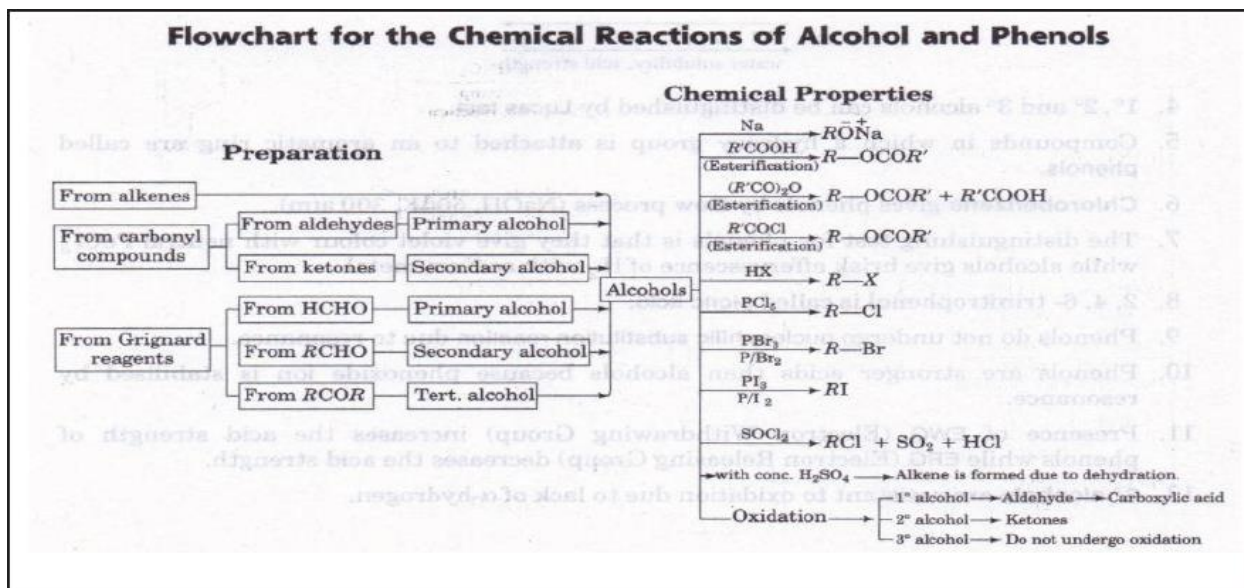
- To distinguish between Primary (1^o), Secondary (2^o), & Tertiary (3^o) Alcohols)
- **Lucas reagent:** ZnCl₂/HCl

- (i) **Primary (1^o)** + Lucas reagent(ZnCl₂/HCl) → No Turbidity at room temperature
- (ii) **Secondary (2^o)** + Lucas reagent(ZnCl₂/HCl) → Turbidity after some time (5-10 min)
- (iii) **Tertiary (3^o)** + Lucas reagent (ZnCl₂/HCl) → Turbidity at once (immediately)

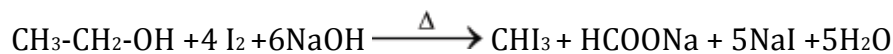
2. Iodoform test (Alcohols)

<ul style="list-style-type: none"> ● Alcohols containing linkage like Ethanol, Propan-2-ol etc.) ● Reagent: I₂ / NaOH ● Test: Alcohols containing CH₃-CH(OH)-linkage on reaction I₂ / NaOH gives Yellow Ppt of CHI₃. 	$\begin{array}{l} \text{OH} \\ \\ \text{CH}_3-\text{CH}_2 + \text{I}_2 + \text{NaOH} \rightarrow \text{CHI}_3 + \text{HCOONa} + \text{NaI} + \text{H}_2\text{O} \\ \text{Ethanol} \qquad \qquad \qquad \text{Yellow ppt} \end{array}$ $\begin{array}{l} \text{OH} \\ \\ \text{CH}_3-\text{CH}-\text{CH}_3 + \text{I}_2 + \text{NaOH} \rightarrow \text{CHI}_3 + \text{CH}_3\text{COONa} + \text{NaI} + \text{H}_2\text{O} \\ \text{Propan-2-ol} \qquad \qquad \qquad \text{Yellow ppt} \end{array}$
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Iodoform test:-alcohol containing the group $\text{CH}_3\text{-CH-}$ is heated with iodine and aqueous NaOH or Na_2CO_3 solution, a yellow ppt of iodoform is obtained.

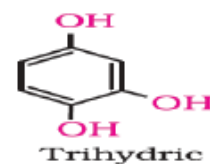
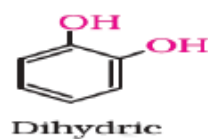
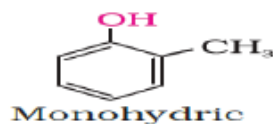
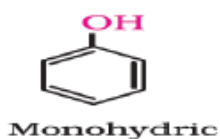


Phenol

Introduction: The replacement of hydrogen atom(s) in an aromatic hydrocarbon by -OH group results in the formation of Phenols. e.g $\text{C}_6\text{H}_5\text{OH}$

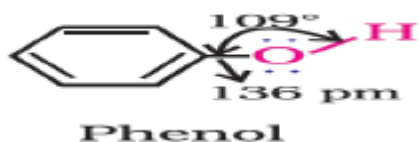
Classification of Phenols:

Phenols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively.



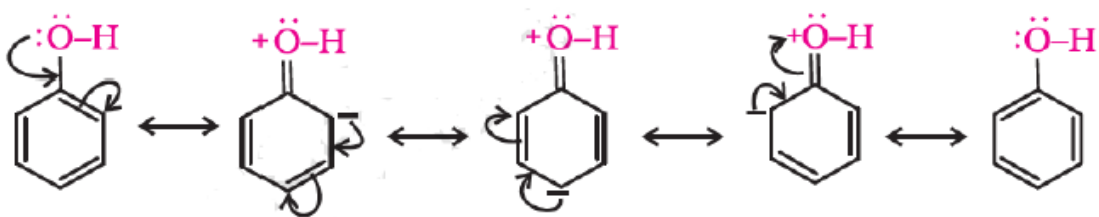
Structures of Functional Groups:

In phenols, the -OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol (142 pm).



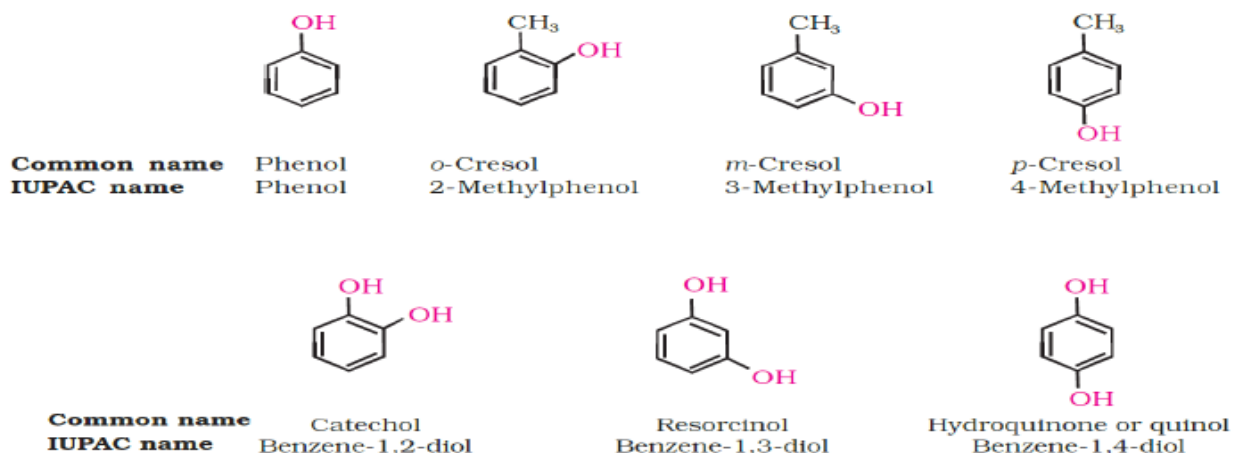
This is due to

- (i) partial double bond character because of resonance and
- (ii) sp^2 hybridised state of carbon to which oxygen is attached.



Nomenclature of Phenols:

The simplest hydroxy derivative of benzene is phenol. It is its common name and IUPAC name. For disubstituted compounds the terms ortho (1,2- disubstituted), meta (1,3 disubstituted) and para (1,4-disubstituted) are often used in the common names.

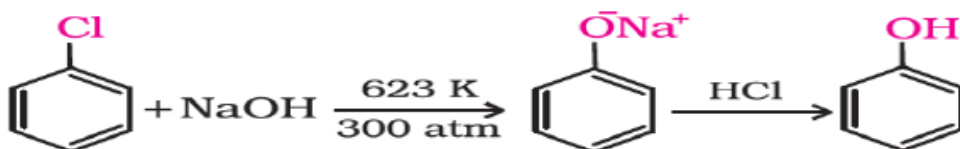


Preparation of Phenols:

Phenol, also known as carboic acid, was first isolated in the early nineteenth century from coal tar.

(1) From haloarenes-

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure to give sodium phenoxide. Phenol is obtained by acidification of sodium phenoxide.

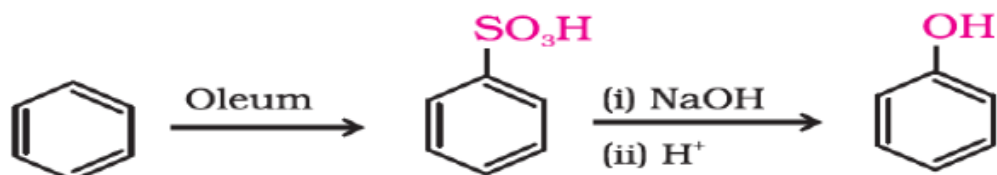


(2) From benzenesulphonic acid-

Benzene is sulphonated with oleum to give benzene sulphonic acid.

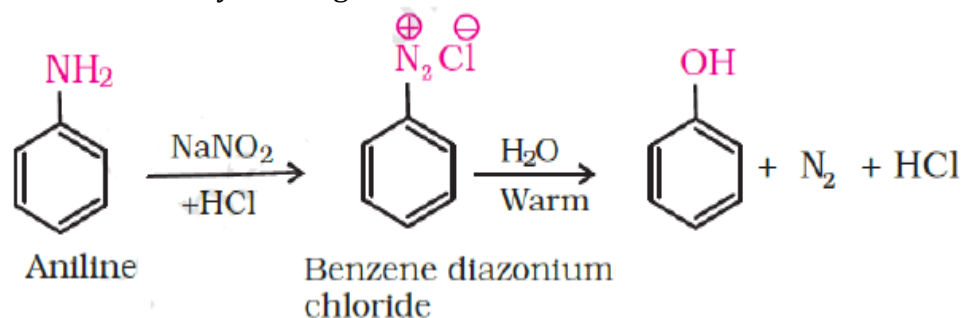
Benzene sulphonic acid converted to sodium phenoxide on heating with molten sodium hydroxide.

Acidification of the sodium salt gives phenol.



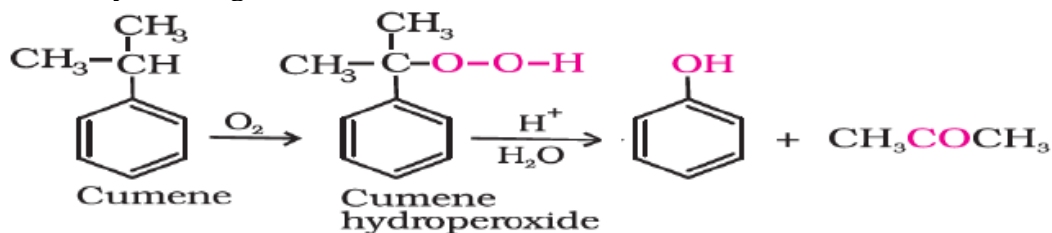
(3) From diazonium salts:

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



(4) From cumene-

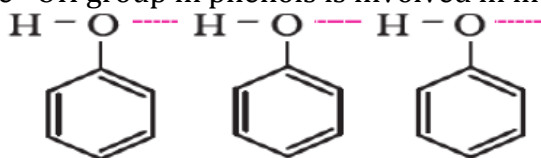
Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid.



Physical Properties of Phenols:

(1) Boiling Point: The boiling points of phenols increase with increase in the number of carbon atoms (increase in van der Waals forces).

The $-\text{OH}$ group in phenols is involved in intermolecular hydrogen bonding.



Due to the presence of intermolecular hydrogen bonding, boiling points of phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses.

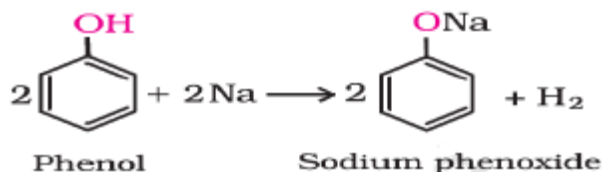
(2) Solubility: Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.

Chemical Reactions of Phenols:

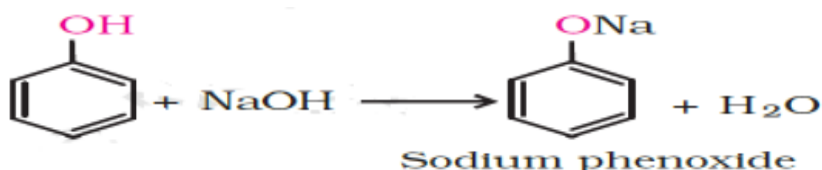
(1) Reactions involving cleavage of O–H bond:

(a) Acidity of phenols:

(i) **Reaction with metals:** Phenols react with active metals such as sodium, potassium and aluminium to yield corresponding phenoxides and hydrogen.



Phenols react with aqueous sodium hydroxide to form sodium phenoxides.



These reactions show that phenols are acidic in nature.

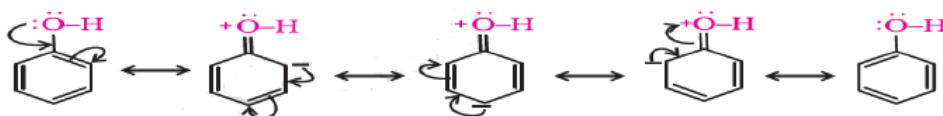
(ii) **Acidity of phenols:** The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature.

The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water.

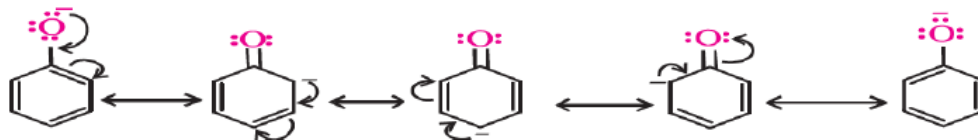
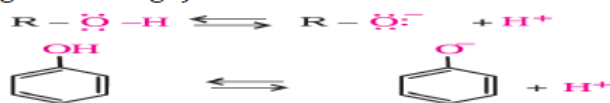
Reasons:- Three reasons are there:

(i) The hydroxyl group, in phenol is directly attached to the sp^2 hybridized carbon. The sp^2 carbon is more electronegative hence O–H bond in phenols is more polar. It results in an increase in ionisation of phenols than that of alcohols.

(ii) Due to resonance in phenols the oxygen of –OH group acquires positive charge, which results in more polarity of O–H bond.



(iii) Phenoxide ion formed after ionization is stable due to resonance (Delocalization of negative charge). While no resonance in alkoxide ion.



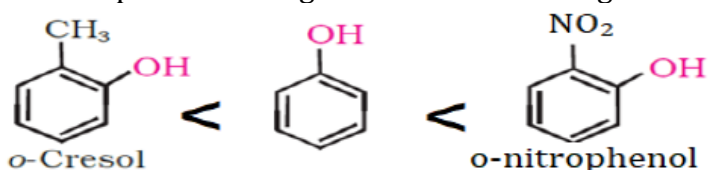
Although there is also charge delocalization in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.

Effect of substituents on acid strength of phenols:

In substituted phenols, the presence of electron withdrawing groups (-I effect) such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalization of negative charge in phenoxide ion when substituent is at ortho or para position.

On the other hand, electron releasing groups, (+I effect) such as alkyl groups do not favour the formation of phenoxide ion resulting in decrease in acid strength.

For example: increasing order of acidic strength:



At a given temperature T, K_a is a measure of the strength of the acid i.e., larger the value of K_a , the stronger is the acid.

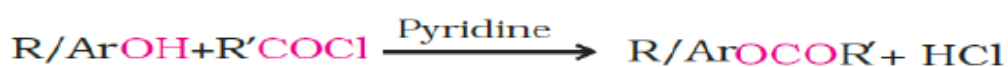
$$pK_a = -\log K_a$$

larger the value of K_a , smaller the value of pK_a , the stronger is the acid.

pK _a Values of some Phenols and Ethanol		
Compound	Formula	pK _a
<i>o</i> -Nitrophenol	<i>o</i> -O ₂ N-C ₆ H ₄ -OH	7.2
Phenol	C ₆ H ₅ -OH	10.0
<i>o</i> -Cresol	<i>o</i> -CH ₃ -C ₆ H ₄ -OH	10.2
Ethanol	C ₂ H ₅ OH	15.9

(b) Esterification:

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

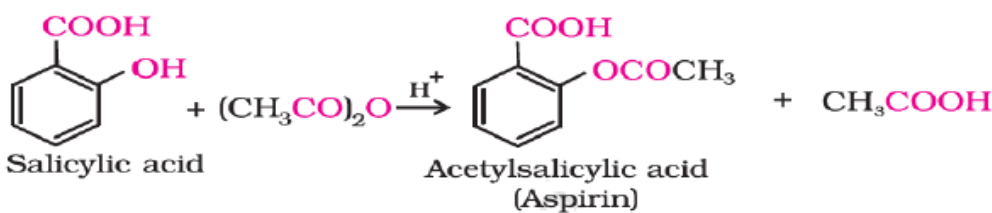


The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, therefore, water is removed as soon as it is formed.

The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side.

Acetylation:

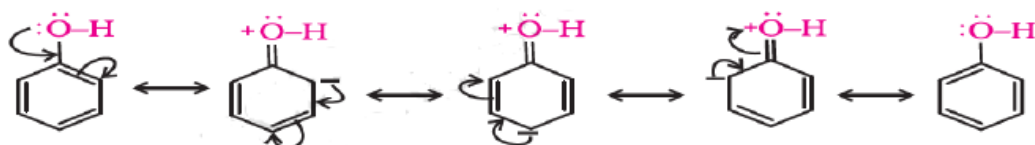
The introduction of acetyl (CH₃CO) group in phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.



Aspirin is used for pain relief (analgesic) and to bring down a high temperature of body (antipyretic).

(2) Electrophilic aromatic substitution on aromatic ring of Phenol:

-OH group is activating and ortho and para directing. Due to resonance electron density is more at o- and p- position, hence, electrophile is directed to ortho and para position.



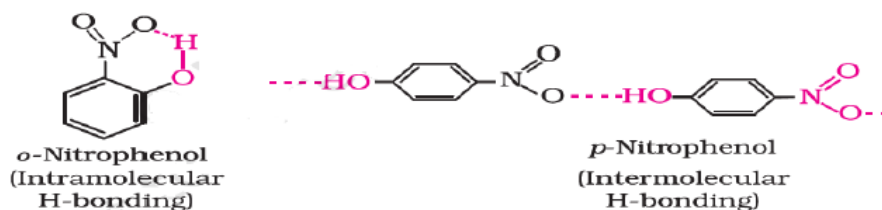
(i) Nitration:

(a) With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenols.

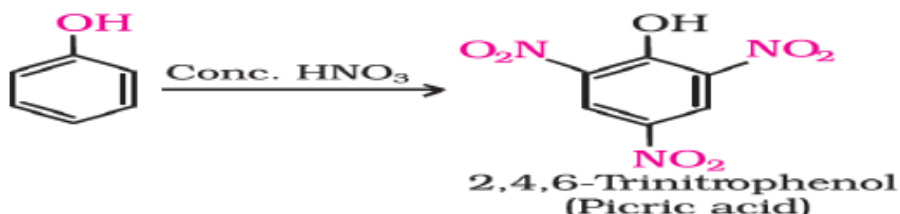


The ortho and para isomers can be separated by steam distillation.

o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



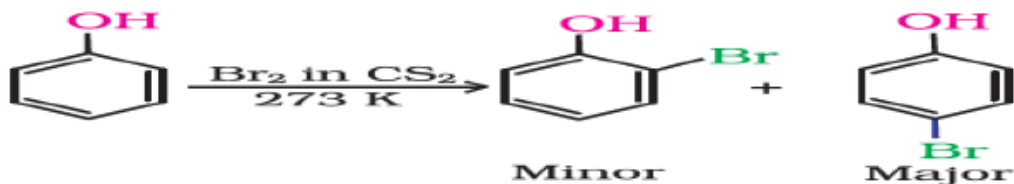
(b) With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid.



(ii) Halogenation:

On treating phenol with bromine, different reaction products are formed under different experimental conditions.

(a) When the reaction is carried out in solvents of low polarity such as CHCl_3 or CS_2 and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as FeBr_3 , which polarises the halogen molecule.

In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid.

It is due to the highly activating effect of $-\text{OH}$ group attached to the benzene ring.

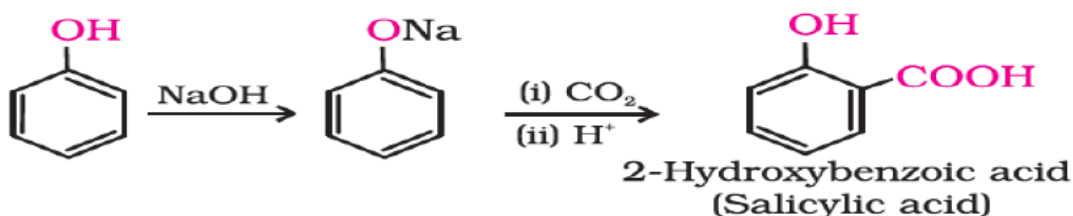
(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



(3) Kolbe's reaction:

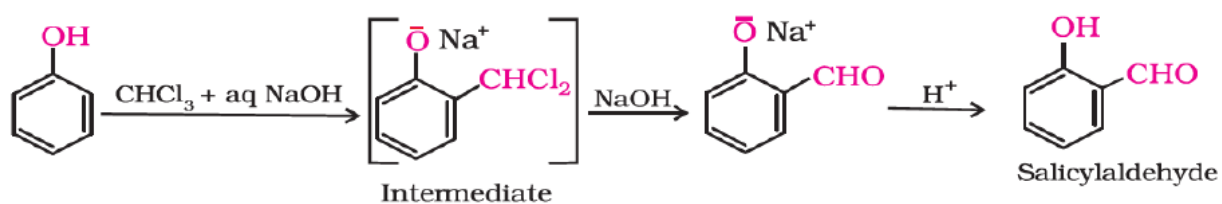
Sodium phenoxide undergoes electrophilic substitution with carbon dioxide, a weak electrophile.

Ortho hydroxybenzoic acid is formed as the main reaction product.

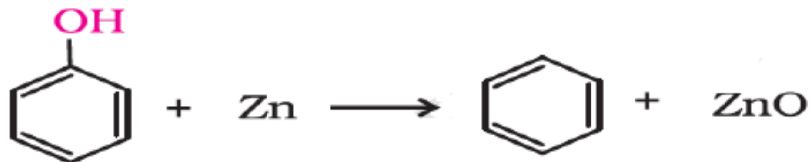


(4) Reimer-Tiemann reaction:

On treating phenol with chloroform in the presence of sodium hydroxide, a $-\text{CHO}$ group is introduced at ortho position of benzene ring. This reaction is known as Reimer-Tiemann reaction. The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.

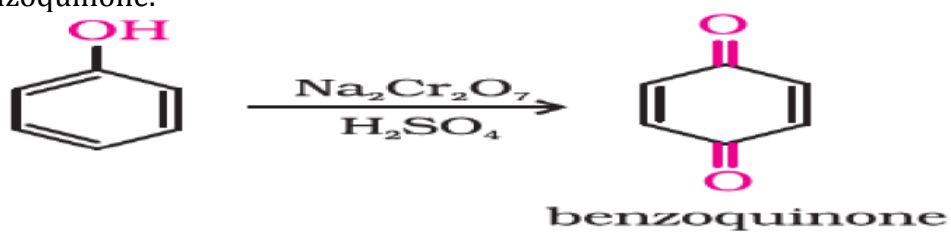


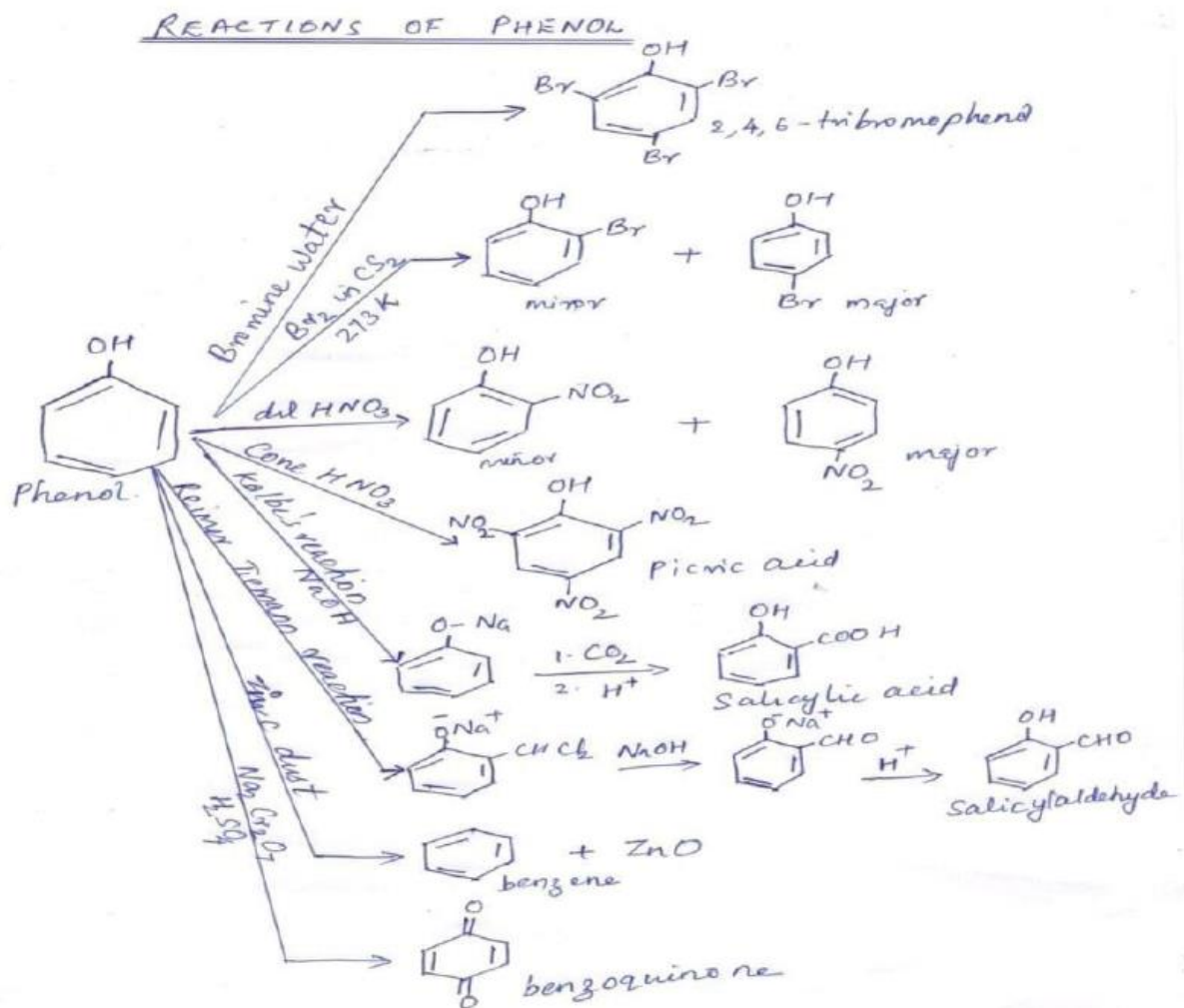
(5) Reaction of phenol with zinc dust:



(6) Oxidation:

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.

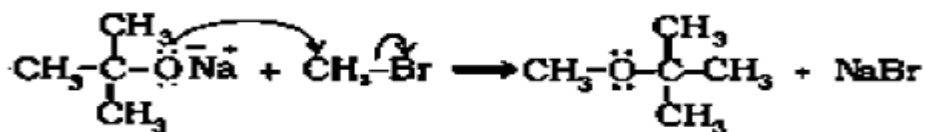
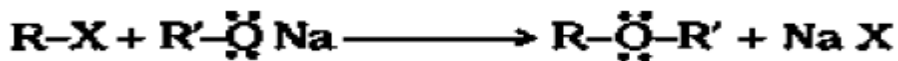




ETHERS

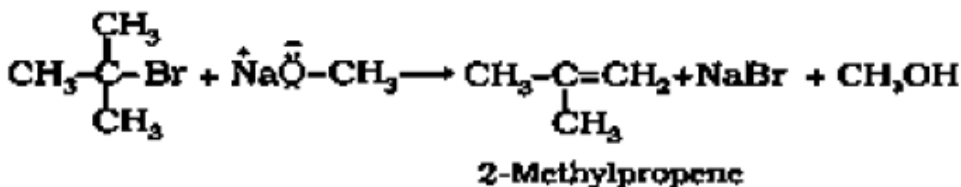
Preparation of ethers

1. Williamson's synthesis : In this method an alkyl halide (Better results are obtained if the alkyl halide is primary) reacts with a sodium alkoxide to form symmetrical or unsymmetrical ethers.

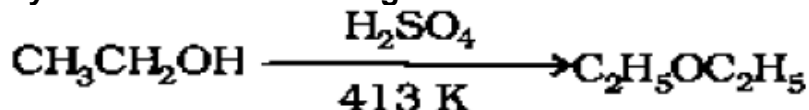


Limitation In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(\text{CH}_3)_3\text{C-Br}$ gives

exclusively 2-methylpropene. It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

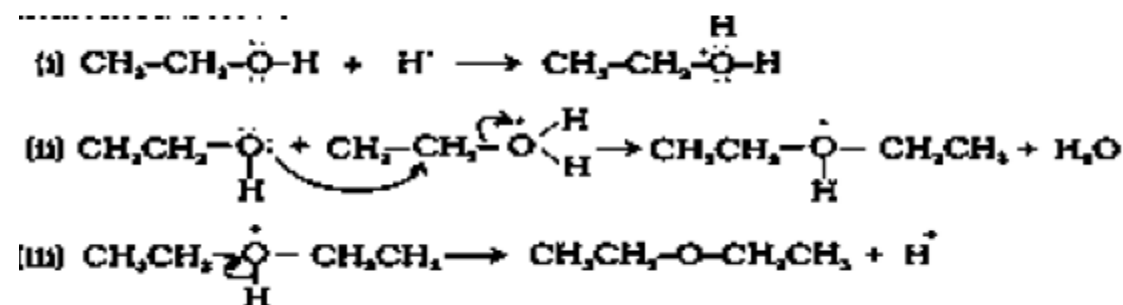


2. Dehydration of alcohols to give ethers



Mechanism for the acidic Dehydration of alcohols to give ethers

Mechanism



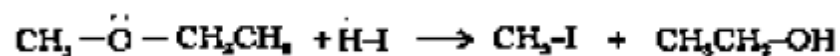
Chemical Properties of Ethers:

1. Reaction of Ethers with hydrogen halides.(HX)

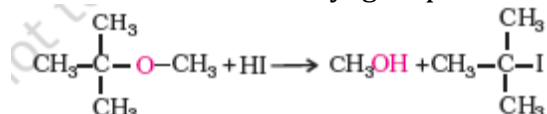
- Order of reactivity of hydrogen halides is as follows: HI > HBr > HCl
- The reaction of dialkyl ether gives two alkyl halide molecules.



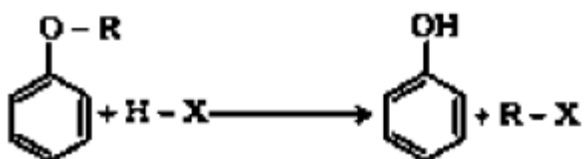
- Ethers with two different alkyl groups:
- When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).



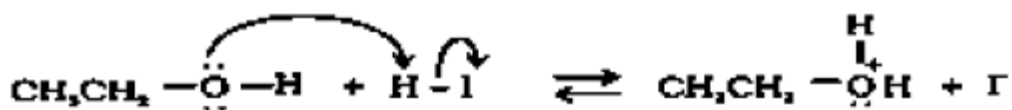
- When one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



- Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.

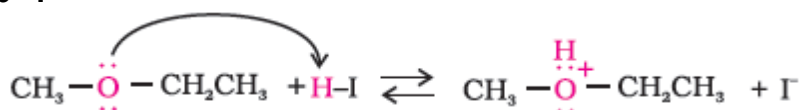


When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

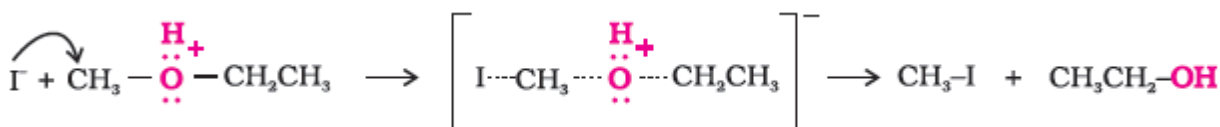


● Mechanism for the reaction of HI on Ethoxymethane

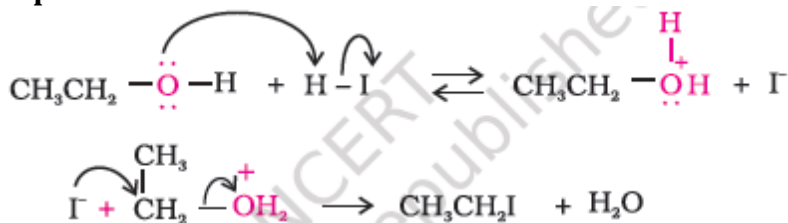
Step -1



Step-2

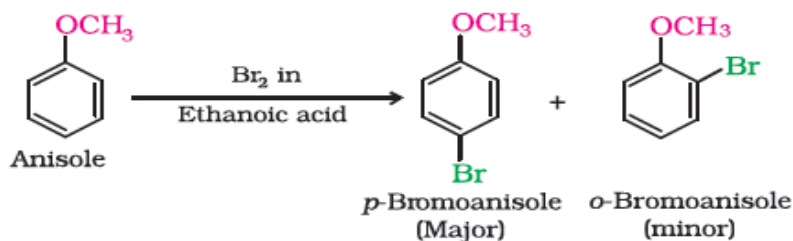


Step-3



2. Electrophilic substitution in Alkyl aryl ethers (Anisole)

(i) Halogenation



(ii) Nitration:



(iii) Friedel crafts alkylation in anisole:

