

11. Alcohols, Phenols & Ethers

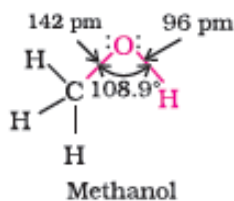
ALCOHOLS

→ Alcohols are hydroxy derivatives of aliphatic hydrocarbons.

Ex. CH_3OH

ELECTRONIC STRUCTURE OF HYDROXYL GROUP

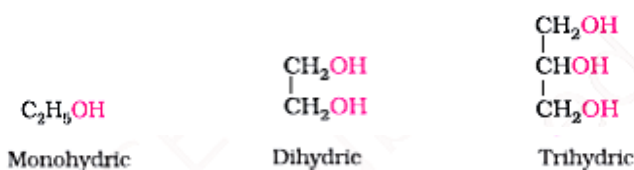
- In alcohols, the oxygen of the $-\text{OH}$ group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. The $\text{C}-\text{O}-\text{H}$ bond angle in alcohols is slightly less than the tetrahedral angle ($109^\circ-28'$). It is due to the repulsion between the unshared electron pairs of O.



CLASSIFICATION (also applicable for phenols)

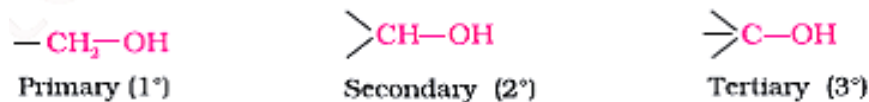
(i) On the basis of the number of hydroxyl groups

- monohydric** (contain only one $-\text{OH}$ group)
- dihydric** (contain two $-\text{OH}$ groups)
- polyhydric** (contain more than two $-\text{OH}$ groups).

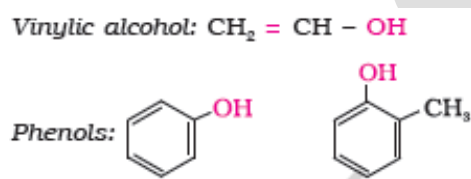


(ii) According to the hybridisation of the C-atom, sp^3 or sp^2 to which the $-\text{OH}$ group is attached.

- Compounds containing sp^3 C-OH bond: Here the $-\text{OH}$ group is attached to an sp^3 hybridised C-atom of an alkyl group. They are further classified as follows: Primary, secondary and tertiary alcohols.



- Compounds containing sp^2 C-OH bond: These alcohols contain $-\text{OH}$ group bonded to a C-C double bond. These may be vinylic alcohols or phenols.



NOMENCLATURE

Common Name: By adding 'alcohol' to the name of alkyl group (i.e. word root + yl alcohol)

IUPAC Name: By replacing 'e' of alkane by 'ol'. (i.e. *alkanol*)

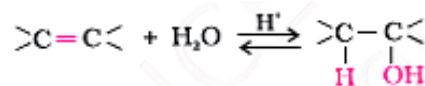
Compound	Common name	IUPAC name
$\text{CH}_3 - \text{OH}$	Methyl alcohol	Methanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	n-Propyl alcohol	Propan-1-ol
$\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_3$	Isopropyl alcohol	Propan-2-ol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	n-Butyl alcohol	Butan-1-ol
$\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{CH}_3$	sec-Butyl alcohol	Butan-2-ol
$\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{OH}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\text{CH}_3 - \text{C}(\text{OH})(\text{CH}_3)_2$	tert-Butyl alcohol	2-Methylpropan-2-ol
$\text{CH}_2(\text{OH}) - \text{CH}(\text{OH}) - \text{CH}_2(\text{OH})$	Glycerol	Propane -1, 2, 3-triol

METHODS OF PREPARATION

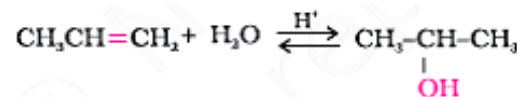
(1) By hydration of alkenes

(i) In presence of an acid

Alkenes, in presence of acid (as catalyst), react with water to form alcohols.

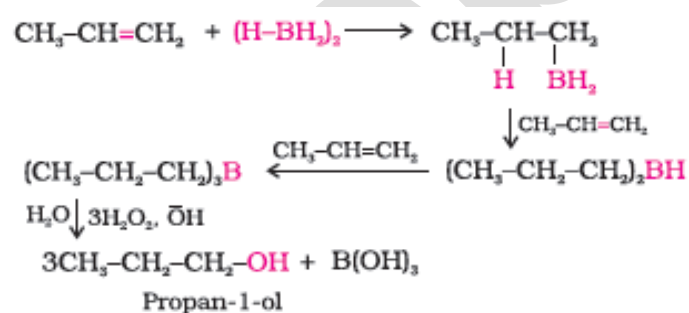


In case of **unsymmetrical alkenes**, the addition reaction takes place in accordance with **Markovnikov's rule**. (Mechanism: See text, page 321)



(ii) By hydroboration-oxidation reaction

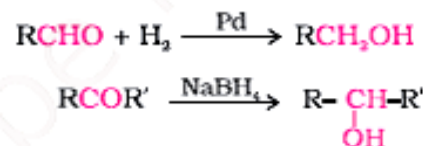
Diborane reacts with alkenes to give **trialkyl boranes**. This on oxidation by H_2O_2 in the presence of aq. NaOH to form alcohols.



The net reaction is the addition of a water molecule to the alkene as a/c to **anti-Markovnikov's rule**.

(2) From carbonyl compounds by catalytic reduction

- (i) On **catalytic hydrogenation** (using finely divided platinum, palladium or nickel) of **aldehydes and ketones** or
- (ii) Treating with **sodium borohydride** (NaBH_4) or **lithium aluminium hydride** (LiAlH_4) gives corresponding alcohols.
- Aldehydes yield 1° alcohols whereas ketones give 2° alcohols.

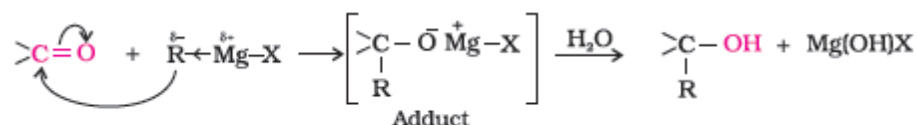


Commercially, acids are reduced to alcohols by converting them to the **esters**, followed by their reduction using hydrogen in the presence of catalyst (**catalytic hydrogenation**).



(3) From the action of Grignard reagents

The nucleophilic addition of Grignard reagent to the carbonyl group form an **adduct**. Hydrolysis of the adduct yields an alcohol.



PROPERTIES

Physical:

- ✓ **Boiling point:** Alcohols are higher boiling than hydrocarbons, ethers and haloalkanes of comparable molecular masses.
Reason:- Due to the presence of intermolecular H-bonding in them
- ✓ **Solubility:** Soluble in water.
Reason:- The ability to form intermolecular H-bonding with water.

Chemical:

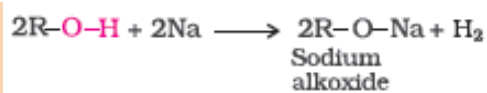
- ✓ Alcohols are **acidic** in nature.
Reason:- Due to the polar nature of O-H bond.

An electron releasing group (like $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc.) increases the electron density on oxygen and hence decrease the polarity of O-H bond. This decreases the acid strength in the order:



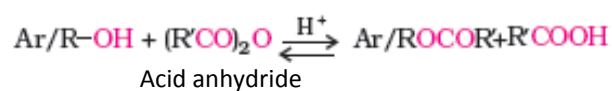
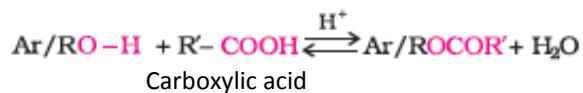
REACTIONS:-

- (i) **Reaction with metals:** Alcohols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides.

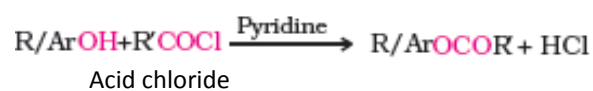


- (ii) **Reaction with carboxylic acids, acid chlorides and anhydrides** form **esters**:

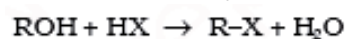
The reaction with carboxylic acid and acid anhydride are carried out in the presence of con. H_2SO_4 .



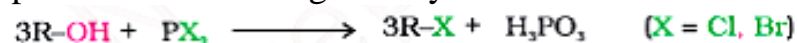
The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl formed during the reaction.



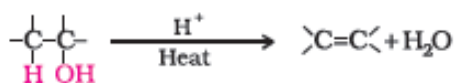
- (iii) **Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides.



- (iv) **Reaction with phosphorus trihalides (PX_3):** Alcohols react with phosphorus trihalides to give alkyl halides.



- (v) **Dehydration** of alcohols gives alkenes.



(Mechanism: See text, page 331)

IDENTIFICATION OF 1°, 2° AND 3° ALCOHOLS

	Test	1° alcohol	2° alcohol	3° alcohol
1	Reaction with Lucas reagent ($HCl + ZnCl_2$)	No turbidity at room temp. Give turbidity on heating.	Produce turbidity within 5 minutes	Produce turbidity immediately
2	Oxidation with mild oxidising agents	Yield aldehydes	Yield ketones	No reaction (Resistant to oxidation)
3	Oxidation with strong oxidising agents	Yield carboxylic acids	Yield ketones	No reaction. At elevated temp., yield carboxylic acids with lesser number of C-atoms
4	Vapours when passed through hot Cu at 573K	Yield aldehydes	Yield ketones	Yield alkenes

SOME COMMERCIALY IMPORTANT ALCOHOLS

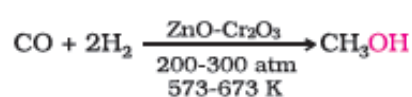
A. Methanol

Methanol, also known as '**wood spirit**', was produced by the **destructive distillation of wood**.

- It is **highly poisonous**- Ingestion of small quantities of methanol cause blindness and large quantities causes death.

Preparation:-

Catalytic hydrogenation of CO in the presence of $ZnO - Cr_2O_3$ catalyst.



Uses:- As solvent in paints, varnishes and for making formaldehyde.

- **Methanol + copper sulphate + pyridine = Denatured spirit**
(to give colour) (for foul smell)

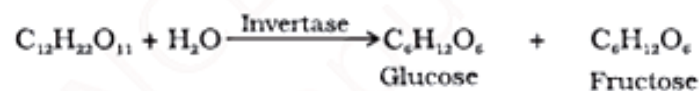
These are added to make sure that it will not be used for beverages. This process is known as **denaturation of alcohol**.

B. Ethanol

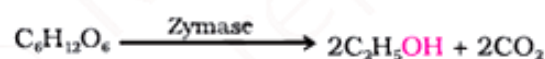
Ethanol, known as **spirit** or **grain alcohol**, is a colourless liquid.

Preparation:-

1. The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose, in the presence of an enzyme, **invertase**.



Glucose and fructose undergo fermentation in the presence of enzyme, **zymase** to give ethanol and CO_2 .



2. **Commercially ethanol made by hydration of ethene.**

Uses:- It is used as a solvent in paint industry.

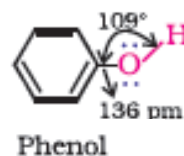
PHENOLS

➔ **Phenol** are **hydroxy derivatives of aromatic hydrocarbons** in which the $-OH$ group(s) directly attached to C- atom of the ring.

Ex. C_6H_5OH .

ELECTRONIC STRUCTURE OF HYDROXYL GROUP

- In phenols, the $-OH$ group is attached to sp^2 hybridised carbon of an aromatic ring. The C-O bond length (136 pm) in phenol is slightly less than that in alcohol. This is due to -
 - (i) Partial double bond character of unshared electron pair of oxygen with the aromatic ring and
 - (ii) sp^2 hybridised state of carbon to which oxygen is attached.



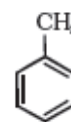
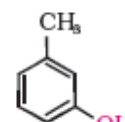
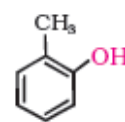
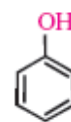
NOMENCLATURE

- ✚ **Common names:** The parent member is **phenol**. The position of the substituents is indicated by the prefixes *ortho* (for 1, 2-disubstituted), *meta* (for 1, 3) and *para* (for 1, 4).

NB: Some substituted phenols are popularly known by their trivial names.

Ex: **Cresol** (hydroxy derivatives of toluene)

- ✚ **IUPAC Name:** Named as derivatives of phenols. The position of the substituents w.r.t. $-OH$ group is indicated by arabic numerals (with the carbon carrying $-OH$ group being numbered 1).



Common name
IUPAC name

Phenol
Phenol

o-Cresol
2-Methylphenol

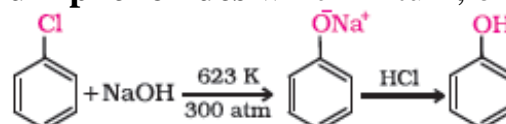
m-Cresol
3-Methylphenol

p-Cresol
4-Methylphenol

METHODS OF PREPARATION

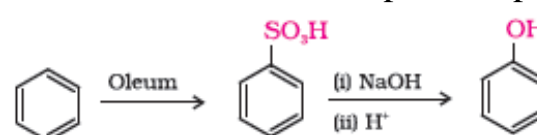
- (1) **Substitution of halogen atom in haloarenes**

Chlorobenzene fuse with **NaOH** at 623K and 320 atm to produce **sodium phenoxides** which in turn, on acidification produce phenol.



- (2) **From benzene sulphonic acid:**

Benzene is sulphonated with **oleum** to form **benzene sulphonic acid**, which on treating with **NaOH** produces **sodium phenoxide** which in turn, on acidification produce phenol.



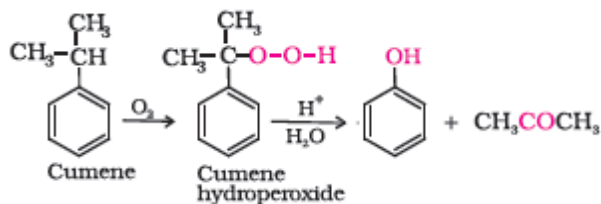
(3) By hydrolysis of diazonium salts

An aromatic 1^o amine is treated with **nitrous acid** ($\text{NaNO}_2 + \text{HCl}$) at 273-278 K, a diazonium salt is formed, which on warming with water or treating with dilute acids, produce phenol.



(4) Industrially from cumene

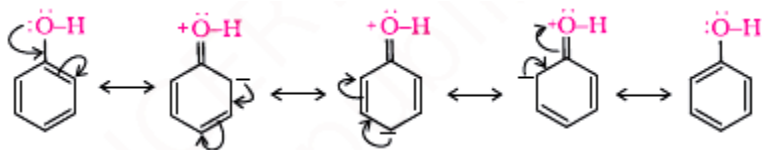
Cumene (isopropylbenzene) is oxidized in the presence of air to **cumene hydroperoxide** followed by acid hydrolysis produce phenol (and acetone).



PROPERTIES

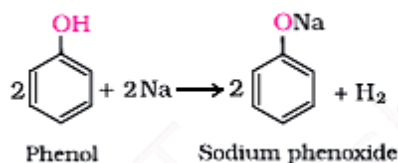
Chemical:

- ✓ **Acidity:** Phenols are **acidic** in nature.
- Electron withdrawing groups** in phenol increase its acidic strength and **electron releasing groups** decrease it.
- ✓ The presence of $-\text{OH}$ group in phenols activates the aromatic ring towards **electrophilic substitution** and directs the incoming group to *ortho* and *para* positions due to resonance effect.



REACTIONS:-

- (i) **Reaction with metals:** Phenols react with metals to yield phenoxides.



- (ii) **Reaction with carboxylic acids, acid chlorides and anhydrides** form esters

- (iii) **Acetylation of salicylic acid produces aspirin** (an analgesic).



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

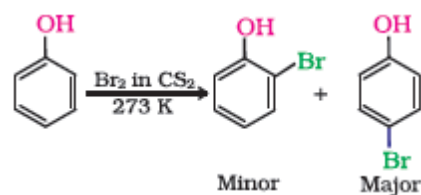


Separation: o-Nitrophenol is steam volatile due to intramolecular H-bonding while p-nitrophenol is less volatile due to intermolecular H-bonding which causes the association of molecules.

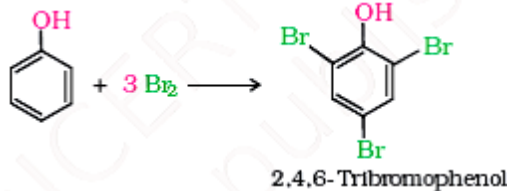
- Phenol reacts with Conc. Nitric acid to give 2,4,6-trinitrophenol commonly called **picric acid**.



- (v) **Halogenation:** When phenol is brominated in CHCl_3 or CS_2 at low temperature, a mixture of *ortho* and *para*-bromophenols are formed.



- When phenol is treated with bromine water, a white precipitate of 2,4,6-tribromophenol are formed.

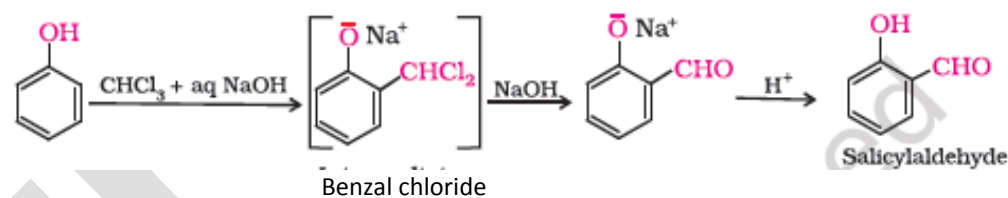


- (vi) **Reaction in alkaline medium (Kolbe's reaction):**

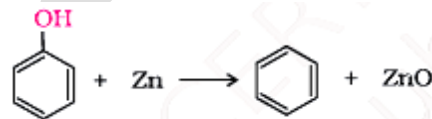
Phenol when treated with NaOH gives **sodium phenoxide** which on treating with CO_2 followed by acidification yields **orthohydroxybenzoic acid**, commonly called **Salicylic acid**.



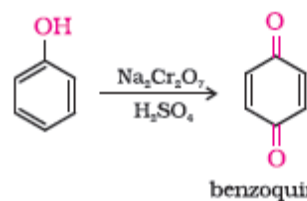
- (vii) **Reimer-Tiemann reaction** of phenol yields salicylaldehyde



- (viii) **Reaction with zinc dust:** Phenol when heated with Zn dust, yield benzene.



- (ix) **Oxidation:** Phenol oxidised with chromic acid (mild agent) forms a conjugated diketone known as **benzoquinone**.



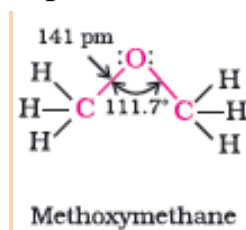
ETHERS

➔ **Ether** are the compounds in which the H-atoms of a hydrocarbon is substituted by alkoxy (R-O) or aryloxy (Ar-O) groups.

Ex. CH_3OCH_3 .

ELECTRONIC STRUCTURE

- In ethers, the 4 electron pairs, (the 2 bond pairs and 2 lone pairs) on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky ($-\text{R}$) groups.



CLASSIFICATION

Ethers are classified on the basis of groups attached to the O-atom.

- **Simple / symmetrical-** The alkyl or aryl groups attached to the O-atom are the same.

Ex. Diethyl ether $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$.

- **Mixed / unsymmetrical-** The alkyl or aryl groups attached to the O-atom are different.

Ex. $\text{C}_2\text{H}_5\text{OCH}_3$ or $\text{C}_2\text{H}_5\text{OC}_6\text{H}_5$

NOMENCLATURE

Common Name: By adding the word '*ether*' to the names of alkyl/aryl groups written as separate words in alphabetical order.

Ex. Ethylmethyl ether: $\text{CH}_3\text{-O-C}_2\text{H}_5$

If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group.

Ex. Diethyl ether: $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$

IUPAC Name: As '*Alkoxyalkane*'. The larger alkyl (R) group is chosen as the parent hydrocarbon.

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6\text{-CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{-O-CH(CH}_3\text{)-CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH}_2\text{-CH(CH}_3\text{)-CH}_3$	Phenyl isopentyl ether	3-Methylbutoxybenzene
$\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-OCH}_3$	—	1,2-Dimethoxyethane
$\text{H}_3\text{C-C(CH}_3\text{)}_2\text{-OC}_2\text{H}_5$	—	2-Ethoxy-1,1-dimethylcyclohexane

METHODS OF PREPARATION

(i) By acidic dehydration of alcohols

Alcohols undergo dehydration in the presence of H_2SO_4 to give ethers.



(ii) Williamson's ether synthesis

Alkyl halide reacts with sodium alkoxide to form ether.



PROPERTIES

Physical:

✓ **Boiling point:** Lower than isomeric alcohols.

Reason:- Incapable of forming inter molecular H-bond.

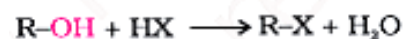
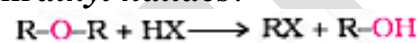
✓ **Solubility:** Lower ethers are soluble in water

Reason:- Ability to form H-bond with water.

CHEMICAL REACTIONS:-

(i) Reaction with HX:

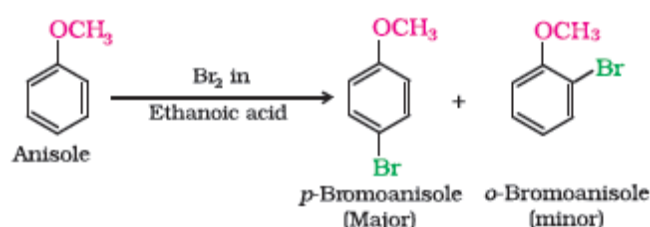
Ethers on reaction with *Hydrogen halide*, cleave the C-O bond and form *alkyl halides*.



In the case of ethers containing two different alkyl groups (primary and secondary), the lower alkyl group forms the alkyl halide (1° alkyl halide).

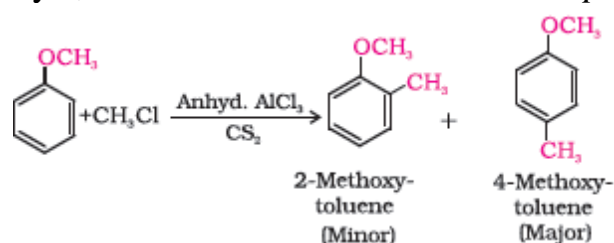
- In **electrophilic substitution**, the alkoxy group activates the aromatic ring and directs the incoming group to *ortho* and *para* positions.

a) **Halogenation:** Anisole on bromination with bromine in ethanoic acid gives a mixture of *o*-bromoanisole and *p*-bromoanisole



b) Friedel-Crafts reactions:

i) **Alkylation:** Anisole undergoes Friedel-Crafts alkylation reaction in presence of **anhydrous aluminium chloride** (a Lewis acid) as catalyst, results in a mixture of *ortho* and *para* alkylated anisole.



ii) Acylation:



c) **Nitration:** Anisole reacts with a mixture of conc. sulphuric acid and conc. nitric acid to give a mixture of *ortho* and *para* nitroanisole.

