

# Chapter # 7

# Alcohols,

# Phenols and

# Ethers





## INTRODUCTION

- Alcohols, Phenols and Ethers are three classes of oxygen containing organic compounds.
- Alcohols and Phenols are derived by replacing one hydrogen atom of water with an alkyl and aryl group respectively but ethers are formed by replacing both hydrogen atoms of water with alkyl or aryl groups.
- Alcohols, phenols and ethers have a wide range of industrial as well as pharmaceutical applications.
- Methanol and Ethanol are good car fuels with high octane rating,
- Isopropyl alcohol is a common sanitizer, Ethylene glycol is frequently used as automotive antifreeze.
- Phenol is the oldest mild antiseptic agent and ethers are known for their anesthetic properties.

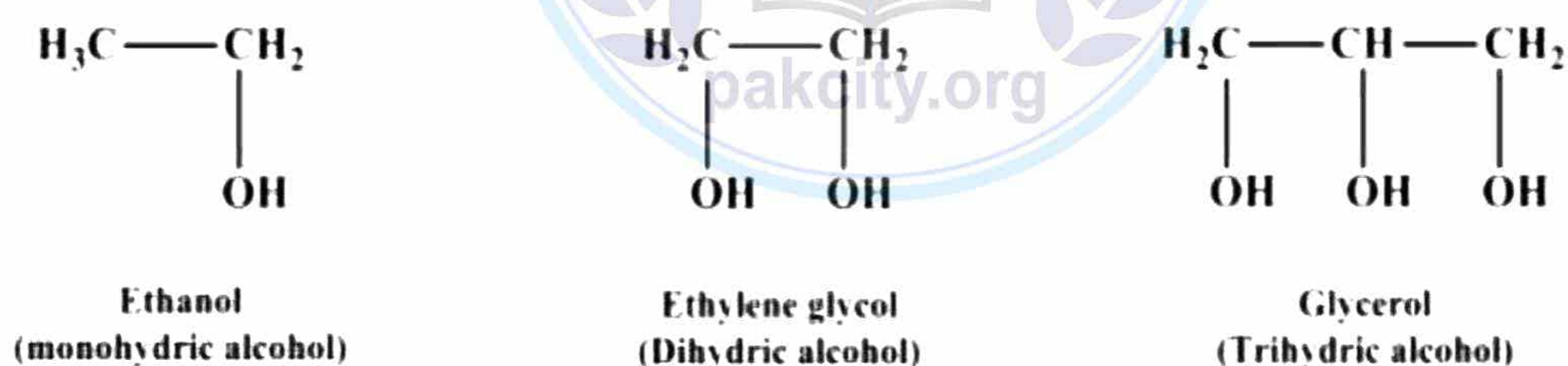
## ALCOHOL

Alcohol is a class of organic compounds in which hydroxyl group (-OH) is attached aliphatic carbon atom.

They are classified according to the number of hydroxyl groups present in the molecule.

Monohydric alcohols contain one hydroxyl group.

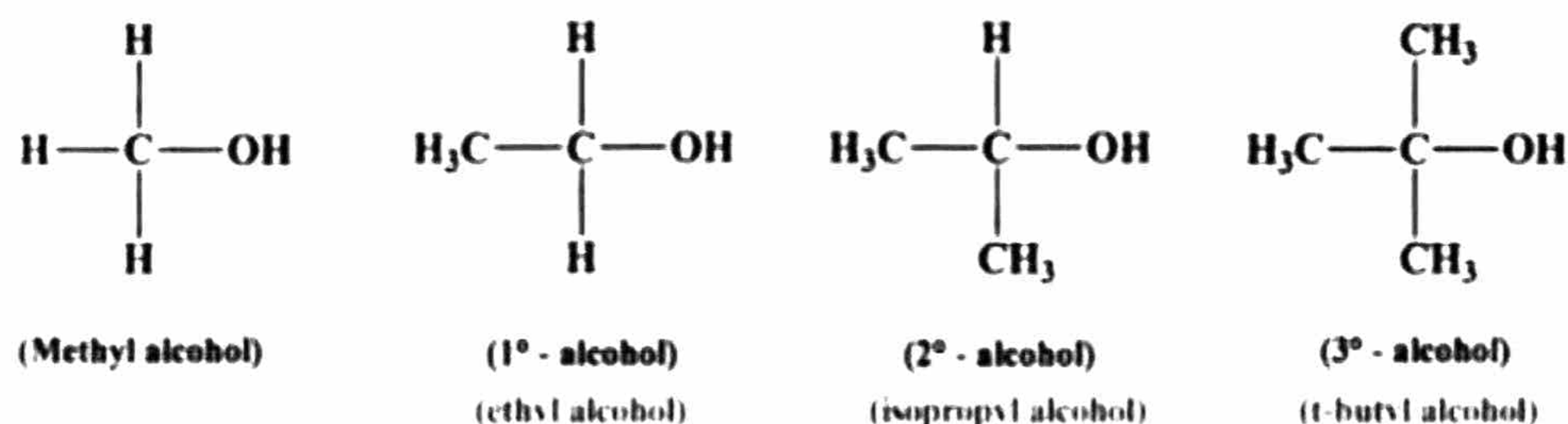
If two or more hydroxyl groups (-OH) are present in the molecule, these are identified as dihydric and polyhydric alcohols respectively.



Monohydric alcohols are represented by a general formula R-OH or  $\text{C}_n\text{H}_{2n+1}\text{OH}$ .

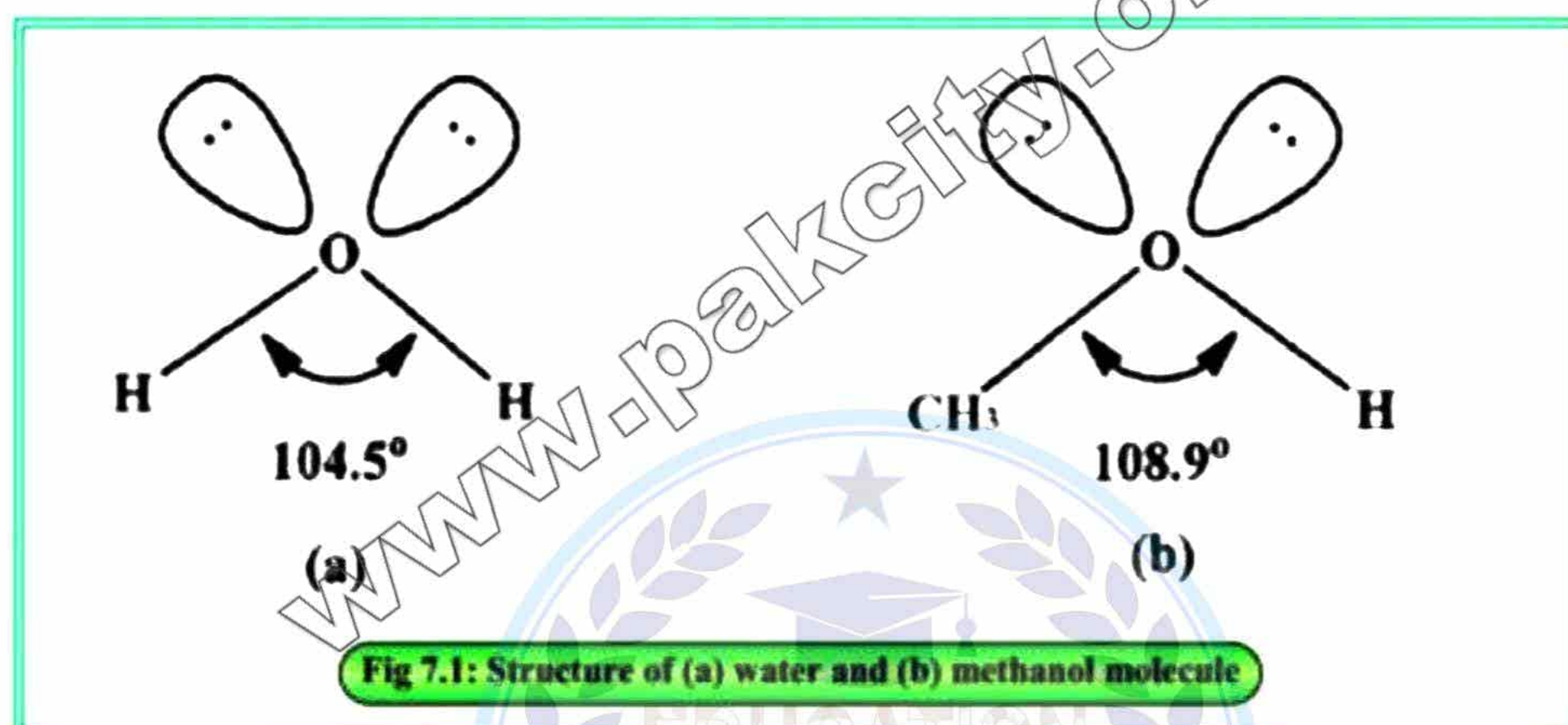
Monohydric alcohols are further classified into primary ( $1^\circ$ - alcohol), secondary ( $2^\circ$ -alcohol) and tertiary ( $3^\circ$ -alcohol) depending upon whether the hydroxyl group is attached to primary, secondary or tertiary carbon atom.





### Structure of Alcohol

The structure of an alcohol molecule is similar to that of water molecule. The carbon atom which is bonded to hydroxyl group is  $\text{sp}^3$ -hybridized. The oxygen atom of  $-\text{OH}$  group is also  $\text{sp}^3$  hybridized. Oxygen atom utilizes its two  $\text{sp}^3$  hybrid orbitals in the formation of sigma bond with carbon and hydrogen atoms while the remaining two  $\text{sp}^3$  hybrid orbitals of oxygen contain lone pairs of electrons. The C-O-H bond angle is  $108.9^\circ$ , which is slightly higher than exists in water molecule ( $104.5^\circ$ ).



### Physical Properties

#### Physical State:

Alcohols of lower molecular mass (up to butanol) are colorless liquids with characteristic sweet smell.

#### Boiling Point:

Boiling point of alcohol is much higher than that of alkanes and ethers of comparable molecular mass.

#### Solubility:

Alcohols are generally soluble in water since they form hydrogen bonds with water molecules. However, solubility decreases with increasing the number of alkyl groups in the molecule

#### Acidity of Alcohol:

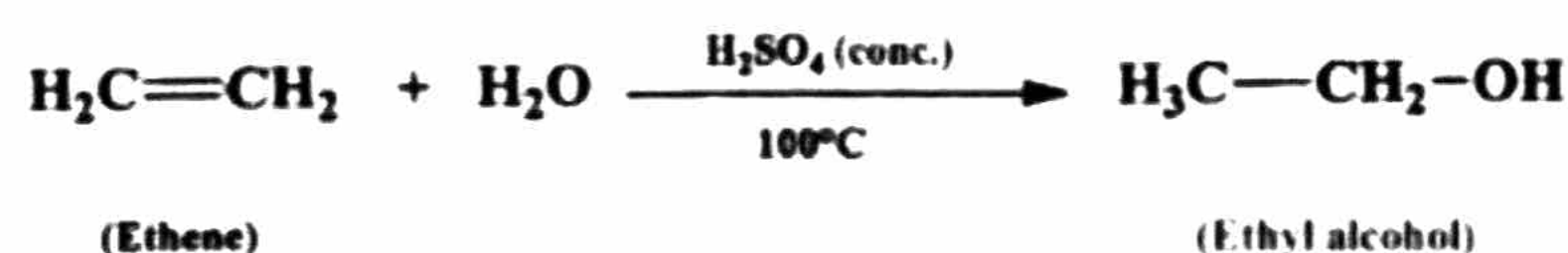


Alcohols are generally classified as weak acids due to their ability to donate a proton to a strong base.

### Preparations of Alcohols

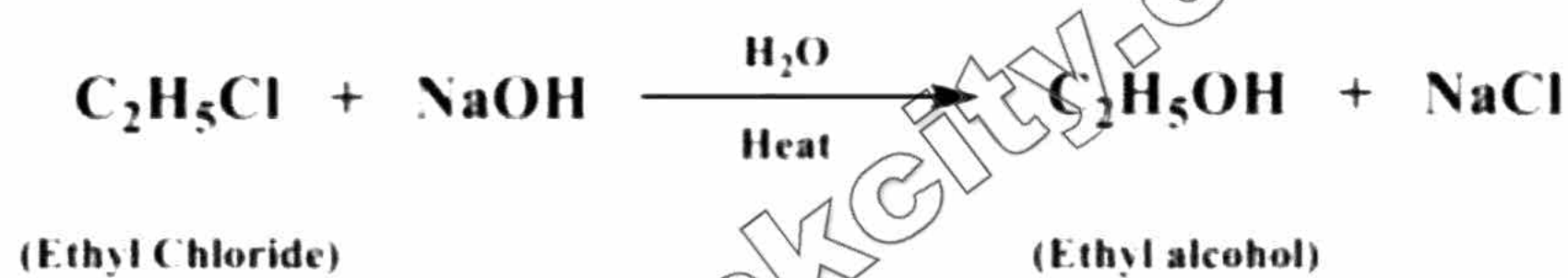
#### Hydration of an Alkene

Alkene when boils with water in the presence of concentrated sulphuric acid to give corresponding alcohol.



#### Hydrolysis of an Alkyl halide

When an alkyl halide is heated with aqueous alkali (NaOH, KOH), it gives corresponding alcohol.



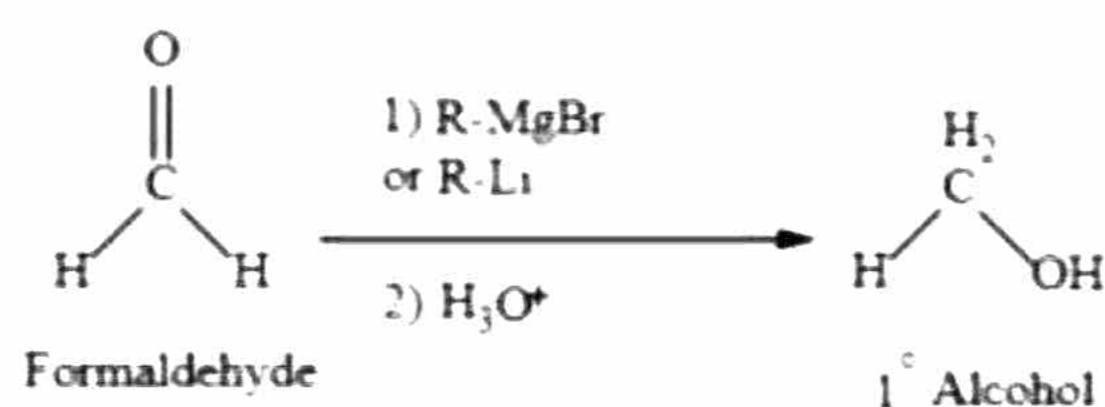
#### Reaction of Grignard reagent with Aldehyde and Ketone

Grignard reagent when reacts with a formaldehyde, acetaldehyde and acetone molecule, it gives primary, secondary and tertiary alcohols respectively.



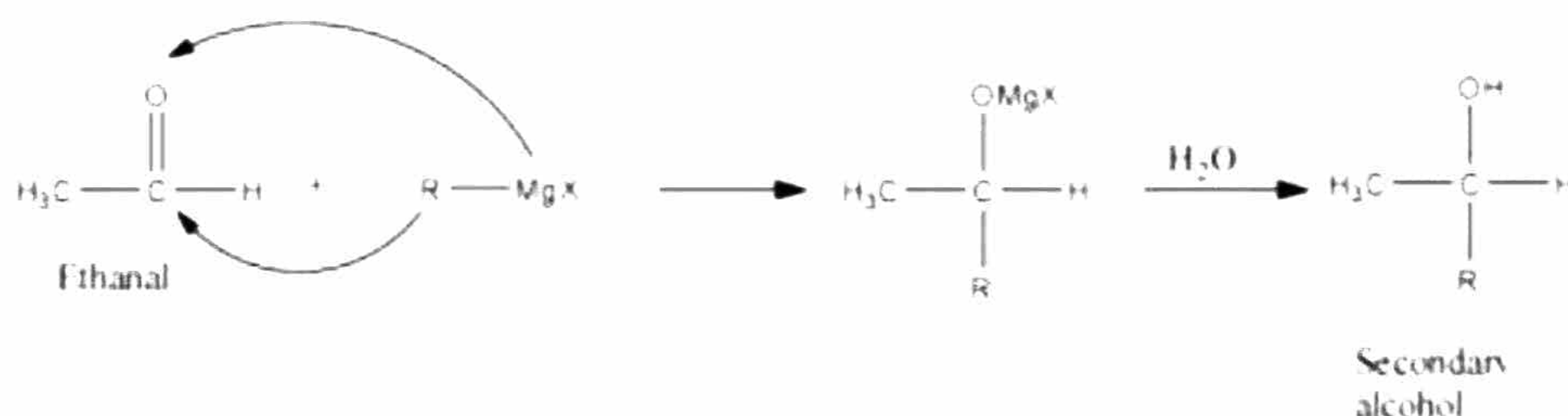
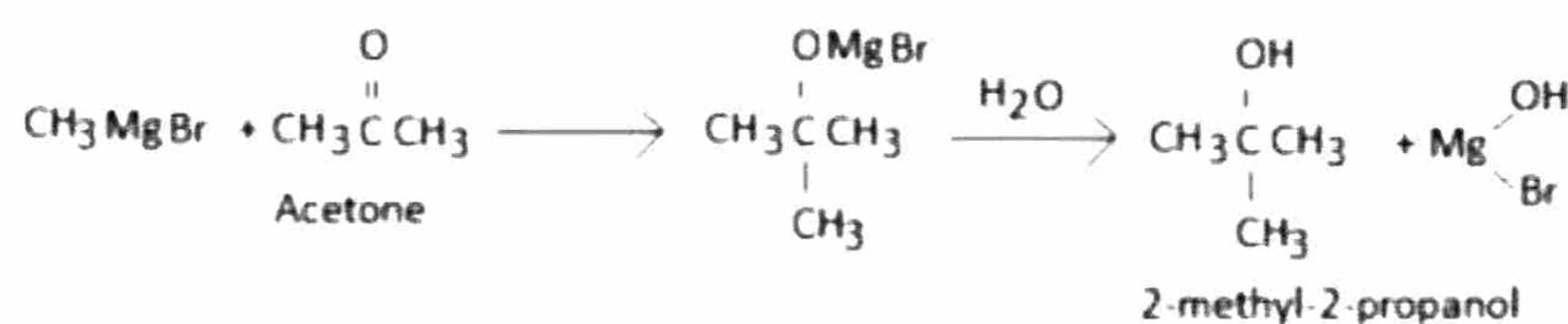
#### Preparation of primary, secondary and tertiary alcohol

##### (i) Reaction with formaldehyde



##### (ii) Reaction with acetaldehyde (ethanal)



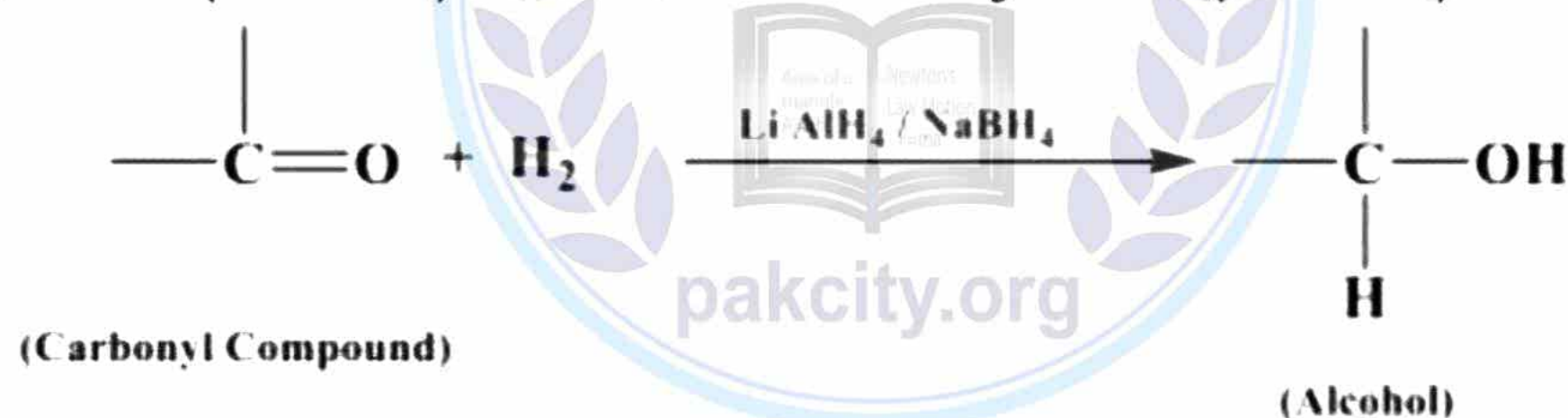
**(iii) Reaction with acetone****Reduction of Aldehydes and Ketones**

Aldehydes and Ketones can be reduced to alcohols by using any one of the following two methods:

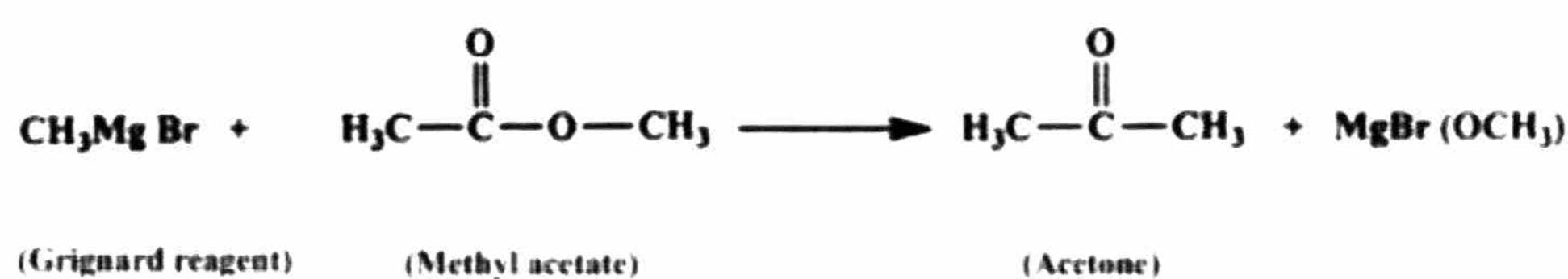
(a) Hydrogenation of aldehyde and ketone at high temperature and pressure in the presence of catalyst like nickel (Ni), platinum (Pt) or palladium (Pd).



(b) Reaction of aldehyde and ketone with a reducing agent like lithium aluminum hydride (LiAlH<sub>4</sub>) or sodium borohydride (NaBH<sub>4</sub>).

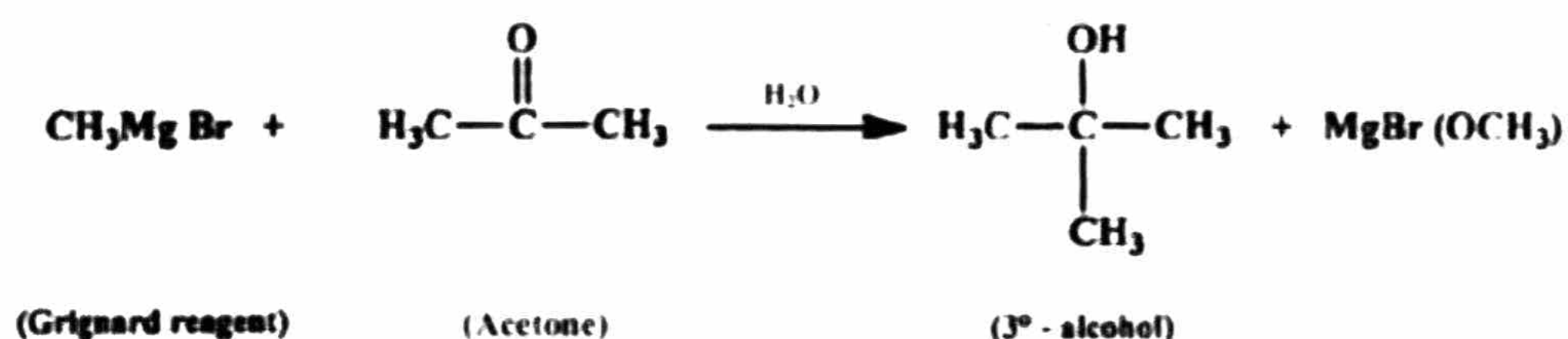
**Reaction of Grignard reagent with Esters**

When a Grignard reagent is mixed with an ester, it chemically changes into carbonyl compound (aldehyde or ketone).



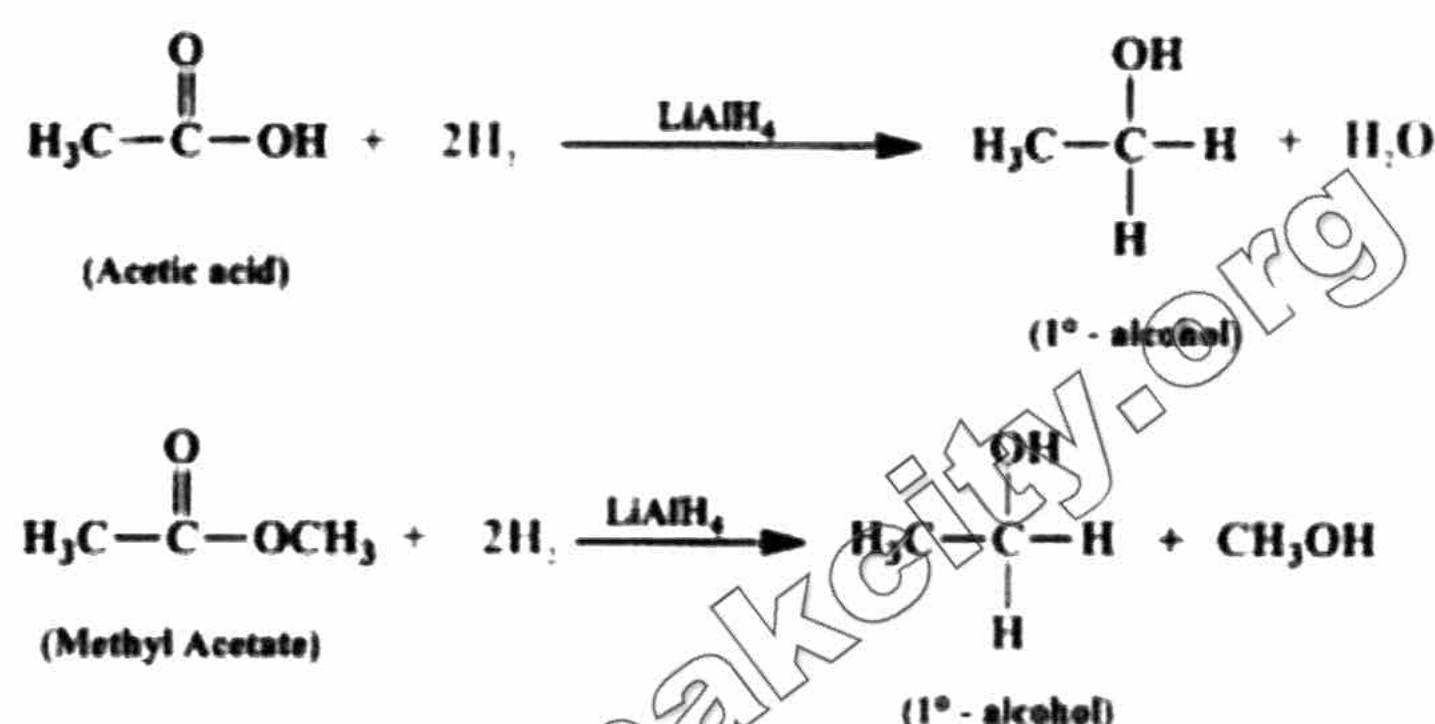


The carbonyl compound thus formed then reacts with another molecule of Grignard reagent and finally gives an alcohol (Discussed in Chap. 18).



### Reduction of Carboxylic acids and Esters

Carboxylic acids and esters can be reduced to the primary alcohols (1°-alcohols) in the presence of a very strong reducing agent such as lithium aluminum hydride.



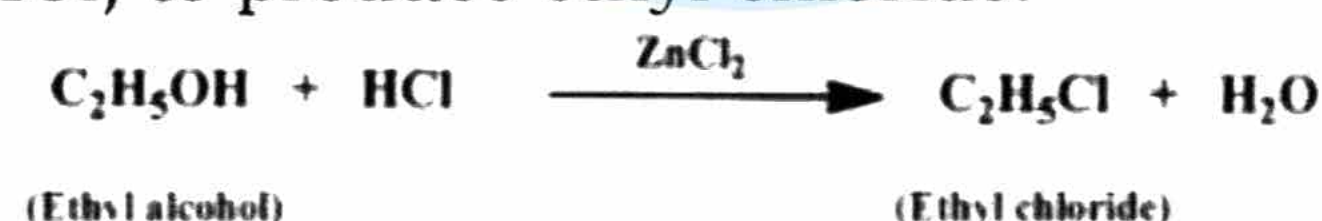
### Reactivity of Alcohol

The reactivity of alcohol can be attributed to the breaking of either C-OH bond with the removal of OH group or by the breaking O-H bond with the removal of hydrogen (H). The common reactions of alcohol are substitution, elimination and oxidation.

### Reactions of Alcohols

#### Reaction with Halogen acids (HX)

In the presence of a catalyst, zinc chloride ( $\text{ZnCl}_2$ ), ethyl alcohol reacts with hydrochloric acid (HCl) to produce ethyl chloride.

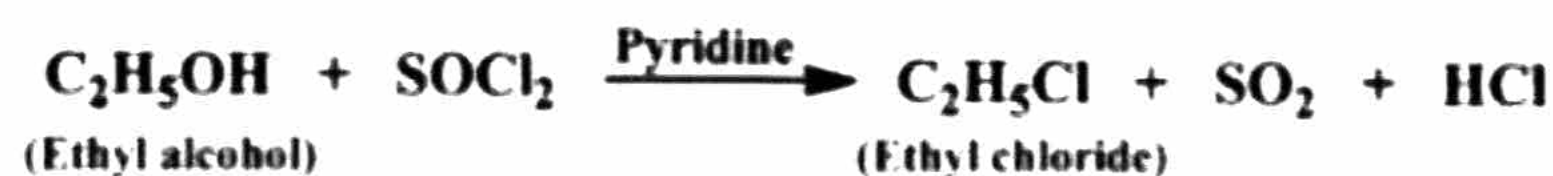


The mixture of concentrated HCl  $\text{ZnCl}_2$  is called "Lucas reagent" and used to distinguish between primary, secondary and tertiary alcohol.

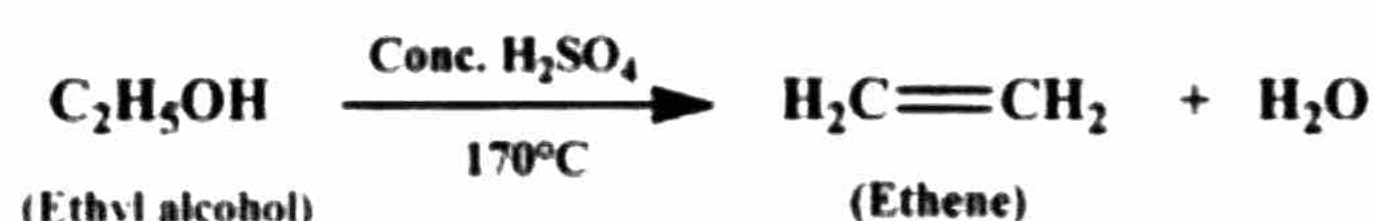
#### Reaction with $\text{SOCl}_2$ and $\text{PX}_3$

When alcohol is treated with Phosphorus tri halide ( $\text{PX}_3$ ) or thionyl chloride ( $\text{SOCl}_2$ ), it gives corresponding alkyl halide





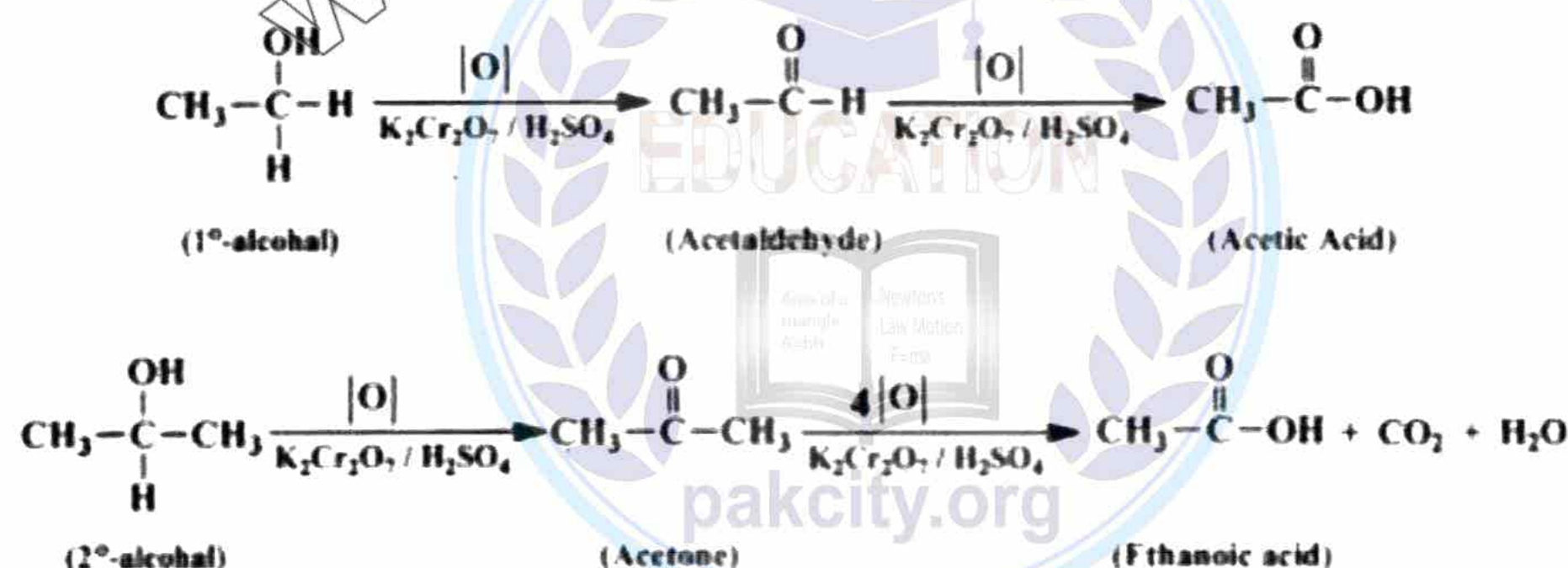
When an alcohol is heated with concentrated sulphuric acid at  $170^{\circ}\text{C}$ , it undergoes a dehydration process, resulting in the formation of an alkene. In this process, a water molecule is eliminated.



## Oxidation Reaction

Primary and secondary alcohols oxidize in the presence of strong oxidizing agents such as acidified potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) or potassium permanganate ( $\text{KMnO}_4$ ) to give carboxylic acid through an aldehyde or ketone intermediate.

Tertiary alcohol cannot be oxidized due to the unavailability of hydrogen on its hydroxyl-bearing carbon.



Since the oxidation of ketone involves the breaking of carbon-carbon sigma bond, it is a relatively slow process.

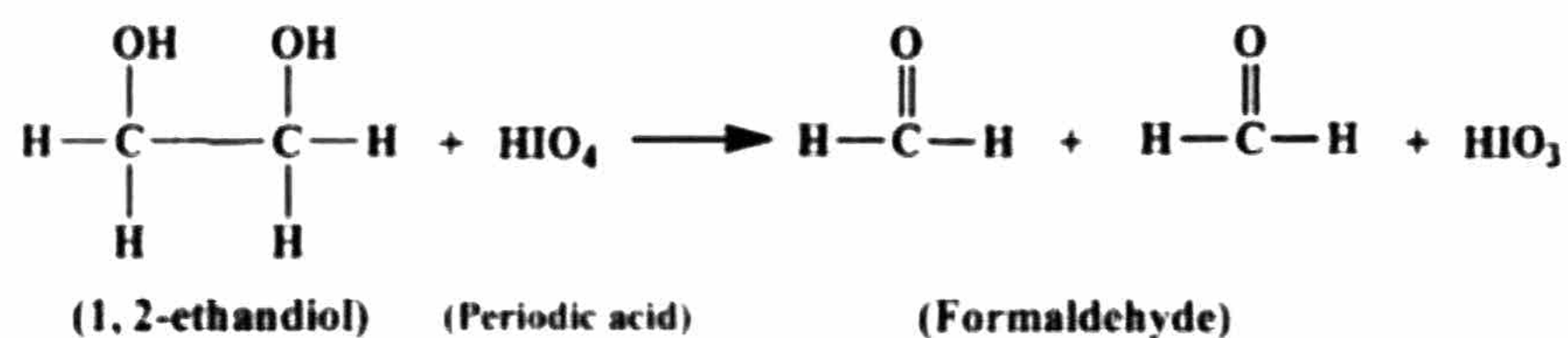
An alcohol molecule in which two hydroxyl groups (-OH) are attached on position 1 and 2 is called as 1, 2 diol or vicinal diol.

When a 1, 2-diol molecule is treated with per iodic acid ( $\text{HIO}_4$ ), an oxidative cleavage occurs between carbon 1 and carbon 2 atoms resulting in the formation of two carbonyl molecules. These carbonyl molecules may be



aldehyde or Ketone depending upon the number of alkyl groups attached to the carbon atom bearing hydroxyl groups. In this reaction periodic acid ( $\text{HIO}_4$ ) is reduced into iodic acid ( $\text{HIO}_3$ ).

For example, ethylene glycol (1, 2- ethanediol) is broken down into two formaldehydes molecules if treated with per iodic acid.



### Uses of Alcohol

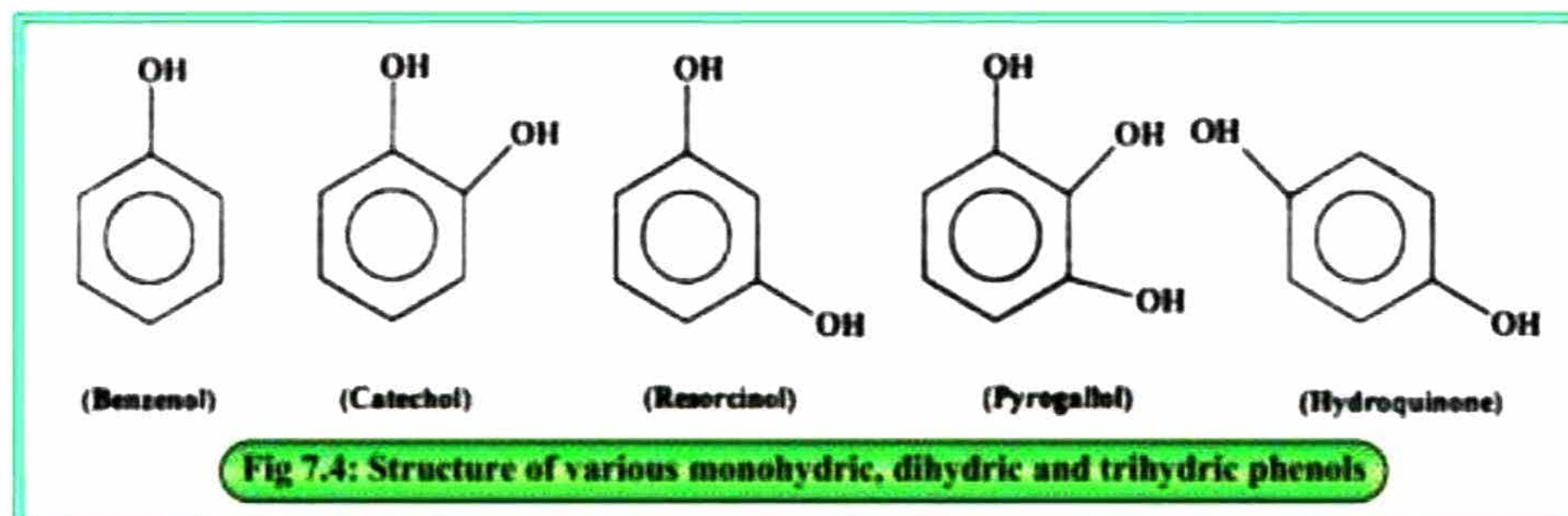
- (i) Methanol is used as antifreeze solution and also in the preparation of perfumes, dyes, drugs etc.
- (ii) Ethanol is used as a raw material in the synthesis of a variety of organic compounds such as gums, resins, tinctures, chloroform, esters, acetone and acetic acid.
- (iii) The mixture of isopropyl alcohol in water is used as rubbing alcohol (antiseptic).

### PHENOLS

Organic compounds in which hydroxyl group ( $-\text{OH}$ ) is directly attached to benzene ring are called Phenols.

The parent compound of this family is monohydroxy benzene which is also known as carbolic acid or benzenol.

On the basis of number of hydroxyl groups ( $-\text{OH}$ ) attached to aromatic ring, Phenols are classified into monohydric, dihydric and trihydric Phenols



### Structure of Phenol



In the molecule of phenol, the carbon atom of aromatic ring is attached to an OH group. The oxygen atom in the -OH group is  $sp^3$  hybridized, while the carbon atoms in the aromatic ring are  $sp^2$  hybridized. An  $sp^3$ - $sp^2$  sigma bond is formed between oxygen atom of -OH group and carbon atom of aromatic ring.

The C -O- H bond angle is set at  $109^\circ$  which is almost the same as the bond angle of tetrahedral geometry ( $109.5^\circ$ ) but due to two non-bonded electron pairs of oxygen atom, the geometry is slightly distorted from a normal tetrahedron and exists in a bent shape.

### Physical Properties

#### (i) Physical State:

Pure phenol is a white crystalline solid at room temperature however it may appear in red colour due to the presence of some oxidized products as impurities.

#### (ii) Boiling Point:

The boiling point of phenol is higher than that of other compounds of comparable size because the presence of OH group

#### (iii) Toxicity:

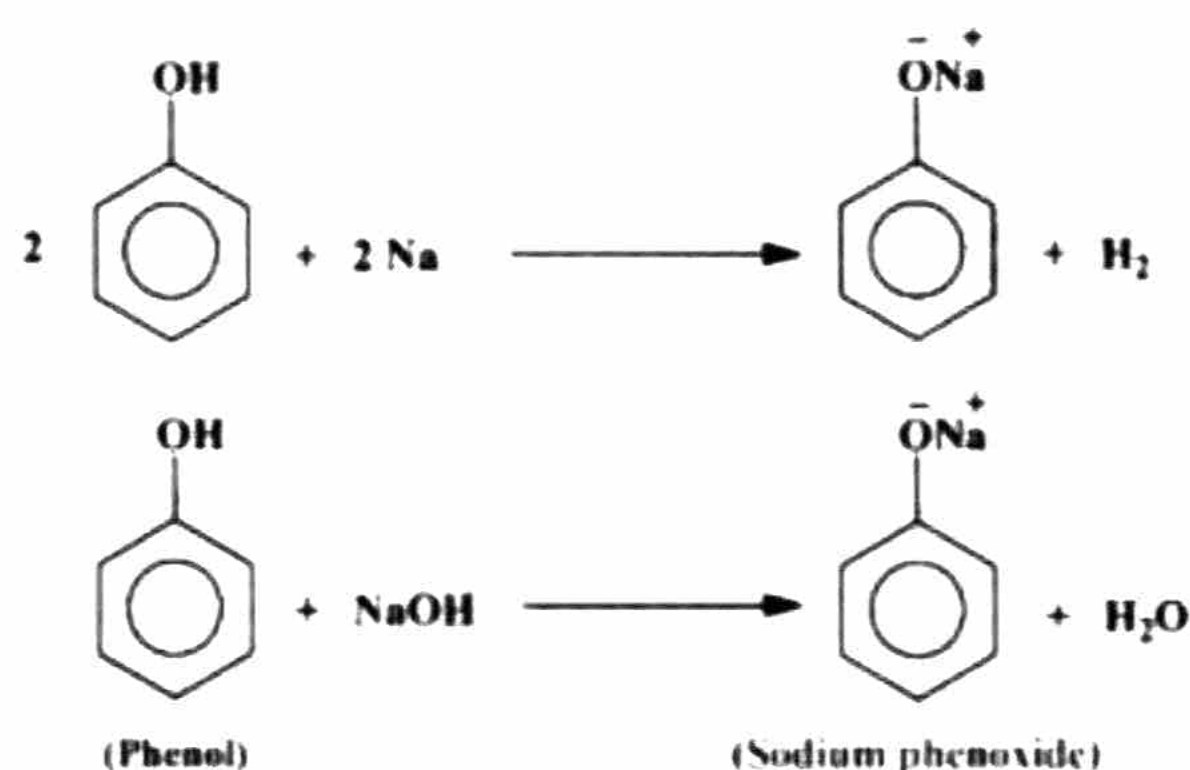
Phenol is toxic and corrosive in nature. When it comes into contact with skin it can lead to a severe burns and tissue damage.

#### (iv) Solubility:

The hydroxyl group attached to the aromatic ring allows phenol to make hydrogen bond with water molecules that is why it is soluble in water.

### Acidity of Phenol

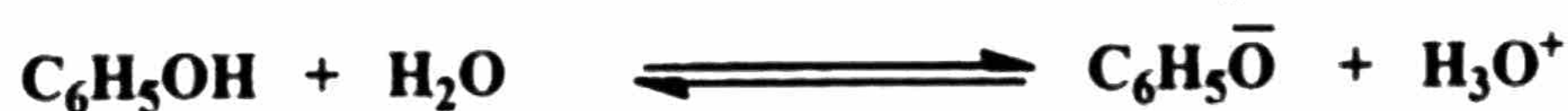
Phenol is fairly acidic since it reacts with an alkali or alkali metal to form salt.





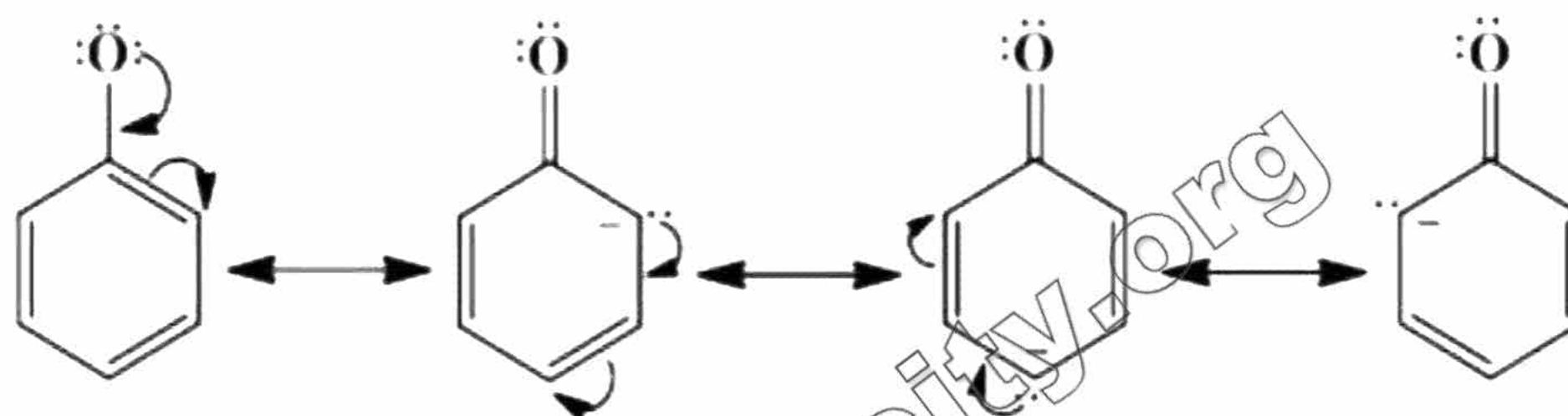
The pka value of phenol is approximately 10, which is far less than carboxylic acid (pka 5) but much higher than alcohol (pka = 15 – 18) that is why phenol is much weaker acid than carboxylic acid but stronger than alcohol.

Comparing phenoxide ion with ethoxide ion, it is noted that the negative charge on oxygen atom of phenoxide ion is delocalized over the entire ring through a process called as resonance and make the phenoxide ion stable.



(Phenol)

(Phenoxide ion)



On the other hand, in ethoxide ion the negative charge is localized on the Oxygen atom due to the absence of aromatic ring result in a less stable structure compared to phenoxide ion.



(Ethanol)

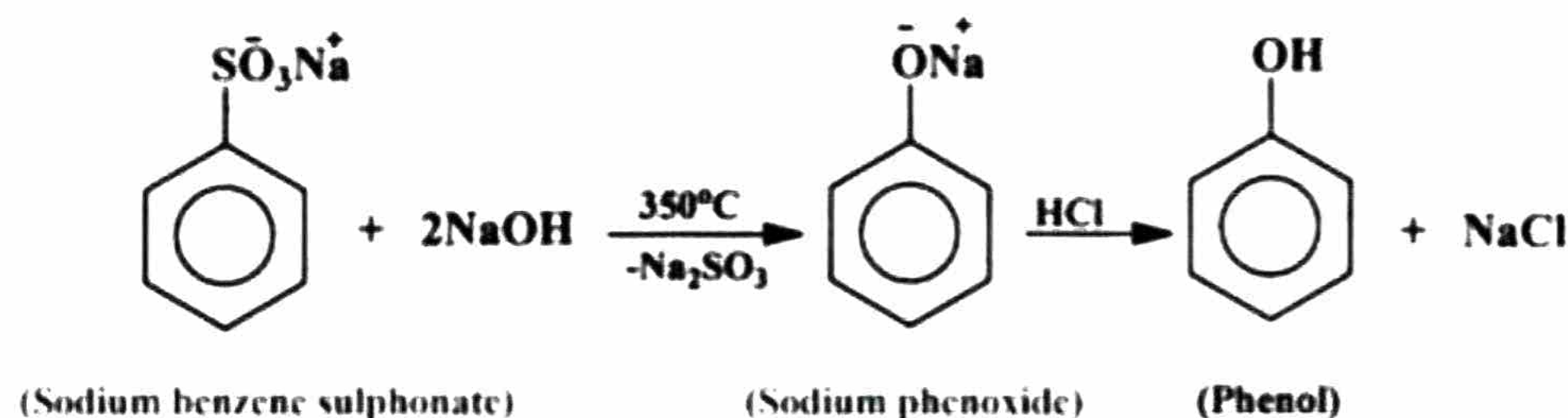
(Ethoxide ion)

### Preparation of Phenol

Phenol can be prepared by various methods. The two most common methods are described below.

#### From Sodium Benzene Sulphonate

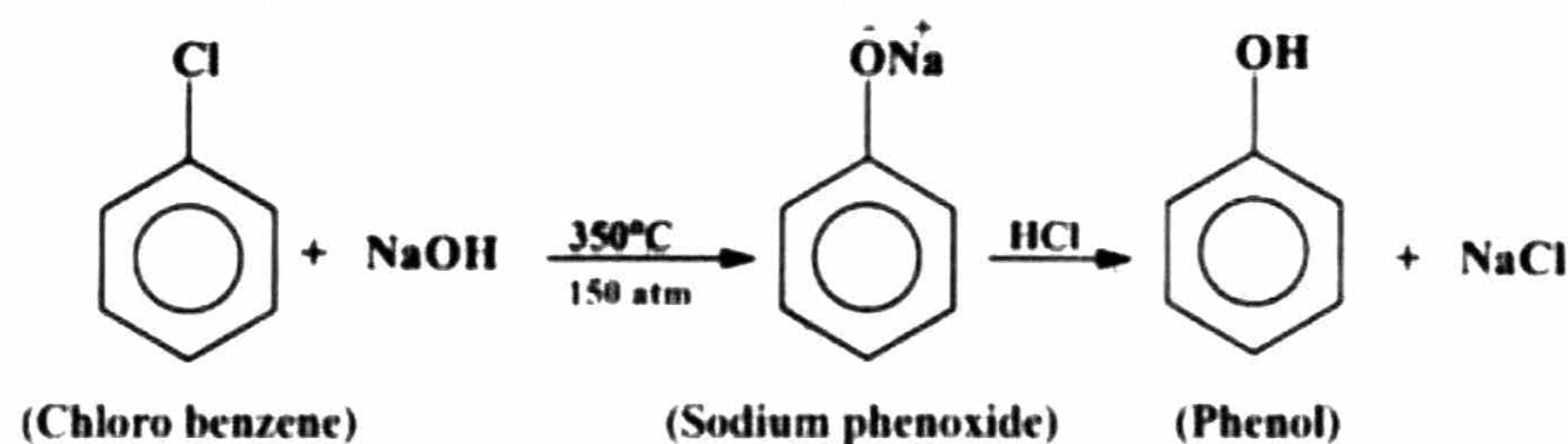
Sodium benzene sulphonate when fused with sodium hydroxide at 300 - 350°C, produces sodium phenoxide which on acidification yield phenol.



#### From Chlorobenzene (Dow's Process)

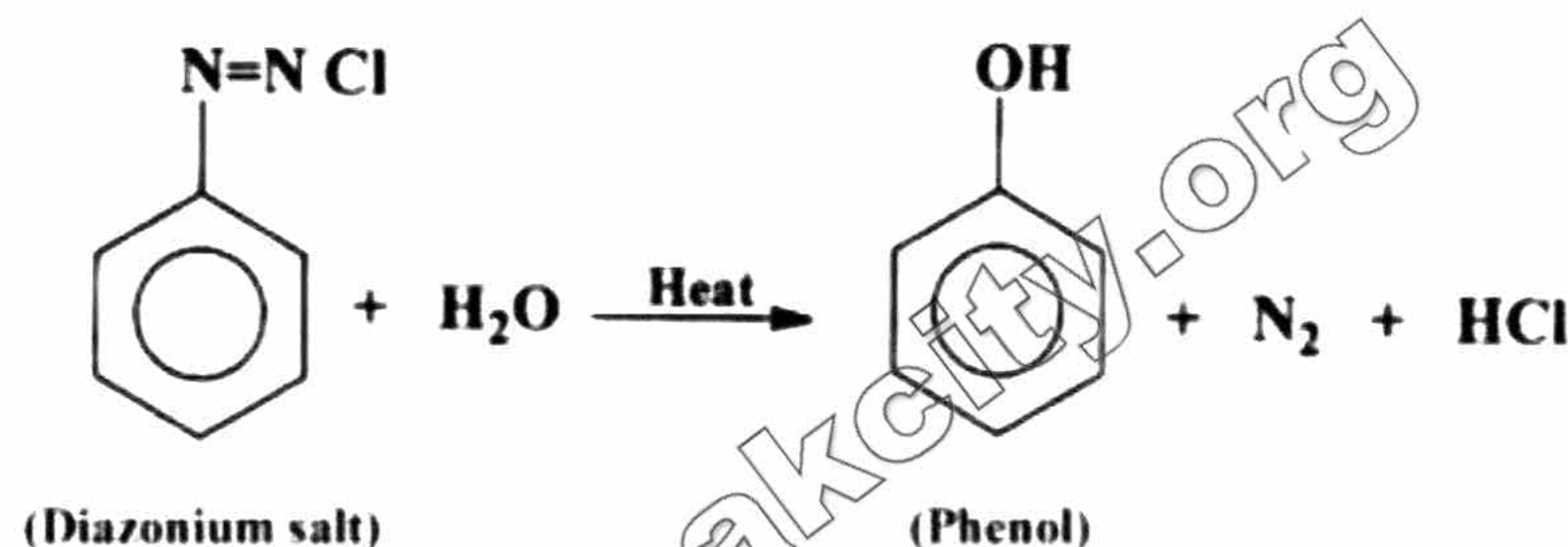


Chlorobenzene when fused with aqueous sodium hydroxide (NaOH) at 350°C and 150 atmospheric pressures, it gives sodium phenoxide which then acidified with dilute hydrochloric acid to yield phenol.



### Hydrolysis of Diazonium salt

It is a laboratory method for the preparation of phenol. Benzene diazonium chloride on heating with water, changes into phenol with the release of nitrogen gas.



Diazonium salt is a class of organic compounds that contain a functional group -N<sub>2</sub>Cl attached with alkyl or aryl carbon chain.

### Reactivity of Phenol

The aromatic part of phenol is similar to benzene which favors the electrophilic substitution reactions.

### Reactions of Phenol

Phenol typically undergoes two types of reactions; those involving the hydroxyl group and those involving the aromatic ring.

In the first type of reactions, the -OH part usually broken to form substances such as salts and esters, which are similar to those of alcohols.

In the second type of reactions, the aromatic ring of phenol undergoes electrophilic substitution reactions.

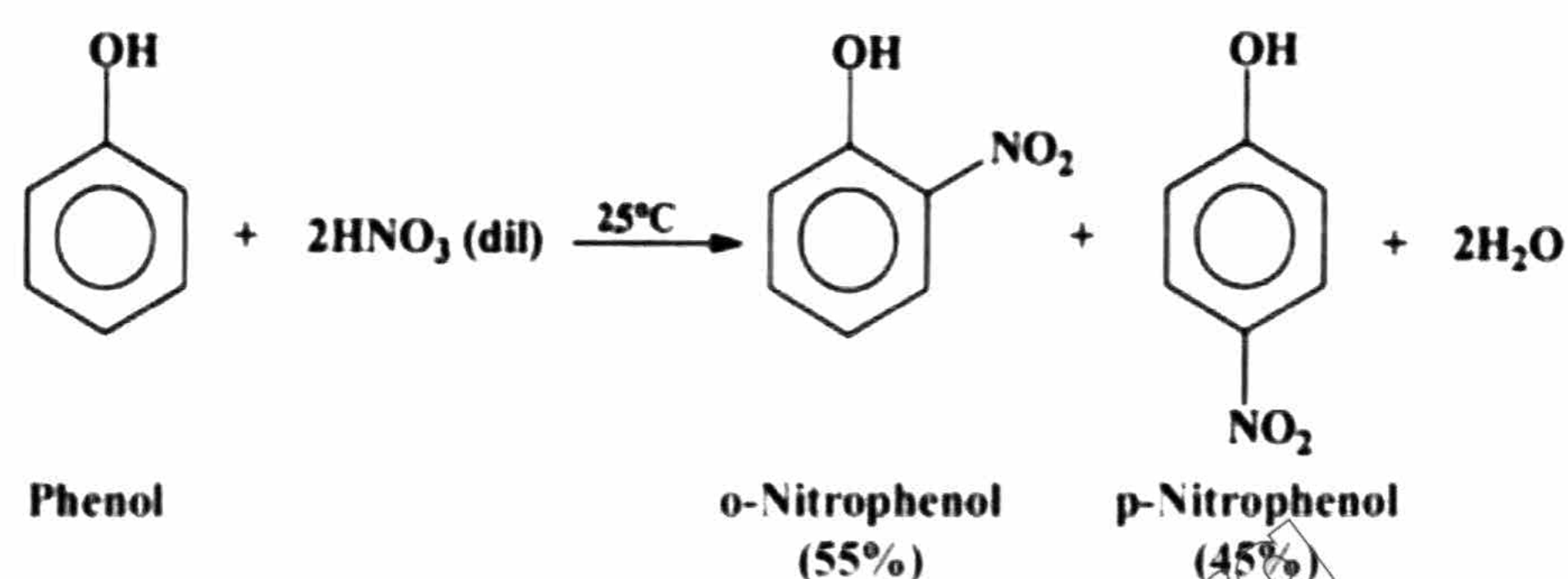
### Electrophilic Aromatic Substitutions



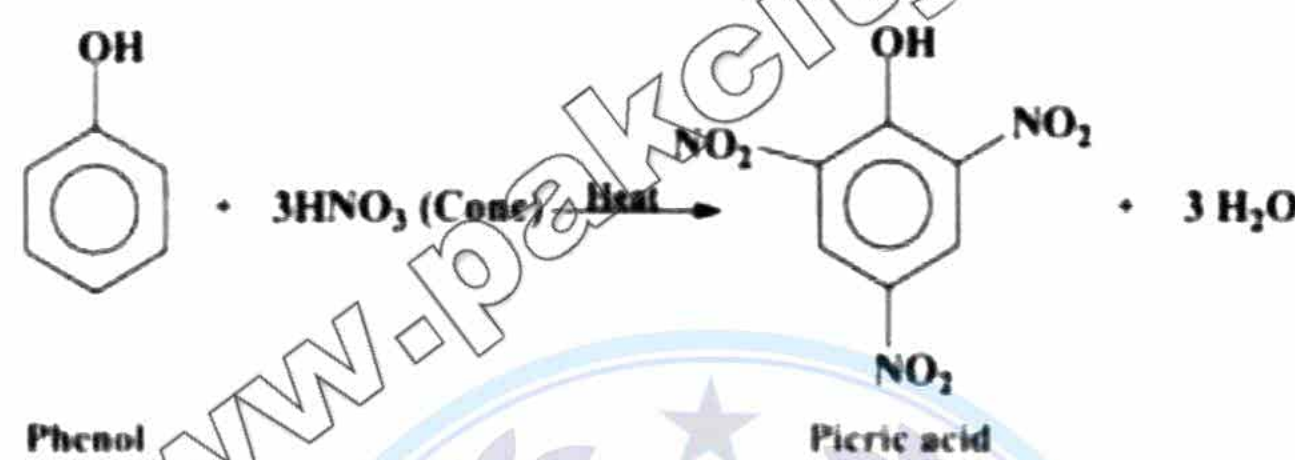
These reactions occur due to aromatic part of molecule. Most common electrophilic aromatic substitution reactions of phenol are nitration, Sulphonation and halogenation.

### Nitration

Phenol on treating with dilute nitric acid at 25°C gives a mixture of o-nitrophenol and p-nitrophenol.



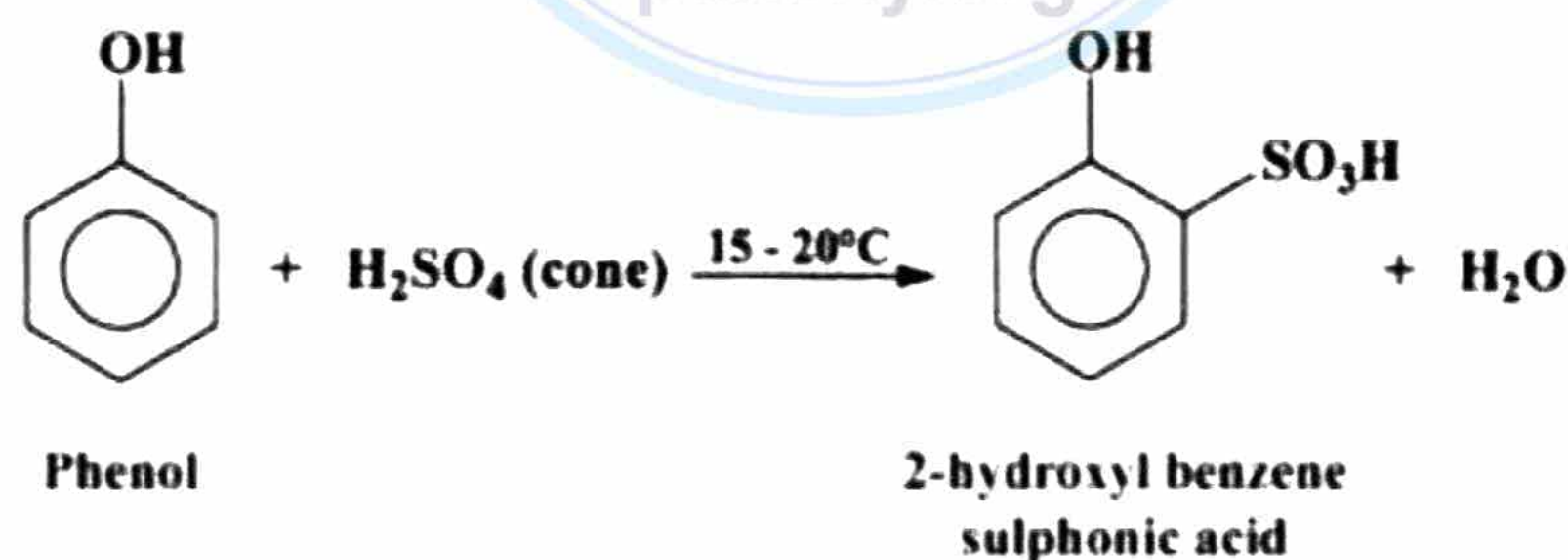
When phenol heated with concentrated nitric acid, it gives 2, 4, 6-trinitrophenol (picric acid).



### Sulphonation explosion.

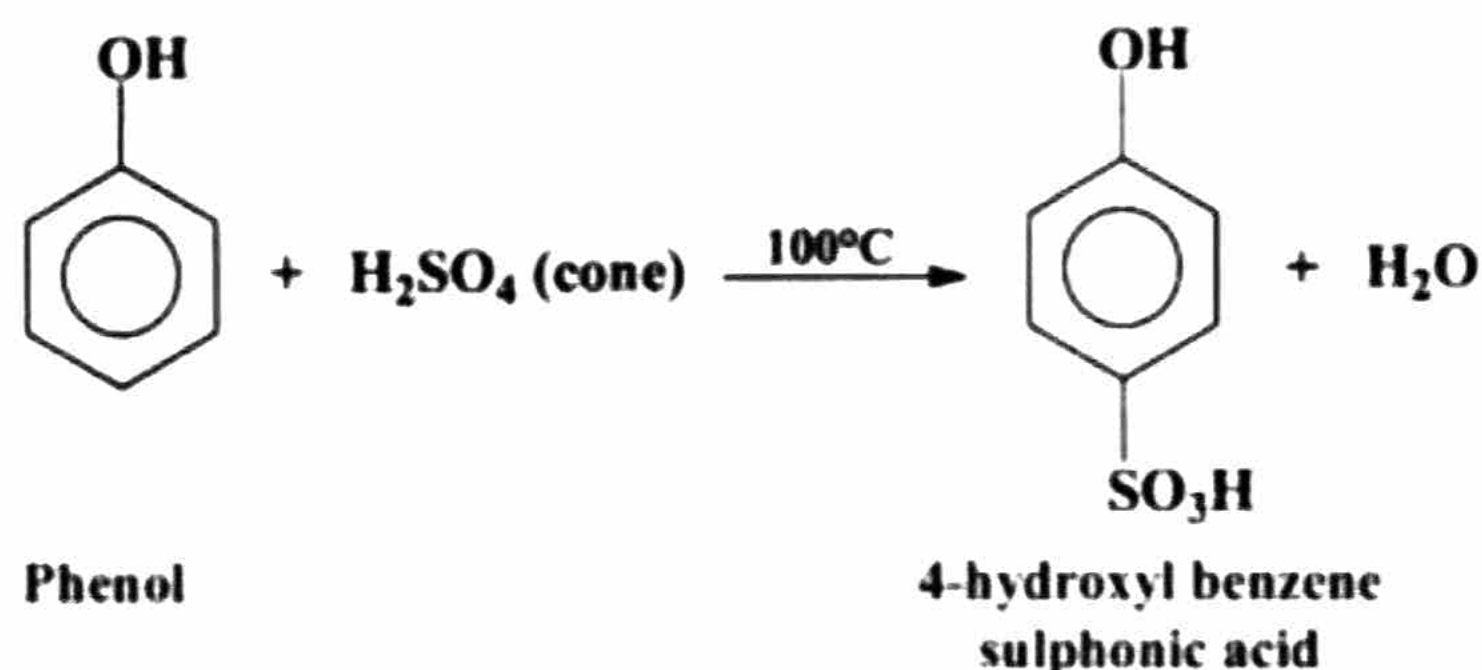
When phenol is treated with sulphuric acid, it gives Phenol sulphonic acid, however the relative proportion of isomers depends upon temperature.

(a) On heating at 15° - 20°C, ortho phenol sulphonic acid is formed as major proportion.



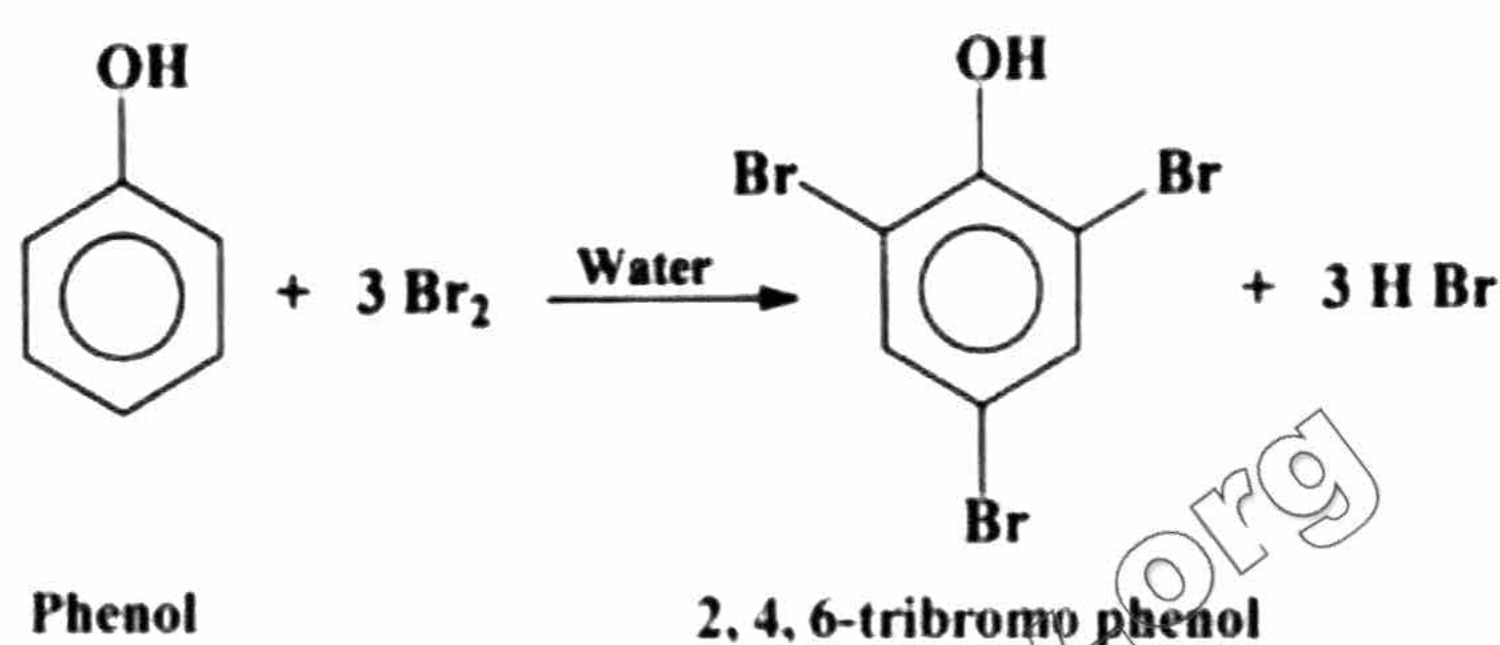
(b) On heating at 100°C it gives major product of para phenol sulphonic acid.



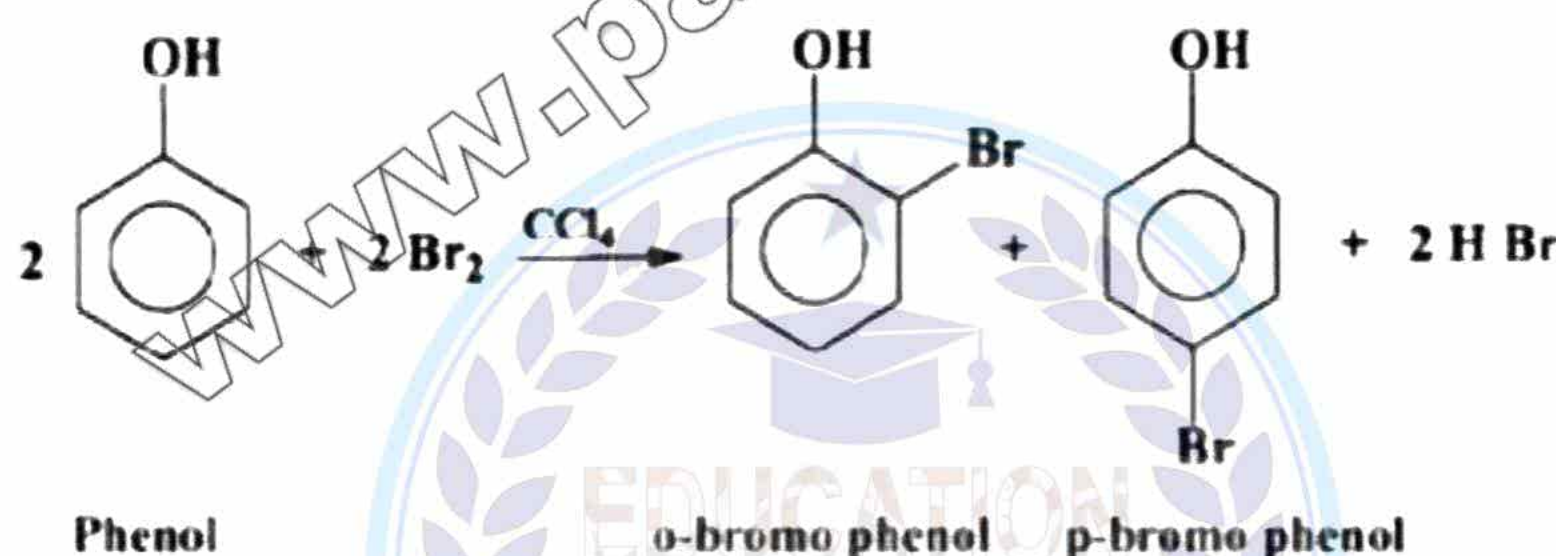


### Halogenation

Phenol if reacts with aqueous bromine, it produces 2, 4, 6 - tribromophenol

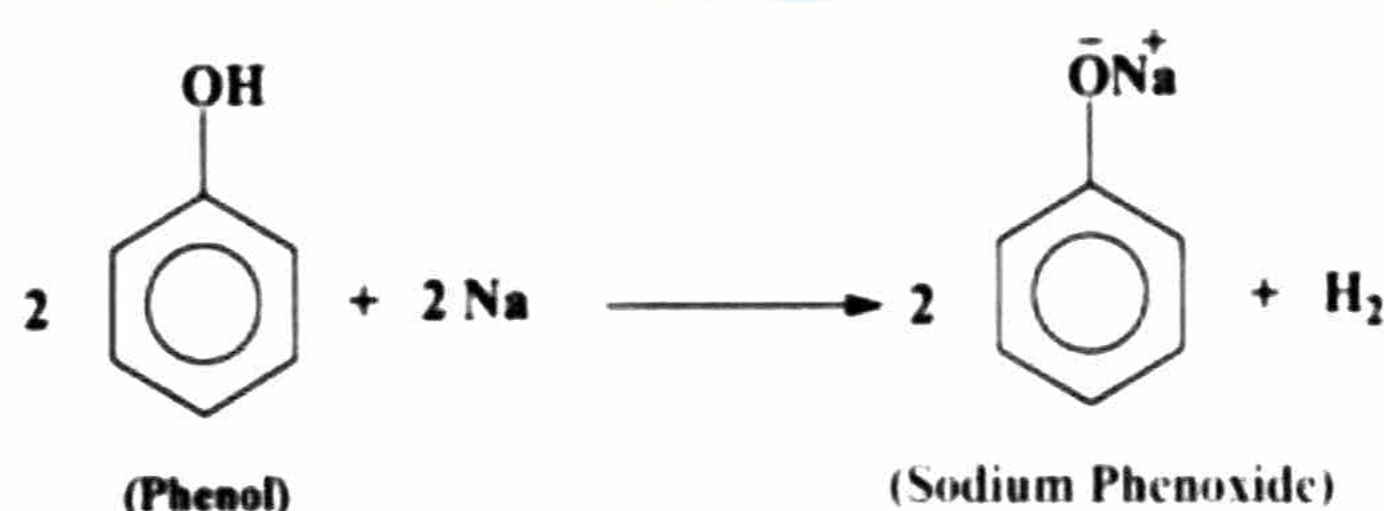


Phenol reacts with Bromine in carbon tetra chloride, it gives a mixture of ortho and para bromophenol.



### Reaction with Sodium Metal

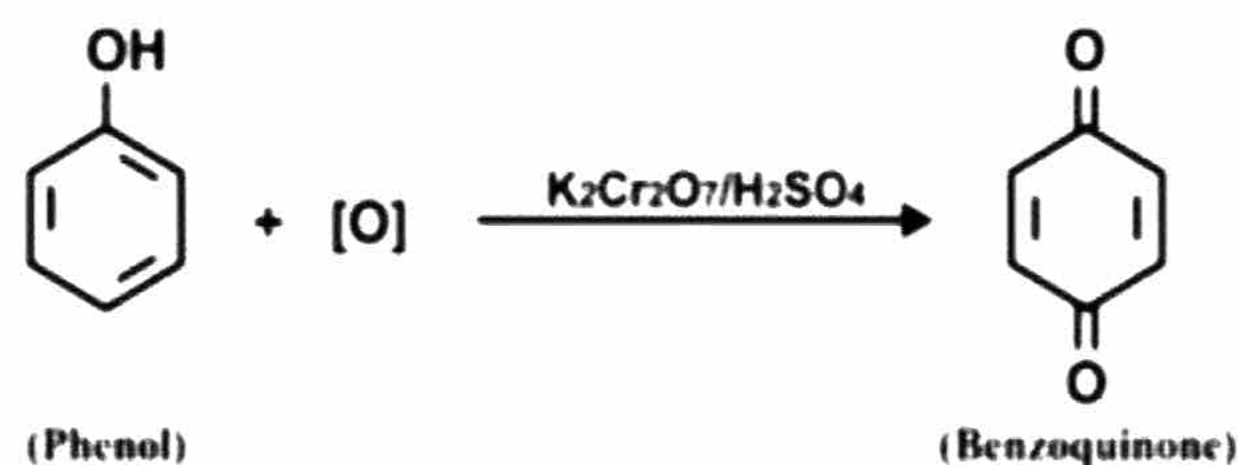
Phenol when reacts with highly active metal such as sodium, the sodium donate an electron to the Oxygen atom of the hydroxyl group in phenol forming sodium phenoxide



### Oxidation of Phenol

In this reaction potassium dichromate acts as oxidizing agent and the Sulphuric acid serves as catalyst. Phenol is oxidized to yellow colored benzoquinone (conjugated diketone).





### Difference between Alcohol and Phenol

Property	Alcohol	Phenol
Functional Group	-OH attached to alkyl carbon (R-OH)	-OH attached to aryl carbon (Ar-OH)
Hydrogen Bonding	Can form intermolecular hydrogen bonding	Can form stronger hydrogen bonding
Boiling Point	Generally lower than phenol	Generally higher than alcohols
Acidity	Weaker acids (higher pKa values)	Stronger acids (lower pKa values)
Solubility in Water	Readily soluble in water	Lower solubility in water
Aromatic Properties	Lacks aromatic properties Contains an aromatic ring	Contains an aromatic ring

### Uses of Phenol

- (i) It is used as an antiseptic and disinfectant
- (ii) It is used in the manufacturing of soap, Plastics, ointments and lozenges etc.
- (ii) It is used in the preparation of picric acid and, phenolphthalein.
- (iv) It is used as ink preservative.

### Identification tests for Alcohols and Phenols

#### Tests of identification of Alcohol

##### (i) Sodium metal test

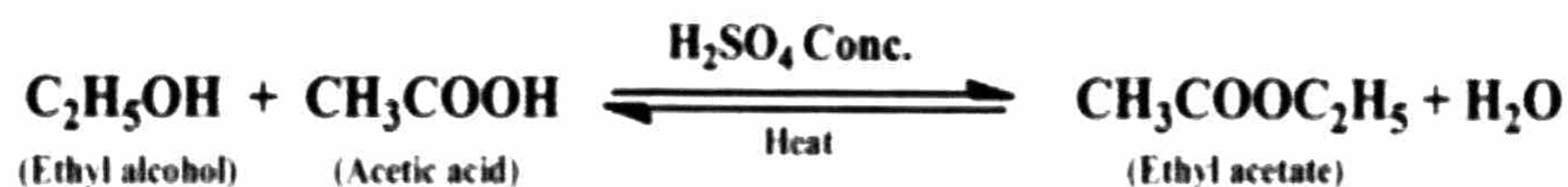
Alcohol readily reacts with sodium metal at room temperature to form sodium alkoxide with the liberation of hydrogen gas.



##### (ii) Ester test

Alcohol when heated with acetic acid in the presence of small amount of concentrated sulphuric acid, it forms an ester.



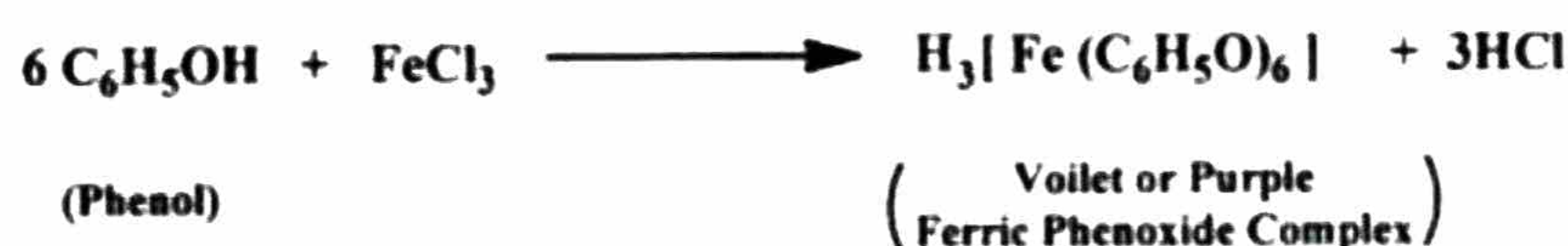


Fruity smell of ester indicates the presence of alcoholic group in the given organic compound.

### Tests for identification of Phenol

#### (i) Ferric chloride test

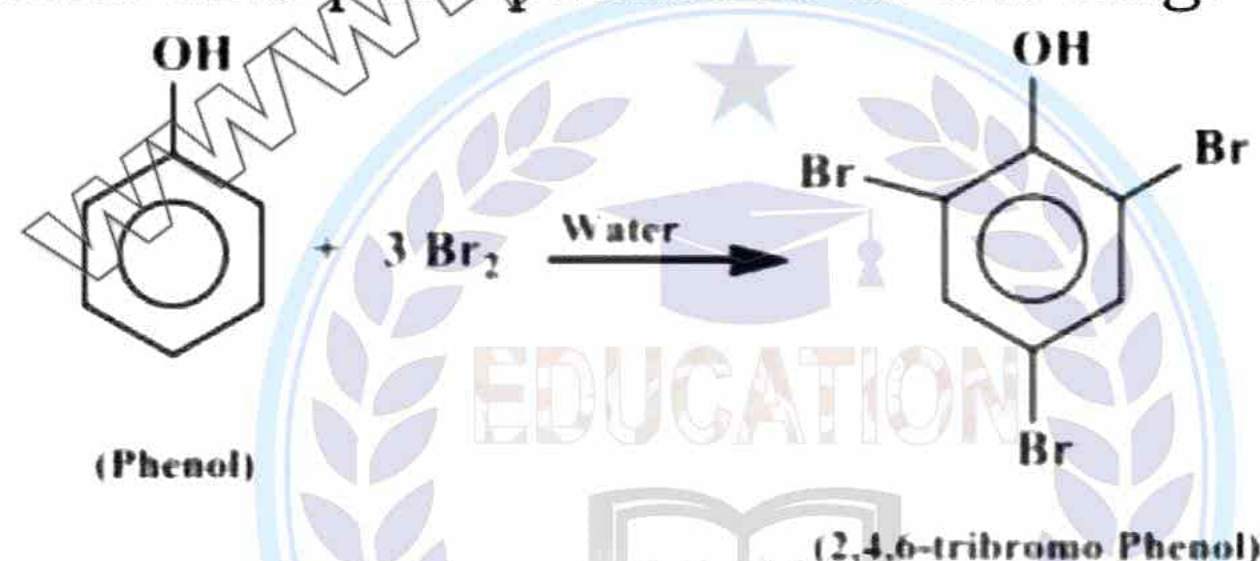
When freshly prepared aqueous solution of ferric chloride ( $\text{FeCl}_3$ ) is added to phenol, it forms a ferric phenoxide complex.



Appearance of violet, blue or purple coloration indicates the formation of complex and identifies the presence of phenol.

#### (ii) Bromine water test

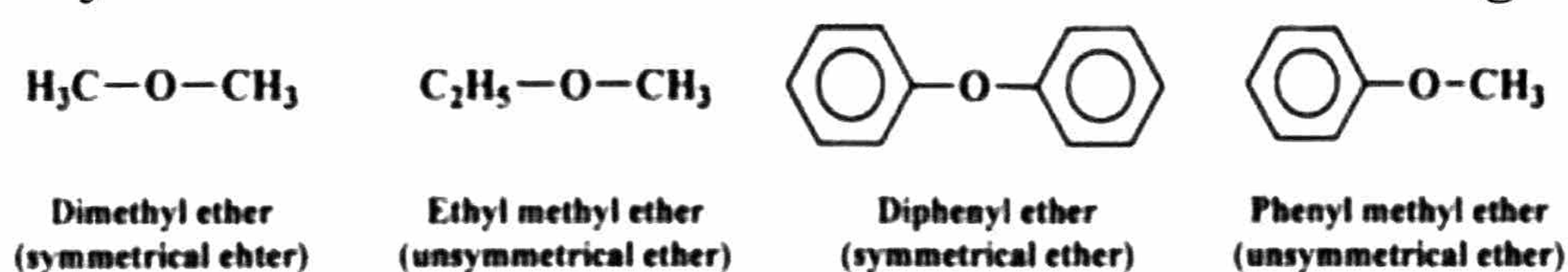
When bromine water is added to phenol, an electrophilic substitution reaction occurs on ortho and para positions of the ring.



Disappearance of brown color of bromine and appearance of white precipitates of 2,4,6-tribromophenol identifies the presence of phenols

### ETHERS

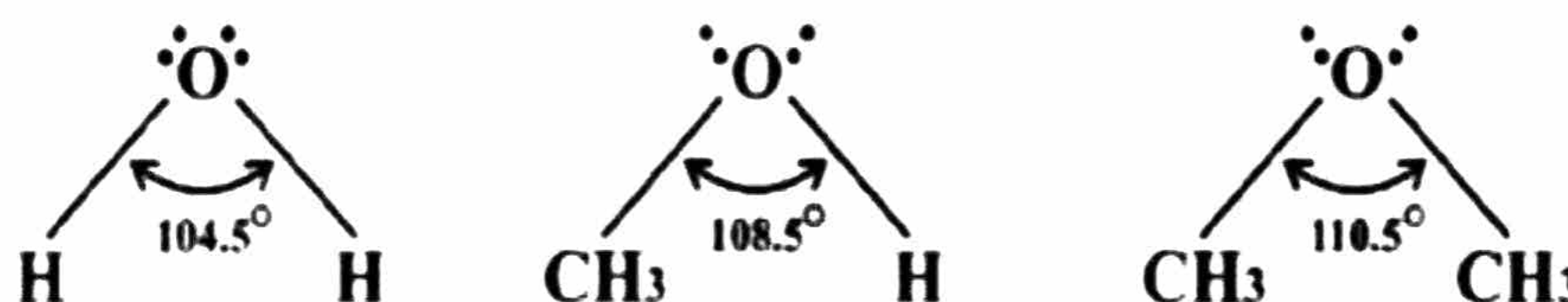
Ethers are an organic compounds having a general formula  $\text{R-O-R}$ , characterized by an Oxygen atom bonded to two alkyl or aryl groups. A symmetrical or simple ether is that in which both groups are of same type whereas unsymmetrical or mixed ether consists of two different groups.





### Structure of Ether

The geometry of ether molecule is bent shaped similar to alcohol and water, however the bond angle of C-O-C in ether molecule is  $110.5^\circ$  which is larger than water ( $104.5^\circ$ ) and alcohol ( $108.5^\circ$ ). The hybridization of oxygen atom is  $sp^2$  while the hybridization of carbon depends on the nature substituent group (alkyl or aryl) attached to the oxygen atom.



The greater (C-O-C) bond angle in ether is due to greater internal repulsion of hydrocarbon part than the external repulsion of lone pair on Oxygen.

### Preparation of Ether

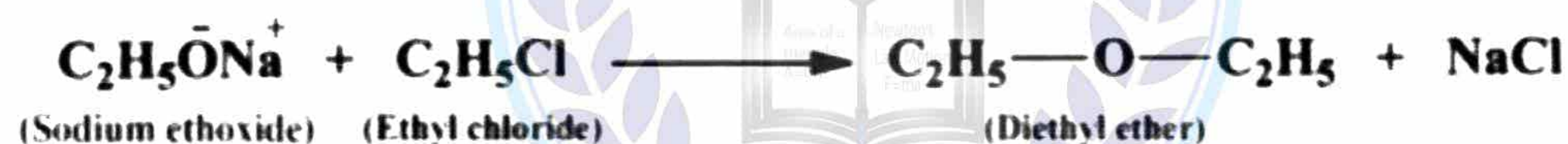
#### (i) Dehydration of alcohol

Excess of alcohol when heated with concentrated  $H_2SO_4$  at  $140^\circ C$ , an intermolecular dehydration occurs to give ether.



#### (ii) Williamson synthesis

It is a well-known method for the preparation of ethers. In this method an alkoxide ion acts as a nucleophile and reacts with an alkyl halide to produce ether.



The alkoxide is obtained by treating an alcohol with sodium metal.



### Physical Properties

(i) Dimethyl ether and ethyl methyl ether are gases, however other higher members of ether family exist in volatile liquid state at room temperature.

(ii) The boiling point of ether is lower than alcohol due to the absence of intermolecular hydrogen bond.

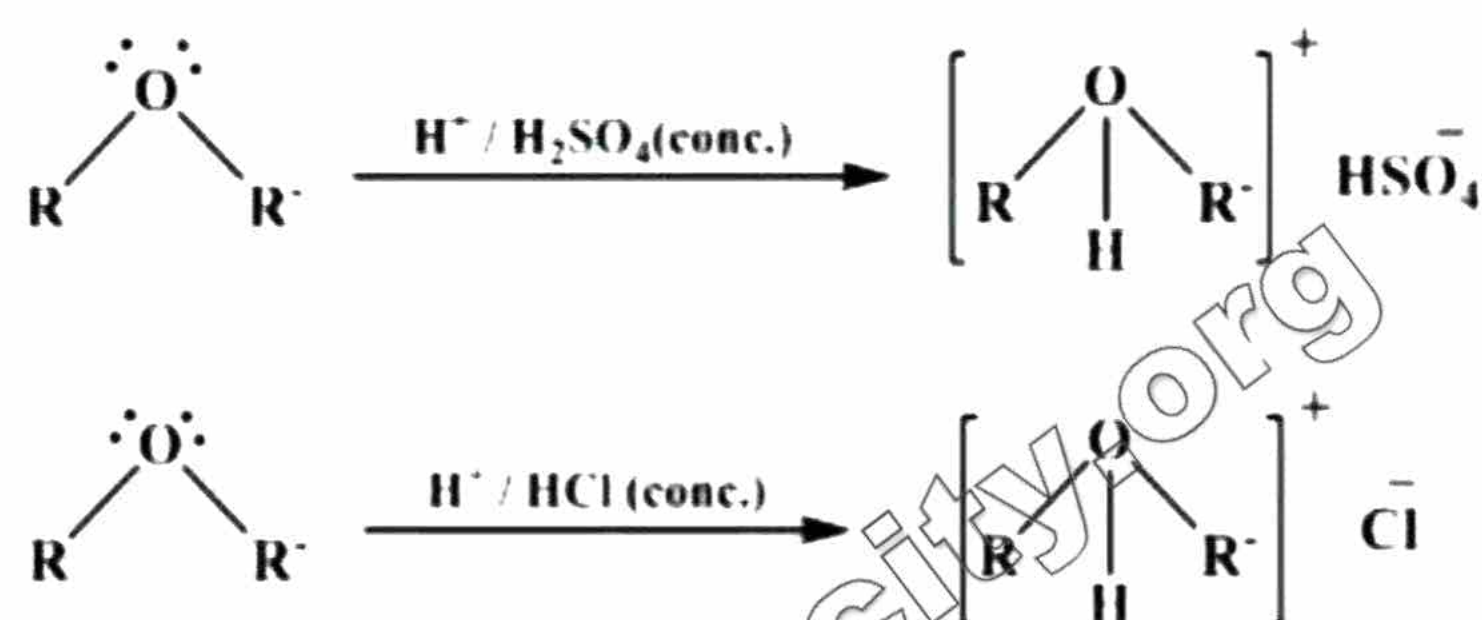


(iii) Ethers are moderately soluble in water since the presence of oxygen makes the molecule polar. However, solubility decreases with increasing the number of carbons of alkyl or aryl groups.

### Chemical Reactivity

Ethers are relatively less reactive organic compounds compared to other functional group because the C-O bond of ether is stable and shows low reactivity towards nucleophile or electrophile. The relatively low reactivity of ethers makes them useful as solvents and anesthetics.

Since oxygen atom of ether possess lone pairs of electrons, they serve as weak base and hence can react with strong acids to form oxonium salt.



The oxonium salt of ether remains stable if acid is concentrated but on dilution with water, it dissociates to reform ether and acid. The reason is that water is stronger Lewis acid than ether.

### Uses of Ethers

- (i) Ether is used as solvent in the manufacturing of waxes, gums, resins, oils etc.
- (ii) Diethyl ether is used as solvent in Wurtz reaction and in the preparation of Grignard reagent.



### Short Questions

1. Define Phenol? Write the equations for the preparation of Phenol from.

(i) Chlorobenzene

(ii) Sodium benzene sulphonate

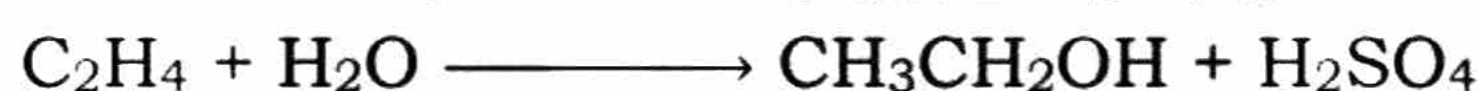
Notes

2. Write the equations for the following chemical Process

**Reduction of acetic acid with  $\text{LiAlH}_4$ :**



**Hydration of ethene with hot concentrated  $\text{H}_2\text{SO}_4$ :**



**Oxidation of ethanol with acidified dichromate:**



**Hydrolysis of diazonium salt:**



3. Explain the following with scientific reason

(i) Boiling point of ether is less than alcohol?

(ii) Alcohols are soluble in water?

(ii) Ethanol is liquid but ethyl chloride is gas at room temperature?

**(i) Boiling Point of Ether vs. Alcohol:**

The key lies in **intermolecular forces**:

- **Alcohol:** Has an -OH group, allowing **hydrogen bonding** between molecules. These bonds are strong and require more energy to break, leading to a **higher boiling point**.
- **Ether:** Contains an oxygen atom but lacks the -OH group, preventing hydrogen bonding. Instead, weaker **dispersion forces** exist. Breaking these weaker forces requires less energy, resulting in a **lower boiling point** compared to alcohol.

For example, ethanol (alcohol) boils at  $78.5^\circ\text{C}$ , while diethyl ether (comparable-sized ether) boils at  $34.6^\circ\text{C}$ .

**(ii) Solubility of Alcohols in Water:**

It's about **intermolecular forces**:

- **Alcohol:** The -OH group in alcohols can form **hydrogen bonds** with water molecules. These bonds pull the alcohol molecules into the water structure, making them **soluble**.
- **Water:** Highly polar molecule with strong hydrogen bonding ability.



The more carbon atoms in an alcohol, the fewer -OH groups relative to the hydrocarbon chain, reducing solubility.

**(iii) Ethanol vs. Ethyl Chloride:**

**Intermolecular forces and molecular size** play a role:

- **Ethanol:** Polar molecule with -OH group for hydrogen bonding and a larger size. Hydrogen bonding dominates, leading to a **liquid** state at room temperature.
- **Ethyl Chloride:** Smaller molecule with polar C-Cl bond but no hydrogen bonding capacity. Weaker dispersion forces are insufficient to overcome thermal energy at room temperature, resulting in a **gas** state.

**4. Identify each of following with two laboratory tests.**

**(i) Phenol**

**(ii) Alcohol**

Notes

**5. What is Lucas reagent? Describe its use to distinguish between primary, secondary and tertiary alcohol.**

Notes

**6. What is oxonium ion? How can ether form oxonium ion?**

Notes

**Descriptive Questions**

**1. (a) What are alcohols? How alcohols are they classified?**

**(b) Starting from Grignard reagent how is primary, secondary and tertiary alcohol prepared?**

Notes

**2. Write the equations for the following possible conversions.**

**(i) Ethyl alcohol to diethyl ether**

**(ii) Phenol to benzoquinone**

**(iii) Ethyl bromide to ethanol**

**(iv) 2°- alcohol to carboxylic acid**



**3 Differentiate between alcohol and phenol on the basis of**

**(i) Solubility in water**

**(ii) Boiling Point**



**(ii) Acidic character**

Notes

**4. Write the equation and name the final product when phenol reacts with the following**

- (i) Hot and concentrated nitric acid.**
- (ii) Concentrated sulphuric acid at 100°C**
- (ii) Bromine water**
- (iv) Sodium metal**

Notes

**5. Enlist the commercial applications of Alcohol, Phenol and ether**  
**Alcohols**

- **Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ):** The most common alcohol, ethanol is used in a variety of products, including:
  - **Beverages:** As the alcohol in alcoholic drinks such as beer, wine, and liquor.
  - **Fuel:** As a biofuel, either blended with gasoline or used pure in specially designed engines.
  - **Solvents:** In paints, varnishes, cosmetics, and pharmaceuticals.
  - **Disinfectants:** To kill bacteria and viruses.
  - **Antiseptic:** To clean and sterilize wounds.

**Methanol ( $\text{CH}_3\text{OH}$ ):** Also known as wood alcohol, methanol is used in a variety of products, including:

- **Antifreeze:** To prevent car engines from freezing in cold weather.
- **Solvents:** In paints, varnishes, and plastics.
- **Fuels:** As a racing fuel and in fuel cells.
- **Chemicals:** In the production of formaldehyde, acetic acid, and other chemicals.

**Isopropanol ( $\text{CH}_3\text{CHOHCH}_3$ ):** Also known as rubbing alcohol, isopropanol is used in a variety of products, including:

- **Disinfectants:** To clean and sterilize wounds and surfaces.
- **Solvents:** In paints, varnishes, and electronics.
- **Cosmetics:** In astringents and toners.
- **Antifreeze:** In some windshield washer fluids.

**Phenols**

- **Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ):** Also known as carbolic acid, phenol is a powerful disinfectant that is used in a variety of products, including:



- **Medical disinfectants:** To sterilize surgical instruments and medical equipment.
- **Household disinfectants:** In cleaners and sanitizers.
- **Chemical industry:** In the production of plastics, resins, and nylon.
- **[Pharmaceuticals:** In the production of aspirin and other drugs

### Ethers

- **Diethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ):** Also known as ether, diethyl ether is a volatile solvent that was once widely used in anaesthesia. Today, it is used in a variety of products, including:
  - **Solvents:** In paints, varnishes, and adhesives.
  - **Starting materials:** In the production of other chemicals.
  - **Fuels:** As a racing fuel and in fuel cells.

