

CHAPTER 7

Alcohols, Phenols and Ethers



ALCOHOL



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

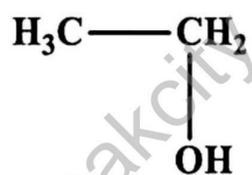
CLASSIFICATION OF ALCOHOL:

Alcohols are classified into three types on the basis of number of hydroxyl group attached to carbon.

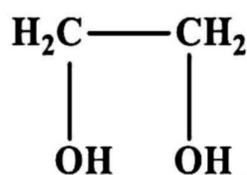
(i) **Monohydric Alcohol** – It contains 1 OH group

(ii) **Dihydric Alcohol** – It contains 2 OH groups

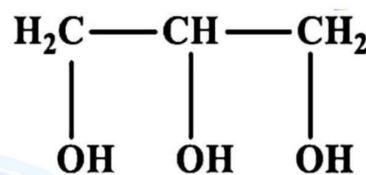
(iii) **Trihydric Alcohol** – It contains 3 OH groups



Ethanol
(monohydric alcohol)



Ethylene glycol
(Dihydric alcohol)



Glycerol
(Trihydric alcohol)

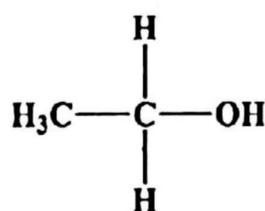
CLASSIFICATION OF MONOHYDRIC ALCOHOLS:

Monohydric alcohols can be further classified into three types.

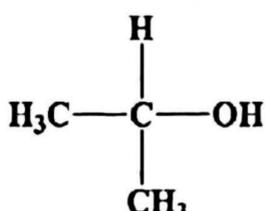
(a) **Primary or 1° Alcohols** – 1 Alkyl radical is attached to α carbon

(b) **Secondary or 2° Alcohols** – 2 Alkyl radicals is attached to α carbon

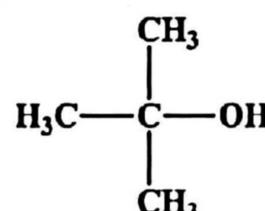
(c) **Tertiary or 3° Alcohols** - 3 Alkyl radicals is attached to α carbon



(1° - alcohol)
(ethyl alcohol)



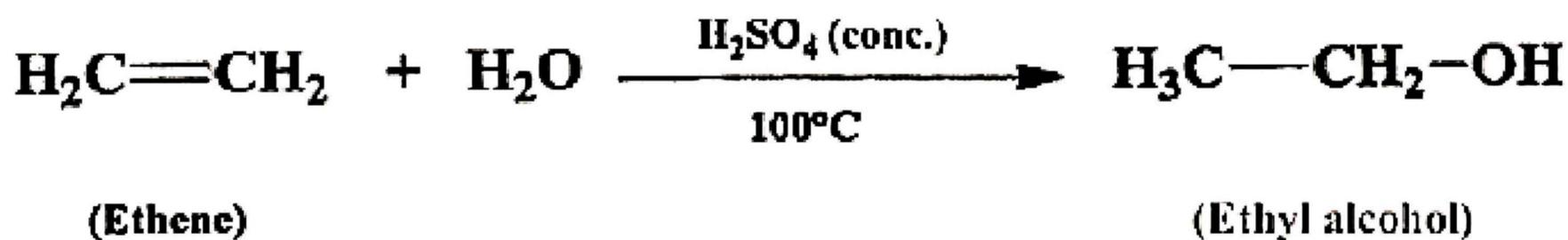
(2° - alcohol)
(isopropyl alcohol)



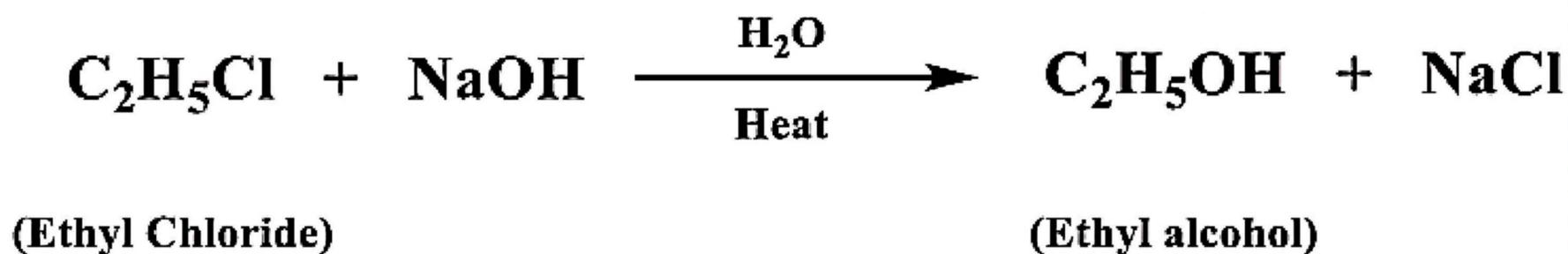
(3° - alcohol)
(t-butyl alcohol)

Preparations of Alcohols pakcity.org

1. Hydration of Alkenes:



2. Hydrolysis of an Alkyl Halide:



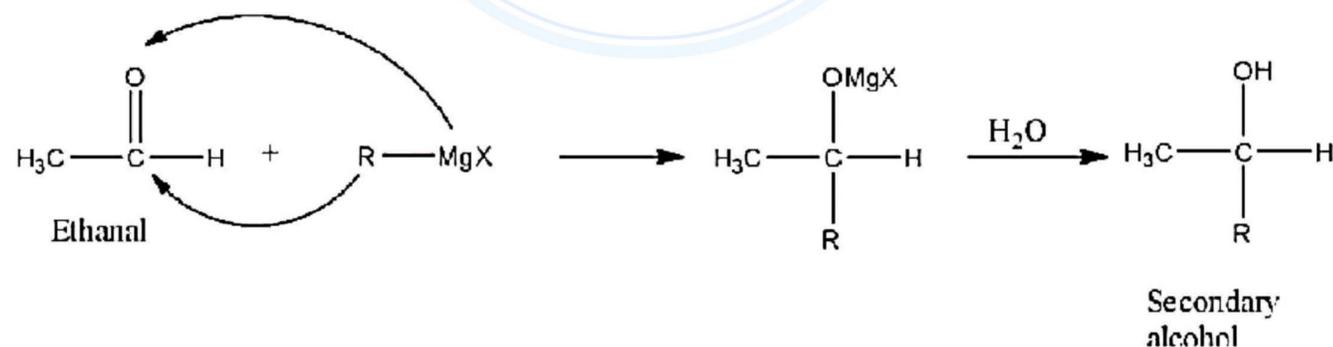
3. Reaction of Grignard's Reagent with Aldehyde & Ketone:

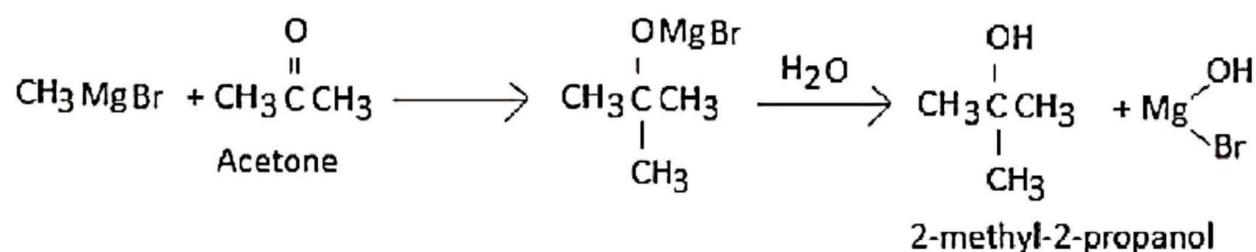
Grignard reagent when reacts with a formaldehyde, acetaldehyde and acetone molecule, it gives primary, secondary and tertiary alcohols respectively.

(i) Reaction with formaldehyde

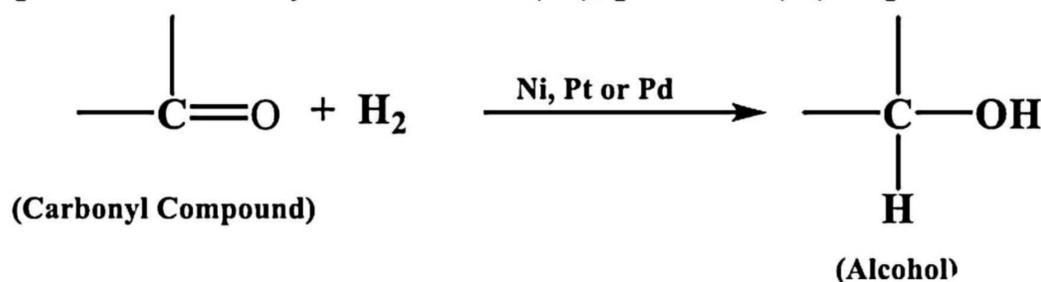


(ii) Reaction with acetaldehyde (ethanal)

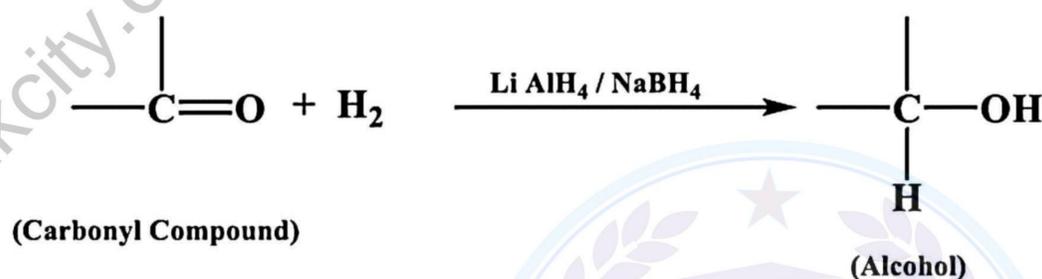


(iii) Reaction with acetone**4. Reduction of Aldehyde and Ketone:**

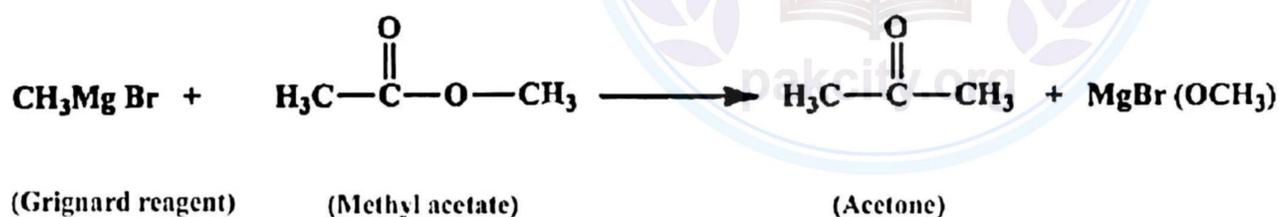
- (a) Hydrogenation of aldehyde and ketone at high temperature and pressure in the presence of catalyst like nickel (Ni), platinum (Pt) or palladium (Pd).



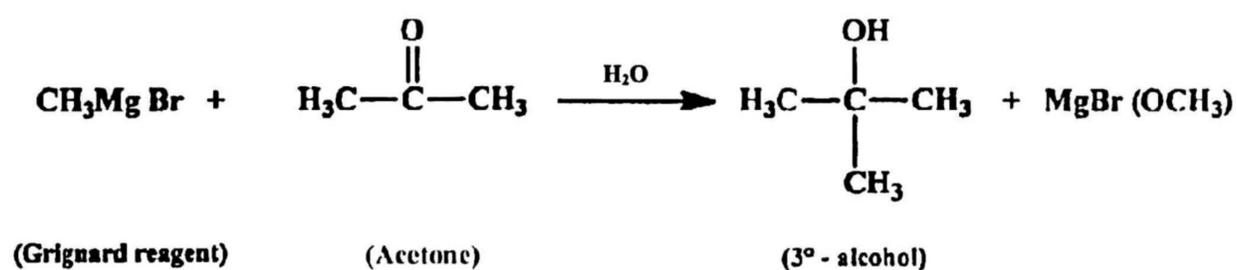
- (b) Reaction of aldehyde and ketone with a reducing agent like lithium aluminum hydride (LiAlH₄) or sodium borohydride (NaBH₄).



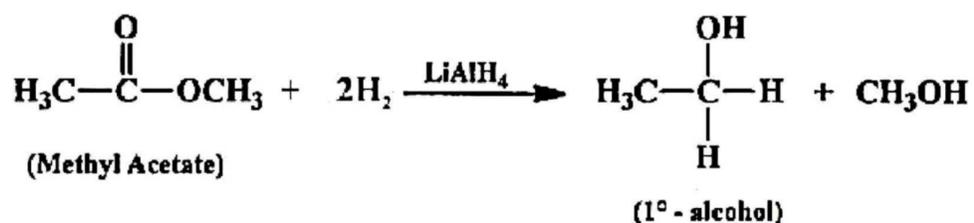
It is important to note that aldehydes on reduction give primary alcohols, and ketones on reduction give secondary alcohols.

5. Reaction of Grignard's reagent with esters:

The carbonyl compound thus formed then reacts with another molecule of Grignard's reagent and finally gives an alcohol.



6. Reduction of Carboxylic Acid & Esters



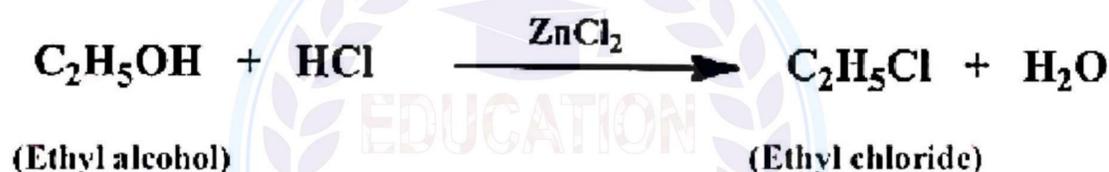
Reactions of Alcohols



- (i) The C-O bond in an alcohol molecule breaks when it is attacked by a nucleophile.
 (ii) The H-O bond in an alcohol molecule breaks when it is attacked by an electrophile.

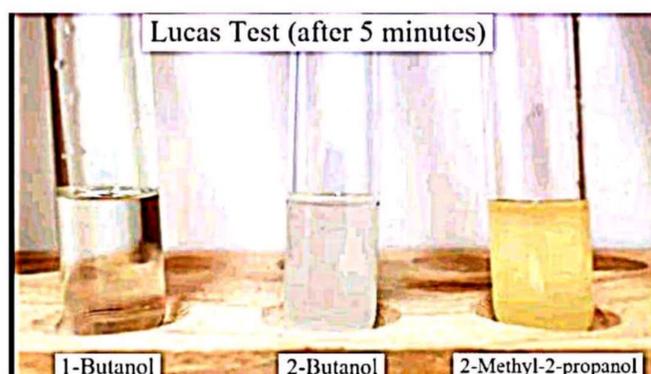
Type of Bond Breaking	Type of Attacking Reagent	Order of reactivity of alcohols
O-H	Electrophile	1° > 2° > 3°
C-O	Nucleophile	3° > 2° > 1°

1. Reaction with Halogen Acids (HX)

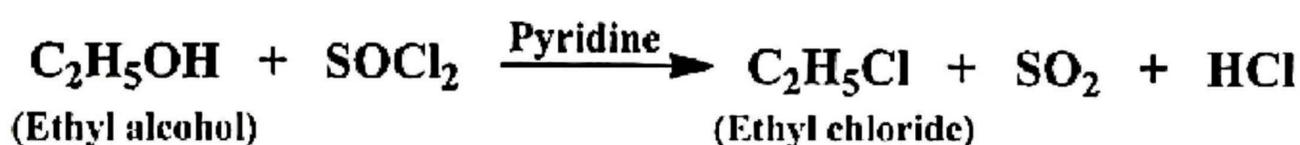
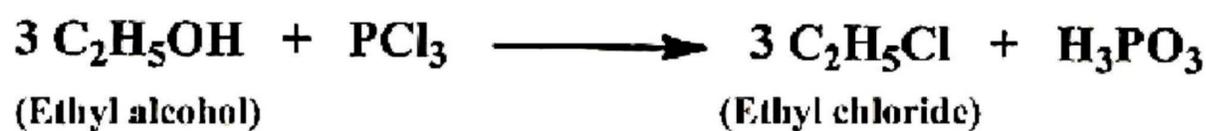


The mixture of concentrated HCl and ZnCl₂ is called "Lucas Reagent" and it is used to distinguish between primary, secondary and tertiary alcohol.

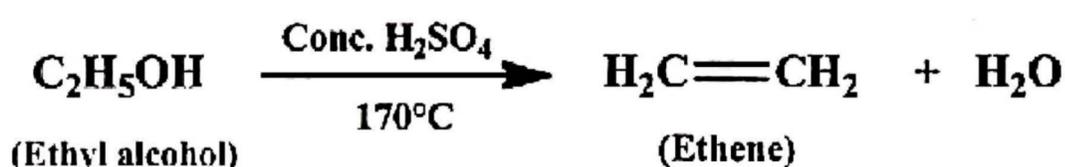
In the Lucas test, primary alcohols show no immediate reaction, secondary alcohols form turbidity within few minutes, and tertiary alcohols produce an immediate and vigorous formation of cloudy precipitate.



2. Reaction with SOCl_2 and PX_3



3. Dehydration of Alcohol



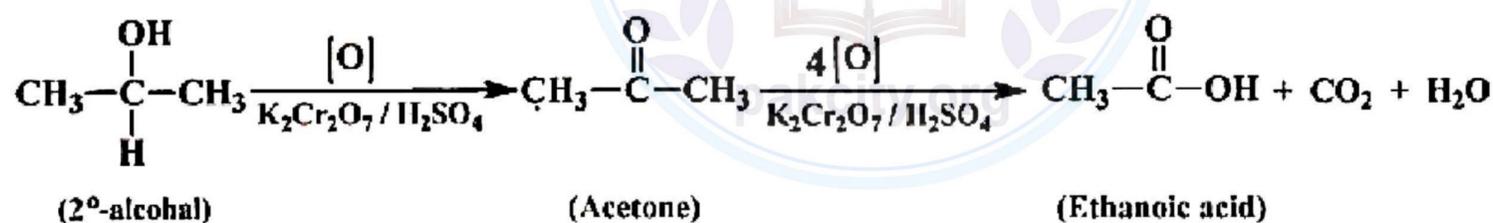
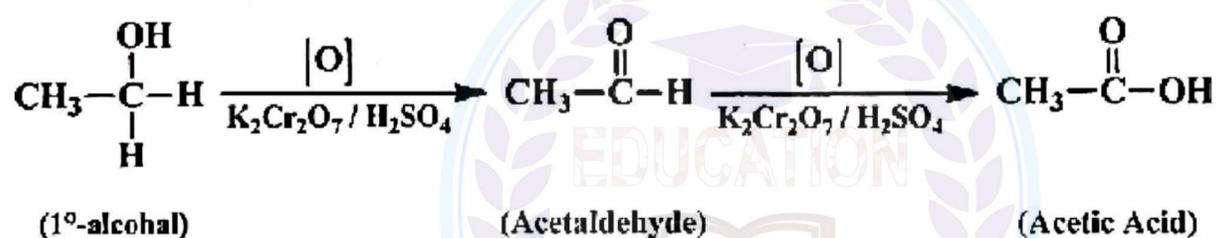
The ease of acid catalyzed dehydration of alcohol is given as
 $3^\circ\text{-alcohol} > 2^\circ\text{-alcohol} > 1^\circ\text{-alcohol}$

4. Oxidation of Alcohol

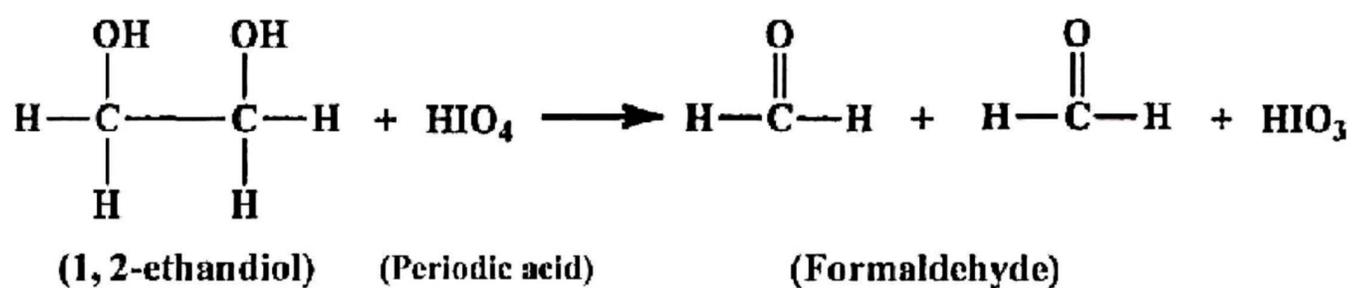
Primary alcohols yield aldehyde on oxidation.

Secondary alcohols yield ketone on oxidation.

Tertiary alcohols cannot be oxidized.



5. Cleavage of 1,2-diols





Self-Assessment

Mention the reagents required for the following conversions.

- | | |
|------------------------------|--------------------------------------|
| (i) Ethanol to Ethene | (ii) Acetic acid to Ethanol |
| (iii) Ethanol to Acetic acid | (iv) Ethylene glycol to formaldehyde |

- (i) Concentrated H_2SO_4 (ii) LiAlH_4 (iii) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (iv) HIO_4

Uses of Alcohol

- Methanol is used as antifreeze solution and also in the preparation of perfumes, dyes, drugs etc.
- 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.
- The mixture of isopropyl alcohol in water is used as rubbing alcohol (antiseptic).

PHENOLS



Organic compounds in which hydroxy group (-OH) is directly attached to benzene ring are called phenols. The parent compound of this family is hydroxy benzene which is also known as carbolic acid or benzenol.

CLASSIFICATION OF PHENOLS

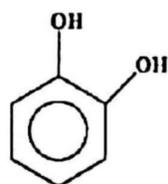
Phenols can be classified into three types:

- (a) Monohydroxy phenol – It contains 1 OH group

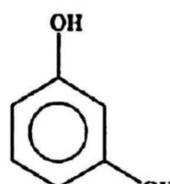


(Benzenol)

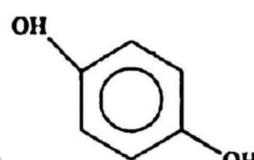
- (b) Dihydroxy phenol – It contains 2 OH groups



(Catechol)

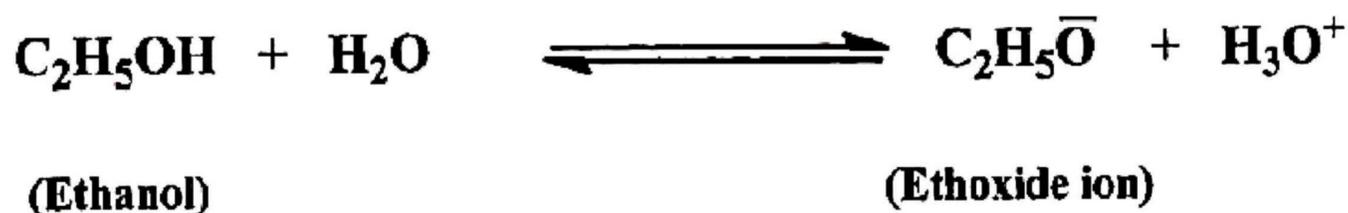


(Resorcinol)



(Hydroquinone)

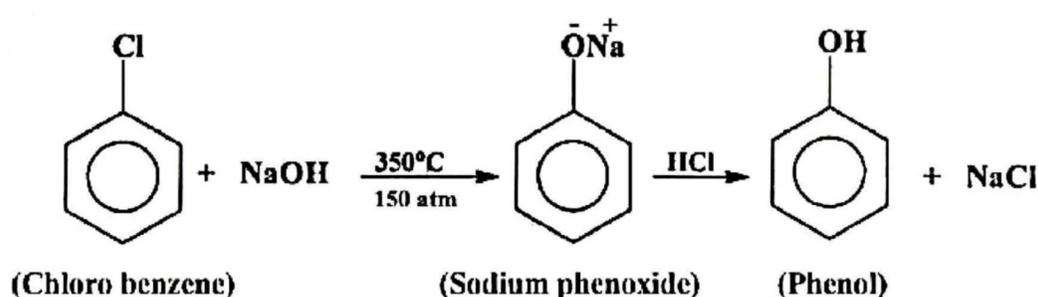
On the other hand, in ethoxide ion the negative charge is localized on the oxygen atom due to the absence of aromatic ring result in a less stable structure compared to phenoxide ion.



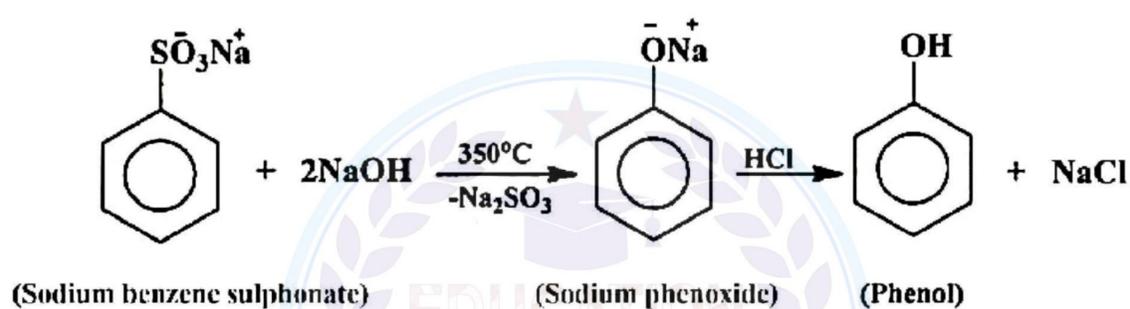
Preparation of Phenol



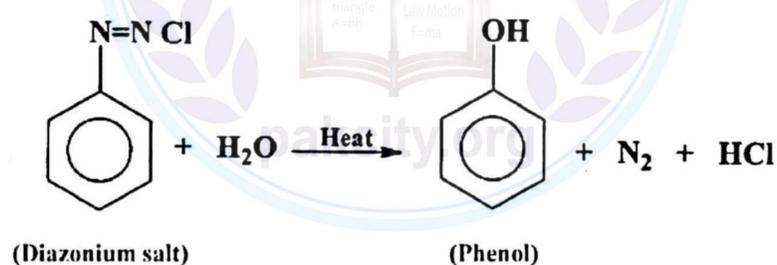
1. From Chlorobenzene (Dow's Process)



2. From Sodium Benzene Sulphonate



3. Hydrolysis of Diazonium Salt



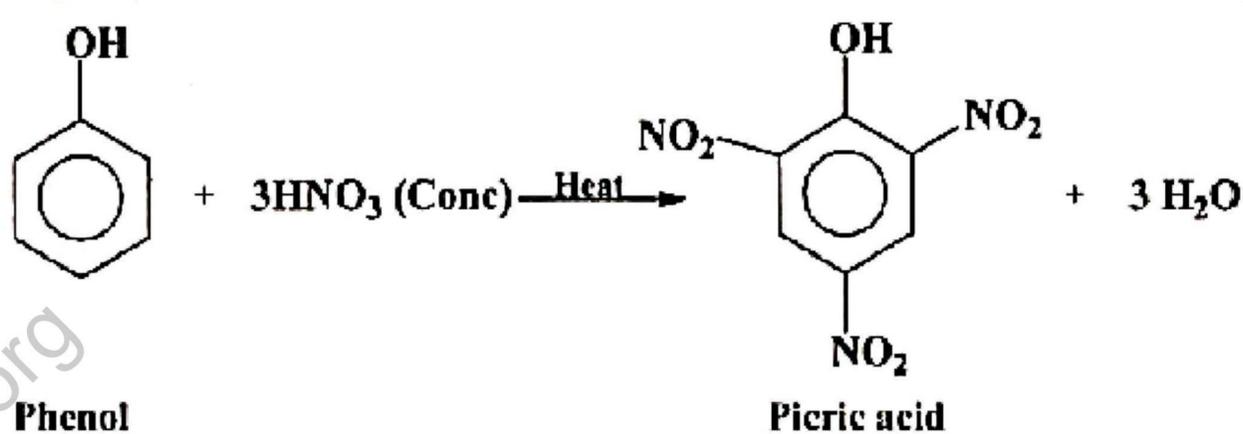
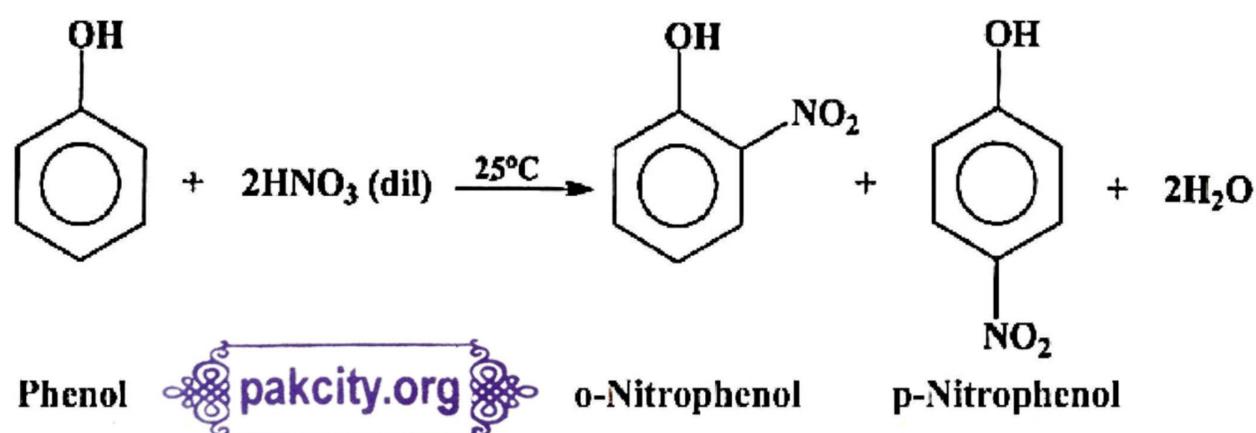
Reactions of Phenol

Phenol typically undergoes two types of reactions:

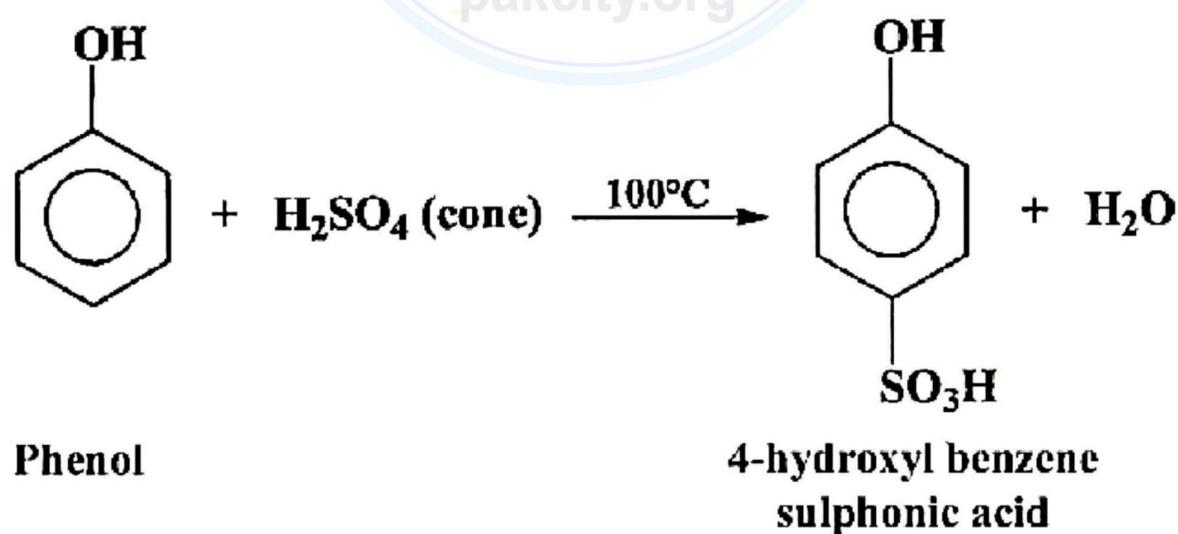
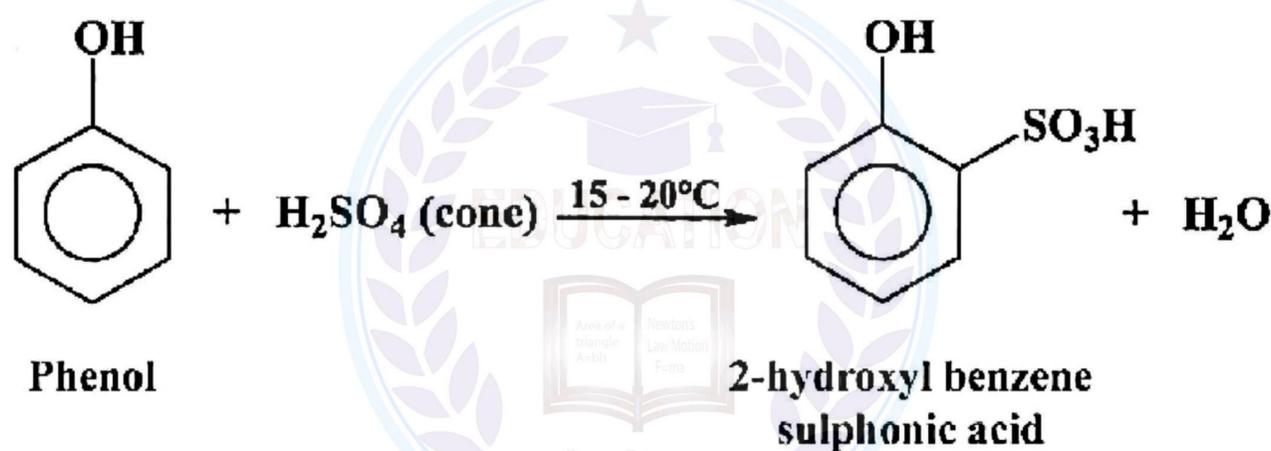
- Those reactions in which hydroxyl group is involved
- Those reactions in which aromatic ring is involved

Electrophilic Aromatic Substitutions

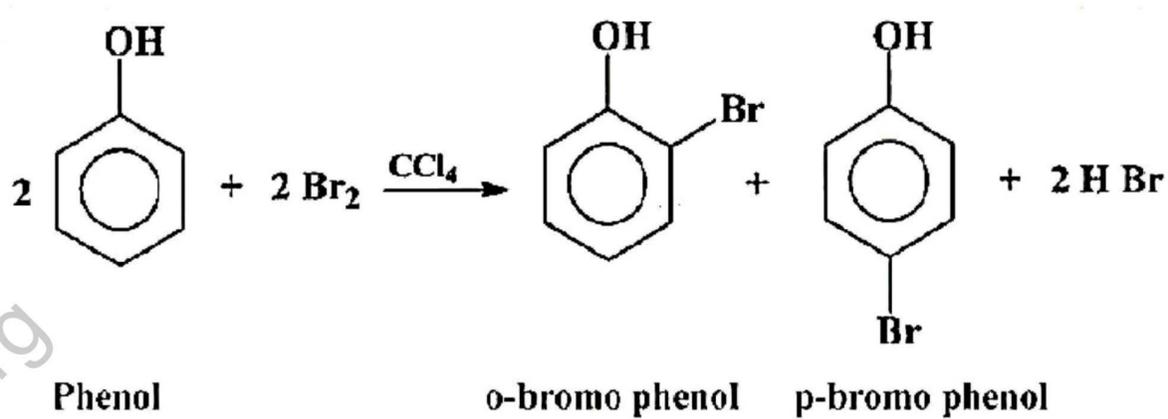
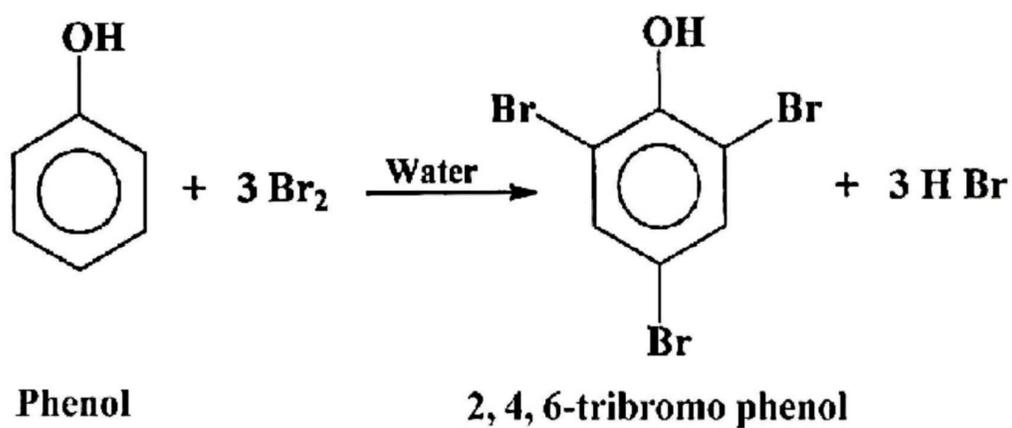
1. Nitration of Phenol



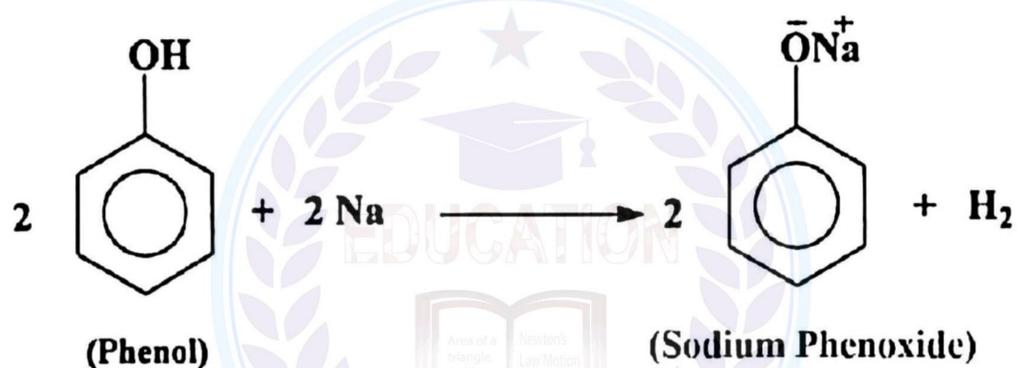
2. Sulphonation of Phenol



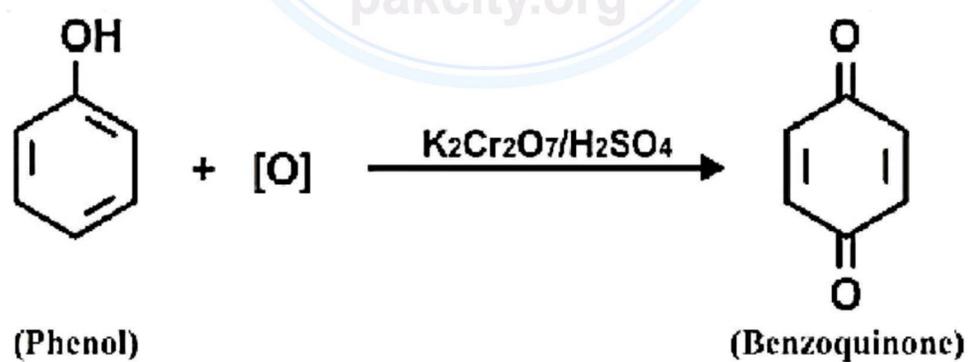
3. Halogenation of Phenol



Reaction with Sodium Metal



Oxidation of Phenol



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

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.
- (iii) It is used in the preparation of picric acid and, phenolphthalein.
- (iv) It is used as ink preservative.

ETHERS

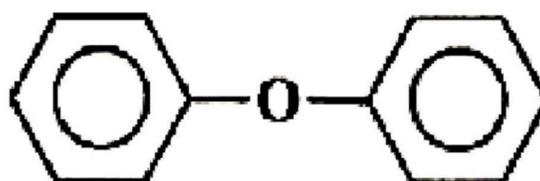
Ethers are organic compounds having a general formula $R-O-R'$, characterized by an oxygen atom bonded to two alkyl or aryl groups. It has low reactivity and it is commonly used as solvent in various chemical reactions.

Ethers can be classified into two types:

(i) Symmetrical ethers or Simple Ethers (Both the alkyl radicals are same.)

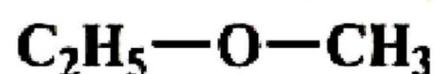


Dimethyl ether

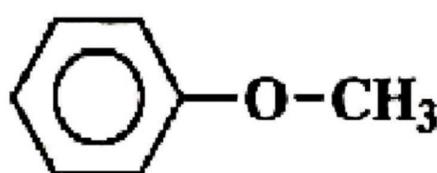


Diphenyl ether

(ii) Asymmetrical ethers or Mixed ethers (Both the alkyl radicals are different)



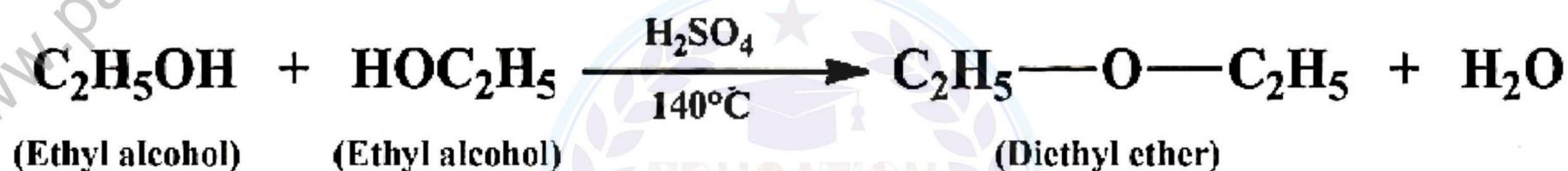
Ethyl methyl ether



Phenyl methyl ether

Preparation of Ether

(i) Dehydration of alcohol



(ii) Williamson synthesis



Physical Properties of Ether

1. Dimethyl ether ($\text{CH}_3\text{-O-CH}_3$) and Ethyl Methyl Ether ($\text{CH}_3\text{-O-C}_2\text{H}_5$) are gases. Other higher members of ether family are volatile liquids.
2. The boiling point of ether is less than alcohol due to the absence of hydrogen bond.

3. Ethers are moderately soluble in water due to its polar nature because of the presence of oxygen atom. Solubility decreases with increase in number of alkyl group as it increases the non-polar nature of molecules.

Chemical Reactivity of Ether



Ethers are less reactive organic compounds due to the presence of alkyl radicals on both sides of the oxygen atom which produces a steric hindrance and makes the molecule stable.



Self-Assessment

- Provide an example of a symmetrical ether.
 - Can ethers form hydrogen bonds with water? Why or why not?
-
- An example of a symmetrical ether is dimethyl ether ($\text{CH}_3\text{-O-CH}_3$)
 - Ethers can form hydrogen bonds with water due to the presence of an oxygen atom in its molecule.

Uses of Ethers

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

Multiple Choice Questions

- (i) In the molecule of phenol, the carbon atom which is attached to the hydroxyl group is.

(a) sp -hybridized	(b) sp^2 -hybridized
(c) sp^3 -hybridized	(d) Unhybridized

- (ii) Which of the following is a trihydric phenol?

(a) Resorcinol	(b) Cresol
(c) Pyrogallol	(d) Catechol

- (iii) Ethanol reacts with PCl_3 to form.
- (a) Diethyl ether (b) Ethene
(c) Ethyl chloride (d) Ethanoic acid
- (iv) Which of the following alcohols has highest boiling Point
- (a) Ethyl alcohol (b) n-pentyl alcohol
(c) iso-pentyl alcohol (d) neo-pentyl alcohol
- (v) Which of the following Products is mainly formed if ethanol is dehydrated with concentrated sulphuric acid at 170°C ?
- (a) Ethene (b) Ethyne
(c) Ethanol (d) Diethyl ether
- (vi) Lucas reagent is a mixture of
- (a) Zn and Hg (b) Zn and HCl
(c) ZnCl_2 and HCl (d) NaOH and CaO
- (vii) Oxidative cleavage of 1, 2 – diol occur in the presence of
- (a) $\text{K}_2\text{Cr}_2\text{O}_7$ (b) KMnO_4
(c) HNO_3 (d) HIO_4
- (viii) Which of the following molecule cannot form hydrogen bonding with water molecule?
- (a) Phenol (b) Resorcinol
(c) Ethyl chloride (d) Ethyl alcohol
- (ix) Secondary alcohols, undergo oxidation with potassium dichromate to produce carboxylic acid through an intermediate product known as:
- (a) Aldehyde (b) Ketone
(c) Ether (d) Alkyl halide
- (x) Which of the following is an anaesthetic agent
- (a) Phenol (b) Ethyl alcohol
(c) Diethyl ether (d) Acetone

Short Questions

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

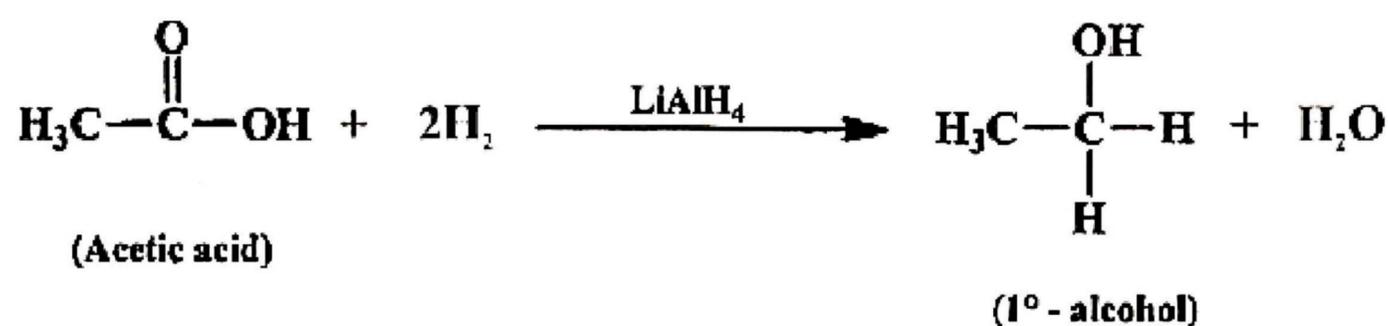
- (i) Chlorobenzene
 (ii) Sodium benzene sulphonate



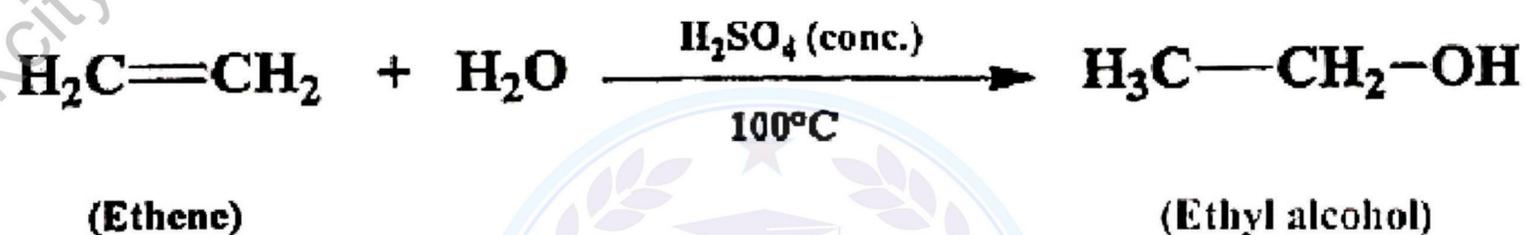
ALREADY DISCUSSED ABOVE

2. Write the equations for the following chemical Process

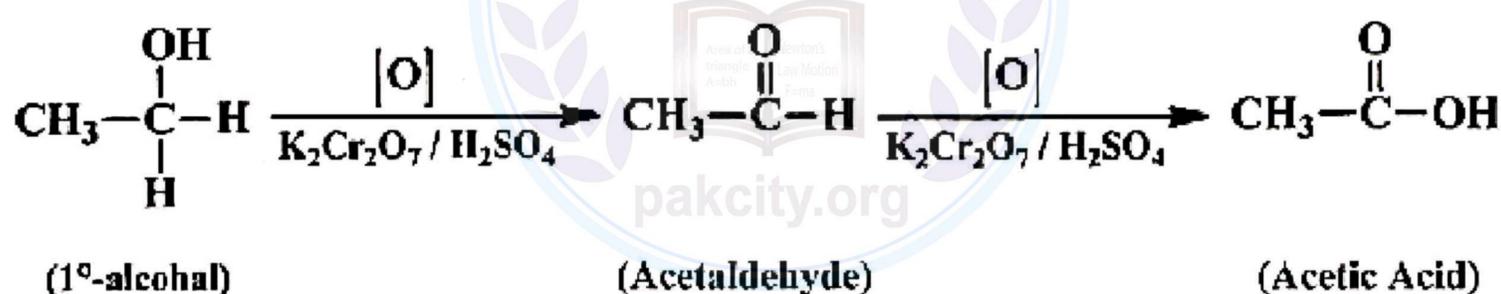
(i) Reduction of acetic acid with LiAlH_4 .



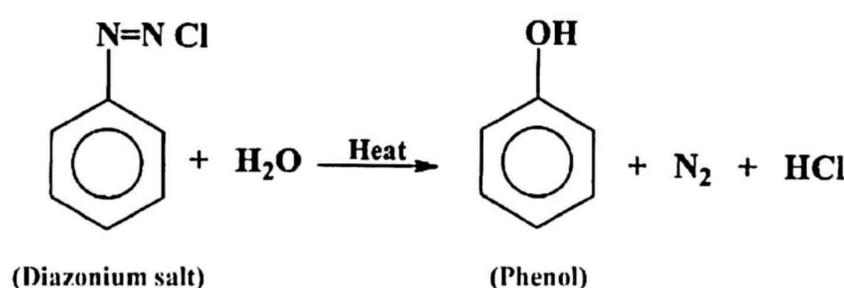
(ii) Hydration of ethene with hot concentrated H_2SO_4



(iii) Oxidation of ethanol with acidified dichromate.



(iv) Hydrolysis of diazonium salt



3. Explain the following with scientific reason
 (i) Boiling point of ether is less than alcohol?

Ans. Boiling point of ether is less than alcohol because ether do not contain hydrogen bonding. Hence, they have low boiling point due to the presence of weaker intermolecular forces.

- (ii) Alcohols are soluble in water? 

Ans. Alcohols are soluble in water due to the presence of hydrogen bonding.

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

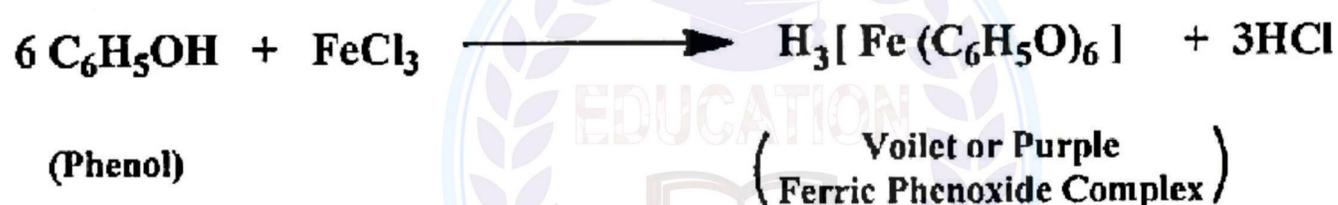
Ans. Ethanol contains hydrogen bonding that's why it is a liquid but ethyl chloride does not contain hydrogen bonding that's why it is a gas at room temperature.

4. Identify each of following with two laboratory tests.

- (i) Phenol
 (ii) Alcohol

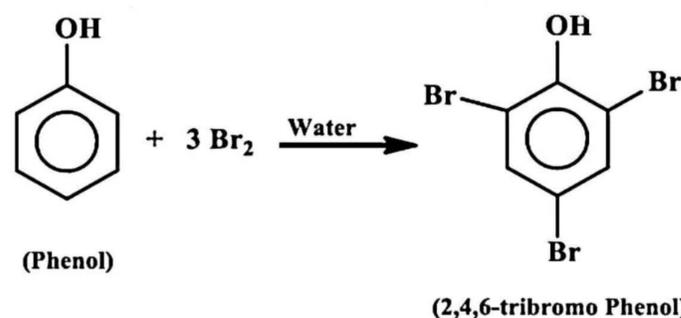
Tests for identification of Phenol

(i) Ferric chloride test



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

(ii) Bromine water test



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

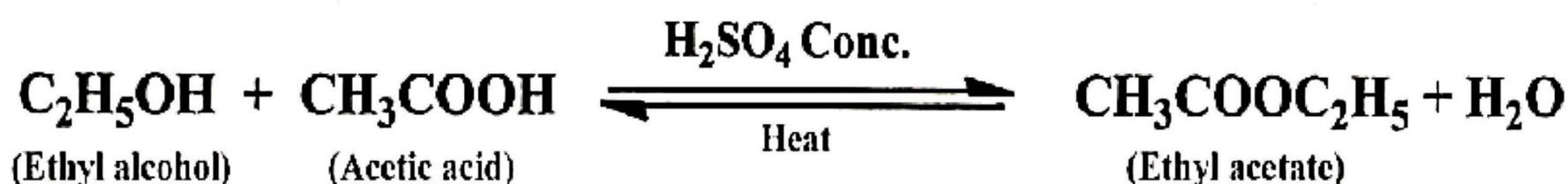
Tests of identification of Alcohol

(i) Sodium metal test



Brisk effervescence in the solution indicates the presence of alcoholic group in the given organic molecule.

(ii) Ester test



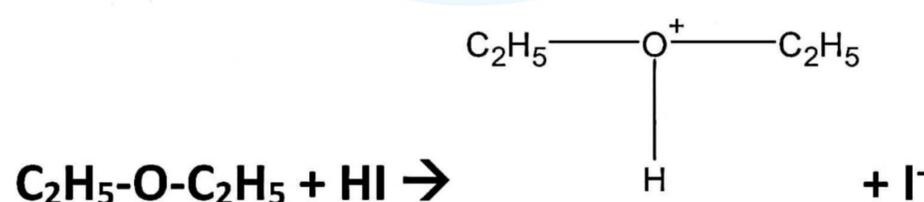
Fruity smell of ester indicates the presence of alcoholic group in the given organic compound.

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

ALREADY DISCUSSED ABOVE

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

Ans. If oxygen contains a positive charge, then it is called an oxonium ion. It is denoted by O^+ . Ether can form oxonium ions by reaction with hydrogen iodide (HI)



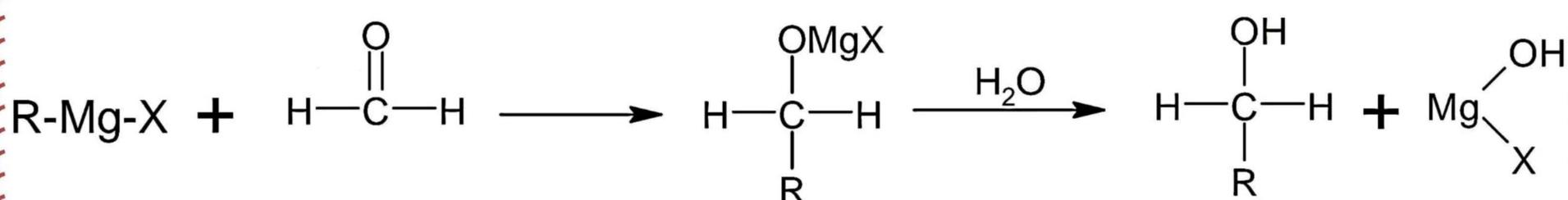
Descriptive Questions

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

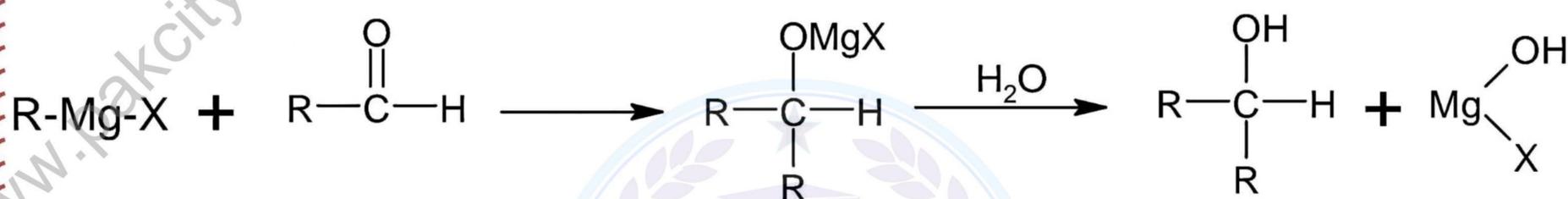
ALREADY DISCUSSED ABOVE

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

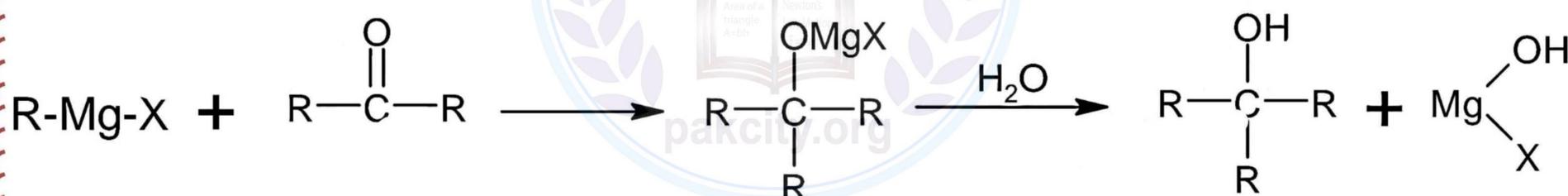
Ans. Primary alcohols can be prepared by the reaction of Grignard's reagent with form aldehyde.



Secondary alcohols can be prepared by the reaction of Grignard's reagent with aldehyde other than form aldehyde.

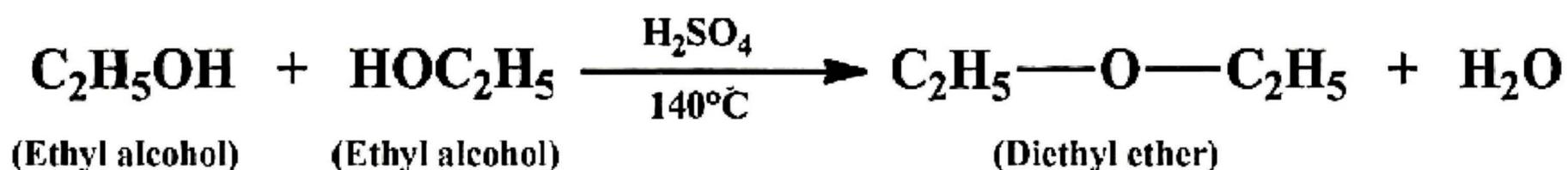


Tertiary alcohols can be prepared by the reaction of Grignard's reagent with ketones.

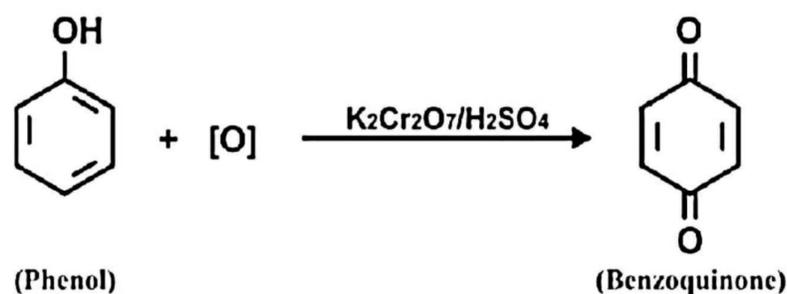


2. Write the equations for the following possible conversions.

- (i) Ethyl alcohol to diethyl ether

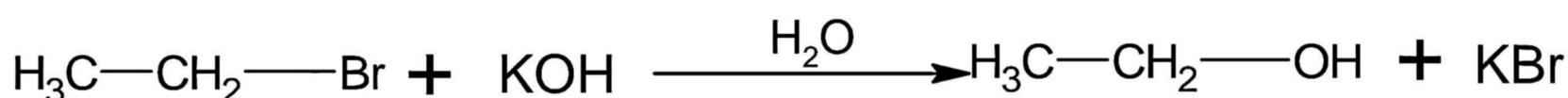


(ii) Phenol to benzoquinone

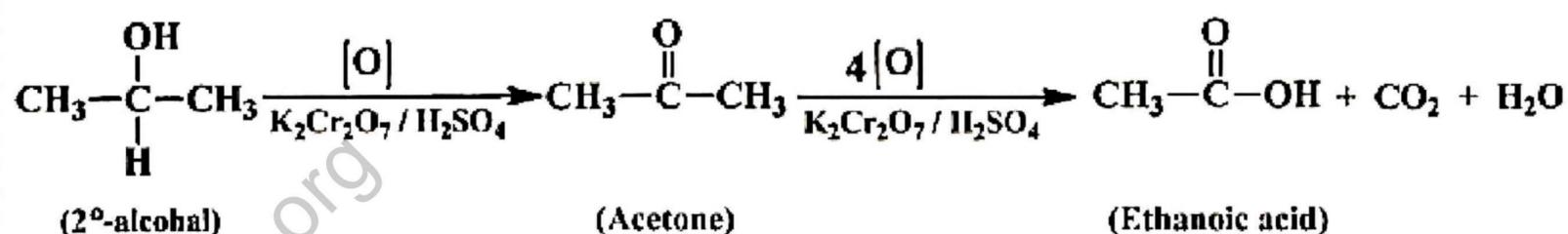




(iii) Ethyl bromide to ethanol



(iv) 2°- alcohol to carboxylic acid



3 Differentiate between alcohol and phenol on the basis of

- (i) Solubility in water
- (ii) Boiling Point
- (iii) Acidic character

ALREADY DISCUSSED ABOVE

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
- (iii) Bromine water
- (iv) Sodium metal

ALREADY DISCUSSED ABOVE

5. Enlist the commercial applications of alcohol, phenol and ether.**Ans. Commercial Applications of Alcohol:**

- (i) Alcohols are used as beverage for drinking purpose.
- (ii) Wood spirit is used as a fuel. 
- (iii) Isopropyl alcohol is used as rubbing alcohol.
- (iv) Ethyl alcohol is used to make perfume.
- (v) Ethanol is used as petrol substitute.
- (vi) Ethanol is used for making thermometers.
- (vii) Ethanol is used to make tincture.

Commercial Applications of Phenol:

- (i) Phenol is used as antiseptic.
- (ii) Phenol is used to make ointments and lozenges.
- (iii) Phenol is used to make picric acid which is an explosive.
- (iv) Phenol is used to make plastics such as Bakelite.

Commercial Applications of Ether:

- (i) Diethyl ether is used as anesthesia.
- (ii) Diethyl ether is mixed with ethanol to form Bloor's reagent which can dissolve lipids.
- (iii) Ethers are used as solvent in many chemical reactions such as Wurtz Reactions, preparation of Grignard's Reagent etc.