
CHAPTER

11

ALCOHOLS, PHENOLS AND ETHERS

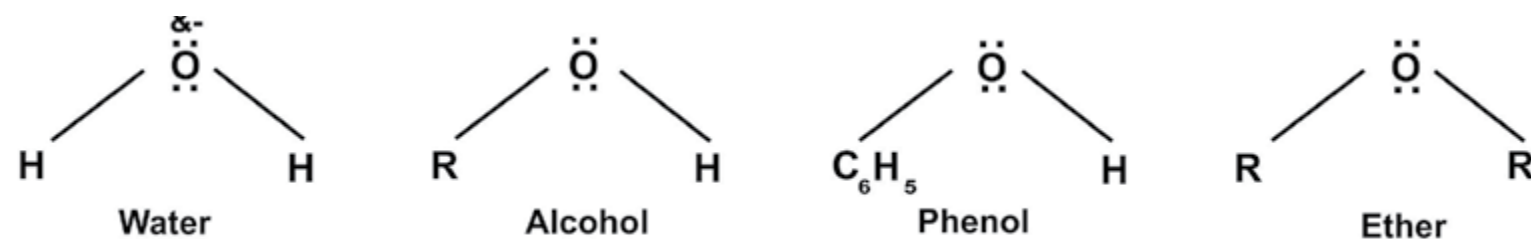
Animation 11.1: Hanau Alcohol Torch
Source and Credit : reddit

IN THIS CHAPTER YOU WILL LEARN:

1. How to name simple monohydric and polyhydric alcohols and their classification as primary, secondary and tertiary alcohols.
2. The important synthetic reactions leading to alcohols and industrial processes for the manufacture of methanol and ethanol.
3. The nature of OH group and its reactivity when O-H bond is broken and when C-O bond is broken.
4. To distinguish chemically between the primary, secondary and tertiary alcohols.
5. The methods of preparation of phenol and its acidic nature.
6. The importance of phenol as starting material for the preparation of five industrially important compounds.
7. How to name ethers and preparation of diethyl ether.
8. The physical and chemical behaviour of diethyl ether and its inertness towards chemical reagents.

11.1 INTRODUCTION

Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water.



Alcohols and phenols are much more close to one another in structure and properties. Both contain hydroxyl (-OH) group so they may also be termed as hydroxy derivatives of alkanes and benzene respectively. In ether both hydrogens of water are replaced by alkyl or phenyl groups.

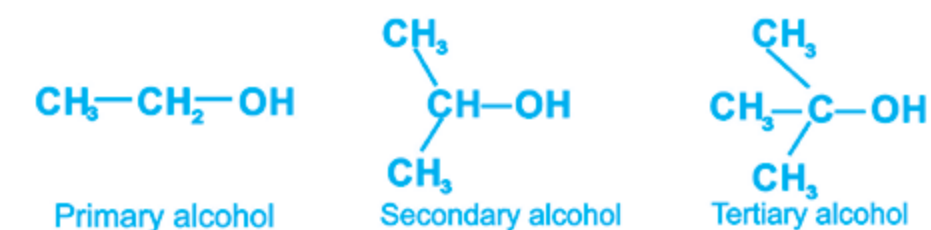
11.2 ALCOHOLS

They are represented by a general formula ROH where R is an alkyl group which may be CH_3- , CH_3CH_2- , $(\text{CH}_3)_2\text{CH}-$ and $\text{C}_6\text{H}_5-\text{CH}_2-$, etc.

Classification

Alcohols are classified into monohydric and polyhydric alcohols. Monohydric alcohols contain one -OH group while polyhydric alcohols may contain two, three or more OH groups and named as dihydric or trihydric alcohols, etc.

Monohydric alcohols are further classified into primary, secondary and tertiary alcohols. In primary alcohols, -OH functional group is attached with primary carbon atom, in secondary alcohols with secondary carbon atom and in tertiary alcohols it is attached with a tertiary carbon atom.



11.2.1 NOMENCLATURE OF ALCOHOLS

There are two systems of naming alcohols

Common or Trivial Names

(a) Lower and simpler alcohols are usually known by their common or trivial names, obtained by adding the name of alcohol after the name of the alkyl group to which the OH group is attached, e.g.,



(b) I.U.R.A.C Names

In this system the alcohols are named according to the following rules.

(i) The longest chain of carbon atoms containing the hydroxyl group is taken as parent hydrocarbon. The ending 'e' of alkane is replaced by ol, e.g;



Methanol



Propanol



Pentanol

(ii) The position of OH group is indicated by a number placed before the name. The carbon chain is numbered, starting from the end where carbon atom attached with OH group gets the lowest possible number, e.g;

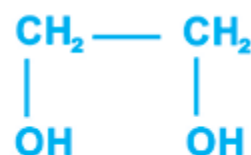


1-Butanol

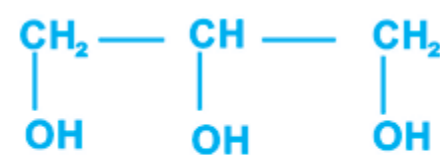


2-Butanol

(iii) If more than one OH groups are attached, they are indicated by an appropriate suffix diol, triol, etc., e.g;

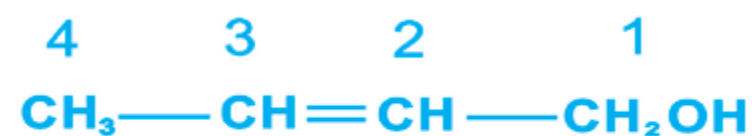


1,2-Ethandiol (Glycol)



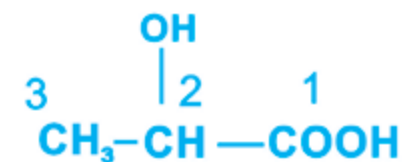
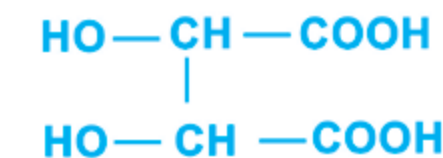
1,2,3-Propanetriol (Glycerol)

(iv) The unsaturated alcohols are numbered in such a way that hydroxyl group rather than the point of unsaturation gets the lower number, e.g.



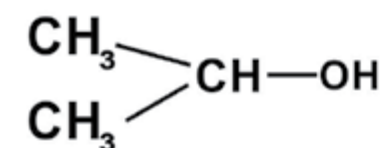
2-Buten-1-ol

(v) When hydroxyl group is not a preferred functional group as in hydroxy acids, aldehydes and ketones, the substituent name hydroxy is used as a prefix to indicate the position of OH group, e.g.;

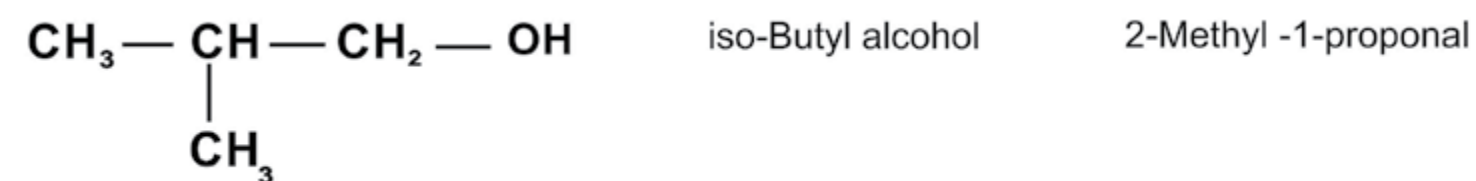
2-Hydroxy propanoic Acid
(Lactic Acid)2,3-Dihydroxy butane-1,4-dioic acid
(Tartaric Acid)

The names of some alcohols in the two systems are given below

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	methanol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Propyl alcohol	1-Propanol



Isopropyl alcohol 2-Propanol



11.2.2 Industrial Preparation of Alcohols

Methanol

Formerly methanol was prepared by distillation of wood. That is why it is also called as wood spirit. Now-a-days methanol is prepared from carbon monoxide and hydrogen or water gas as follows:

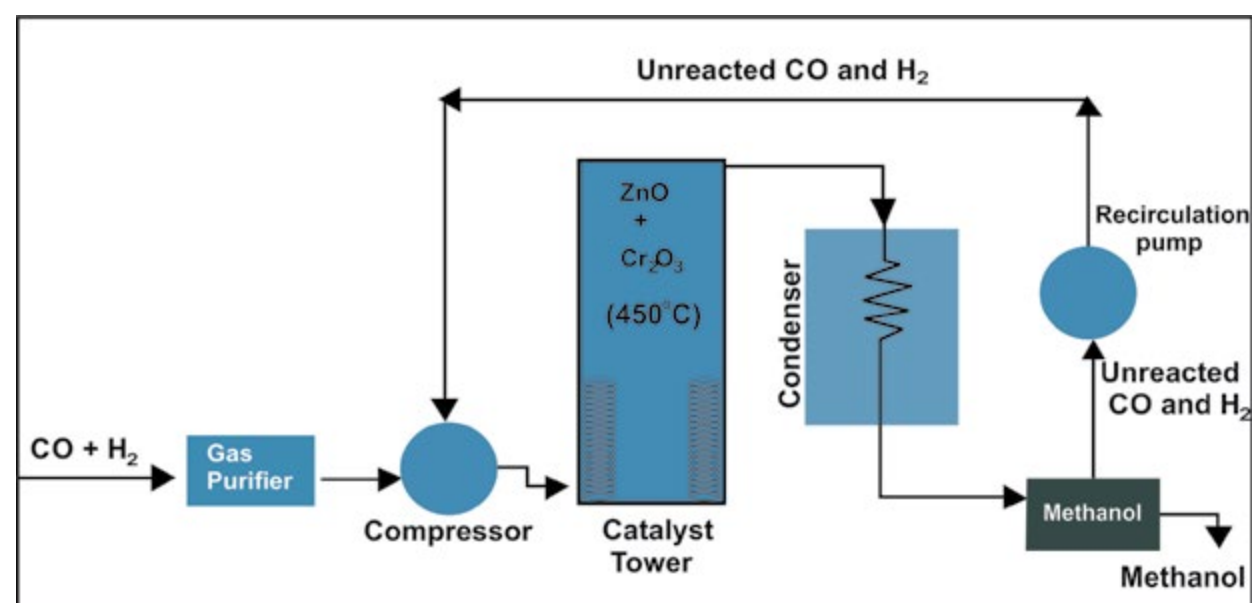
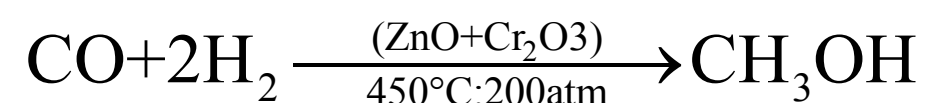


Fig. 11.1 Flow sheet diagram for the manufacturing of methanol

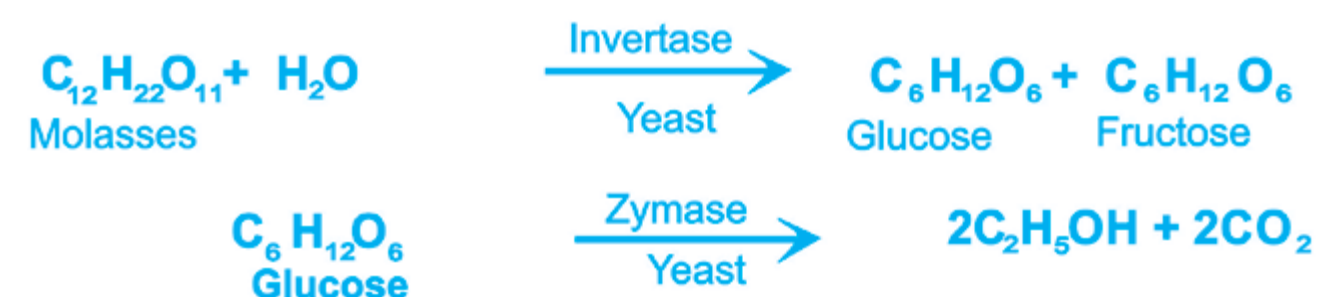
First of all a mixture of carbon monoxide and hydrogen is purified. It is compressed under a pressure of 200 atmospheres and taken into a reaction chamber by means of coiled pipes. Here the catalyst is heated up to 450-500 °C. Gases react to form methanol vapours. These vapours are passed through a condenser to get methanol. Unreacted gases are recycled through compressor to reaction chamber.

Ethanol

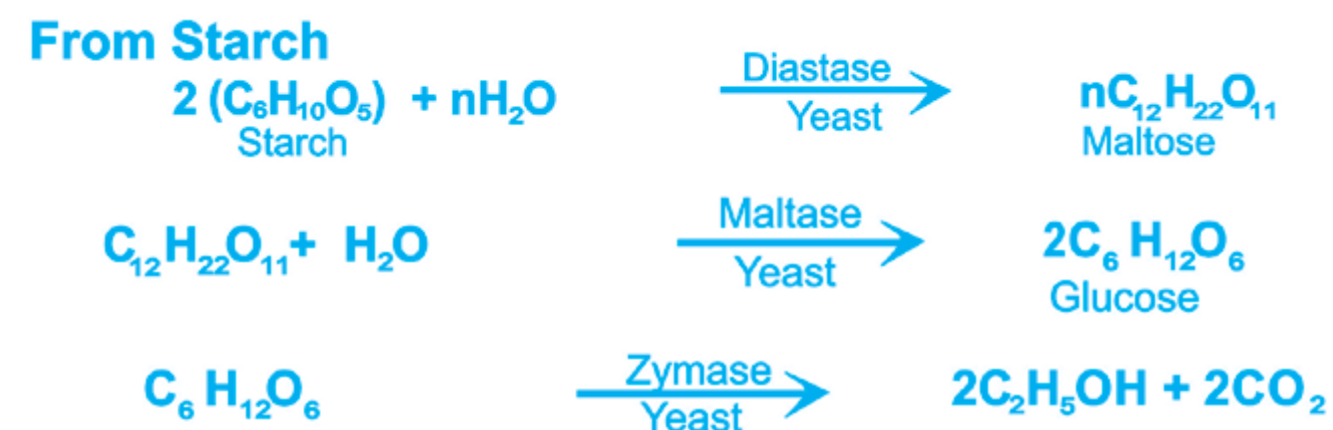
Ethanol is prepared on industrial scale world over, by the process of fermentation. Fermentation is a biochemical process which occurs in the presence of certain enzymes secreted by microorganisms such as yeast. Optimum temperature for this process of fermentation is 25-35°C. Moreover, proper aeration, dilution of solution and the absence of any preservative are essential conditions for fermentation. In Pakistan ethanol is prepared by the fermentation of molasses starch grains or fruit juices.

From Molasses

The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called molasses. It undergoes fermentation in the presence of enzymes present in yeast to give ethanol.



From Starch



Alcohol obtained by fermentation is only up to 12% and never exceeds 14% because beyond this limit enzymes become inactive. This alcohol is distilled again and again to obtain 95% alcohol which is called rectified spirit. Absolute alcohol can also be obtained by redistillation of rectified spirit in the presence of CaO which absorbs its moisture.

Denaturing of Alcohol

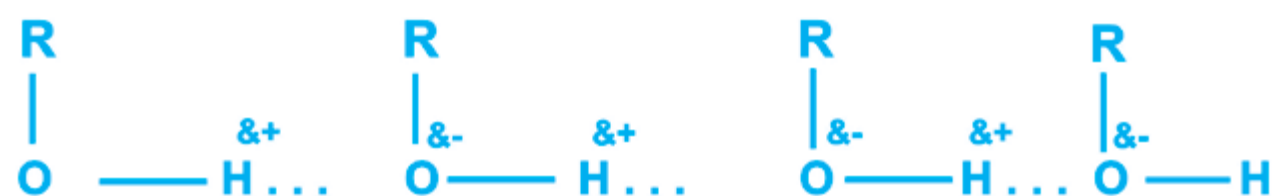
Sometimes ethanol is denatured by addition of 10% methanol to avoid its use for drinking purposes. Such alcohol is called methylated spirit. A small quantity of pyridine or acetone may also be added for this purpose.

Other Methods of Preparation of Alcohols

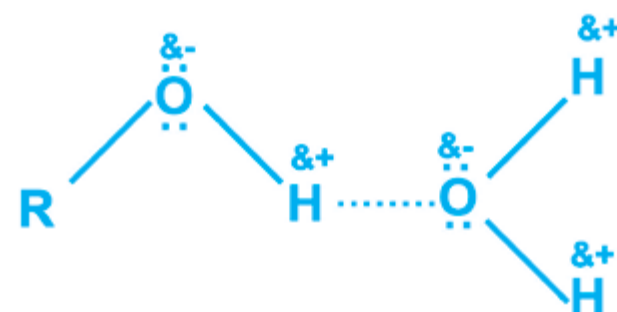
Alcohols can be obtained by the hydration of alkenes and by the reaction of Grignard reagents with aldehydes or ketones. Both these methods have already been discussed in the previous chapter.

11.2.3 Physical Properties

Lower alcohols are generally colourless toxic liquids with characteristic sweet smell and burning taste. They are readily soluble in water but solubility decreases in higher alcohols. The solubility of alcohols is due to hydrogen bonding which is prominent in lower alcohols but diminishes in higher alcohols.



Hydrogen bonding in alcohol



Hydrogen bonding between water and alcohol

Melting and boiling points of alcohols are higher than corresponding alkanes. Methyl alcohol and ethyl alcohol are liquids while methane and ethane are gases. This is also due to hydrogen bonding which is present in alcohols but absent in alkanes.

11.2.4 Reactions of Alcohols

Alcohols react with other reagents in two ways

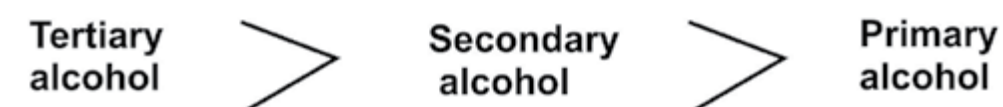
- (i) Reactions in which C — O bond breaks
- (ii) Reactions in which O — H bond breaks

Which bond will break depends upon the nature of the attacking reagent.

If a nucleophile attacks, it is the C — O bond which breaks. On the other hand, if an electrophile attacks on alcohol, it is the O — H bond which breaks.



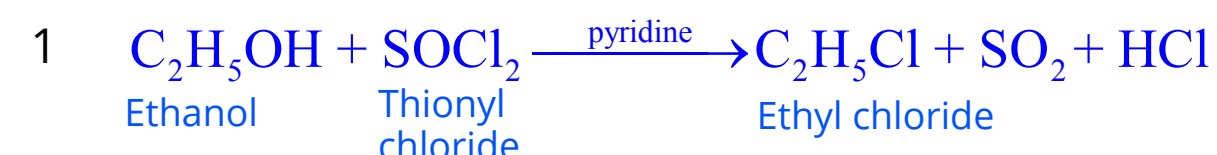
The order of reactivity of alcohols when C — O bond breaks:

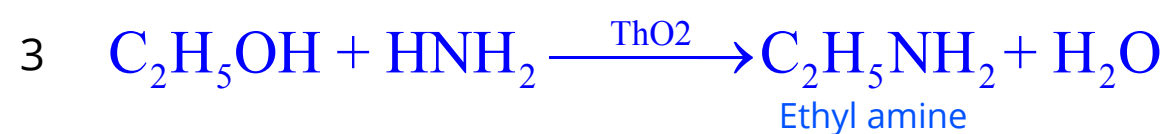


The order of reactivity of alcohols when O — H bond breaks:

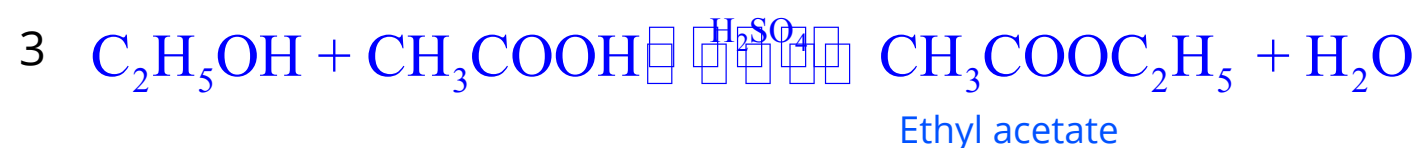
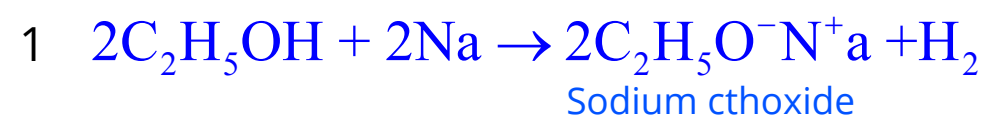


11.2.5 Reactions in which C — O Bond is Broken.





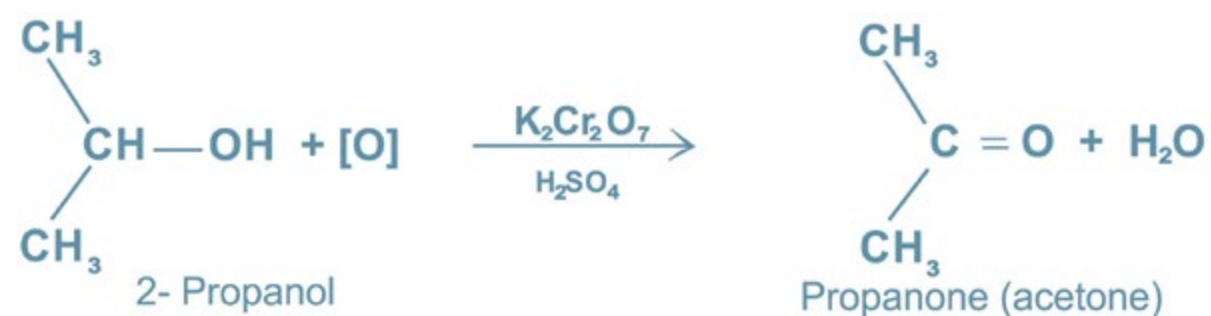
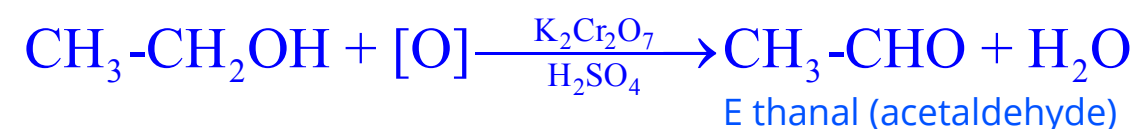
11.2.6 Reactions Involving the Cleavage of O – H bond.



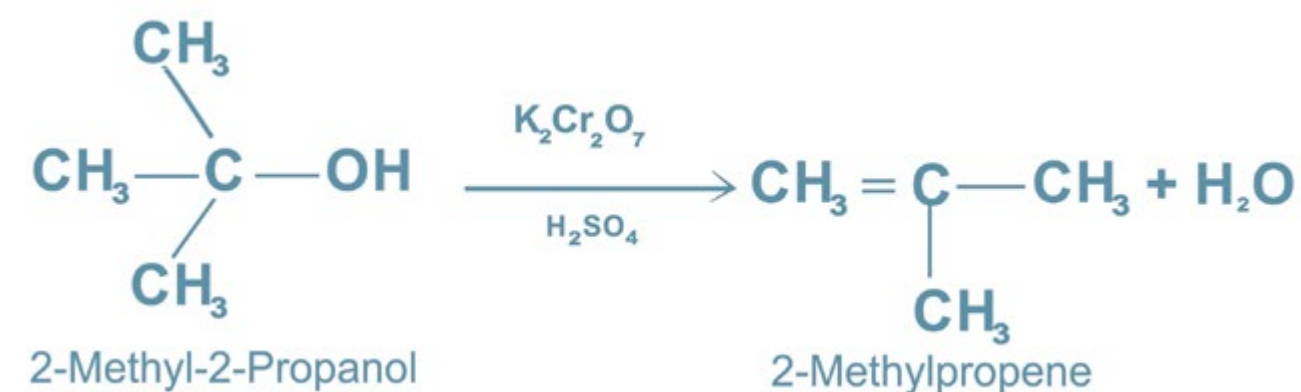
11.2.7 Some Other Reactions of Alcohols

(i) Oxidation

Oxidation of alcohols convert them into aldehydes and ketones. The best reagent for this purpose is acid dichromate.

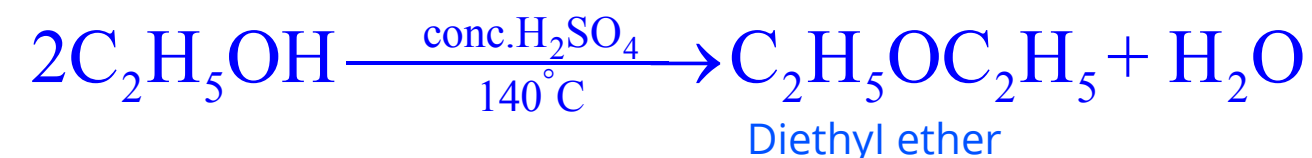
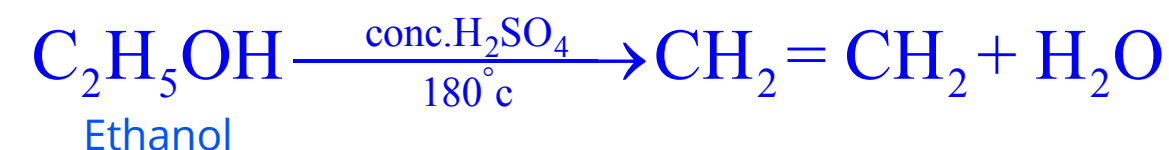


Tertiary alcohols are resistant to oxidation. In the presence of acid dichromate they undergo elimination reactions to give alkenes.



(ii) Dehydration

Alcohols react with con. H_2SO_4 and give different products at different temperatures.



(iii) Reactions with Phosphorus Halides PCl_3 , PCl_5

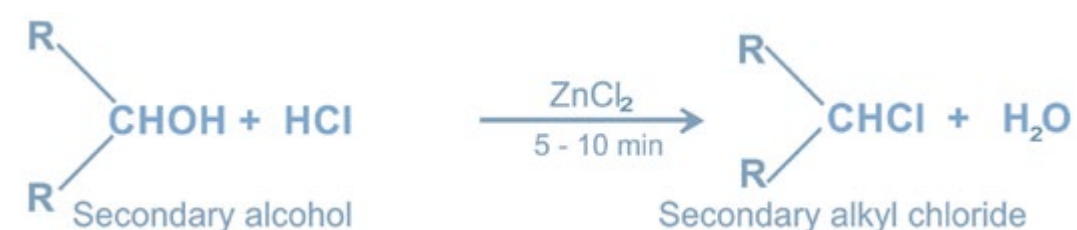
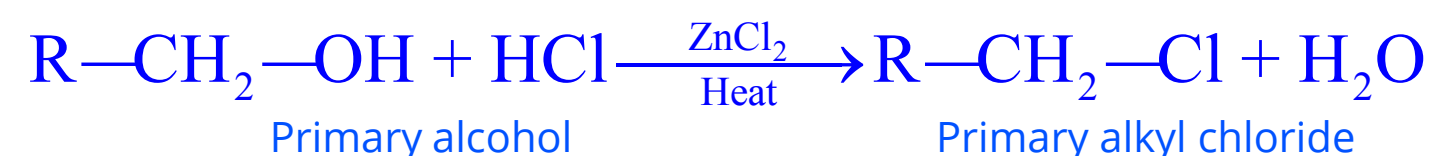


11.3 DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

Lucas Test

Primary, secondary and tertiary alcohols are identified and distinguished by reacting them with con. HCl in anhydrous ZnCl_2 . An oily layer of alkyl halides separates out in these reactions.

1. Tertiary alcohols form an oily layer immediately
2. Secondary alcohols form an oily layer in five to ten minutes.
3. Primary alcohols form an oily layer only on heating.



Distinction between Methanol and Ethanol

Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals indicate that the alcohol is ethanol. Methanol does not give iodoform test.



11.4 USES OF ALCOHOLS

Methanol is used as a solvent for fats oils, paints, varnishes. It is also used as antifreeze in the radiators of automobiles and for denaturing of alcohol.

Ethanol is used as a solvent, as a drink and as a fuel in some countries. Moreover it is used in pharmaceutical preparations and as a preservative for biological specimen.

11.5 PHENOL

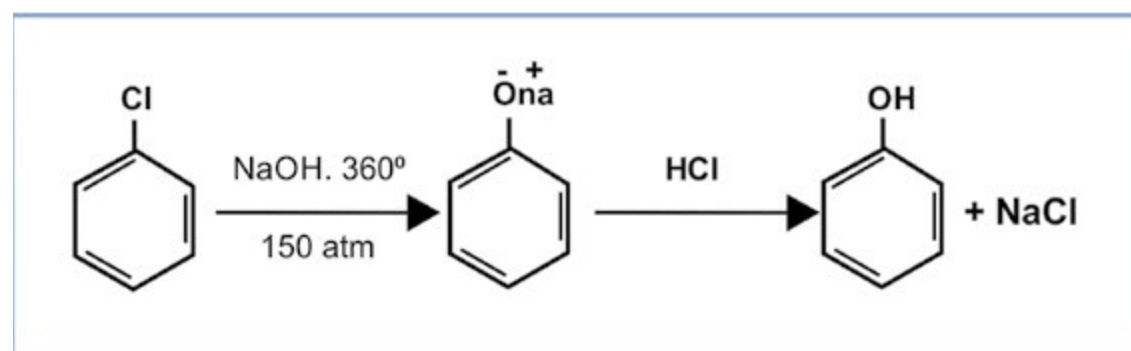
Aromatic compounds which contain one or more OH groups directly attached with carbon of benzene ring are called Phenols. The simplest example is phenol which is also known as Carboic acid i.e. $\text{C}_6\text{H}_5\text{OH}$. It was first obtained from coaltar by Runge in 1834.

11.5.1 Preparation of Phenol

1) From Chlorobenzene (Dow's Method)

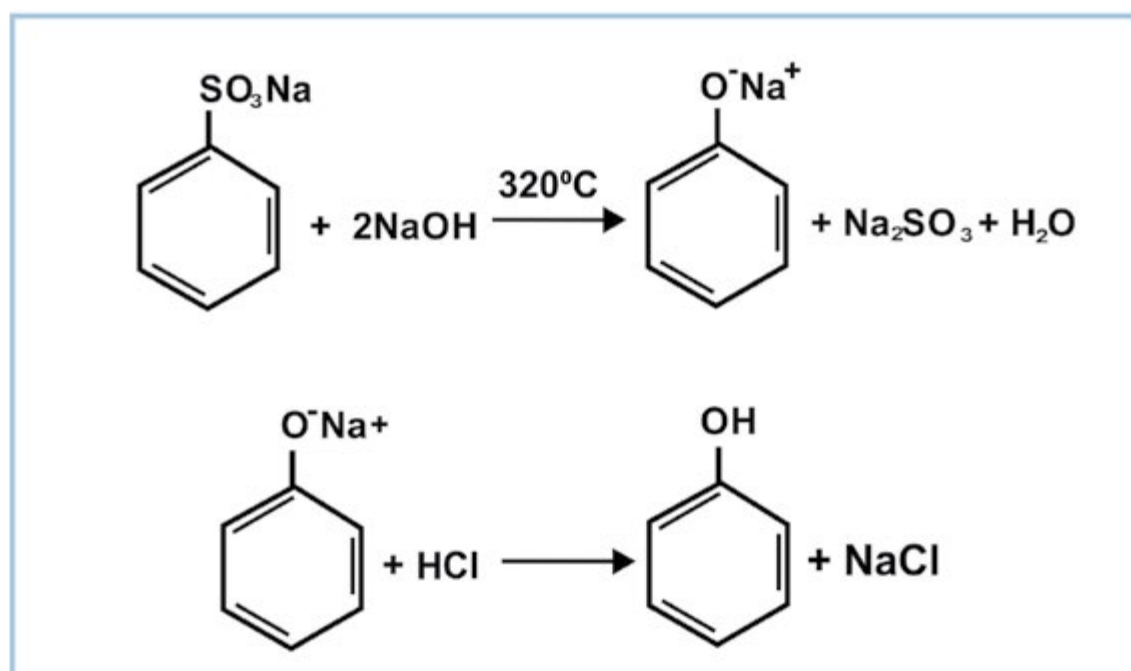
In this method chlorobenzene is treated with 10% NaOH at 360°C and 1150 atmospheres pressure. Sodium phenoxide is produced which on treating with HCl gives phenol.

*Animation 11.4: Phenol
Source and Credit : chem*



2) From Sodium Salt of Benzene Sulphonic Acid

Sodium salt of benzene sulphonic acid reacts with NaOH at 320°C to give sodium phenoxide which on treatment with HCl gives phenol.



The phenol is recovered by steam distillation.

11.5.2 Physical Properties

Phenol is a colourless, crystalline, deliquescent solid with characteristic phenolic odour having melting point 41°C and boiling point 182°C. It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C. It is poisonous and used as a disinfectant in hospitals and washrooms.

Animation 11.5: Physical Properties of phenol
Source and Credit : chemwiki

11.5.3 Reactions of Phenol

Phenol shows two types of reactions.

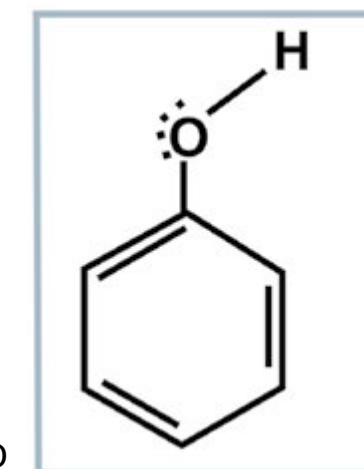
1. Reactions due to —OH group
2. Reactions due to benzene ring

Phenols are less reactive to nucleophiles so nucleophilic attack is less favoured, i.e. —OH is not easy to replace while electrophilic attack on the ring is easy.

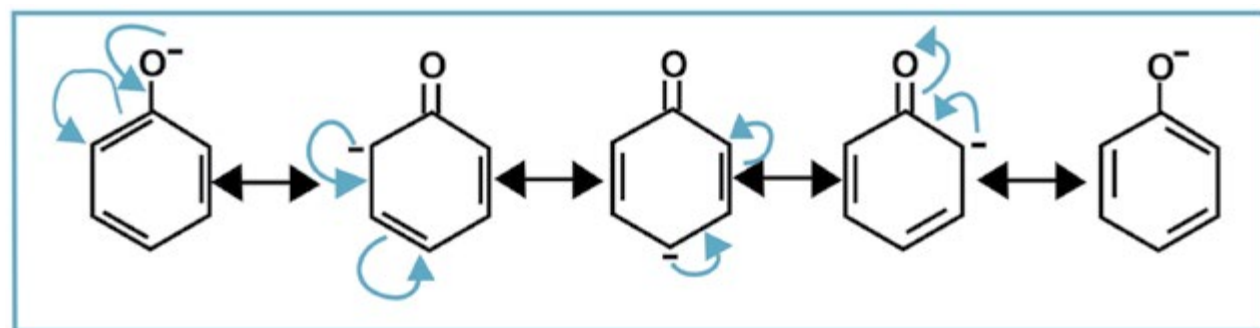
11.5.4 Acidic Behaviour of Phenol

Phenol is much more acidic than alcohols but less acidic than carboxylic acids. It dissolves readily in alkalies but it is too weak to affect the litmus paper or to evolve CO₂ from carbonates. Its dissociation constant (K_a) is 1.3 × 10⁻¹⁰.

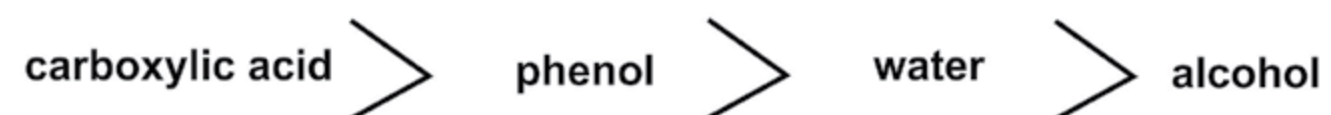
Phenol is partially soluble in water and its solution has a pH of around 5 or 6. This makes phenol different from aliphatic alcohols.



The reason why phenol is acidic lies in the nature of the phenoxide ion. The negative charge on oxygen atom can become involved with the π -electron cloud on the benzene ring. The negative charge is thus delocalized in the ring and the phenoxide ion becomes relatively stable. This type of delocalization is not possible with alcohols.



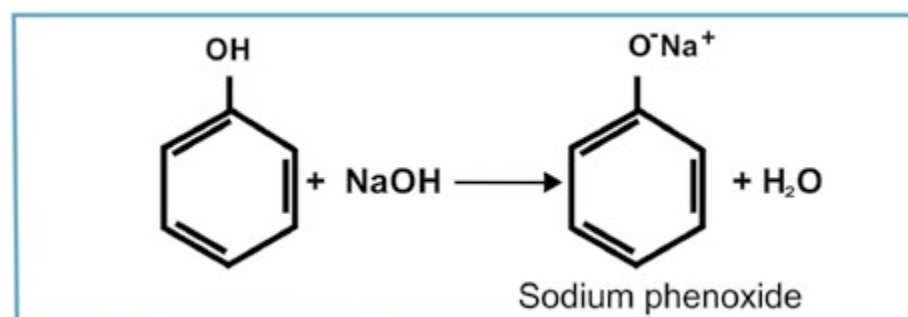
Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows,



11.5.5 Reactions of Phenol Due to -OH Group.

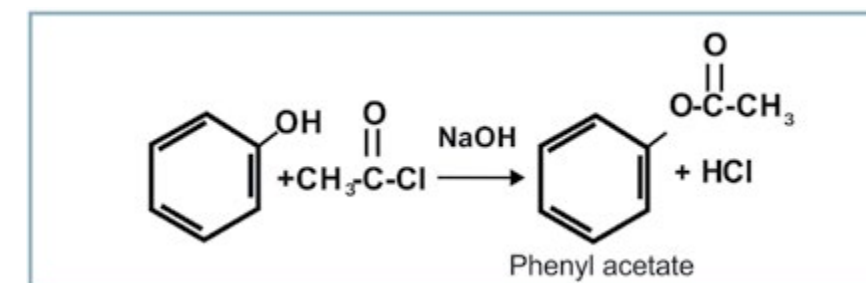
Salt Formation

Phenol reacts with alkalis to form salts, e.g;

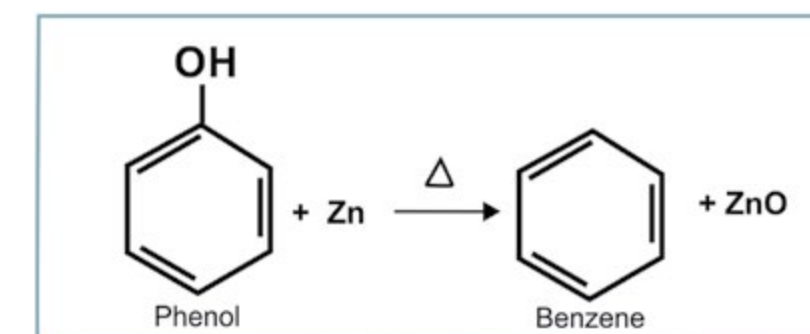


Ester Formation

Phenol reacts with acetyl chloride in the presence of a base to form ester.



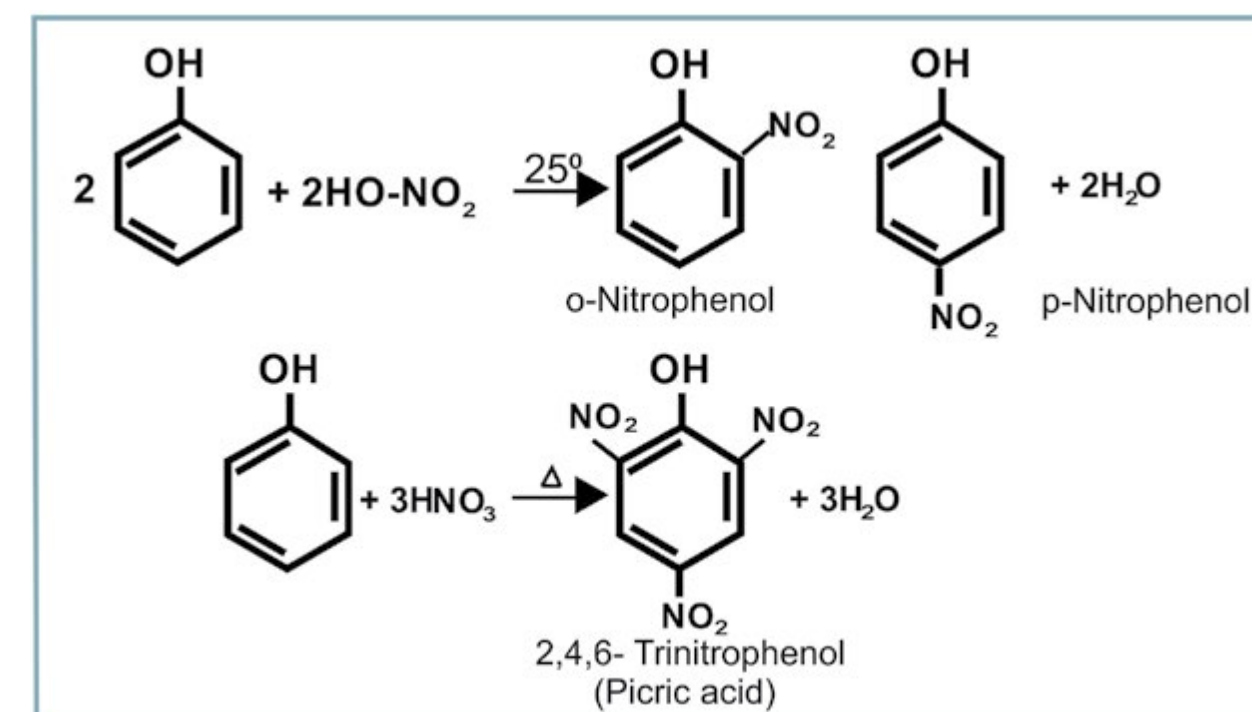
Reduction with Zn



11.5.6 Reactions of Phenol Due to Benzene Ring

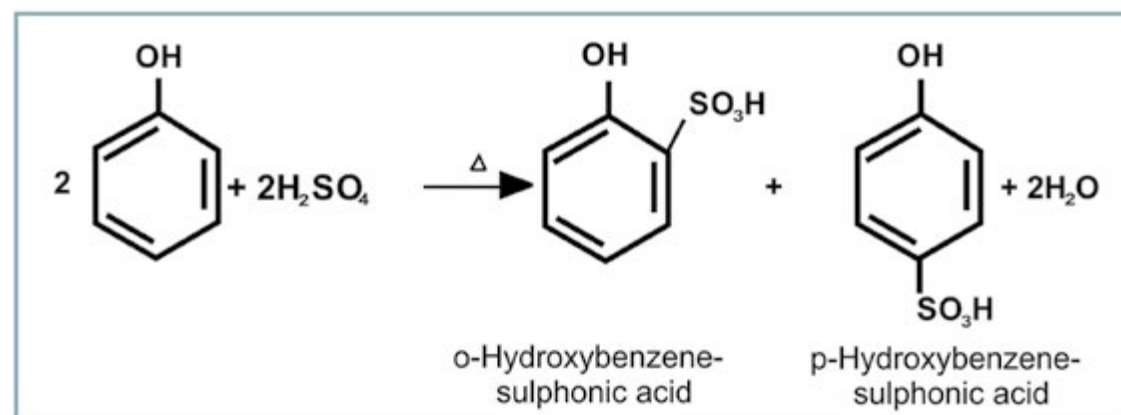
Nitration

Phenol reacts with dil. and conc. HNO₃ at different temperatures as follows.



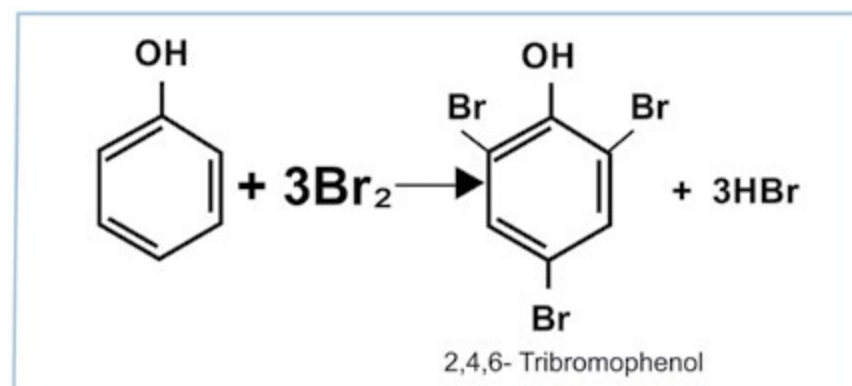
Sulphonation

Phenol reacts with conc. H_2SO_4 at room temperature giving ortho and para hydroxy benzene sulphonic acids.



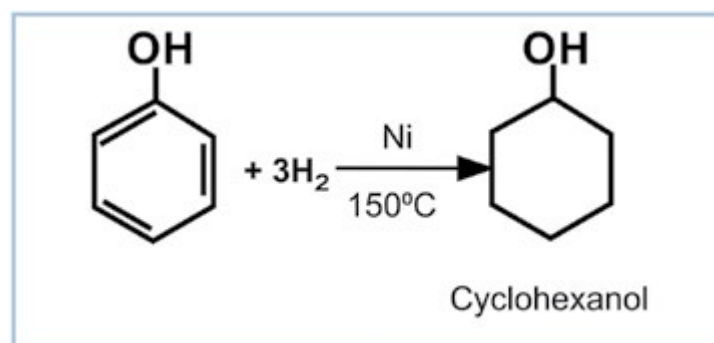
Halogenation

An aqueous solution of phenol reacts with bromine water to give white ppt. of 2,4,6-tribromophenol.



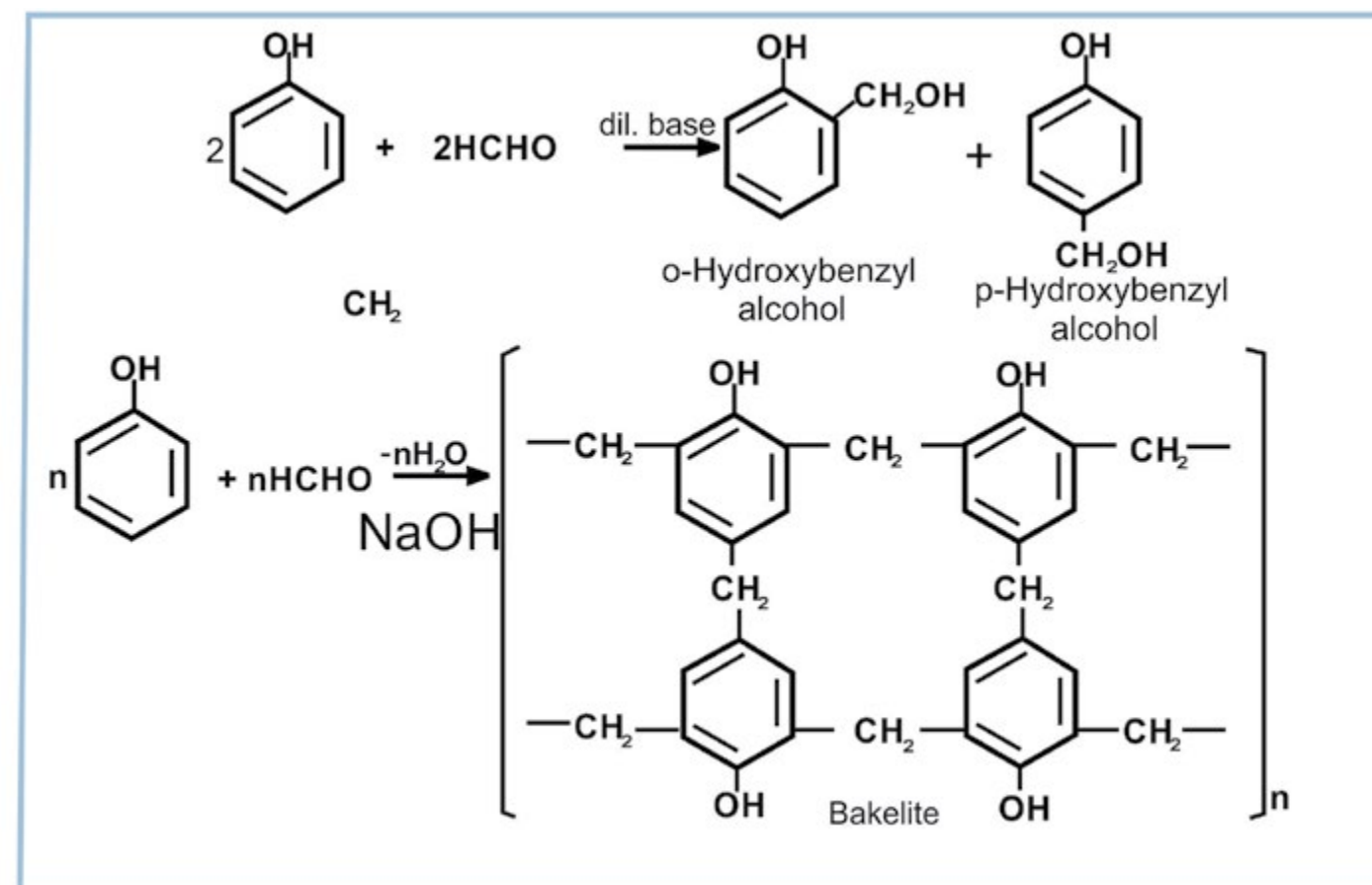
Hydrogenation

When hydrogen is passed through phenol at 150°C in the presence of Ni catalyst it gives cyclohexanol.



Reaction with formaldehyde

Phenol reacts with formaldehyde (methanal) in the presence of acid or alkali to give hydroxy benzyl alcohol which on further reaction with other phenol molecules yield a polymer called bakelite.



11.6 ETHERS

Ethers are classified into two categories

1. Simple or symmetrical ethers, which contain two same alkyl groups e.g. dimethyl ether CH_3OCH_3 and diethyl ether $\text{CH}_3\text{—CH}_2\text{—O—CH}_2\text{—CH}_3$.
2. Mixed or unsymmetrical ethers, which contain different alkyl or phenyl groups, e.g., ethyl methyl ether $\text{CH}_3\text{—O—CH}_2\text{—CH}_3$.

11.6.1 Nomenclature

Ethers are named either by I.U.P.A.C. system or by common names. In I.U.P.A.C. system the large alkyl (R) group is taken as parent molecule and given the last name (suffix) while the smaller alkyl group along with oxygen is used as prefix and given the name alkoxy (e.g. methoxy, ethoxy, propoxy, etc).

I. U. P. A. C. names are not common as they are difficult. Usually ethers are known by their common names, as given below;

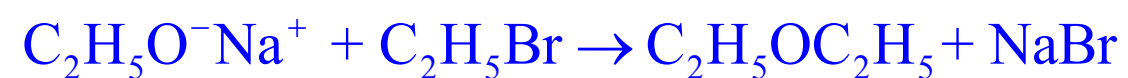
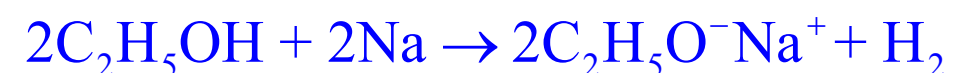
Formula	Common Names	I.U.P.A.C
CH ₃ OCH ₃	Dimethyl ether	Methoxy methane
CH ₃ OC ₂ H ₅	Methyl ethylether	Methoxy ethane
C ₂ H ₅ OC ₂ H ₅	Diethyl ether	Ethoxy ethane
C ₂ H ₅ OCH ₂ —CH ₂ —CH ₃	Ethyl n-propylether	Ethoxy propane
CH ₃ OC ₆ H ₅	Methyl phenyl ether	Methoxy benzene

11.6.2 Preparation of Ethers

Ethers are prepared from alcohols either directly or indirectly. Usually they are obtained by the following methods.

(i) By Williamsons synthesis

Alcohols are reacted with metallic sodium to form alkoxides. This alkoxide ion is a strong nucleophile and readily reacts with alkyl halide to produce an ether.



(ii) Alkyl halides are heated with dry silver oxide to form ethers



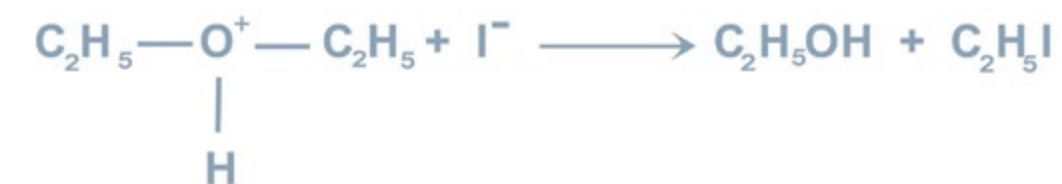
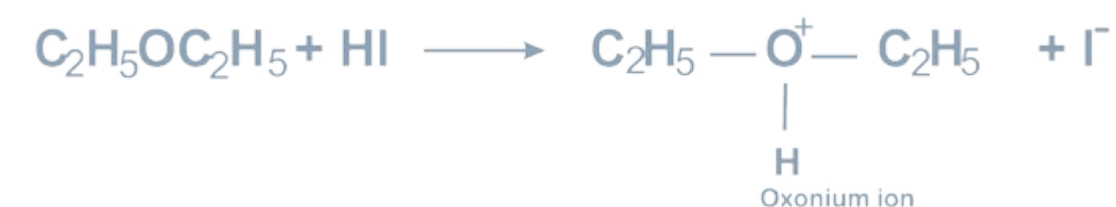
11.6.3 Physical Properties

Usually ethers are volatile liquids, highly inflammable with low boiling points. They are slightly soluble in water but freely soluble in organic solvents. Ether molecules do not show hydrogen bonding with one another but they show weak hydrogen bonding with water molecules due to which they are slightly soluble in water.

11.6.4 Chemical Reactivity

Ethers are comparatively inert substances. The reagents like ammonia, alkalies, dilute acids and metallic sodium, have no action on ethers in cold state. Moreover, they are not oxidized or reduced easily. However ethers show some reactions, e.g.

1. With hydrogen iodide ethers give alcohols which can react further to give alkyl iodides.



2. Ethers also react with hot phosphorus pentachloride to give alkyl chloride.



KEY POINTS

1. Alcohols and Phenols are hydroxy derivatives of aliphatic and aromatic hydrocarbons.
2. General formula for alcohol is ROH, for Phenol is Ph OH, and for ether it is ROR.
3. Alcohols are usually named by replacing 'e' for the alkane with 'ol'.
4. In Pakistan ethanol is prepared commercially from molasses.
5. Fermentation is a biochemical phenomenon which may occur naturally or artificially.
6. Ethyl alcohol obtained by fermentation is less than 12% concentrated.
7. Ethyl alcohol gives different products when reacts with H_2SO_4 of different concentrations.
8. Ethyl alcohol is used as a solvent, as a beverage and as a fuel.
9. Primary, secondary and tertiary alcohols can be distinguished by Lucas test.
10. Picric acid is a phenol which behaves like an acid.

EXERCISE

1. Primary, secondary and tertiary alcohols can be identified by _____ test.
2. Oxidation of _____ alcohols give ketones.
3. Alcohols on heating with _____ give alkenes at high temperature.
4. Alcohols have _____ boiling points than ethers due to stronger hydrogen bonding.
5. Williamsons synthesis is used to prepare _____ .
6. _____ is also called wood spirit.
7. Carboic acid is the other name of _____ .
8. Primary, secondary and tertiary alcohols can be prepared by reacting Grignard reagent with _____ , _____ and _____ .
9. Alcohols and _____ react to produce esters.
10. _____ is used as anti-freezing agent in automobile radiator.
11. The process of conversion of starch into alcohol with the help of microorganisms is called _____ .
12. Ketones on reduction give _____ alcohols.

Q.2. Indicate True or False

1. Methylated spirit contains 95% methyl alcohol and 5% ethyl alcohol.
2. Ethyl alcohol is a very good anti-freezing agent.
3. Methanol is also called wood spirit.
4. Only 14% ethyl alcohol can be prepared by fermentation.
5. Ethers do not show hydrogen bonding.
6. Alcohols are more acidic than phenols.
7. Phenol is more soluble in water than lower alcohols.
8. Alcohols are more basic than ethers.
9. Ethers have higher boiling points than alcohols and phenols.
10. Methanol and ethanol can be distinguished by iodoform test.

Q.3. Multiple Choice Questions. Encircle the correct answer.

- i) Which compound shows hydrogen bonding
 a) C_2H_6 b) C_2H_5Cl c) CH_3-O-CH_3 d) C_2H_5OH
- ii) Which compound shows maximum hydrogen bonding with water?
 a) CH_3OH b) C_2H_5OH c) CH_3-O-CH_3 d) C_6H_5OH
- iii) Which compound is more soluble in water
 a) C_2H_5OH b) C_6H_5OH c) CH_3COCH_3 d) n-Hexanol
- iv) Which compound will have the maximum repulsion with H_2O ?
 a) C_6H_6 b) C_2H_5OH c) $CH_3CH_2CH_2OH$ d) CH_3-O-CH_3
- v) Ethanol can be converted into ethanoic acid by
 a) Hydrogenation b) Hydration c) Oxidation d) Fermentation
- vi) Which enzyme is not involved in fermentation of starch?
 a) Diastase b) Zymase c) Urease d) Invertase
- vii) Which compound is called a universal solvent?
 a) H_2O b) CH_3OH c) C_2H_5OH d) CH_3-O-CH_3

- viii) Methyl alcohol is not used
 a) as a solvent
 b) as an anti-freezing agent
 c) as a substitute for petrol
 d) for denaturing of ethyl alcohol
- ix) Rectified spirit contains alcohol methyl about
 a) 80% b) 85% c) 90% d) 95%
- x) According to Lewis concept ethers behave as
 a) Acid b) Base
 c) Acid as well as a base d) None of them

Q.4. What are alcohols. How are they classified? How will you distinguish between primary, secondary and tertiary alcohols?

Q.5. How is methyl alcohol obtained on large scale? How it may be distinguished from ethyl alcohol?

Q.6. What is fermentation? Which compound may be obtained on industrial scale by fermentation?

Q.7. Explain the following terms.
 Absolute alcohol, Methylated spirit, Rectified spirit, Denaturing of alcohols.

Q.8. How does ethyl alcohol react with the following reagents?
 i) $\text{Conc. H}_2\text{SO}_4$ ii) Na iii) PCl_5 iv) CH_3COOH v) SOCl_2

Q.9. How will you obtain primary, secondary and tertiary alcohols by reacting Grignard reagent with suitable carbonyl compounds.

Q.10. How will you distinguish between
 i) an alcohol and a phenol ii) an alcohol and an ether
 iii) methanol and ethanol iv) a tertiary alcohol and a primary alcohol
 v) 1-propanol and 2-propanol

Q.11. Give reasons for the followings:

- i) Ethyl alcohol is a liquid while methyl chloride is a gas.
 ii) Ethanol has higher boiling point than diethyl ether.
 iii) Absolute alcohol cannot be prepared by fermentation process.
 iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.
 v) Water has higher boiling point than ethanol.

Q.12. How will you convert

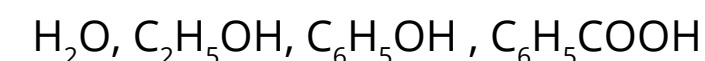
- i) Methanol into ethanol ii) Ethanol into methanol
 iii) Ethanol into isopropyl alcohol iv) Formaldehyde into ethyl alcohol
 v) Acetone into ethyl alcohol

Q.13. Explain the following terms using ethyl alcohol as an example.

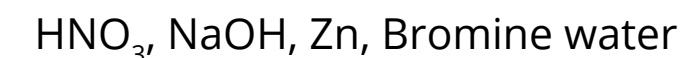
- i) Oxidation ii) Dehydration iii) Esterification
 iv) Ether formation

Q.14. Compare the reactions of phenol with those of ethanol. Discuss the difference if any.

Q.15. Arrange the following compounds in order of their increasing acid strength and give reasons.



Q.16. Write down two methods for preparing phenol. What is the action of following on phenol.



Q.17. Give the uses of phenols. How bakelite is prepared from it.

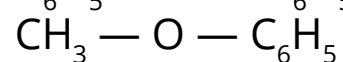
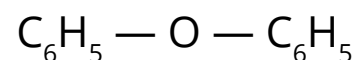
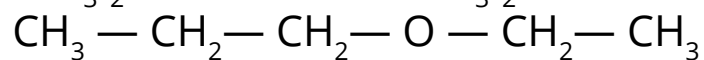
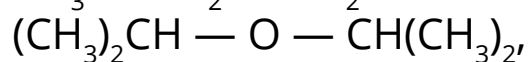
Q.18. (a) Write I.U.P.A.C. names of the following compounds.



(b) Write structure formulas for the following compounds.

Glycol, Glycerol, Carbolic Acid, Acetophenone, Picric Acid

Q.19. (a) Name the following compounds



(b). Write down structural formulas of the following compounds. Methoxy ethane, ethoxy benzene, sodium ethoxide, sodium phenoxide, propoxy propane.