Chapter 18

Alcohols, Phenols and Ethers

Major Concepts

18.1 Alcohols
18.2 Phenols
18.3 Ethers

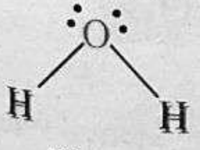
Learning Outcomes:

Students will be able to:

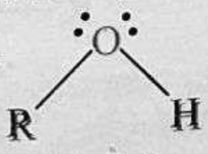
- Explain nomenclature, structure and acidity of alcohols as exemplified by ethanol. **(Understanding)**
- Describe the preparation of alcohols by reduction of aldehydes, ketones, carboxylic acids and esters. **(Applying)**
- Explain reactivity of alcohols. **(Understanding)**
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidative cleavage of 1,2-diols. **(Applying)**
- Discuss thiols (RSH). **(Understanding)**
- Explain the nomenclature, structure and acidity of phenols. **(Applying)**
- Describe the preparation of phenol from benzene sulphonic acid, chlorobenzene, acidic oxidation of cumene and hydrolysis of diazonium salts. **(Applying)**.
- Discuss the reactivity of phenol and their chemistry by electrophilic aromatic substitution reaction with Na metal and oxidation. **(Applying)**
- Differentiate between alcohol and phenol. **(Understanding)**
- Describe isomerism in alcohols and phenols. **(Understanding)**
- Identify ethers from their formula. **(Understanding)**

Introduction

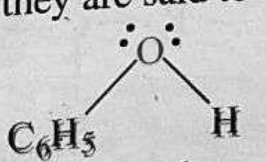
In this chapter, we will focus on those hydrocarbon derivatives whose functional groups contain one oxygen atom participating in two single bonds (alcohols, phenols and ethers). Alcohols, phenols and ethers are organic compounds containing hydroxyl groups. They are very close to each other in structures. They have structures like water. Because of this, they are said to be derivatives of water.



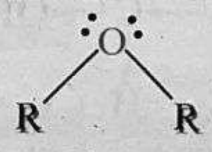
Water



Alcohol



Phenol

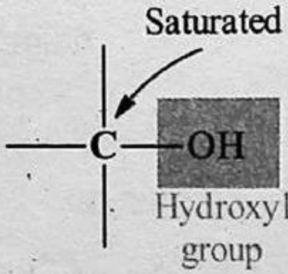


Ether

Alcohols and phenols both have hydroxyl (–OH) groups in their structures. Alcohols are hydroxyl derivatives of alkanes while phenols are hydroxyl derivatives of benzene. They (alcohols, phenols and ethers) occur widely in nature. They have many pharmaceutical, biological and industrial applications.

18.1 Alcohols

Alcohols are compounds in which hydroxyl group (–OH) is bonded to saturated carbon atom. A saturated carbon atom is a carbon atom, which is bonded to four other carbon atoms.

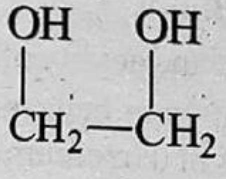


On the basis of number of hydroxyl groups, alcohols are classified into two major types: Monohydric alcohols and polyhydric alcohols.

Monohydric alcohols have only one hydroxyl group in their molecules while polyhydric alcohol have two or more hydroxyl groups in their molecules. Ethyl alcohol and tertiary butyl alcohol are examples of monohydric alcohols whereas glycol and glycerol are examples of polyhydric alcohols.

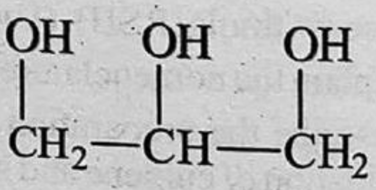
$CH_3CH_2—OH$

Ethyl alcohol
(Monohydric alcohol)



$\underset{\text{OH}}{CH_2}—\underset{\text{OH}}{CH_2}$

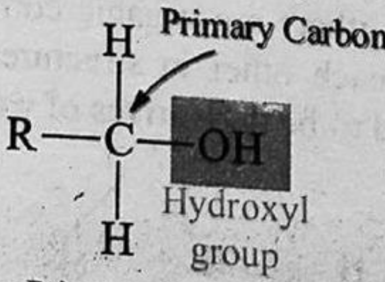
Glycol
(Polyhydric alcohol)



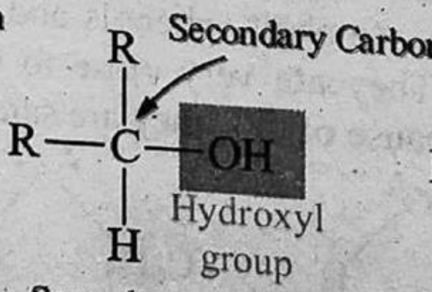
$\underset{\text{OH}}{CH_2}—\underset{\text{OH}}{CH}—\underset{\text{OH}}{CH_2}$

Glycerol
(Polyhydric alcohol)

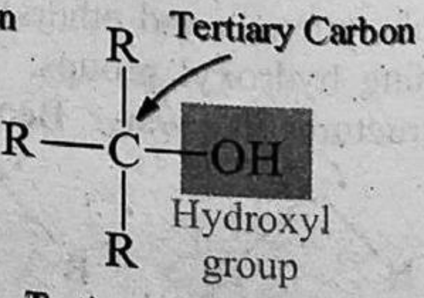
Monohydric Alcohols are further classified as primary (1°) alcohols, secondary (2°) alcohols, or tertiary (3°) alcohols, depending on whether the OH group is bonded to a primary, secondary, or tertiary carbon. In primary alcohols, the hydroxyl group is directly bonded to primary carbon. In secondary alcohols, the hydroxyl group is directly bonded to secondary carbon. In tertiary alcohols, the hydroxyl group is directly bonded to tertiary carbon.



Primary alcohol



Secondary alcohol



Tertiary alcohol

18.1.1 Nomenclature of Alcohols

Alcohols are named by two systems: common system and IUPAC system.

18.1.1.1 Common System

The common names are obtained by adding the word alcohol after the name of alkyl group. All of the carbon atoms are named as a single alkyl group of the molecule. We can say that, in this system, they are named as alkyl alcohols.

Examples are:

$CH_3—OH$

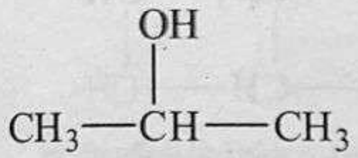
Methyl alcohol

$CH_3—CH_2—OH$

Ethyl alcohol

$CH_3—CH_2—CH_2—OH$

n-Propyl alcohol



$$CH_3—\overset{\overset{OH}{|}}{CH}—CH_3$$

Isopropyl alcohol

$(CH_3)_3C—OH$

Tert.butyl alcohol

Common names exist generally for those alcohols which have simple (C_1 to C_4) alkyl groups.

18.1.1.2 IUPAC System

In this system, alcohols are considered as derivatives of alkanes in which one of the hydrogen atoms has been replaced by hydoxyl group and are named as ***alkanols***. The IUPAC names of alcohols are one-word names. The rules for naming alcohols are:

Step 1: Select the longest continuous chain of carbon atoms containing the hydroxyl group.

Step 2: Drop the final ***–e*** from the alkane name and add the suffix ***–ol*** to give the root name.

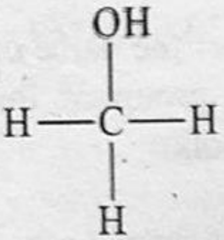
Step 3: Number the carbon chain from that end which is nearer to hydroxyl group. The hydroxy group takes precedence over alkyl groups, halogen atoms, double and triple bonds while numbering the parent chain.

Step 4: Indicate the position of hydroxyl group and other substituents by the number of carbon atoms to which they are bonded.

When two or more hydroxyl groups are present in a chain, then alcohols are named as diols (for alcohols containing two hydroxyl groups), triols (for alcohols containing three hydroxyl groups), tetraols (for alcohols containing four hydroxyl groups), etc.

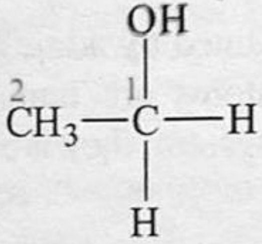
Step 5: When hydroxy group is present in the structures of carbonyl compounds such as aldehydes, ketones, carboxylic acids and their derivatives, the preference in numbering the chain is not given to hydroxyl group. The hydroxyl group is taken as a side group in the carbonyl compounds. Use the word hydroxy for –OH group and indicate the position of this group by the number of carbon to which it is bonded.

Examples are:



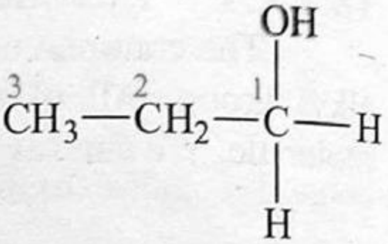
$$\mathrm{H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$

Methanol



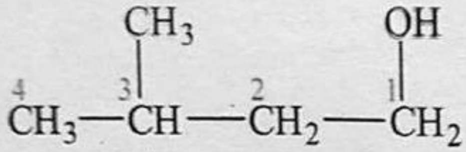
$$\mathrm{{}^{2}CH_3-{}^{1}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$

Ethanol



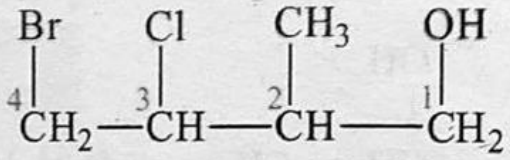
$$\mathrm{{}^{3}CH_3-{}^{2}CH_2-{}^{1}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$

1-Propanol



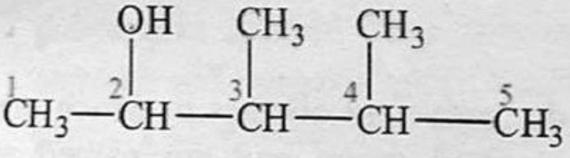
$$\mathrm{{}^{4}CH_3-{}^{3}\overset{\overset{CH_3}{|}}{CH}-{}^{2}CH_2-{}^{1}\overset{\overset{OH}{|}}{CH_2}}$$

3-Methyl-1-butanol



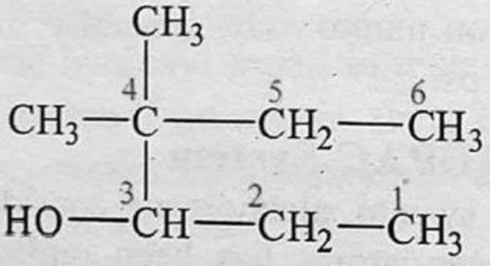
$$\mathrm{{}^{4}\overset{\overset{Br}{|}}{CH_2}-{}^{3}\overset{\overset{Cl}{|}}{CH}-{}^{2}\overset{\overset{CH_3}{|}}{CH}-{}^{1}\overset{\overset{OH}{|}}{CH_2}}$$

4-Bromo-3-Chloro-2-methyl-1-butanol



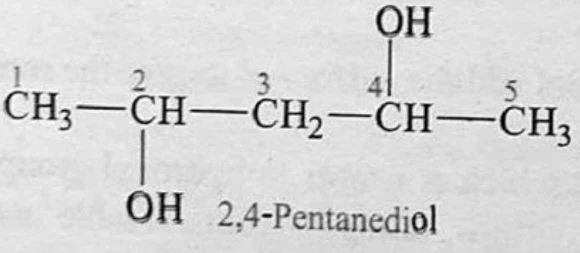
$$\mathrm{{}^{1}CH_3-{}^{2}\overset{\overset{OH}{|}}{CH}-{}^{3}\overset{\overset{CH_3}{|}}{CH}-{}^{4}\overset{\overset{CH_3}{|}}{CH}-{}^{5}CH_3}$$

3,4-dimethyl-2-pentanol



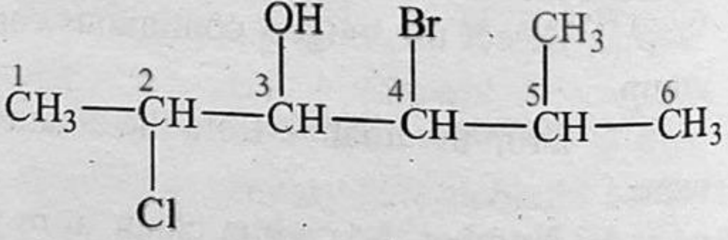
$$\mathrm{CH_3-{}^{4}\underset{\underset{HO-{}^{3}CH-{}^{2}CH_2-{}^{1}CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-{}^{5}CH_2-{}^{6}CH_3}$$

4,4-Dimethyl-3-hexanol



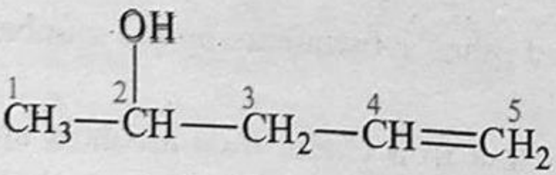
$$\mathrm{{}^{1}CH_3-{}^{2}\underset{\underset{OH}{|}}{CH}-{}^{3}CH_2-{}^{4}\overset{\overset{OH}{|}}{CH}-{}^{5}CH_3}$$

2,4-Pentanediol



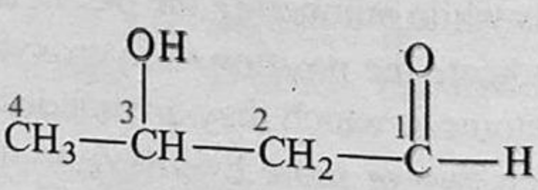
$$\mathrm{{}^{1}CH_3-{}^{2}\underset{\underset{Cl}{|}}{CH}-{}^{3}\overset{\overset{OH}{|}}{CH}-{}^{4}\overset{\overset{Br}{|}}{CH}-{}^{5}\overset{\overset{CH_3}{|}}{CH}-{}^{6}CH_3}$$

4-Bromo-2-chloro-5-methyl-3-hexanol



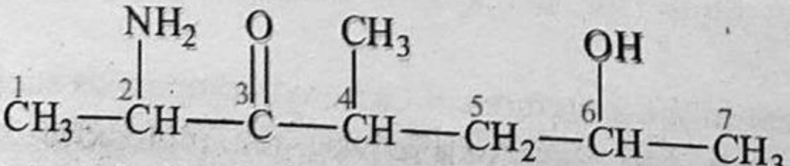
$$\mathrm{{}^{1}CH_3-{}^{2}\overset{\overset{OH}{|}}{CH}-{}^{3}CH_2-{}^{4}CH{=}{}^{5}CH_2}$$

4-Penten-2-ol



$$\mathrm{{}^{4}CH_3-{}^{3}\overset{\overset{OH}{|}}{CH}-{}^{2}CH_2-{}^{1}\overset{\overset{O}{\|}}{C}-H}$$

3-Hydroxybutanal



$$\mathrm{{}^{1}CH_3-{}^{2}\overset{\overset{NH_2}{|}}{CH}-{}^{3}\overset{\overset{O}{\|}}{C}-{}^{4}\overset{\overset{CH_3}{|}}{CH}-{}^{5}CH_2-{}^{6}\overset{\overset{OH}{|}}{CH}-{}^{7}CH_3}$$

2-Amino-6-hydroxy-4-methyl-3-heptanone

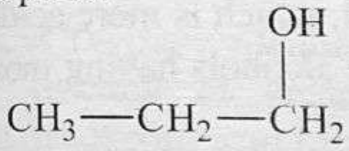
Isomerism in Alcohols

Alcohols with two or more carbon atoms can show functional isomerism with ethers. Thus alcohols and ethers have same molecular formula but have different functional groups. For example, dimethyl ether is the functional isomer of ethyl alcohol.

$CH_3—CH_2—OH$ **Ethyl alcohol**

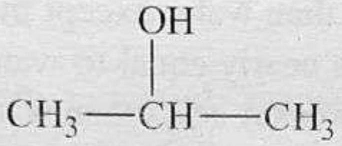
$CH_3—O—CH_3$ **Dimethyl ether**

Alcohols with three or more carbon atoms can show position isomerism due to different position of hydroxyl groups. For example, 2-propanol is the position isomer of 1-propanol.



$$CH_3—CH_2—\overset{\overset{\large OH}{|}}{C}H_2$$

1-Propanol



$$CH_3—\overset{\overset{\large OH}{|}}{C}H—CH_3$$

2-Propanol

18.1.2 Physical Properties of Alcohols

i) Lower alcohols are colourless liquids. The higher members are colourless waxy solids.

ii) They have characteristic alcoholic smell and burning taste.

iii) They are volatile and inflammable.

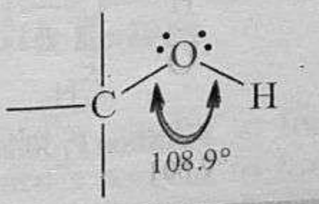
iv) They have higher boiling points than corresponding alkanes, ethers and haloalkanes.

v) They are readily soluble in water up to four carbon atoms. Higher alcohols, from carbon five onwards, are insoluble in water. The solubility is due to the presence of the intermolecular hydrogen bonding in the molecules of alcohol and water. Solubility of alcohols in water decreases with increase in the size of the alkyl groups and increases with increase in the branching of alkyl groups.

vi) They (esp. monohydric alcohols) are lighter than water. The density of methanol is 0.792 g/mL and that of ethanol is 0.789 g/mL at 20°C. The density of water at 20°C is 0.998 g/mL.

18.1.3 Structure of Alcohols

The oxygen atom of an alcohol is sp^3 hybridized and has four sp^3 hybrid orbitals. Two sp^3 hybrid orbitals of oxygen atom form σ-bonds to atoms of carbon and hydrogen, and the remaining two sp^3 hybrid orbitals each contain a lone pair of electrons.



The C$\hat{O}$H bond angle in methanol is 108.9°. The carbon-oxygen bond length is 142 pm and the oxygen-hydrogen bond length is 96 pm.

18.1.4 Acidity of Alcohols

Alcohols are acidic in nature due to presence of polar O—H bond. Greater the polarity of –OH group, greater would be the acidity of alcohols. Primary alcohols are more acidic than secondary alcohols which in turn are more acidic than tertiary alcohols. The polarity of –OH group decreases by increase in the number of electron releasing groups, namely alkyl groups bonded to α-carbon. For example, tert-butyl alcohol is weaker acid than either methyl alcohol or ethyl alcohol.

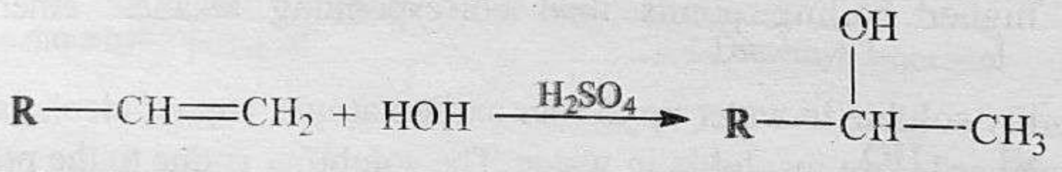
Alcohols are less acidic than water except methanol, which is more acidic than water. The acidity of ethanol is nearly equal to water. The alcohols having more than two carbon atoms are slightly weaker acids than water.

18.1.5 Preparations of Alcohols

The alcohols can be prepared by the methods given below:

18.1.5.1 Hydration of Alkenes

Alkenes react with water in the presence of cold concentrated sulphuric acid to produce an alcohol. The predominant product of alcohol can be obtained by using Markovnikov's rule.



$$\mathrm{R{-}CH{=}CH_2 + HOH \xrightarrow{H_2SO_4} R{-}\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_3}$$

18.1.5.2 Hydrolysis of Alkyl Halides

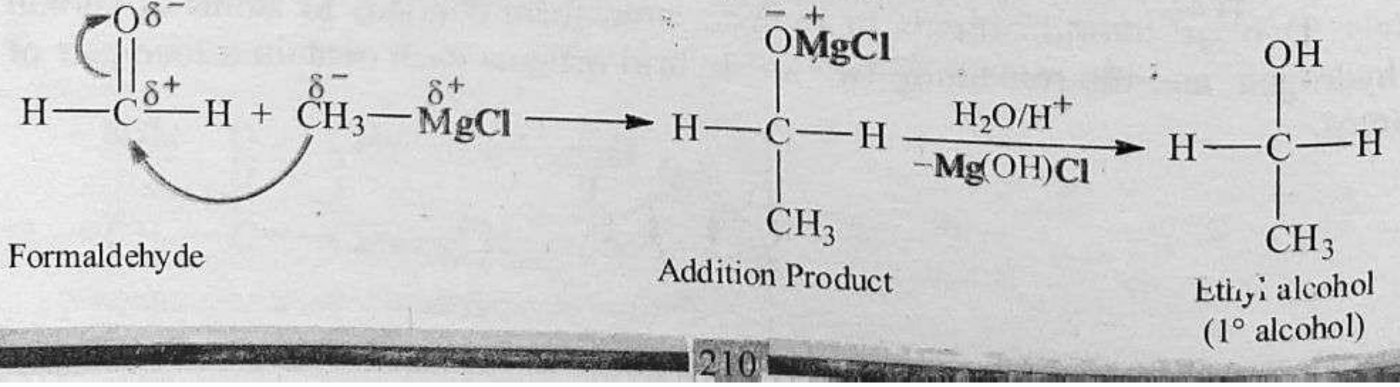
Alkyl halides react with aqueous NaOH or KOH to produce alcohols.

$$\mathrm{CH_3{-}CH_2{-}Br + KOH \xrightarrow[Heat]{H_2O} CH_3{-}CH_2{-}OH + KBr}$$

18.1.5.3 Reaction of RMgX with Aldehydes and Ketones

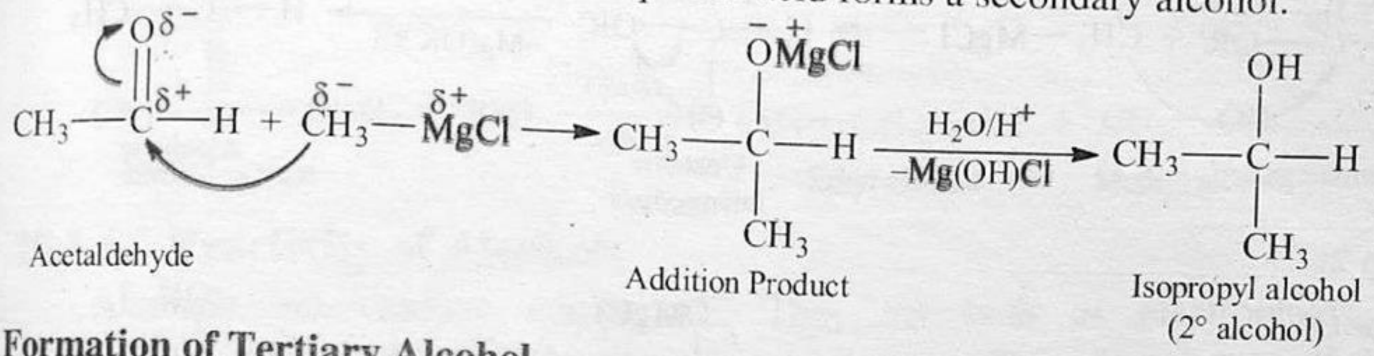
Formation of Primary Alcohol

The reaction of formaldehyde with Grignard reagent (RMgX) is followed by protonation in aqueous acid forms a primary alcohol.



Formation of Secondary Alcohol

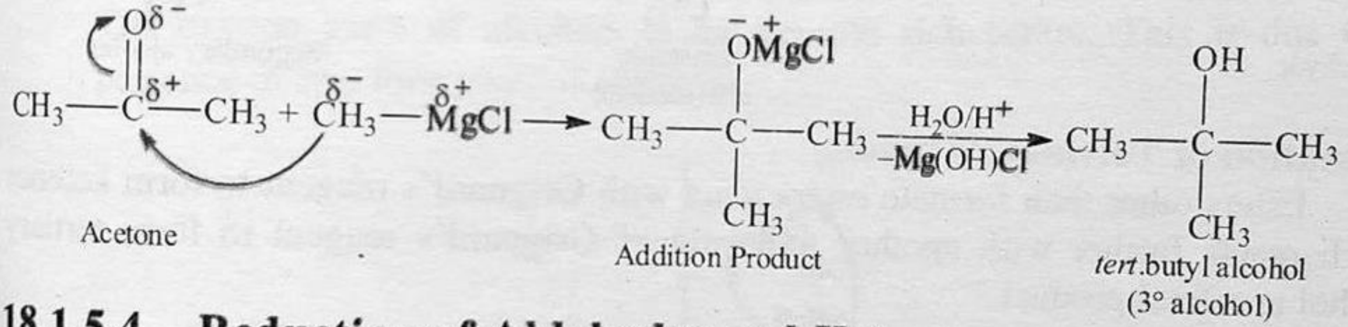
The reaction of aldehydes other than formaldehyde with Grignard reagent (RMgX) followed by protonation in aqueous acid forms a secondary alcohol.



$$CH_3-\overset{\overset{\delta-}{O}}{\overset{\|}{C}}{}^{\delta+}-H + \overset{\delta-}{C}H_3-\overset{\delta+}{Mg}Cl \longrightarrow CH_3-\underset{CH_3}{\overset{\overset{-\;+}{O}MgCl}{C}}-H \xrightarrow[-Mg(OH)Cl]{H_2O/H^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-H$$

Formation of Tertiary Alcohol

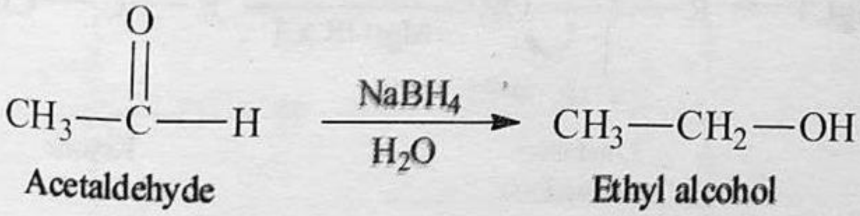
The reaction of ketones with Grignard reagent (RMgX) followed by protonation in aqueous acid forms a tertiary alcohol.



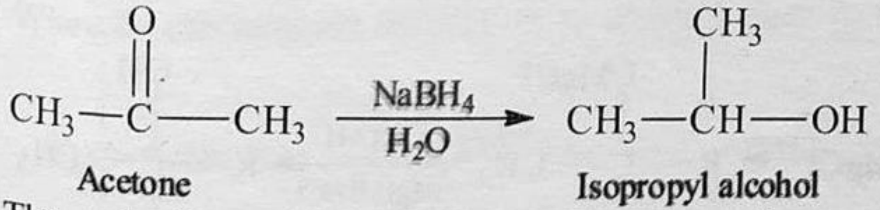
$$CH_3-\overset{\overset{\delta-}{O}}{\overset{\|}{C}}{}^{\delta+}-CH_3 + \overset{\delta-}{C}H_3-\overset{\delta+}{Mg}Cl \longrightarrow CH_3-\underset{CH_3}{\overset{\overset{-\;+}{O}MgCl}{C}}-CH_3 \xrightarrow[-Mg(OH)Cl]{H_2O/H^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

18.1.5.4 Reduction of Aldehydes and Ketones

Metal hydrides such as $NaBH_4$ (sodium borohydride) or $LiAlH_4$ (lithium aluminiumhydride) reduce aldehydes to primary alcohols and ketones to secondary alcohols.



$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H_2O]{NaBH_4} CH_3-CH_2-OH$$



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[H_2O]{NaBH_4} CH_3-\overset{\overset{CH_3}{|}}{CH}-OH$$

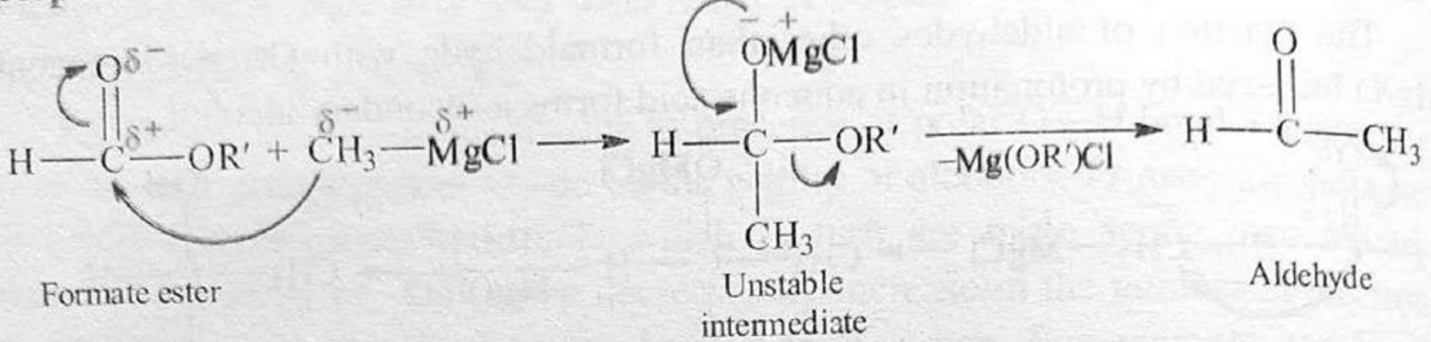
The reduction with $NaBH_4$ needs polar solvents such as water and ethyl alcohol.

18.1.5.5 Reaction of RMgX with Esters

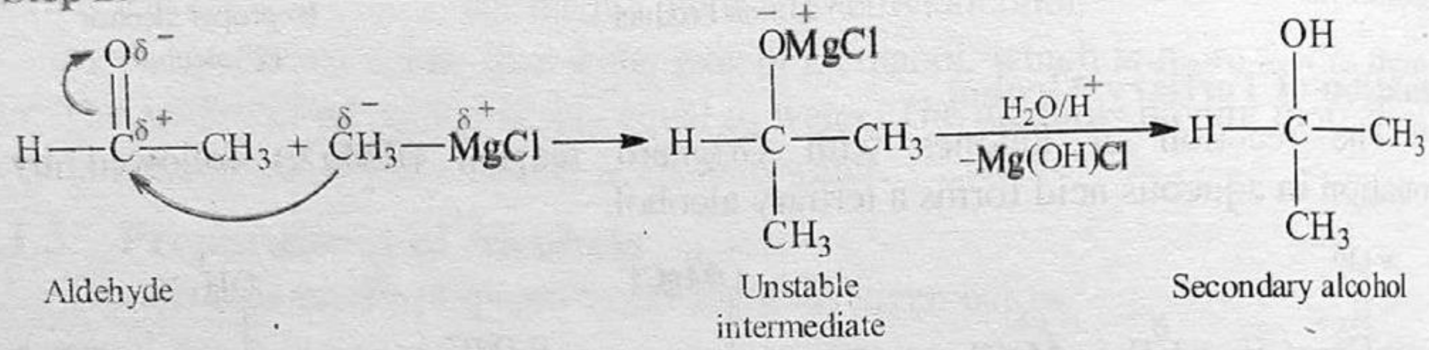
Formation of Secondary Alcohol

Formate esters react with Grignard's reagent to form aldehydes which reacts further with another molecule of Grignard's reagent to form secondary alcohols as a final product.

Step 1:



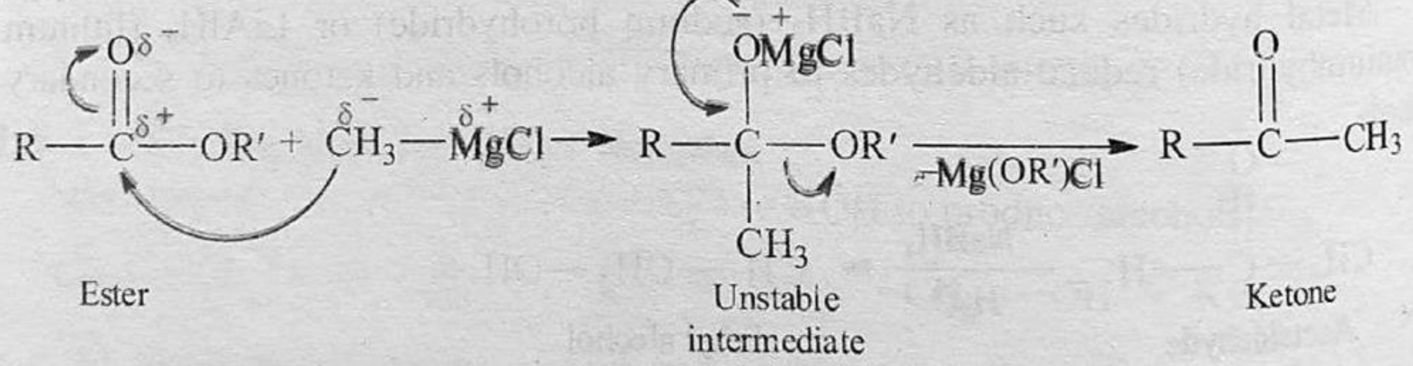
Step 2:



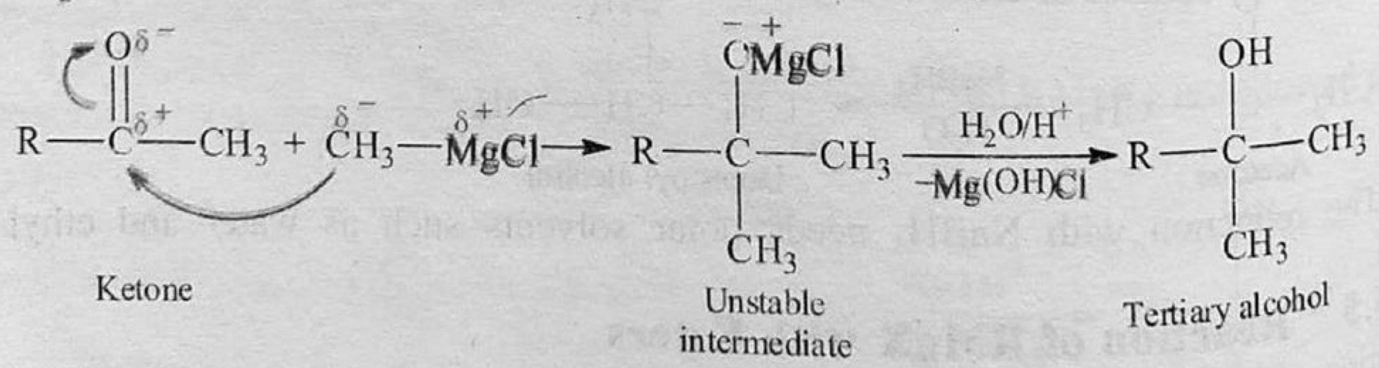
Formation of Tertiary Alcohol

Esters other than formate esters react with Grignard's reagent to form ketones which reacts further with another molecule of Grignard's reagent to form tertiary alcohol as a final product.

Step 1:

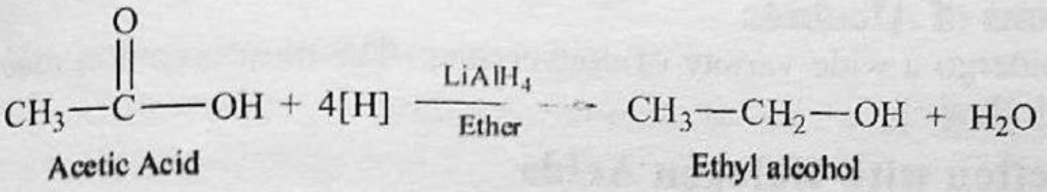


Step 2:



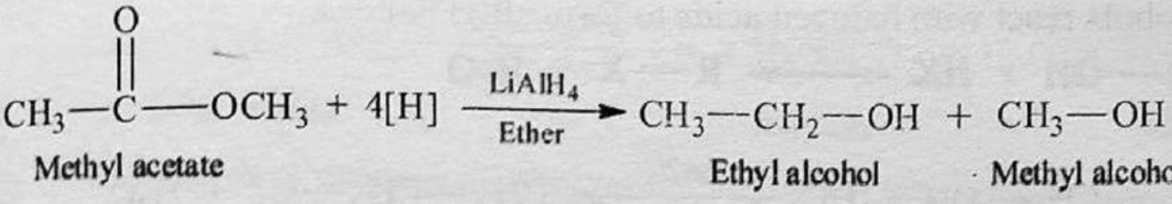
18.1.5.6 Reduction of Carboxylic Acids and Esters

Carboxylic Acids and Esters are easily reduced by strong reducing agents such as $LiAlH_4$. Both carboxylic acids and esters are reduced to alcohols.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} CH_3-CH_2-OH + H_2O$$

Acetic Acid — Ethyl alcohol



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} CH_3-CH_2-OH + CH_3-OH$$

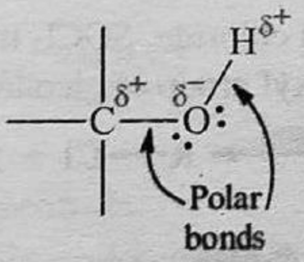
Methyl acetate — Ethyl alcohol — Methyl alcohol

18.1.6 Reactivity of Alcohols

Alcohols are reactive compounds. They act both as electrophiles and nucleophiles. They are attacked by polar or ionic reagents. This is for the reason that:

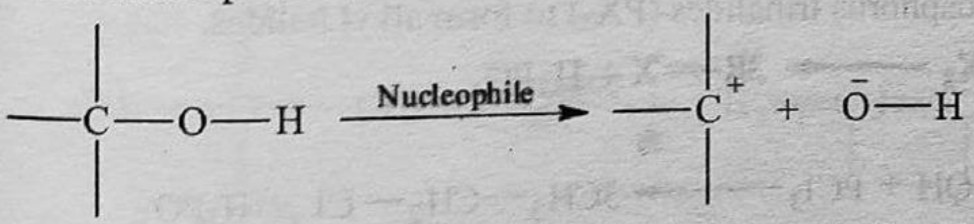
i) The carbon-oxygen (C—O) and hydrogen-oxygen (O—H) bonds are polar due to presence of highly electronegative oxygen atom.

ii) The oxygen atom of alcohols is an electron rich centre. This is due to the presence of two lone pairs of electrons.



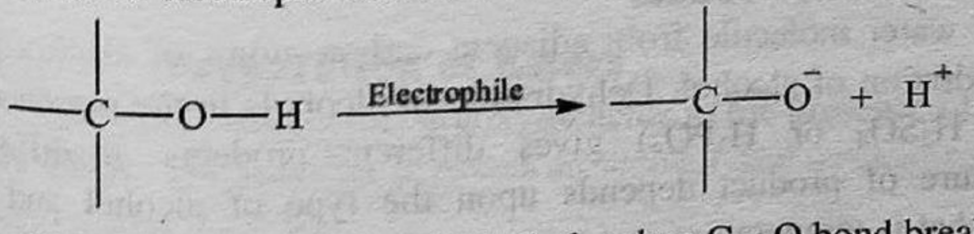
Alcohols react with other reagents in two ways:

i) When nucleophile attacks on an alcohol, then its C—O bond breaks.



$$-\overset{|}{\underset{|}{C}}-O-H \xrightarrow{\text{Nucleophile}} -\overset{|}{\underset{|}{C^+}} + \bar{O}-H$$

ii) When an electrophile attacks on an alcohol, then its O—H bond breaks.



$$-\overset{|}{\underset{|}{C}}-O-H \xrightarrow{\text{Electrophile}} -\overset{|}{\underset{|}{C}}-\bar{O} + \overset{+}{H}$$

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

Tertiary alcohols > Secondary alcohols > Primary alcohols > CH_3OH

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

CH_3OH > Primary alcohols > Secondary alcohols > Tertiary alcohols

18.1.7 Reactions of Alcohols

Alcohols undergo a wide variety of conversions. The most common reactions of alcohols are as follows:

18.1.7.1 Reaction with Halogen Acids

Alcohols react with halogen acids to form alkyl halides.

$$R{-}OH + HX \longrightarrow R{-}X + H_2O$$

For example:

$$CH_3{-}CH_2{-}OH + HCl \xrightarrow{ZnCl_2} CH_3{-}CH_2{-}Cl + H_2O$$

HBr and HI react in the same way but in the absence of catalyst. The reaction of alcohols with HCl in the presence of $ZnCl_2$ is called Lucas test. This test is used to differentiate between primary, secondary and tertiary alcohols due to different speed of reactions. The order of reactivity for halogen acids is:

$$HI > HBr > HCl$$

18.1.7.2 Reaction with $SOCl_2$ and PX_3

Reaction with $SOCl_2$

Alcohols react with thionyl chloride, $SOCl_2$ in the presence of pyridine catalyst to form alkyl chloride. The hydroxyl group of alcohol is replaced by chlorine atom.

$$R{-}OH + SOCl_2 \xrightarrow{\text{Pyridine}} R{-}Cl + SO_2 + HCl$$

For example:

$$CH_3{-}CH_2{-}OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3{-}CH_2{-}Cl + SO_2 + HCl$$

Reaction with PX_3

Alcohols react with phosphorus trihalides (PX_3) to form alkyl halides.

$$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3$$

For example:

$$3CH_3{-}CH_2{-}OH + PCl_3 \longrightarrow 3CH_3{-}CH_2{-}Cl + H_3PO_3$$

18.1.7.3 Dehydration of Alcohols

The removal of water molecule from adjacent carbon atoms of alcohol in a reaction is called dehydration of alcohol. Dehydration of alcohols in the presence of acid catalyst (conc. H_2SO_4 or H_3PO_4) gives different products at different temperatures. The nature of product depends upon the type of alcohol and the conditions of reaction that is temperature and concentration of an acid. The hydroxyl group is removed from α-carbon and hydrogen is removed from β-carbon. The ease of dehydration of alcohols follows the order: 3° > 2° > 1°. This is also the order of the ease of stability of carbocations.

Dehydration of Primary Alcohols

Dehydration of primary alcohols is the most difficult. It requires high temperature and strong acid.

$$CH_3—CH_2—OH \xrightarrow[170–180°C]{Conc.\ H_2SO_4} CH_2{=}CH_2 + H_2O$$

Ethyl alcohol **Ethylene**

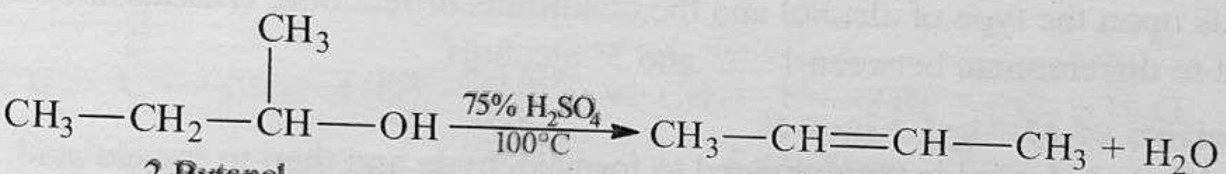
The excess of primary alcohol (ethyl alcohol) at low temperature gives ether.

$$2\,CH_3—CH_2—OH \xrightarrow[140°C]{Conc.\ H_2SO_4} CH_3—CH_2—O—CH_2—CH_3 + H_2O$$

Ethyl alcohol **Diethyl ether**

Dehydration of Secondary Alcohols

The secondary alcohols undergo dehydration at somewhat lower temperatures (100-140°C).

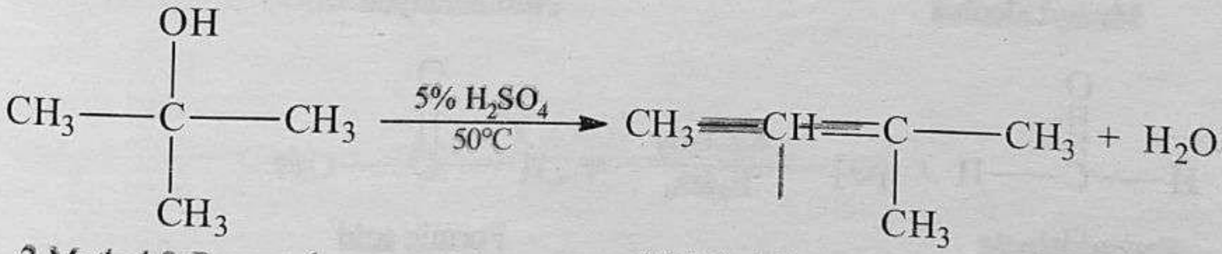


$$CH_3—CH_2—\overset{\overset{\large CH_3}{|}}{CH}—OH \xrightarrow[100°C]{75\%\ H_2SO_4} CH_3—CH{=}CH—CH_3 + H_2O$$

2-Butanol **2-Butene**

Dehydration of Tertiary Alcohols

Tertiary alcohols generally undergo dehydration at temperatures only slightly above room temperature (25-80°C).



$$CH_3—\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}—CH_3 \xrightarrow[50°C]{5\%\ H_2SO_4} CH_3{=}CH{=}\underset{\underset{\large CH_3}{|}}{C}—CH_3 + H_2O$$

2-Methyl-2-Propanol **2-Methyl-1-propene**

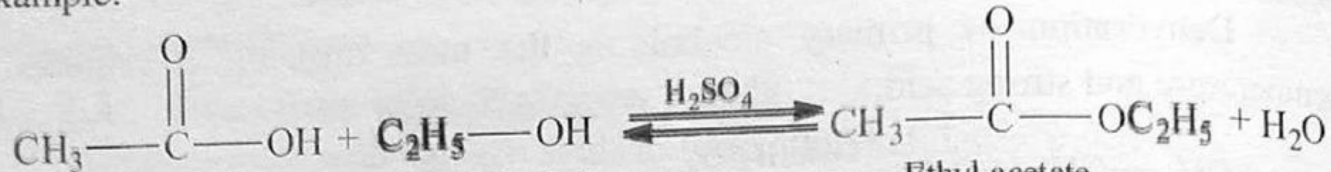
18.1.7.4 Preparation of Esters

Alcohols react with carboxylic acids in the presence of conc. H_2SO_4 catalyst to form esters. The reaction between an alcohol and an acid to form an ester is called esterification.

$$R—\overset{\overset{\large O}{||}}{C}—OH + R—OH \xrightleftharpoons{H_2SO_4} R—\overset{\overset{\large O}{||}}{C}—OR + H_2O$$

Carboxylic acid **Alcohol** **An ester**

For example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + C_2H_5-OH \xrightleftharpoons{H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 + H_2O$$

Acetic acid **Ethyl Alcohol** **Ethyl acetate**

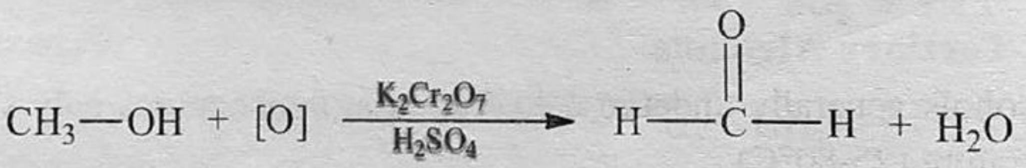
This reaction is reversible. Its reversibility can be controlled by the addition of conc. H_2SO_4 to remove water from the product. In this way, nearly all of the mass of the reactants is converted to products.

18.1.7.5 Oxidation of Alcohols

The addition of oxygen to alcohol molecule in a reaction is called oxidation of alcohol.The oxidation of alcohols in the presence of oxidizing agents gives different products. The reagent most commonly used for the oxidation of alcohols to acids is potassium dichromate dissolved in aqueous sulphuric acid. The nature of product depends upon the type of alcohol and the conditions of reaction. Oxidation of alcohols is used to differentiate between 1°, 2° and 3° alcohols.

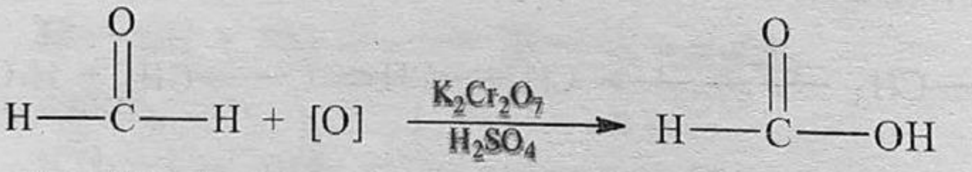
Oxidation of Methyl Alcohol

Methyl alcohol is first oxidized to formaldehyde and then to formic acid.



$$CH_3-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

Methyl alcohol **Formaldehyde**



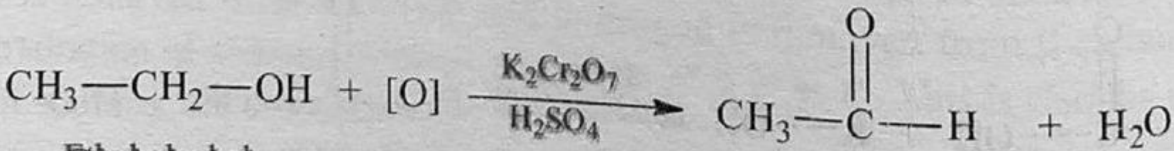
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Formaldehyde **Formic acid**

The reaction can be stopped at aldehyde stage by removing it from the oxidizing medium.

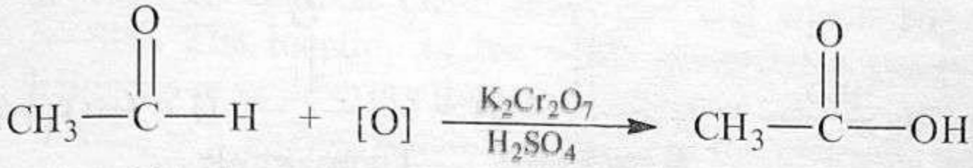
Oxidation of Primary Alcohols

Primary alcohols are first oxidized to aldehydes other than formaldehyde and then to carboxylic acids other than formic acid.



$$CH_3-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

Ethyl alcohol **Acetaldehyde**

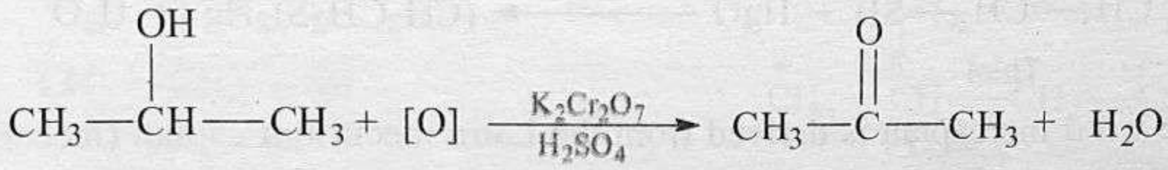


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Acetaldehyde **Acetic Acid**

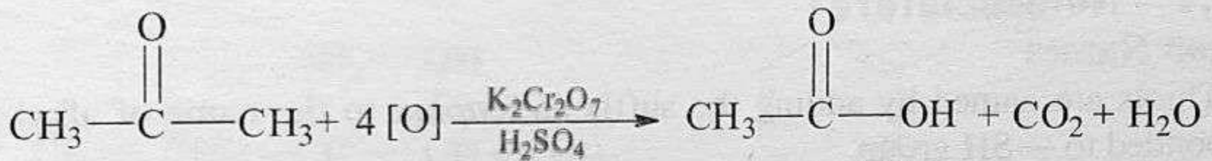
Oxidation of Secondary Alcohols

Secondary alcohols are oxidized to ketones, which are not oxidized further easily. Because they require breaking of carbon-carbon bond. They can be oxidized to acids at drastic conditions.



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

Sec. propyl alcohol **Acetone**

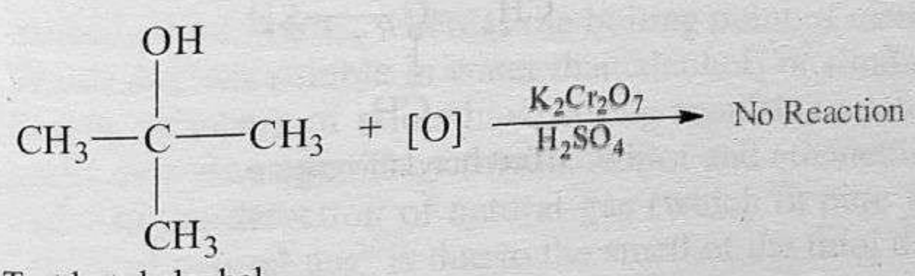


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 4[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CO_2 + H_2O$$

Acetone Acetic Acid

Oxidation of Tertiary Alcohols

Tertiary alcohols are not oxidized under acidic conditions because the carbon bearing the —OH group is attached to three carbon atoms and, hence cannot form a carbon-oxygen double bond.

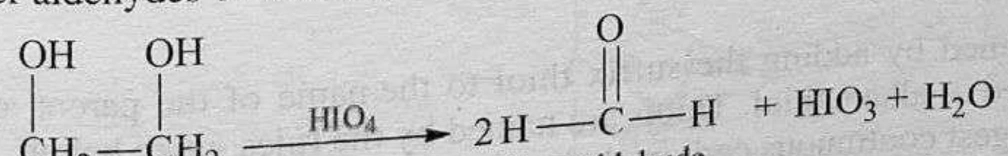


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \text{No Reaction}$$

Tert-butyl alcohol

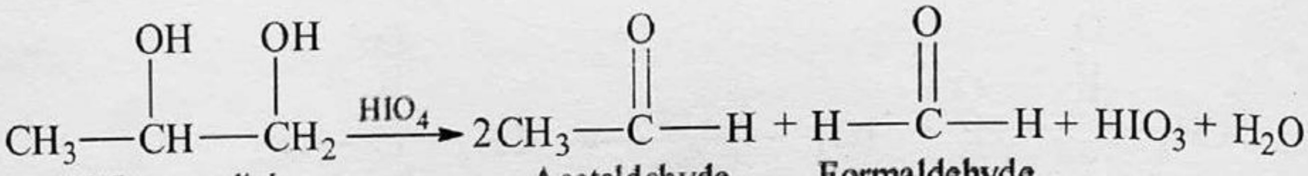
18.1.7.6 Cleavage of 1,2-diols (Glycols)

The vicinal diols are cleaved into two carbonyl compounds by the action of periodic acid, HIO_4 or lead tetraacetate, $(CH_3COO)_4Pb$. The carbonyl compounds can be either aldehydes or ketones.



$$\overset{\overset{\displaystyle OH}{|}}{CH_2}-\overset{\overset{\displaystyle OH}{|}}{CH_2} \xrightarrow{HIO_4} 2H-\overset{\overset{\displaystyle O}{\|}}{C}-H + HIO_3 + H_2O$$

Ethylene glycol **Formaldehyde**



$$CH_3-\overset{OH}{\overset{|}{C}H}-\overset{OH}{\overset{|}{C}H_2} \xrightarrow{HIO_4} 2CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H + HIO_3 + H_2O$$

1,2-Propanediol Acetaldehyde Formaldehyde

18.1.8 The Sulphur Analogous (Thiols, RSH)

Thiols are sulphur analogues of alcohols and are known as thioalcohols. They have mercapto group (—SH) instead of hydroxyl group (—OH). Since they form strong complexes with mercuric oxide that is they capture mercury hence, they are also called mercaptans.

$$2CH_3-CH_2-SH + HgO \longrightarrow (CH_3CH_2S)_2Hg + H_2O$$

Thiol

The word mercaptan is derived from the Latin mecurium captan (mecurium = mercury; captans = capturing).

18.1.8.1 Nomenclature

Common Names

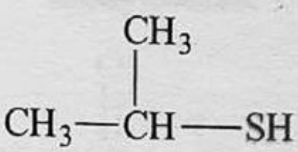
Thiols are named by adding the suffix *mercaptan* to the name of alkyl group that is bonded to —SH group.

CH_3-SH

Methyl mercaptan

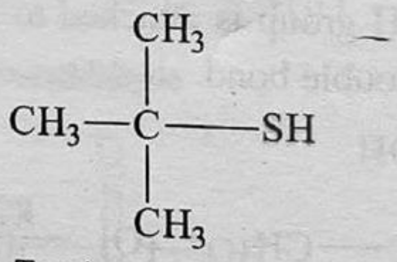
CH_3-CH_2-SH

Ethyl mercaptan



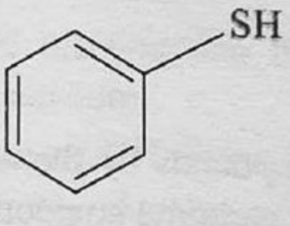
$$CH_3-\overset{\overset{CH_3}{|}}{C}H-SH$$

Isopropyl mercaptan



$$CH_3-\underset{\underset{CH_3}{}}{\overset{\overset{CH_3}{|}}{\underset{|}{C}}}-SH$$

Tert-butyl mercaptan



Phenyl mercaptan

IUPAC Names

Thiols are named by adding the suffix thiol to the name of the parent alkane. Thus they are named as alkanethiol. Thiols are named by the rules given below:

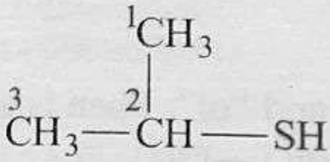
i) Select the longest continuous carbon chain containing the mercapto group.

ii) Number the carbon chain from that end which is nearer to mercapto group (—SH). The location of the —SH group takes priority over alkyl groups and halogens in numbering the parent chain.

iii) If there is a second functional group in the molecule with a higher priority, then the —SH group is indicated by the prefix *sulfanyl*. It may be indicated by the prefix mercapto-. For example, the —OH (higher priority group) takes priority over —SH (lower priority group) in both numbering and naming. Examples are:

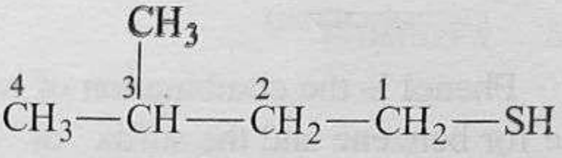
$CH_3—SH$
Methanethiol

$CH_3—CH_2—SH$
Ethanethiol



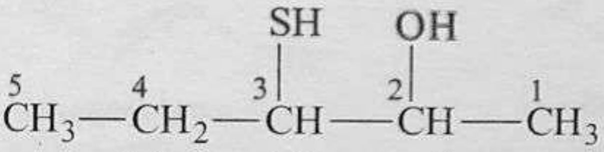
$\overset{3}{C}H_3—\overset{2}{C}H(\overset{1}{C}H_3)—SH$

2-Propanethiol
(Propane-2-thiol)



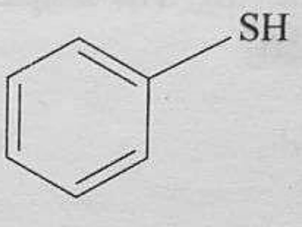
$\overset{4}{C}H_3—\overset{3}{C}H(CH_3)—\overset{2}{C}H_2—\overset{1}{C}H_2—SH$

3-Methyl-1-butanethiol
(3-Methylbutane-1-thiol)



$\overset{5}{C}H_3—\overset{4}{C}H_2—\overset{3}{C}H(SH)—\overset{2}{C}H(OH)—\overset{1}{C}H_3$

3-Sulfanyl-2-pentanol
(β-Mercapto-2-Pentanol)



Benzenethiol

18.1.8.2 Physical Properties

i) Methanethiol is a gas whereas higher members are colourless volatile liquids.

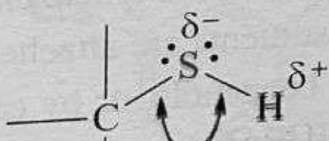
ii) They have considerably lower boiling points than alcohols because they have much weaker intermolecular attractive forces. For example, the boiling point of methanethiol is 6°C, whereas the boiling point of methyl alcohol is 65°C.

iii) Thiols are less soluble in water than alcohols of similar molecular masses.

iv) Lower members of thiols have strong repulsive odours. They smell like that of garlic or rotten egg. They (methanethiol and ethanethiol) are used as odorants to assist in the detection of natural gas (which in pure form is odourless), and the "smell of natural gas" is due to the smell of the thiol used as the odorant.

18.1.8.3 Structure

The functional group of thiol is —SH (mercapto) group bonded to sp^3 hybridized carbon. Their structures are similar to alcohols. The $C\widehat{S}H$ bond angle in methanethiol is 100.3°.



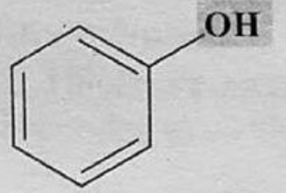
The electronegativity of sulphur and carbon are nearly equal while sulphur is slightly more electronegative than hydrogen. Hence, hydrogen attain partial positive charge and sulphur attains slight negative charge. The sulphur-hydrogen bond is less polar than oxygen-hydrogen bond because sulphur is less electronegative than oxygen.

18.1.8.4 Acidity

Thiols are stronger acids than alcohols. The pK_a value of ethanethiol is 10.5 and that of ethanol is 15.9 in dilute aqueous solution.

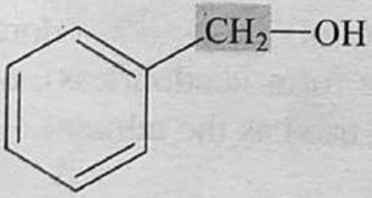
18.2 Phenols

Phenol is the combination of two words that is "phen" and "ol". Phen is an old name for benzene and the suffix "ol" is used for hydroxyl group (—OH). Phenols are those organic compounds in which one or more —OH groups are directly bonded to the carbon of benzene ring. The simplest member of this family is phenol.

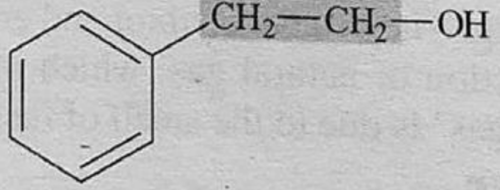


Phenols may be monohydric or polyhydric. It depends on the number of hydroxyl groups attached to the carbon of benzene ring. The phenols containing one —OH are known as monohydric phenols and the phenols containing two or more —OH groups are known as polyhydric phenols.

The aromatic compounds in which hydroxyl (—OH) group is not directly bonded to the benzene ring are not phenols but are called aromatic alcohols. These may be regarded as derivatives of aliphatic alcohols. For example:



Phenylmethanol

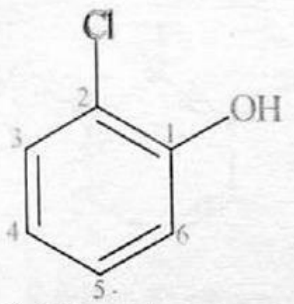


2-Phenylethanol

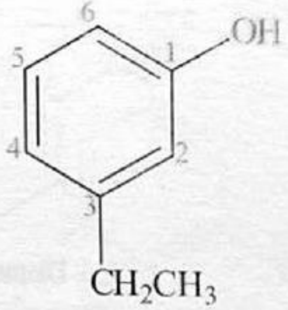
18.2.1 Nomenclature of Phenols

Phenol is the specific name for hydroxybenzene, but the word phenol is also used as the parent name when substituents are attached. We name substituted phenols either as derivatives of phenol, as benzenols, or by common names. Common names are given in parenthesis below IUPAC names. The IUPAC rules for substituted phenols are as:

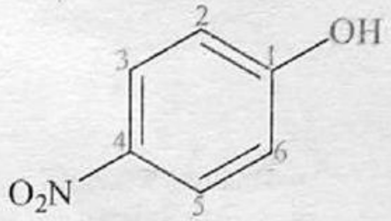
i) In substituted phenols, the position 1 is given to that carbon which has hydroxyl group. For example:



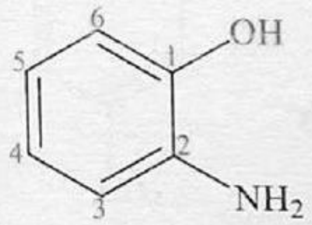
2-Chlorophenol
(*o*-Chlorophenol)



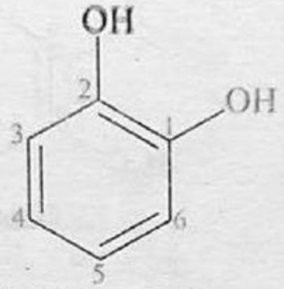
3-Ethylphenol
(*m*-Ethylphenol)



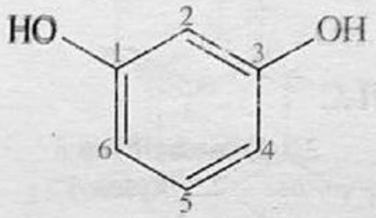
4-Nitrophenol
(*p*-Nitrophenol)



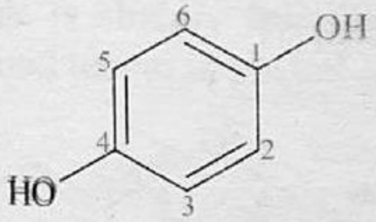
2-Aminophenol
(*o*-Aminophenol)



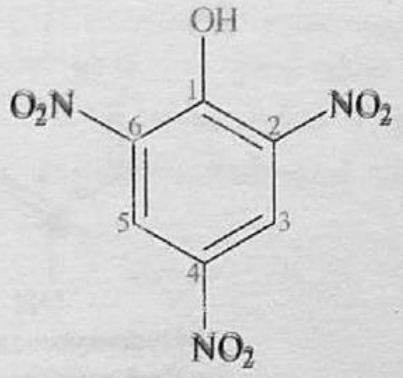
1,2-Benzenediol
(Catechol)



1,3-Benzenediol
(Resorcinol)

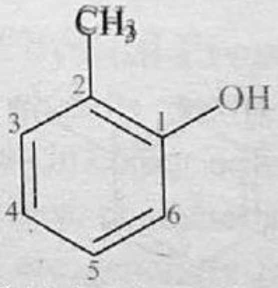


1,4-Benzenediol
(Hydroquinone)

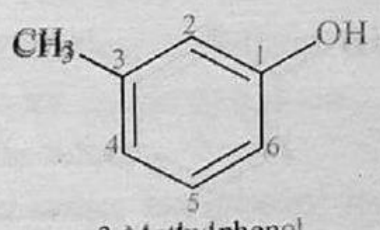


2,4,6-Trinitrophenol
(Picric acid)

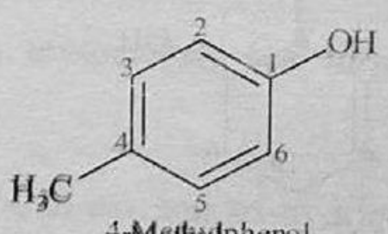
The methylphenols are called cresols.



2-Methylphenol
(*o*-Cresol)

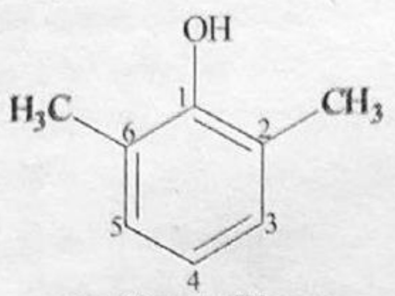


3-Methylphenol
(*m*-Cresol)

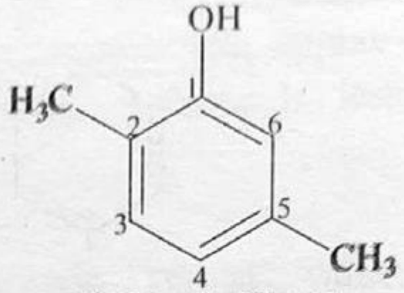


4-Methylphenol
(*p*-Cresol)

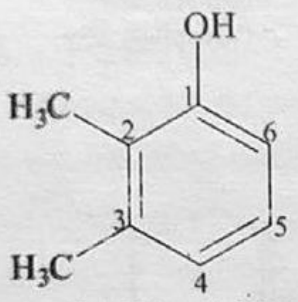
Derivatives of phenols with two methyl groups are called xylenols.



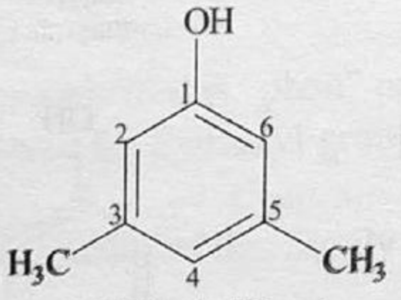
2,6-**DimethylPhenol**
or 2,6-**Xylenol**



2,5-**DimethylPhenol**
or 2,5-**Xylenol**

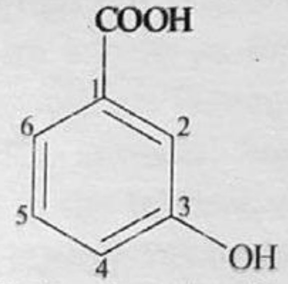


2,3-**DimethylPhenol**
or 2,3-**Xylenol**

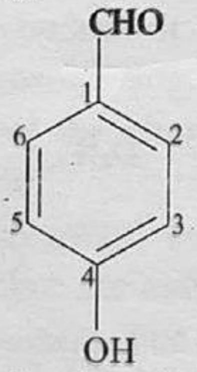


3,5-**DimethylPhenol**
or 3,5-**Xylenol**

ii) If phenol has another functional group which is superior in priority order, then phenols are named as hydroxyl derivatives.



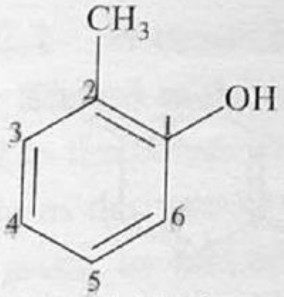
3-**Hydroxy**benzoic acid
(*m*-**Hydroxy**benzoic acid)



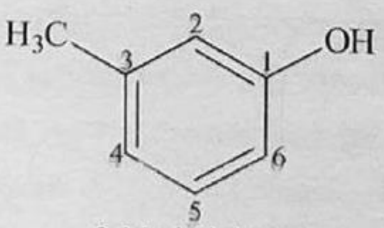
4-**Hydroxy**benzaldehyde
(*p*-**Hydroxy**benzaldehyde)

Isomerism in Phenols

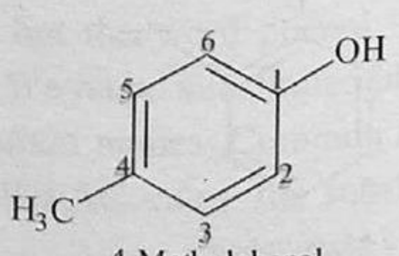
Phenols with two or more substituents can show position isomerism due to different position of substituents. For example, the methylphenol also called cresol has three isomers i.e. *o*-cresol, *m*-cresol and *p*-cresol.



2-Methylphenol
(*o*-Cresol)

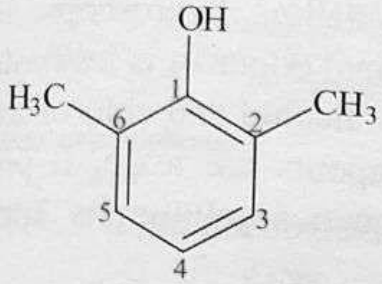


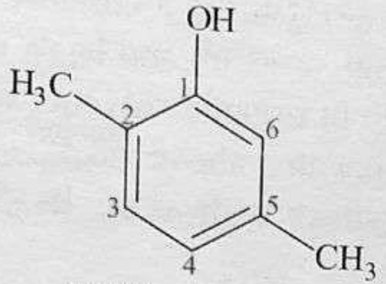
3-Methylphenol
(*m*-Cresol)

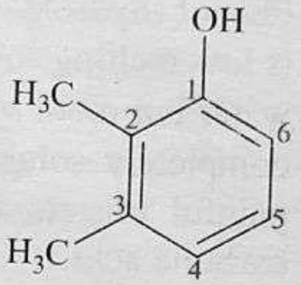


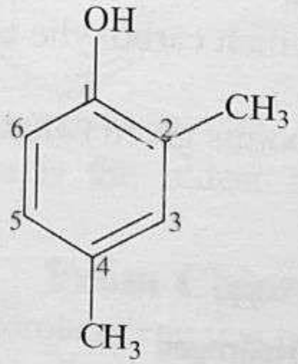
4-Methylphenol
(*p*-Cresol)

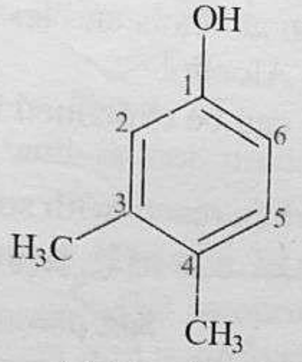
Xylenol has one hydroxyl group and two methyl groups and contains six isomers.

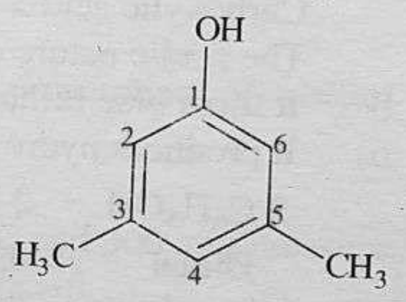

2,6-DimethylPhenol


2,5-DimethylPhenol


2,3-DimethylPhenol

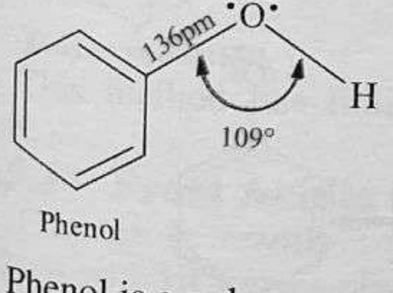

2,4-DimethylPhenol


3,4-DimethylPhenol


3 5-DimethylPhenol

18.2.2 Structure of Phenol

In phenols, the hydroxyl group is bonded to aromatic ring. The oxygen atom of the hydroxyl group has two bond pairs and two lone pairs of electrons, hence, it has bent shape as water molecules. The C$\hat{O}$H bond angle in phenol is 109°. C—O—H bond angle is slightly less than the regular tetrahedral angle (109.5°). the carbon-oxygen bond length in phenol is 136 pm.



Phenol

Phenol is a polar compound and has a dipole moment of 1.54 D.

18.2.3 Physical Properties of Phenols

i) Pure phenols are generally colourless solids at room temperature but turn reddish in colour on exposure to air due to oxidation.

ii) They have characteristic phenolic odour.

iii) They are generally insoluble in water but phenol itself and di- and tri-hydric phenols are fairly soluble.

iv) They usually have higher boiling points than aliphatic alcohols due to presence of strong intermolecular hydrogen bonding and high molecular mass.

v) Phenol (hydroxybenzene) itself is a colourless, crystalline, hygroscopic solid. It is low melting solid (mp. = 43°C) and has a medicinal odour. It is less soluble in water but more soluble in organic solvents such as alcohol and chloroform. It is completely soluble in water above 68.5°. Its vapours are toxic. It produces painful blisters in contact with skin. Its 5% aqueous solution is known as carbolic acid.

18.2.4 Acidity of Phenol

Phenols are more acidic than alcohols and less acidic than carboxylic acids.

Carboxylic acid > Phenol > Alcohol

The acidic nature of phenol can be explained by the points given below:

i) It turns blue litmus red.

ii) It produces hydrogen gas when reacts with sodium.

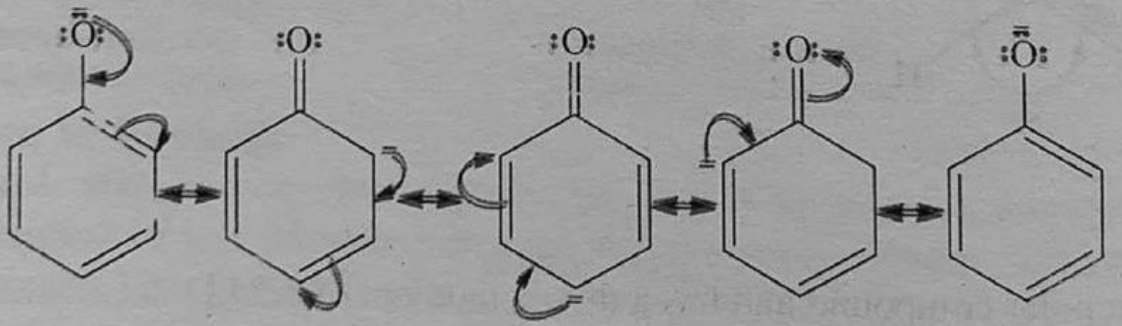
$$\underset{\textbf{Phenol}}{2\,C_6H_5OH} + \underset{\textbf{Sodium}}{2\,Na} \longrightarrow \underset{\textbf{Sod. phenoxide}}{2\,C_6H_5ONa} + \underset{\textbf{Hydrogen}}{H_2}$$

iii) It has ability to produce hydrogen ions in water.

iv) It reacts with a strong base to produce salt and water.

$$\underset{\substack{\textbf{Phenol}\\(\text{Acid})}}{C_6H_5OH} + \underset{\substack{\textbf{Sodium hydroxide}\\(\text{Base})}}{NaOH} \longrightarrow \underset{\substack{\textbf{Sod. phenoxide}\\(\text{Salt})}}{C_6H_5ONa} + \underset{\text{Water}}{H_2O}$$

v) It forms a stable phenoxide ion (phenolate ion) after loss of hydrogen ion. The stability of phenoxide ion as compared to alkoxide ion is due to delocalization of negative charge in the benzene ring. It is shown by the following resonating structures.

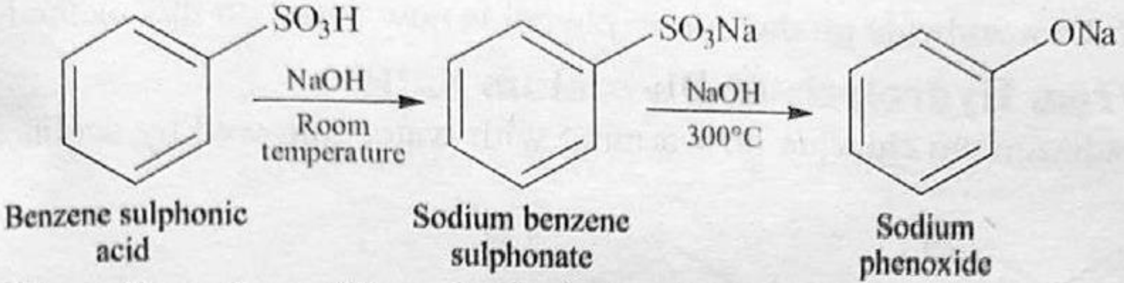


18.2.5 Preparation of Phenol

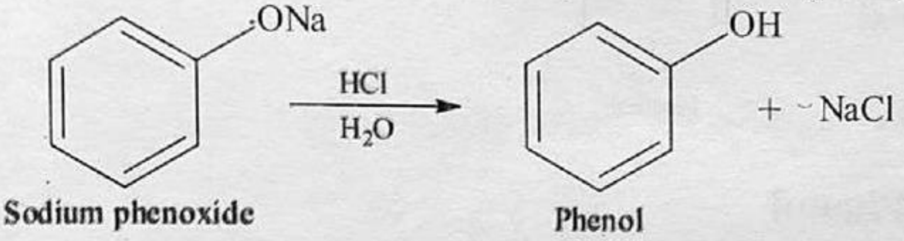
Phenol can be prepared by the following methods:

18.2.5.1 From Benzene Sulphonic Acid

Benzene sulphonic acid reacts with sodium hydroxide to produce sodium benzene sulphonate which on further reaction with NaOH at about 300°C produces sodium phenoxide.



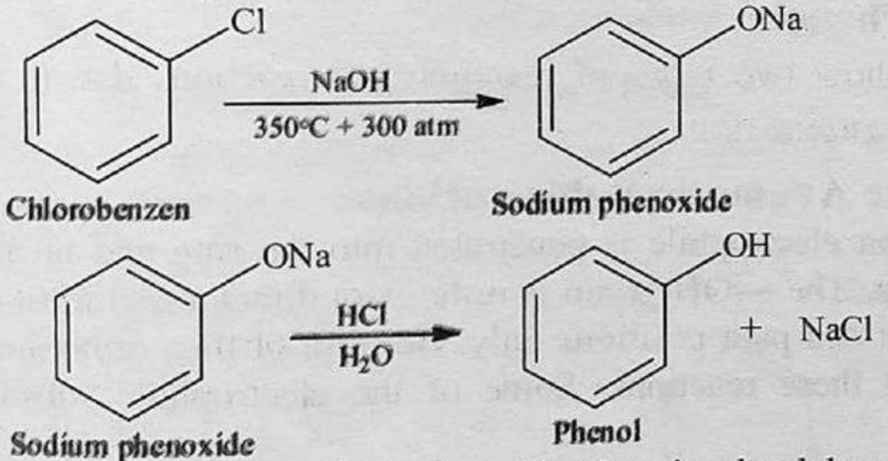
The sodium phenoxide on hydrolysis with HCl gives phenol.



This is the oldest method and is not used for the preparation of phenol nowadays.

18.2.5.2 From Chlorobenzene (Dow's Method)

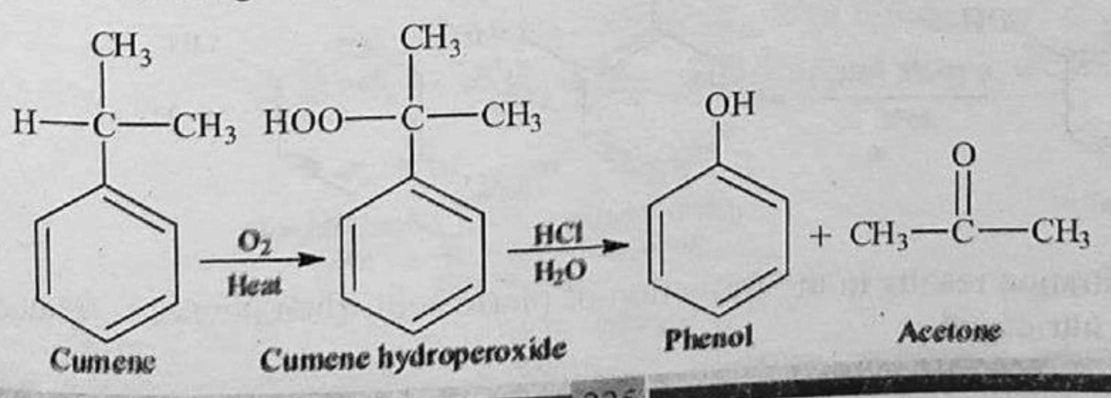
Chlorobenzene reacts with 10% NaOH solution at 350°C and 300 atm pressure to produce sodium phenoxide which on acid hydrolysis gives phenol.



This method has limited application in the laboratory synthesis of simple phenols.

18.2.5.3 From Acidic Oxidation of Cumene

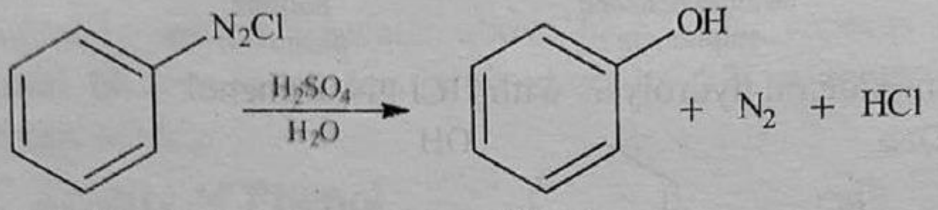
Cumene is readily oxidized by air to produce cumene hydroperoxide on hydrolysis with HCl gives phenol.



Most of the worldwide production of phenol is now based on this method.

18.2.5.4 From Hydrolysis of Diazonium Salts

Benzenediazonium chloride on warming with water followed by acidification, gives phenol.



Benzenediazonium chloride

Phenol

18.2.6 Reactivity of Phenol

The phenolic (—OH) group is electron donating group and increases the electron density at ortho and para positions by donating its electron pair to the benzene ring. This makes the benzene ring of phenol more reactive towards electrophilic substitution reactions. Because of this reason, phenols behave as nucleophiles in most of their reactions.

18.2.7 Reactions of Phenols

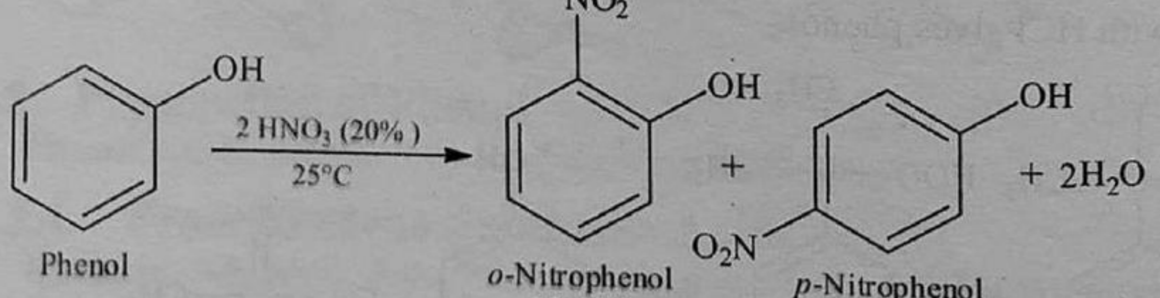
Phenols generally show two types of reactions: (i) reactions due to —OH group (ii) reactions due to benzene ring.

18.2.7.1 Electrophilic Aromatic Substitutions

In these reactions, an electrophile is penetrated into the ring and breaks the electronic cloud of benzene. The —OH group is ortho-para director and most of the substitutions occur at ortho and para positions only. Because of this, ortho and para derivative are obtained in these reactions. Some of the electrophilic substitution reactions of phenols are:

Nitration

Phenol reacts with dilute nitric acid at room temperature to give a mixture of ortho and para nitrophenols.

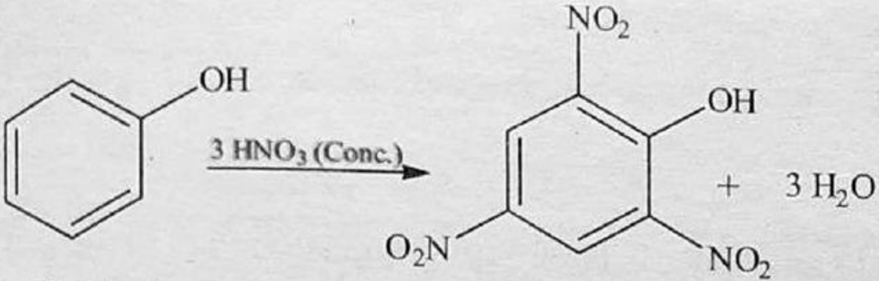


Phenol

o-Nitrophenol 30-40%

p-Nitrophenol 20%

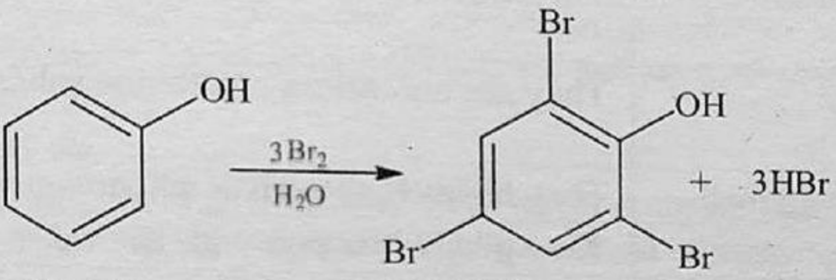
The nitration results in the formation of picric acid when phenol is treated with concentrated nitric acid.



Phenol **2,4,6-trinitrophenol (Picric acid)**

Halogenation

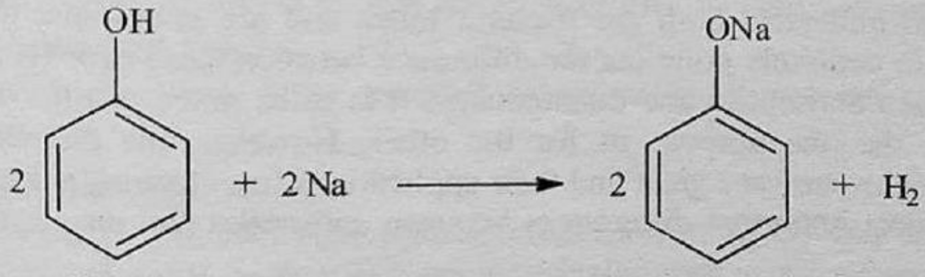
Phenols react with bromine water to produce white precipitate of 2,4,6-tribromophenol.



Phenol **2,4,6-Tribromophenol**

18.2.7.2 Reaction with Sodium Metal

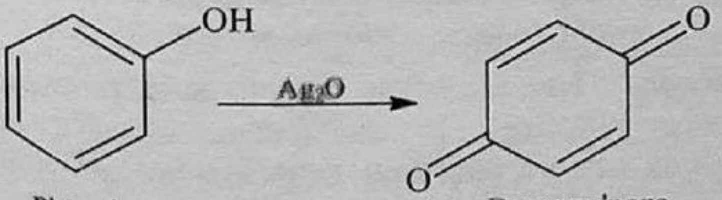
Phenol reacts with sodium metal on warming to form water soluble salt (sodium phenoxide) with release of hydrogen gas.



Phenol **Sodium metal** **Sod. phenoxide**

18.2.7.3 Oxidation

Phenol is oxidized to *p*-benzoquinone in the presence of stronger oxidizing agents. The oxidizing agents used are silver oxide, lead tetraacetate, dichromate, and atmospheric oxygen. Phenols are more easily oxidized than simple alcohols.



Phenol ***p*-Benzoquinone**

18.2.8 Difference between Alcohols and Phenols

The main difference between alcohols and phenols are given in the table:

Alcohol	Phenol
Hydroxyl group is bonded to an alkyl group.	Hydroxyl group is bonded to an aryl group.
Hydroxyl derivatives of alkanes.	Hydroxyl derivatives of benzene.
General formula is R—OH.	General formula is Ar—OH.
They are less acidic.	They are more acidic.
The pK_a value is nearly equal to 16-20.	The pK_a value is nearly equal to 10.
Lower alcohols are generally colourless liquids.	They are colourless crystalline solids.
They have characteristic sweet smell.	They have characteristic phenolic smell.
They have no action with Br_2 water.	They give white ppt. with Br_2 water.
They do not react with NaOH.	They react with NaOH to form phenoxides.

Society, Technology and Science

Antiseptics and Disinfectants

Antiseptic and disinfectants both are bacteria killer and are considered to be antimicrobial. It is hard to definitely point out the difference between these two. There is no real difference between antiseptics and disinfectants. It is to be noted that the same chemicals are used for the one purpose as for the other. However, the differences between these two chemicals are very great and their applications (uses) are significantly different. Some of the most important differences between antiseptics and disinfectants are given in the table.

Antiseptics	Disinfectants
They are mild chemicals that are applied to the skin or body to kill germs.	They are strong chemicals that are applied to the non-living surfaces, spots and places to kill germs.
They are safe and do not harmful to the body of humans and animals. They are used locally outside the body.	They are harmful to the body of humans and animals. They are not applied on the body due to their corrosive nature.
They are used on or in living tissue including skin, oral cavities and open wounds to remove, inhibit the growth of, or inactivate microorganisms.	They are often used to sterilize operation theatres, to disinfectant utensils, doors, floors, etc. and to decontaminate reusable instruments.

Antiseptics	Disinfectants
They are commonly used at healthcare centres or hospitals.	They are commonly found at homes or public places.
Examples are surgical spirit (ethyl alcohol as 60-70% or isopropyl alcohol at least 70%), iodine, dettol, boric acid, listrine, lime, hydrogen peroxide, etc.	Examples are phenol, dettol, formalin, sodium hypochlorite, DDT, etc.

The Role of Disinfectants in Hygiene

Hygiene is a practice or an activity of keeping yourself and your surrounding clean and healthy. Hygiene refers to conditions and practices that prevent illness or the spread of diseases. A good hygiene means to keep your body clean and healthy. Disinfectants are used to kill or inactive germs and other harmful substances.

There are many different chemicals that are used as disinfectants and play key roles in hygiene.

Alcohols

Alcohols such as ethyl alcohol and isopropyl alcohol are widely used as antiseptics and disinfectants. They are used to kill bacteria and viruses.

Phenols

Phenols are widely used as disinfectants in household products.

Sodium Hypochlorite

The 5% solution of sodium hypochlorite is an effective disinfectant for sinks, toilets, etc.

Calcium Hypochlorite

Calcium hypochlorite is used in hospitals as disinfectants for clothing and bedding.

Chlorine and Ozone

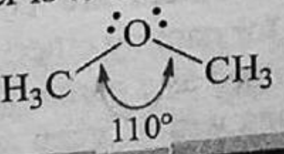
Chorine and ozone gases are used as disinfectants in water treatment to kill harmful bacteria.

Iodine Tincture

It contains 2–7% elemental **iodine** in addition to KI or NaI, dissolved in a mixture of ethanol and water. Iodine tincture is typically used as an antiseptic. It is usually used in hospitals as a disinfectant because it can destroy both bacteria and viruses.

18.3 Ethers

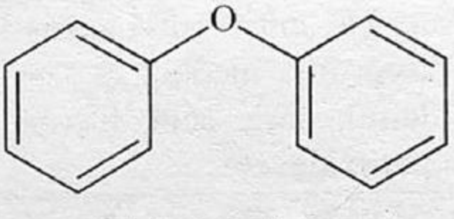
Ethers are compounds in which an oxygen atom is bonded to two alkyl (or aryl) groups. They may be regarded as derivatives of water in which both the hydrogen atoms have been replaced by alkyl (or aryl) groups. They have general formula R—O—R′, where R and R′ may be alkyl or aryl or vinyl groups. The bond angle at the oxygen atom of an ether is to some extent greater than that of water:



There are two types of ethers: (i) symmetrical ethers (ii) unsymmetrical ethers. **In symmetrical ethers**, the two alkyl (or aryl) groups are the same. They are also known as simple ethers. Examples are:

$CH_3—O—CH_3$

Dimethyl ether

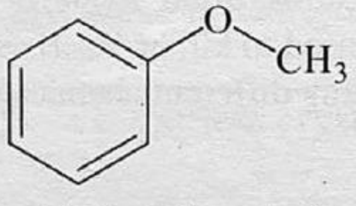


Diphenyl ether

In unsymmetrical ethers, the two alkyl (or aryl) groups are different. They are also known as mixed ethers. Examples are:

$CH_3—O—CH_2—CH_3$

Ethyl methyl ether



Methyl phenyl ether

18.3.1 Nomenclature of Ethers

There are two systems for naming ethers: (i) common system and (ii) IUPAC system. Ethers are usually named by common system. IUPAC system is used for those compounds which have more than one ether linkages.

18.3.1.1 Common System

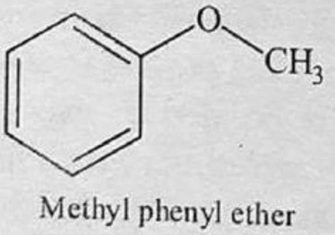
Chemists almost use common names for simple ethers that is, low molecular mass ethers. In common system, the two alkyl (or aryl) groups bonded to oxygen atom are named in alphabetical order and the word ether is added. If the two alkyl (or aryl) groups are similar, then the prefix di- is used. Examples are:

$CH_3—O—CH_3$

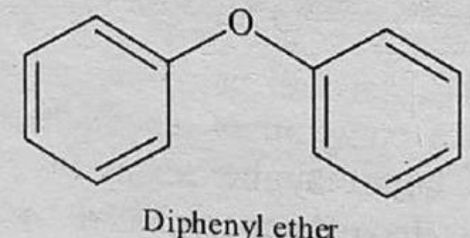
Dimethyl ether

$CH_3—O—CH_2—CH_3$

Ethyl methyl ether



Methyl phenyl ether



Diphenyl ether

18.3.1.2 IUPAC System

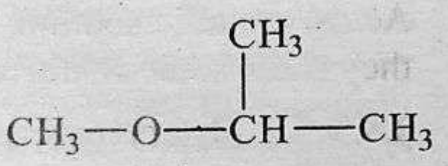
According to this system, ethers are considered as alkoxy derivatives of hydrocarbons. The IUPAC rules for naming ethers are:

i) The larger alkyl group is named as a parent alkane.
ii) The smaller alkyl group along with oxygen atom is taken as alkoxy group.

iii) Number the carbon chain from that end which is nearer to alkoxy group.
Examples are:

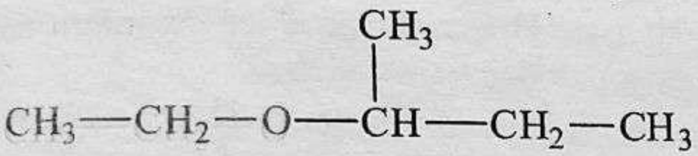
$CH_3—O—CH_3$
Methoxymethane

$CH_3—O—CH_2—CH_3$
Methoxyethane



$$CH_3—O—\overset{\displaystyle CH_3 \atop |}{CH}—CH_3$$

2-Methoxypropane



$$CH_3—CH_2—O—\overset{\displaystyle CH_3 \atop |}{CH}—CH_2—CH_3$$

2-Ethoxybutane

18.3.2 Physical Properties of Ethers

i) Lower ethers such as dimethyl ether and ethyl methyl ether are gases while higher ethers are colourless, volatile liquids.
ii) They have pleasant odour.
iii) They are highly inflammable.
iv) They have low boiling points due to absence of hydrogen bonding.
v) They are slightly soluble in water because they form hydrogen bonds with water. Their solubility decreases with increase in the size of alkyl groups. They are readily soluble in organic solvents such as benzene, chloroform etc.
vi) They are lighter than water.
vii) Ethers are used as a solvent.

18.3.3 Preparation of Ethers

They are prepared by the following methods:

18.3.3.1 Williamson's Synthesis

Alcohols react with sodium metal to give sodium alkoxide which on further reaction with alkyl halide gives ether.

$$2\,R—OH \xrightarrow[-H_2]{2\,Na} 2\,R—ONa \xrightarrow[-NaX]{RX} R—O—R$$

This is the most important and widely used method for the preparation of ethers.

18.3.3.2 Reaction of Alkyl Halides with Dry Silver Oxide

Alkyl halides react with silver oxide on heating to produce ether.

$$2R—X + Ag_2O \longrightarrow R—O—R + 2AgX$$

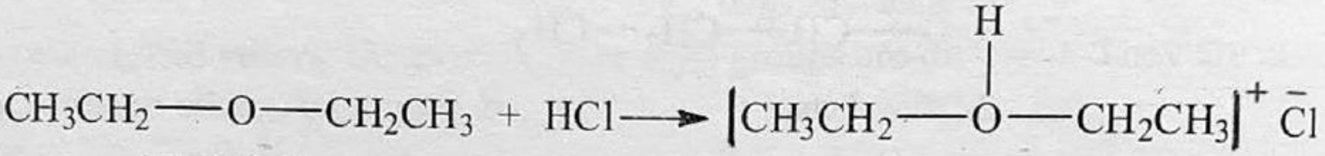
18.3.5 Reactivity of Ethers

Ethers are stable compounds. They are less reactive than alcohols but are considerably reactive than alkanes. They are less reactive because of the absence of active hydrogen bonded to oxygen as present in alcohols. They are reactive only when the oxygen is protonated in an acidic medium. They do not react with bases, dil. Acids, metallic sodium, reducing agents and oxidizing agents in cold state. However, they show some characteristic reactions.

18.3.5 Reactions of Ethers

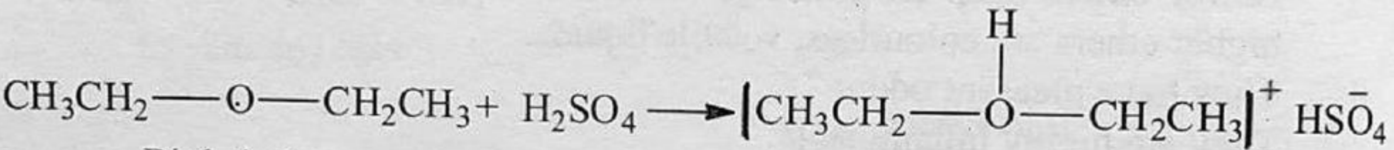
18.3.5.1 Reaction with Cold Conc. Acids

Ethers react with cold conc. HCl or H_2SO_4 to produce oxonium salts. For example:



$$CH_3CH_2—O—CH_2CH_3 + HCl \longrightarrow \left[CH_3CH_2—\overset{\overset{H}{|}}{O}—CH_2CH_3\right]^+ \bar{Cl}$$

Diethyl ether　　Diethyl oxonium chloride

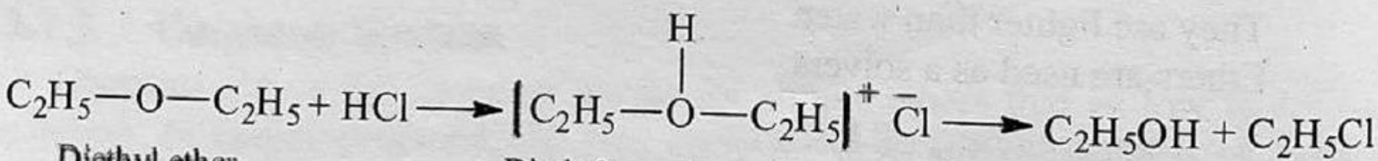


$$CH_3CH_2—O—CH_2CH_3 + H_2SO_4 \longrightarrow \left[CH_3CH_2—\overset{\overset{H}{|}}{O}—CH_2CH_3\right]^+ H\bar{SO_4}$$

Diethyl ether　　Diethyl oxonium hydrogen sulphate

18.3.5.2 Reaction with Hot Concentrated Acids

Ethers react with hot concentrated HCl or HI to produce an alcohol and alkyl halide.



$$C_2H_5—O—C_2H_5 + HCl \longrightarrow \left[C_2H_5—\overset{\overset{H}{|}}{O}—C_2H_5\right]^+ \bar{Cl} \longrightarrow C_2H_5OH + C_2H_5Cl$$

Diethyl ether　　Diethyl oxonium chloride　　Ethyl alcohol　　Ethyl chloride

If an excess of an acid is used, the alcohol so obtained reacts further with HX to give alkyl halides.

$$CH_3CH_2—OH + HCl \longrightarrow CH_3CH_2—Cl + H_2O$$

Ethyl alcohol　　Ethyl chloride

Society, Technology and Science

Use of Ether as Anesthesia

Ether is colourless, volatile and highly flammable liquid with a characteristic smell. Diethyl ether was one of the first chemicals used as an anesthetic in hospitals. **Anesthetic** is a substance that is used to cause loss of sensation or consciousness in order to undergo surgery without pain. The three important early anesthetics were diethyl ether, chloroform and nitrous oxide. Diethyl ether is safer anesthetic than chloroform and more effective than nitrous oxide. Ether was safe, easy to use, and remained the standard general anesthetic until the 1960s. Since then, ether is no longer used in advanced countries (Europe and America) as an anesthetic because it is extremely flammable and has prolonged anesthesia recovery. In these countries, the use of ether was displaced by less flammable and safer fluorinated hydrocarbons such as haloethane. Ether is still used as an anaesthetic these days in some un-developed countries (third world countries) because of its cheapness.

Summary of Facts and Concepts

- Alcohols are hydroxyl derivatives of alkanes while phenols are hydroxyl derivatives of benzene.
- Alcohols are compounds in which hydroxyl group (—OH) is bonded to saturated carbon atom while phenols are those organic compounds in which one or more —OH groups are directly bonded to the carbon of benzene ring. General formula of alcohol is ROH and that of phenol is PhOH.
- Alcohols are categorised into two major groups: (i) Monohydric alcohols (ii) polyhydric alcohols. Monohydric alcohols have only one hydroxyl group while polyhydric alcohol have two or more hydroxyl groups in their structures. Ethyl alcohol is the example of monohydric while glycerine is the example of polyhydric alcohols.
- 95% pure ethyl alcohol is called rectified alcohol and 100% pure ethyl alcohol is called absolute alcohol.
- Alcohols are polar compounds with oxygen carrying a partial negative charge and both the carbon and hydrogen bonded to it carrying partial positive charges.
- The boiling points of alcohols are higher than those of hydrocarbons with similar molecular mass. This is due to presence of hydrogen bonding in alcohols.
- Alcohols are acidic in nature due to presence of polar O—H bond. Greater the polarity of —OH group, greater would be the acidity of alcohols. Primary alcohols are more acidic than secondary alcohols which in turn are more acidic than tertiary alcohols.
- Alcohols are reactive organic compounds. They act both as electrophiles and nucleophiles. They undergo a wide variety of conversions—the majority of which are either oxidation or reduction type reactions.
- An alcohol undergoes dehydration when it is heated with an acid. The major product of alcohol dehydration is the more stable alkene. Tertiary alcohols are the easiest to dehydrate, and primary alcohols are the hardest.
- Thiols are sulphur analogues of alcohols and are known as thioalcohols. They have mercapto group (—SH) instead of hydroxyl group (—OH). Thiols are stronger acids and have lower boiling points than alcohols. Because the S—H

bond is almost nonpolar, the physical properties of thiols are more like those of hydrocarbons of similar molecular mass.

- In an ether, an oxygen atom (—O—) is connected by single bonds to two alkyl or aromatic groups. Ethers are formed by a condensation reaction of two molecules of alcohol. Ethers of low molecular mass have low boiling points, while ethers with larger alkyl groups have higher boiling points due to London dispersion forces between the alkyl groups. Ethers are often used as solvents for organic reactions.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) The hydrogen bonding is present in:

(a) C_6H_6 (b) C_2H_5OH

(c) C_2H_5Br (d) $CH_3—O—CH_3$

ii) Which compound is more soluble in water?

(a) Phenol (b) Ethyl alcohol

(c) Dimethyl ether (d) 1-Hexanol

iii) Oxidation of ethyl alcohol gives:

(a) Formaldehyde (b) Acetaldehyde

(c) Acetone (d) Ether

iv) Methanol is also known as

(a) Absolute alcohol (b) Rectified alcohol

(c) Wood spirit (d) Methylated alcohol

v) Rectified spirit contains about:

(a) 85% ethyl alcohol (b) 90% ethyl alcohol

(c) 95% ethyl alcohol (d) 100% ethyl alcohol

vi) Alcohols are prepared by the:

(a) Hydration of alkenes. (b) Hydrogenation of alkenes.

(c) Halogenation of alkenes. (d) Oxidation of alkenes.

vii) The protonated ether is called:

(a) Oxide ion (b) Carbon ion

(c) Hydronium ion (d) Oxonium ion

viii) Which statement is true about phenol?

(a) It is more acidic than acetic acid

(b) It is more acidic than ethyl alcohol.

(c) It turns red litmus blue.

(d) It does not react with sodium.

ix) Which one of the following is the isomer of dimethyl ether?

(a) CH_3CH_2OH (b) CH_3CHO

(c) CH_3COOH (d) $HCOOCH_3$

x) Which statement is correct about ether?

(a) Lower ethers are liquids at room temperature.

(b) They are crystalline solids at room temperature.

(c) They are highly inflammable.

(d) They are denser than water.

Short Answer Questions

Q.1. Why phenols are more acidic than alcohols?

Q.2. Why the boiling point of alcohol is higher than ether?

Q.3. Can ether form a hydrogen bond with water?

Q.4. Why ethers are considered to be good solvents?

Q.5. Ethers are less dense than liquid water, how?

Q.6. Phenols are more reactive than benzene, why?

Q.7. Explain why the boiling points of alcohols and phenols are much higher than those of alkanes and ethers?

Q.8. Why phenols have higher boiling points than alcohols?

Q.9. Which are more soluble in water, alcohols or phenols?

Q.10. What is the difference between primary and secondary alcohols?

Q.11. What do you know about rectified and absolute alcohols?

Long Answer Questions

Q.1. What are alcohols? How are they classified?

Q.2. How will you distinguish between primary, secondary and tertiary alcohols?

Q.3. Describe the nomenclature of alcohols.

Q.4. Draw structures for the following alcohols:

i) 1-propanol

ii) 2-butanol

iii) 1,3-butanediol

iv) 5-methyl-2-hexanol

v) 4-ethyl-3-heptanol

vi) 2,2,4,4-tetramethyl-3-pentanol

vii) 3-chloro-1,2-propanediol

viii) 2,3,4-pentanetriol

Q.5. Draw structures for the following ethers:

i) Methoxymethane

ii) Phenoxybenzene

iii) 2-methoxypropane
iv) 1,2-diphenoxypropane
v) 1-ethoxy-4-methylbenzene

Q.6. Draw structures and then give IUPAC names to the following compounds.
i) Dimethyl ether
ii) Ethylmethyl ether
iii) Methylphenyl ether
iv) Ethyl alcohol
v) Sec. propyl alcohol
vi) Propylene glycol

Q.7. Explain the structure and acidity of alcohols.

Q.8. Describe the methods for the preparation of alcohols.

Q.9. What do you know about reactivity of alcohols?

Q.10. Give physical and chemical properties of alcohols.

Q.11. What are thiols? Describe the nomenclature of thiols.

Q.12. Give physical properties and explain structure and acidity of thiols.

Q.13. What are phenols? Explain nomenclature of phenols.

Q.14. Describe structure and acidity of phenol.

Q.15. Write down four different methods for the preparation of phenols.

Q.16. Explain reactivity of phenols.

Q.17. Give physical and chemical properties of phenols.

Q.18. What is the difference between alcohols and phenols?

Q.19. What are ethers? What do you know about simple and mixed ethers?

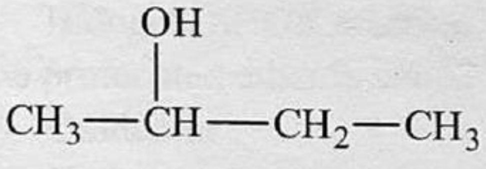
Q.20. Describe nomenclature of ethers.

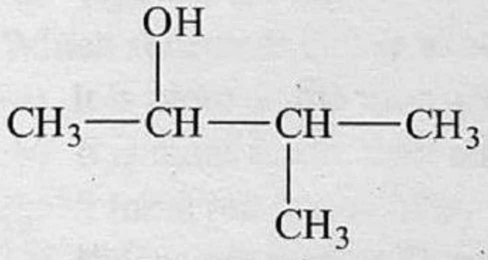
Q.21. Describe the preparation of ethers by (i) Williamson's Synthesis (ii) the reaction of alkyl halides with dry silver oxide.

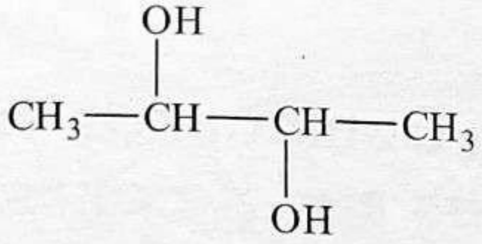
Q.22. Explain reactivity of ethers.

Q.23. What are the physical and chemical properties of ethers?

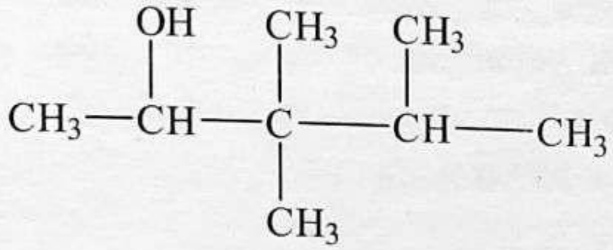
Q.24. Give IUPAC names to the structures given below:

i)

$CH_3-\overset{OH}{CH}-CH_2-CH_3$

ii)

$CH_3-\overset{OH}{CH}-\underset{CH_3}{CH}-CH_3$

iii) 

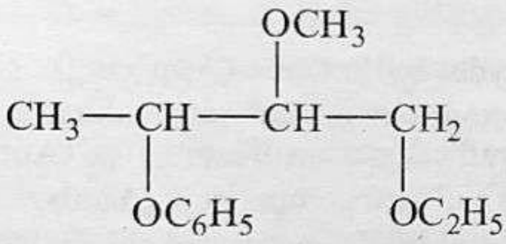
$$CH_3-\overset{OH}{\overset{|}{CH}}-\underset{\underset{OH}{|}}{CH}-CH_3$$

iv) 

$$CH_3-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

v) $CH_3-CH_2-O-CH_3$

vi) $CH_3-CH_2-O-C_6H_5$

vii) 

$$CH_3-\underset{\underset{OC_6H_5}{|}}{CH}-\overset{OCH_3}{\overset{|}{CH}}-\underset{\underset{OC_2H_5}{|}}{CH_2}$$

Q.25. What are locants, prefixes, parent compound and suffixes in 3-methyl-2-pentanol?

Q.26. Describe isomerism in alcohols and phenols.

Q.27. How many isomers are possible for $C_4H_{10}O$? Draw their structures.