28

ALCOHOLS, PHENOLS AND ETHERS

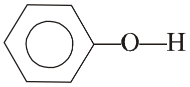
So far you have learnt the chemistry of hydrocarbons which serve as basic skeleton for the attachment of various functional groups to give a large number of their derivatives. In the last lesson, we discussed one such class of compounds *viz halogen derivatives of hydrocarbons*. Another very useful and important catagory of hydrocarbon derivatives is that of compounds containing functional groups in which the carbon atom is linked to an oxygen atom.

We have devoted two lessons for the study of these compounds. In this lesson, you will study about compounds containing carbon-oxygen single bond ($-\text{C}-\text{O}$) whereas the next lesson deals with compounds containing carbon-oxygen double-bond ($\rangle\text{C}=\text{O}$).

Among the compounds with carbon-oxygen single bond are the classes of *alcohols, phenols* and *ethers* having the following general structures.

R—O—H

Alcohol



Phenol

R—O—R′

Ether

R/R′ can also be aromatic

These are very important categories of compounds both in the industry and in the synthesis of other organic compounds. You will study each of these classes of compounds in this Lesson.

Objectives

After reading this lesson, you should be able to

- Classify alcohols as primary, secondary or tertiary;
- Name simple alcohols according to IUPAC system of nomenclature;
- List general methods of preparation of alcohols;
- Discuss the properties of alcohols in the light of their structure;

- Explain various reactions exhibited by alcohols to give other categories of organic compounds;
- Give the names of common phenolic compounds;
- Describe the laboratory and industrial methods of preparation of phenols;
- Explain the greater acidity of phenols as compared to alcohols;
- Discuss the reactions of phenols;
- Name ethers according to the IUPAC system of nomenclature;
- Describe the general methods of preparation of ethers and
- Explain the important reactions of ethers.

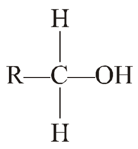
28.1 Alcohols

Alcohols are organic compounds that have one or more hydroxy (-OH) groups bonded to the *carbon atoms in aliphatic compounds*. They occur widely in nature and have many industrial and pharmaceutical applications. For example, methanol and ethanol are two industrially important alcohols.

CH_3-OH	CH_3CH_2-OH
Methanol	**Ethanol**
(Methyl alcohol)	**(Ethyl alcohol)**

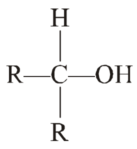
28.1.1 Classification and Nomenclature of Alcohols

Alcohols are classified as *primary* (1º), *secondary* (2º) or *tertiary* (3º) depending upon whether the number of alkyl groups bonded to the carbon atom bearing the hydroxy group is one, two or three, respectively.



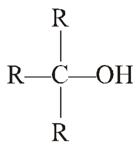
$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

primary alcohol



$$R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-OH$$

secondary alcohol



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-OH$$

tertiary alcohol

According to the IUPAC system of nomenclature, alcohols are called **alkanols**. They are named as the derivatives of the corresponding alkane in which the *-e* of the alkane is replaced by *-ol* .

The procedure for nomenclature involves the following steps:

Step 1: Select the longest carbon chain which contains the carbon atom bearing the –OH group. Count the number of carbon atoms and identify the corresponding alkane. From the name of this alkane, drop the final *e* and suffix *-ol* in its place. This gives the root name or the parent name.

Step 2: Number the carbon chain starting from the end nearest to the hydroxy group. The number of the carbon atom bearing the hydroxy group is indicated before *-ol* in the name.

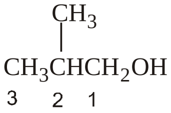
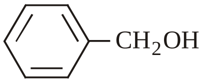
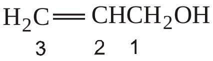
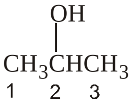
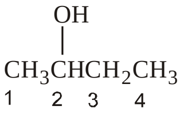
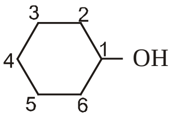
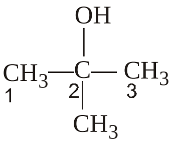
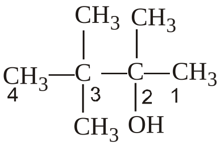
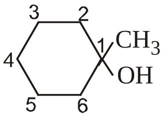
Step 3: Number the other substituents according to their position on the chain.

Step 4: Write the name of the alcohol by listing the substituents in the alphabetical order alongwith their position.

You may remember from Lesson 25 that the hydroxyl group takes precedence over double and triple bonds.

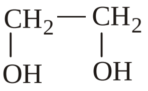
Table 28.1 illustrates some common alcohols and their IUPAC and common names. Go through them in light of the steps given above for nomenclature.

Table 28.1 : Some common Alcohols and their Names

Primary Alcohol	 **2-Methylpropan-1-ol** **(Isobutyl alcohol)***	 **Phenylmethanol** **(Benzyl alcohol)**	 $\underset{3}{CH_3}\underset{2}{CH}\underset{1}{CH_2OH}$ **1-Propanol** **(*n*-Propyl alcohol)**  $\underset{3}{H_2C}{=}\underset{2}{CH}\underset{1}{CH_2OH}$ **Prop-2-en-1-ol**
Secondary Alcohol	 **Propan-2-ol** **(*Iso*propyl alcohol)**	 **Butan-2-ol** **(*sec* Butyl alcohol)**	 **Cyclohexanol** **(Cyclohexyl alcohol)**
Tertiary Alcohol	 **2-Methylpropan-2-ol** **(*tert*-Butyl alcohol)**	 **2,3,3-Trimethylbutan-2-ol**	 **1-Methylcyclohex-1-ol**

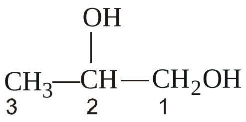
* The names given in the brackets are common names.

In the above examples, only one -OH group is present in the molecule. These alcohols are called **monohydric** alcohols. Alcohols having **two hydroxyl** groups in a molecule are known as **dihydric alcohols** or **diols** or **glycols**. Examples of some diols are shown below :



Ethane-1,2-diol

(Ethylene glycol)

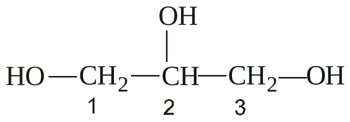


Propane-1,2-diol

(Propylene glycol)

Note that the term *glycol* generally means 1,2-diol or a **vicinal** diol. In these diols, the two hydroxyl groups are present on the adjacent carbon atoms.

Similarly, alcohols having *three* hydroxyl groups are called *trihydric* alcohols. 1,2,3-propanetriol which is commanly known as *glycerol*, is a trihydric alcohol.



$$HO-\underset{1}{CH_2}-\overset{\displaystyle OH}{\underset{2}{CH}}-\underset{3}{CH_2}-OH$$

1,2,3-Propanetriol
(Glycerol)

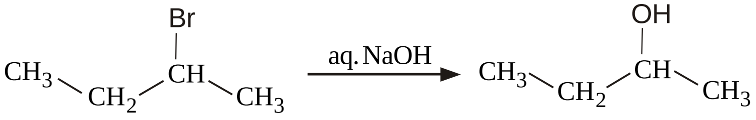
28.1.2 General Methods of Preparation

Alcohols are synthesized by the following general methods. You might have come across some of these methods in previous lessons. Let us now study these methods.

1. Hydrolysis of Haloalkanes

Haloalkanes can be converted to corresponding alcohols using aqueous sodium or potassium hydroxide or water as nucleophiles.

$$\underset{\textbf{Chloroethane}}{CH_3CH_2Cl} + NaOH(aq.) \longrightarrow \underset{\textbf{Ethanol}}{CH_3CH_2OH} + NaCl$$



2-Bromobutane **Butan-2-ol (90%)**

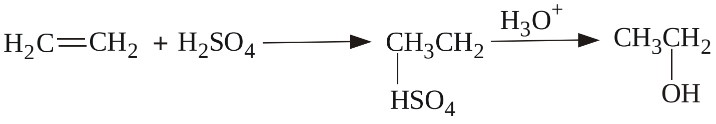
2. From hydration of Alkenes

Hydration means addition of water molecule. In case of alkenes, hydration is the addition of H^+ and OH^- across the double bond to give alcohols.

Alkenes can be hydrated by the following methods:

(i) Acid-catalysed Hydration

Alkenes can be hydrated to yield alcohols in the presence of acid catalysts.

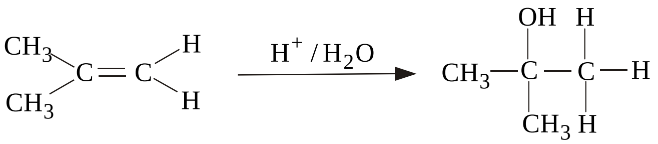


$$\underset{\textbf{Ethene}}{H_2C{=}CH_2} + H_2SO_4 \longrightarrow \underset{\textbf{Ethyl hydrogen sulphate}}{\underset{\displaystyle HSO_4}{CH_3CH_2}} \xrightarrow{H_3O^+} \underset{\textbf{Ethanol}}{\underset{\displaystyle OH}{CH_3CH_2}}$$

Ethene **Ethyl hydrogen sulphate** **Ethanol**

The reaction proceeds via alkyl hydrogen sulphate and this method is used for the industrial preparation of ethanol.

In case of unsymmetric alkenes, the addition follows Markovniokov's rule.



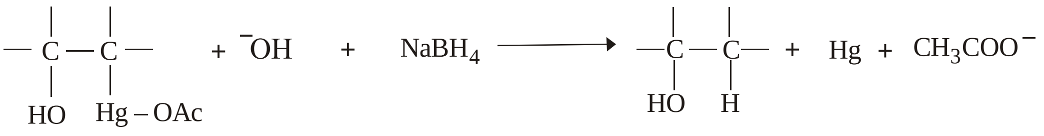
2-Methylpropene **2-Methyl-2-propanol**

(ii) Oxymercuration-demercuration

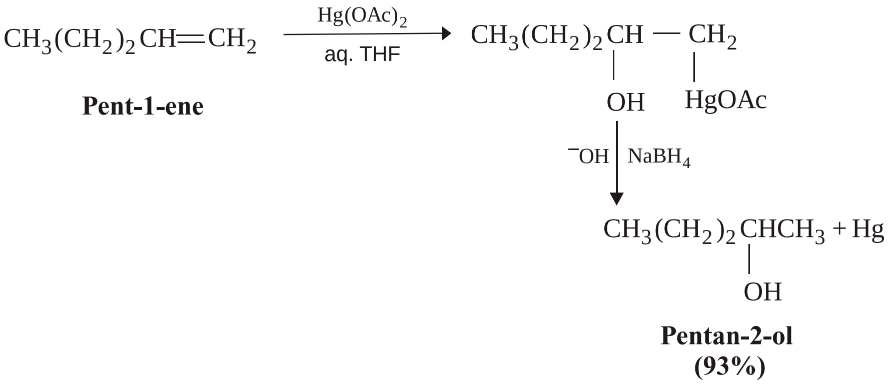
Alkenes react with mercury (II) acetate, i.e. mercuric acetate [$Hg(O\overset{\overset{O}{\|}}{C}CH_3)_2$ also represented as $Hg(OAc)_2$] in aqueous tetrahydrofuran (THF) solvent to give hydroxyalkyl mercury compounds which are reduced to alcohols by sodium borohydride.

Step 1: Oxymercuration

Step 2: Demercuration

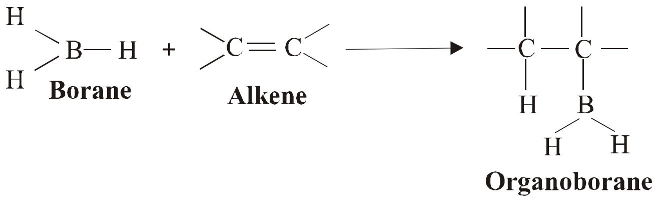


This method gives very good yield of alcohols and here also, the addition takes place in Markovnikov's fashion.

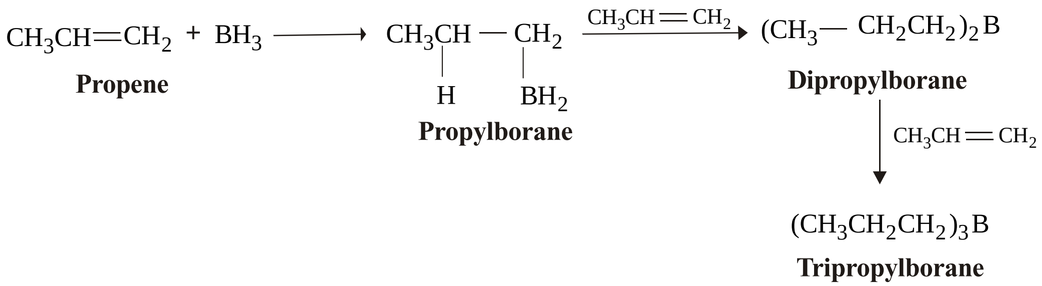


(iii) Hydroboration - Oxidation

When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained.



Since BH_3 has three hydrogens, above addition can occur three times to give trialkylborane (R_3B). This is shown below for propene.



The trialkylborane so obtained is oxidised using alkaline hydrogen peroxide solution to give three molecules of alcohols and boric acid.

$$(CH_3CH_2CH_2)_3B \xrightarrow{H_2O_2/^{-}OH} 3CH_3CH_2CH_2OH + B(OH)_3$$

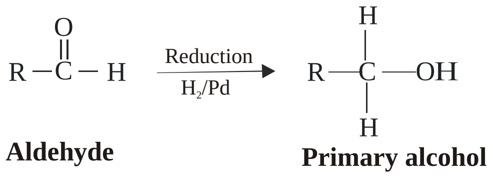
Tripropylborane **Propanol** **Boric acid**

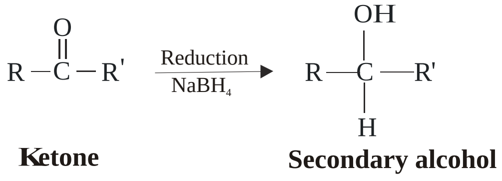
Note that hydroboration-oxidation yields the anti-Markovnikov addition of water although the reaction proceeds according to Markonikov's rule.

3. Reduction of Carbonyl Compounds

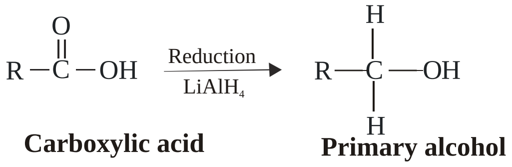
Carbonyl compounds (which contain $\overset{O}{\overset{\|}{-C-}}$ group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols.

Aldehydes give primary alcohols while ketones yield secondary alcohols on reduction.

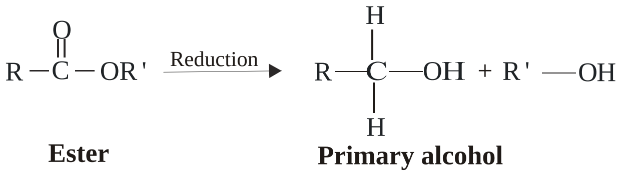




Carboxylic acids and esters also give primary alcohols on reduction.

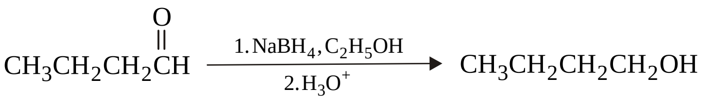


or



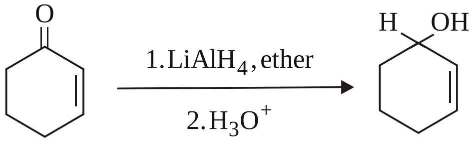
The reduction is carried out using hydride reagents such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). $LiAlH_4$ is stronger and reacts explosively with water while $NaBH_4$ is convenient to handle and reacts slowly.

Lithium aluminium hydride reduces all of the above classes of compounds while sodium borohydride reduces only aldehydes and ketones and does not reduce carboxylic acids and esters. Hence, it can be used to selectively reduce aldehydic/ketonic carbonyl group in presence of carboxylic acid/ester function. Some examples below illustrate the use of these reagents.



$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[2.\,H_3O^+]{1.\,NaBH_4,\,C_2H_5OH} CH_3CH_2CH_2CH_2OH$$

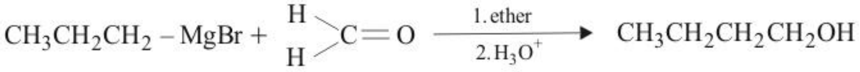
Butanol **Butan-1-ol**



Cyclohex-2-enone **Cyclohex-2-enol**

4. From Aldehydes and Ketones using Grignard Regents

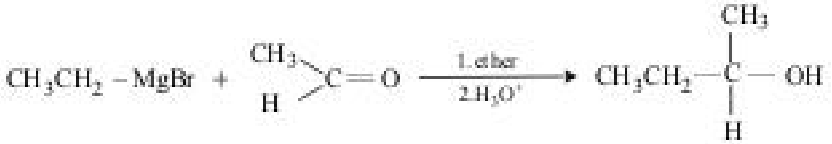
Grignard reagents react with methanal (or formaldehyde) to give a *primary alcohol*.



$$CH_3CH_2CH_2-MgBr + \begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow[2.\,H_3O^+]{1.\,ether} CH_3CH_2CH_2CH_2OH$$

Propyl magnesium bromide **Methanal** **Butan-1-ol (Primary alcohol)**

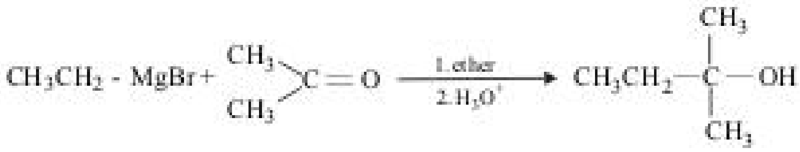
All other aldehydes yield *secondary alcohols* on reaction with Grignard reagents.



$$CH_3CH_2-MgBr + \begin{matrix}CH_3\\H\end{matrix}\!\!>C=O \xrightarrow[2.\,H_3O^+]{1.\,ether} CH_3CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Ethyl magnesium bromide **Ethanal (Acetaldehyde)** **Butan-2-ol (Secondary alcohol)**

With ketones, Grignard reagents give *tertiary alcohols*.



$$CH_3CH_2-MgBr + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow[2.\,H_3O^+]{1.\,ether} CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Ethyl magnesium bromide **Propanone** **2-Methylbutan-2-ol**

5. Diazotization of Primary Aliphatic Amines

This reaction also yields alchols and will be discussed in Lesson 30.

6. Fermentation

Ethanol is prepared on a large scale using fermentation. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes.

The fermentation of sugar is shown below :

$$\underset{\textbf{Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Investase}} \underset{\textbf{Glucose}}{C_6H_{12}O_6} + \underset{\textbf{Fructose}}{C_6H_{12}O_6}$$

$$\downarrow \textbf{Zymase}$$

$$\underset{\textbf{Ethanol}}{2\,C_2H_5OH} + 2\,CO_2$$

28.1.3 Structure and Physical Properties

The structure of alcohols is similar to that of water. The structures of water and methanol molecules are shown in Fig. 28.1.

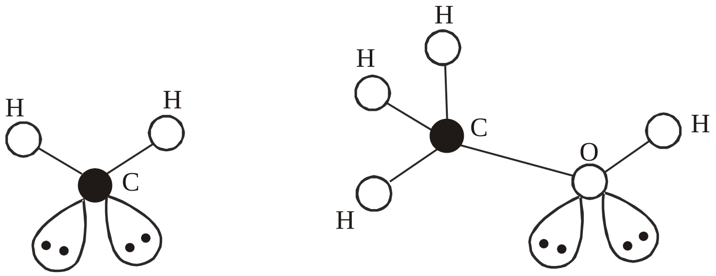


Fig. 28.1: *Water and Methanol molecule*

You know that the electronegativity of oxygen is more than that of hydrogen. Therefore, in alcohols, the O–H bond is polar in nature. In other words, oxygen has a slight negative charge on it whereas hydrogen has a slight positive charge. This bond polarity alone cannot explain the higher boiling points of alcohols as compared to hydrocarbons or similar haloalkanes, as listed in Table 28.2.

Normally, hydrogen bonding is responsible for higher boiling points of alcohols. Hydrogen bonding amongst alcohol molecules is depicted in Fig. 28.2.

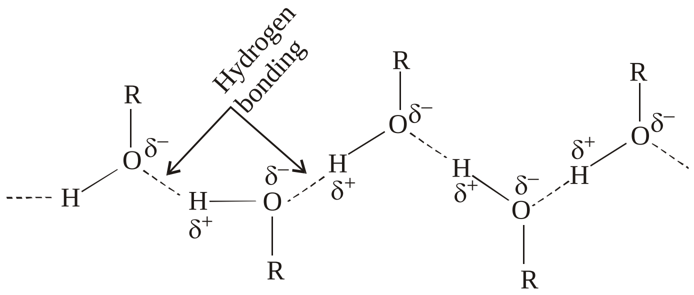
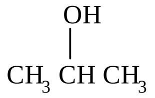
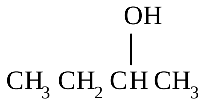


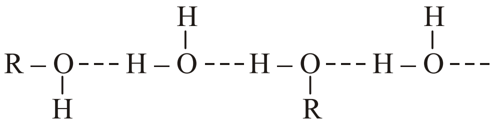
Fig. 28.2: *Hydrogen bonding in alcohol molecules*

You can see that the negatively polarised oxygen atom of one alcohol molecule attracts the positively polarised hydrogen atom of the other molecule. Thus, alcohol molecules are associated or are held together. This force of attraction is to be overcome before a molecule is set free from the liquid state and vaporises. Thus, more heat energy is required to break the hydrogen bonds and hence, the boiling points of alcohols are higher than alkanes and haloalkanes of comparable molecular mass.

Table 28.2: Physical Properties of some Alcohols, Hydrocarbons and related Haloalkanes

Compound	IUPAC Name	Melting Point (K)	Boiling Point (K)	Solubility g/100 mL of water
CH_3OH	Methanol	175.2	322.8	∞
CH_4	Methane	90.5	181.13	–
CH_3Cl	Chloromethane	175.3	248.8	–
CH_3CH_2OH	Ethanol	158.3	351.5	∞
CH_3CH_3	Ethane	189.7	184.4	–
CH_3CH_2Cl	Chloroethane	136.6	285.3	–
$CH_3CH_2CH_2OH$	Propan-1-ol		378.04	∞
$CH_3CH_2CH_3$	Propane	85.3	230.9	–
 $CH_3\overset{OH}{\overset{\vert}{CH}}CH_3$	Propan-2-ol	184	355	∞
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol	183	391	8.3
 $CH_3CH_2\overset{OH}{\overset{\vert}{CH}}CH_3$	Butan-2-ol	159	373	10.0

From the last column of Table 28.2, you must have noticed that alcohols have high solubilities in water. The lower alcohols are completely miscible and their solubilities decrease as the hydrocarbon portion of the molecule becomes larger. The higher solubility of alcohols can be again attributed to the hydrogen bonding. In this case, hydrogen bonding takes place between the alcohol and water molecules as is shown below in Fig. 28.3.



$$R-\underset{\underset{H}{\vert}}{O}---H-\overset{\overset{H}{\vert}}{O}---H-\underset{\underset{R}{\vert}}{O}---H-\overset{\overset{H}{\vert}}{O}---$$

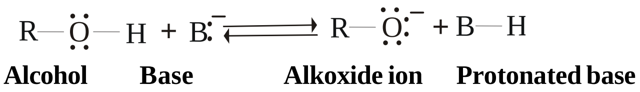
Fig. 28.3: *Hydrogen bonding in a solution of methanol and water*

28.1.4 Reactions of Alcohols

Alcohols exhibit the following reactions:

1. Acidic and Basic behaviour

Alcohol behave both as acids and bases. They are weakly acidic. A strong base such as a hydride ion (H^-) in sodium hydride (NaH), can remove the proton from the alcohol molecule and an alkoxide ion results.



$$R-\ddot{\underset{\cdot\cdot}{O}}-H + B\colon^{-} \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}\colon^{-} + B-H$$

$$CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + B\!:^- \rightleftharpoons CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}\!:^- + BH$$

Ethanol **Base** **Ethoxide ion** **Protonated base**

When water is used as a base, the *acid dissociation constant* (K_a) and pK_a can be written as follows:

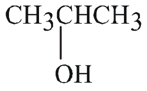
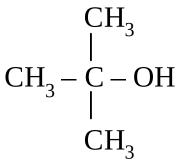
$$R-O-H+H_2O \overset{K_a}{\rightleftharpoons} R-O^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][RO^-]}{[ROH]}$$

$$pK_a = -\log K_a$$

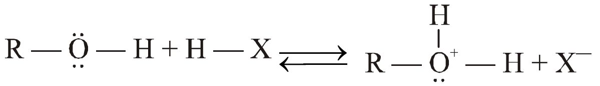
Some pK_a values are listed in Table 28.3.

Table 28.3: pK_a values of some compounds

Compound	pK_a
CH_3OH	15.5
H_2O	15.74
CH_3CH_2OH	15.9
 $CH_3\underset{OH}{\underset{\vert}{C}}HCH_3$	16.5
 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-OH$	18.0

Remember that the lower the pK_a value, higher is the acidity of the compound.

Alcohols can behave as weak bases also. They have lone pair of electrons on oxygen atom and hence they can be protonated by strong acids to give oxonium ions as shown below:



$$R-\ddot{\underset{\cdot\cdot}{O}}-H + H-X \rightleftharpoons R-\overset{H}{\overset{\vert}{\underset{\cdot\cdot}{O^+}}}-H + X^-$$

Alcohol **Acid** **Oxonium ion**

2. Formation of Alkoxides

Alcohols react with sodium or potassium metals to give the respective alkoxides.

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2(g)$$

Ethanol **Sodium metal** **Sodium ethoxide**

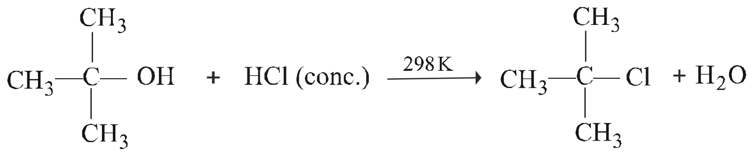
$$(CH_3)_3C-OH + K \longrightarrow (CH_3)_3C-O^-K^+ + \frac{1}{2}H_2(g)$$

***tert*-Butyl alcohol** **Potassium metal** **Potassium *tert*-butoxide**

Alkoxides are used in the synthesis of organic compounds.

3. Conversion to Alkyl Halides

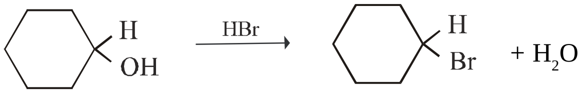
You have already studied in Lesson 27 that alcohols react with a variety of reagents to form alkyl halides. These are hydrogen halides (such as HCl, HBr or HI), phosphorus tribromide (PBr_3) and thionyl chloride ($SOCl_2$). The reaction involves the breaking of $R-OH$ bond of alcohol molecule.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH + HCl\,(conc.) \xrightarrow{298\,K} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + H_2O$$

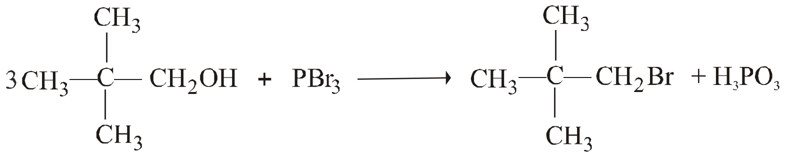
2-Methyl propan-2-ol

2-chloro-2-methyl propane



Cyclohexanol

Bromocyclohexane



$$3\,CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OH + PBr_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2Br + H_3PO_3$$

2, 2-Dimethylpropan-1-ol

1-Bromo-2, 2-Dimethylpropane

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_{2(g)} + HCl_{(g)}$$

Propan-1-ol **1-Chloropropane**

Tertiary alcohols are readily converted to alkyl halides by HCl or HBr while the best method with primary and secondary alcohols is by using PBr_3 or $SOCl_2$ as the reagents. Another advantage of using $SOCl_2$ is that both the by-products in this reaction, i.e. SO_2 and HCl are gases and hence can be easily eliminated to yield pure alkyl halide.

Lucas Test

The formation of alkyl halides from alcohols is the basis of this test. In involves the reaction of the alcohol with Lucas reagent (i.e. anhyd. $ZnCl_2$ + conc. HCl). Since the reactivity of alcohols is in the following order :

primary alcohols < secondary alcohols < tertiary alcohols

With primary alcohols turbidity does not appear. In case of secondary alcohols, turbidity appears within 5 mintues whereas it appears immediately with tertiary alcohols. The turbidity is due to the formation of alkyl chlorides from the corresponding alcohols.

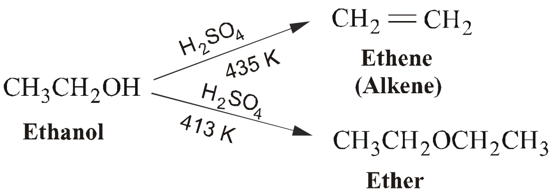
4. Formation of Alkenes

Alcohols can be dehydrated to alkenes. This reaction requires an acidic catalyst and is favoured at higher tempratures. Usually sulphuric and phosphoric acid are used as acidic catalysts. You have come across this reaction in Lesson 26 also. The ease of dehydration follows the following order amongst alcohols.

tertiary alcohols > secondary alcohols > primary alcohols

5. Dehydration to form Ethers

Intermolecular dehydration of alcohols yields ethers. This reaction takes place at a lower temperature than that for dehydration to give alkenes.



The formation of ethers by dehydration is a substitution type of reaction and gives only symmetrical ethers. You will study a better method of synthesis of ethers later under the section of ethers in this lesson.

6. Oxidation

Alcohols can be oxidised to carbonyl compounds. Primary alcohols give aldehydes or carboxylic acids on oxidation while secondary alcohols yield ketones. The tertiary alcohols do not usually undergo oxidation. Normally $KMnO_4$, CrO_3 and $Na_2Cr_2O_7$ or $K_2Cr_2O_7$ are used as oxidising agents.

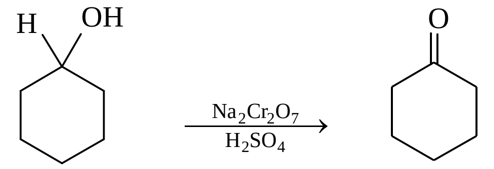
$$\underset{\textbf{Propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow[H_2O]{K_2Cr_2O_7,H_2SO_4} \underset{\textbf{Propanal}}{CH_3CH_2CHO} \xrightarrow{\text{Further oxidation}} \underset{\textbf{Propanoic acid}}{CH_3CH_2COOH}$$

The aldehydes obtained by oxidation of the primary alcohols get further oxidised to carboxylic acids as shown above. You will study more about these classes of compounds in the next lesson.

The oxidation can be controlled and aldehydes are obtained as the products by using pyridium chlorochromate (PCC) which is a mild reagent.

$$\underset{\textbf{Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{PCC} \underset{\textbf{Decanal}}{CH_3(CH_2)_8CHO}$$

Secondary alcohols can be oxidised to ketones as shown below :



Cyclohexanol **Cyclohexanone**

7. Formation of Esters

Alcohols react with carboxylic acids to form esters. This reaction is discussed in the next lesson.

$$\underset{\textbf{Ethanoic acid}}{CH_3COOH} + \underset{\textbf{Ethanol}}{CH_3CH_2OH} \overset{H+}{\rightleftharpoons} \underset{\textbf{Ethyl ethanoate}}{CH_3COOCH_2CH_3} + \underset{\textbf{Water}}{H_2O}$$

This reaction is called **esterification reaction** and is reversible in nature.

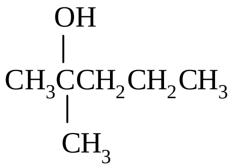
Uses

Alcohols find a large variety of uses as follows :

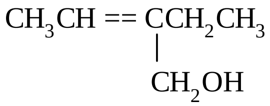
1. As solvents
2. As laboratory reagents
3. In medicines
4. As thinners in paints, varnishes, etc.

Intext Questions 28.1

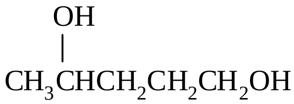
1. Give the IUPAC names of the following alcohols :

(i) 

$CH_3C(OH)(CH_3)CH_2CH_2CH_3$

(ii) 

$CH_3CH{=}C(CH_2OH)CH_2CH_3$

(iii) 

$CH_3CH(OH)CH_2CH_2CH_2OH$

....

2. How will you prepare propan-1-ol from propanal?

....

3. Give the synthesis of 2-methylpropan-2-ol using Grignard reagent.

....

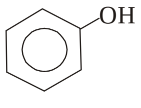
4. Give the product of the following reactions:

(i) Hexan-1-ol $\xrightarrow[H_2O, H^+]{CrO_3}$

(ii) Hexan-1-ol $\xrightarrow[\text{Chlorochromate}]{\text{Pyridium}}$

28.2 Phenols

The name phenol is specifically used for the following compound (hydroxybenzene) in which one hydroxyl group is attached to the benzene ring.

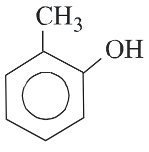


Phenol

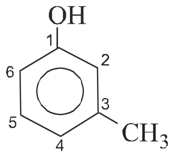
It is also used as a general name for the class of compounds derived from the above compound. Phenol is a disinfactant. Phenols are widely distributed in nature. They are also important in the synthesis of organic compounds such as aspirin and in the preparation of dyes. Phenol is also used in the manufacture of bakelite which is a very useful polymer.

28.2.1 Nomenclature of Phenols

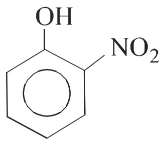
Some representative examples of phenolic compounds are given below:



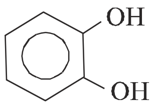
2-Methylphenol
(*o*-Cresol)



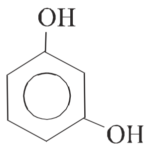
3-Methylphenol
(*m*-Cresol)



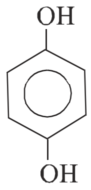
2-Nitrophenol
(*o*-Nitrophenol)



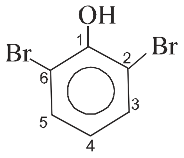
1,2-Benzenediol
(Catechol)



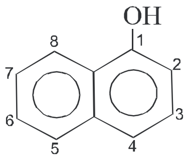
1,3-Benzenediol
(Resorcinol)



1,4-Benzenediol
(Hydroquinone)



2,6-Dibromophenol



1-Naphthol
(α – Naphthol)

Note that the term *phenol* is used as a parent name and the other substituents present in the compound are given a specific number according to their position on the aromatic ring. As done before the common names of the above compounds are given in the brackets below their IUPAC names.

28.2.2 General Methods of Preparation

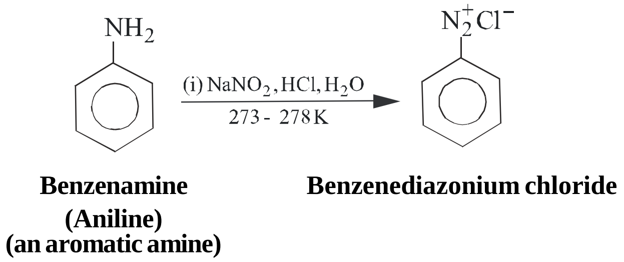
We can categorise the methods of preparation as methods of *laboratory synthesis* and *industrial synthesis* of phenols.

A. Laboratory Synthesis of Phenols

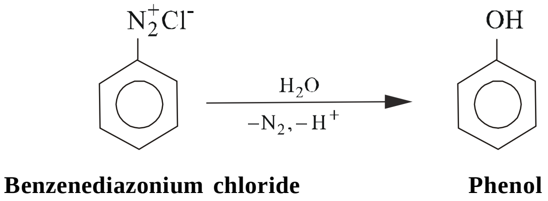
1. From Arenediazonium Salts

It is the most general method of preparation of phenols and requires mild conditions.

Arenediazonium salts or aromatic diazonium salts are obtained by the *diazotization* of primary aromatic amines as given below :



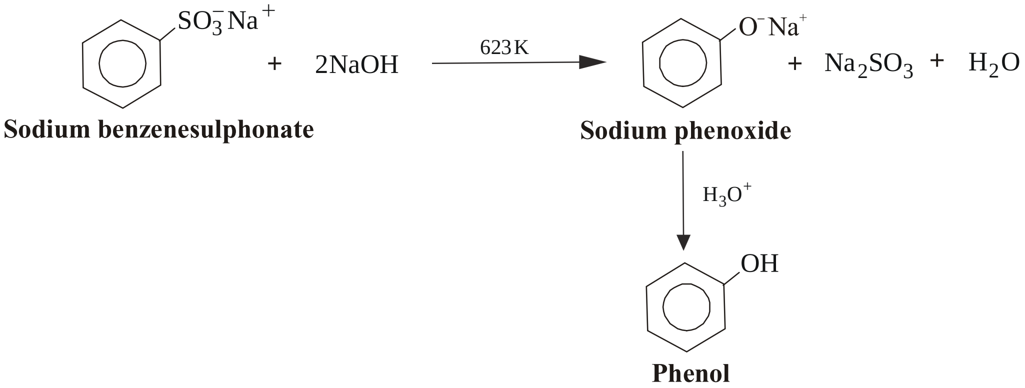
The arenediazonium salt on hydrolysis yields phenol.



2. Alkali Fusion of Sodium Benzenesulphonate

This was the first commercial synthesis of phenol developed in Germany in 1890. It can also be used as a laboratory method for synthesis of phenol.

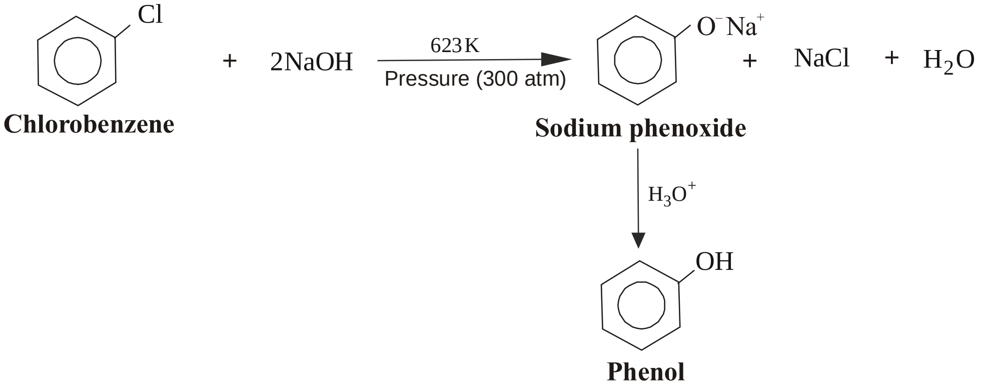
Sodium benzenesulphonate is fused with sodium hydroxide to give sodium phenoxide which on acidification yields phenol.



B. Industrial Synthesis of Phenols

1. Dow Process

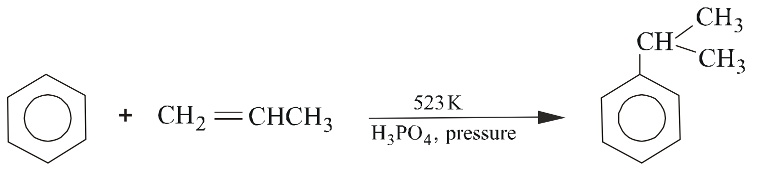
In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.



This method was in use for many years but now phenol is synthesised via cumene hydroperoxide which is discussed below.

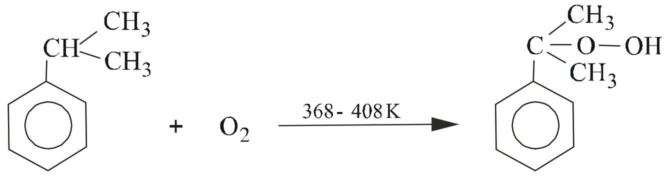
2. From Cumene Hydroperoxide

The reaction between benzene and propene in presence of phosphoric acid yields cumene.



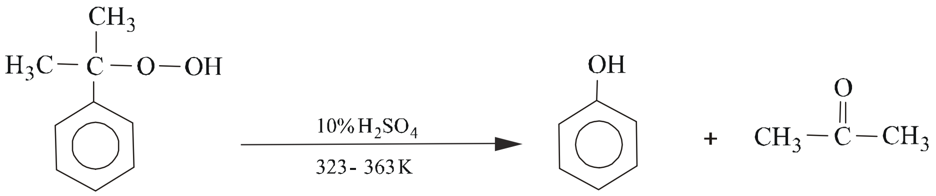
Benzene **Propene** **1-Methylethyl benzene (*Iso*propylbenzene) Cumene**

Cumene is then oxidised to cumene hydroperoxide by air.



Cumene **Cumene hydroperoxide**

In the final step, cumene hydroperoxide is treated with 10% sulphuric acid to give phenol and acetone on hydrolytic rearrangement.

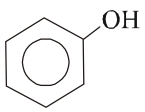


Cumene hydroperoxide **Phenol** **Propanone (Acetone)**

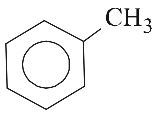
Note that propanone is obtained as a valuable byproduct in this reaction.

28.2.3 Physical Properties

Similar to alcohols, phenols also have hydrogen atom linked to the electronegative oxygen atom. Thus, phenols also exhibit hydrogen bonding and hence have higher boiling points as compared to the hydrocarbons of similar molecular weight.



b.p. = 454.7 K
Phenol



b.p. = 383.6 K
Methylbenzene (Toluene)

Due to their ability to form hydrogen bonds, phenols show some water solubility. For example, the solubility of phenol is 9.3 g per 100 mL of water.

28.2.4 Reactions of Phenols

Let us now study the reactions exhibited by phenols.

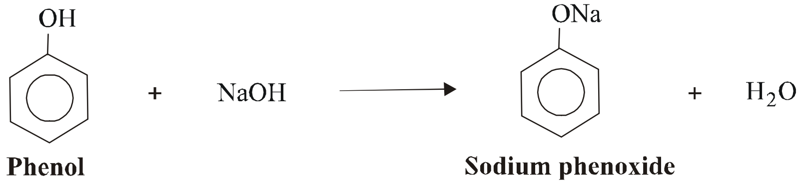
1. Acidic and Basic Nature

Phenols are much more acidic than alcohols. pK_a values of some phenols are listed in Table 28.4.

Table 28.4: pK_a values of phenols

Name	pK_a
Phenol	9.89
2- Methylphenol	10.20
2-Chlorophenopl	8.11
3-Chlorophenol	8.80
2-Nitrophenol	7.17
3-Nitrophenol	8.28
4-Nitrophenol	7.15
2,4,6-Trinitrophenol (Picric acid)	0.38

Since phenols are acidic in nature, they are soluble in dilute sodium hydroxide.



The greater acidity of phenols can be attributed to the resonance stablisation of the phenoxide ion. The resonance structures of pheoxide ion are shown in Fig. 28.4.

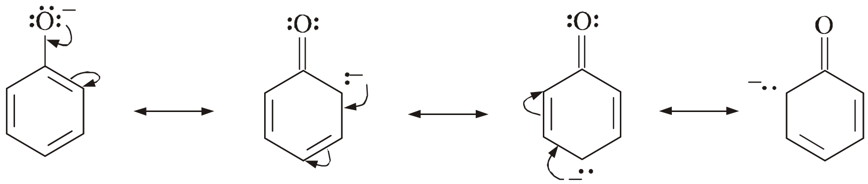


Fig. 28.4: *Resonance structures of phenoxide ion*

The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of alkoxide ions.

Similar resonance is also shown in phenol itself, see Fig 28.5. But the resonance structures of phenol are less stable as compared to those of phenoxide ion as they involve the separation of charge.

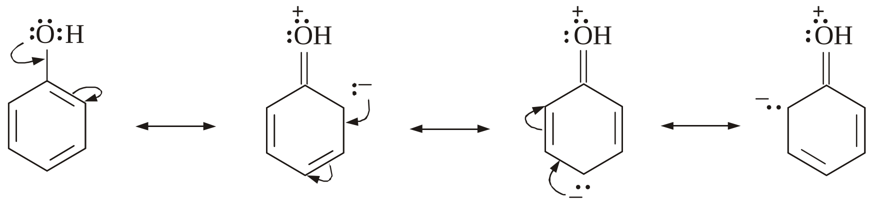
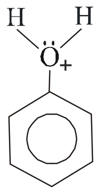


Fig. 28.5: *Resonance structures of phenol*

If you carefully go through the pK_a values given in Table 28.4, you would see that the electron donating substituents such as methyl group decrease the acidity of phenol and hence alkylphenols have greater pK_a values as compared to phenol itself. On the other hand, electron withdrawing substituents increase the acidity and phenols having these substituents (–Cl, –NO_2, etc.) have lower pK_a values than phenol. In fact, 2,4,6-trinitrophenol is more acidic than many carboxylic acids.

Phenols behave as weak bases also. Similar to alcohols, they can also be protonated to give phenyloxonium ion.

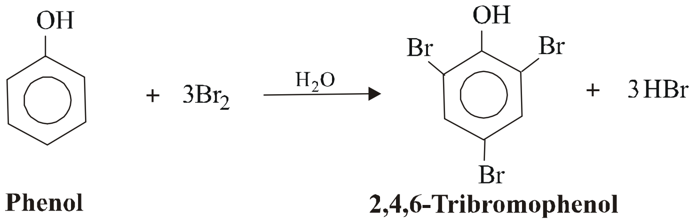


Phenyloxonium ion

2. Electrophilic Substitution Reactions

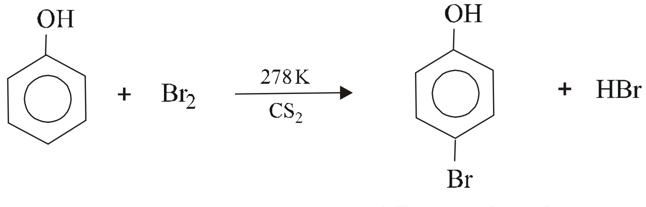
The hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. In this reaction, an **electrophile** (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho* and *para* positions of the phenol are electron rich, the substitution takes place at these positions. Two such reactions are **halogenation** and **nitration** reactions. Let us now study them in details.

(i) Halogenation: Phenol reacts with bromine in aqueous solution to give 2,4,6-tribromophenol in about 100% yield.



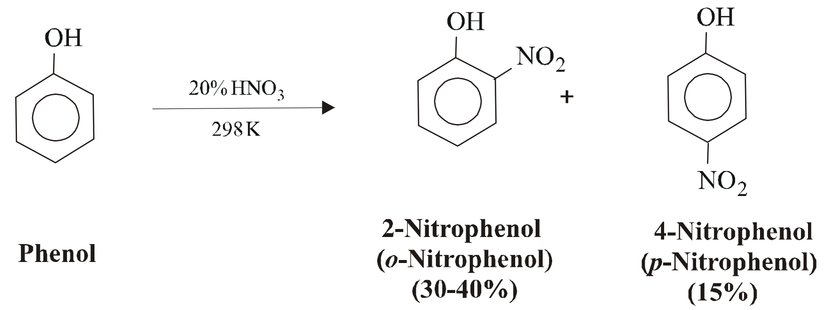
Phenol **2,4,6-Tribromophenol**

Bromination can be limited to monobromination to give mainly 4-bromophenol using low temprature and less polar solvent such as carbon disulphide. The other product formed in minor quantity is 2-bromophenol.



Phenol **4-Bromophenol**

(ii) Nitration: Phenol gives a mixture of 2-nitro and 4-nitrophenols on nitration with dilute nitric acid.



The mixture of nitrophenols so obtained is separated using steam distillation. Both these products show hydrogen bonding. In case of 2-nitrophenol, the hydrogen bonding is **intramolecular** (in the same molecule) whereas in case of 4-nitrophenol, it is **intermolecular** (between different molecules). These are depicted in Fig. 28.5.

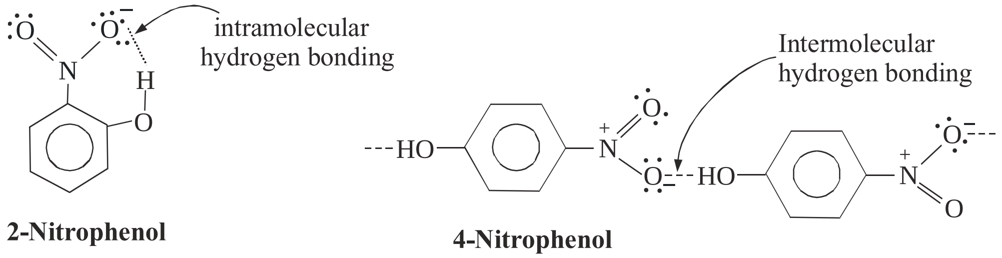


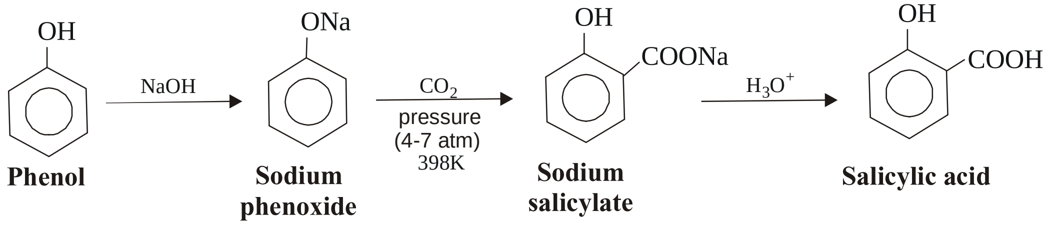
Fig. 28.5 : *Intramolecular and intermolecular hydrogen bonding in nitrophenols*

2-Nitrophenol is steam volatile and distills out on passing steam whereas 4-nitrophenol is less volatile due to intermolecular hydrogen bonding.

Treatment of phenol with a mixture of conc. nitric acid and conc. sulphuric acid at 323K yields 2,4,6-trinitrophenol also known as picric acid.

3. Kolbe Reaction

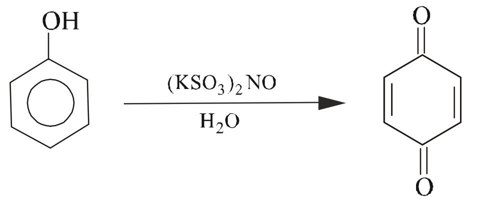
It involves sodium phenoxide which is allowed to absorb carbon dioxide and then heated under a pressure of CO_2 to 398 K. Sodium salicylate so obtained on acidification yields salicylic acid.



By reaction with acetic anhydride, salicylic acid yields *aspirin*, which is the common pain reliever.

4. Oxidation

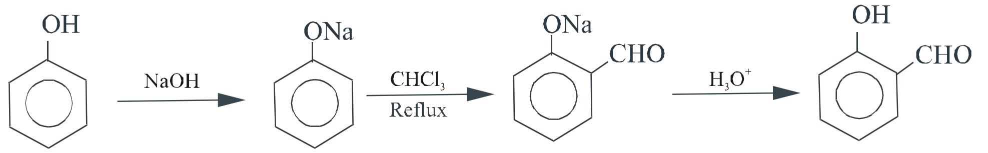
Phenols undergo oxidation reactions to give products which are diffrent from those obtained by alcohols. They can be oxidised using a variety of oxidising agents such as sodium dichromate or silver oxide to give quinones. These days Fremy's salt [$(KSO_3)_2NO$] is preferred for oxidation.



Phenol **Benzoquinone**

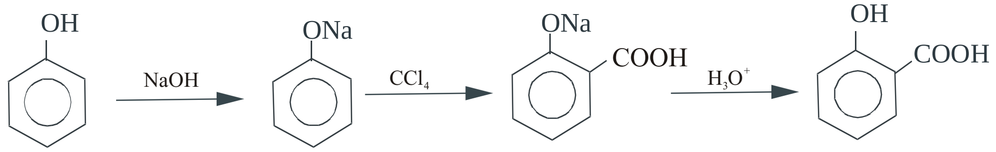
5. Reimer Tiemann Reaction

Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.



Phenol **Sodium phenoxide** **Salicyldehyde**

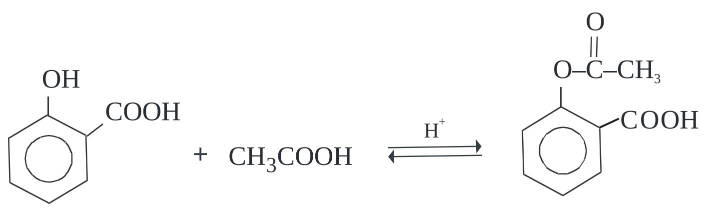
Use of carbon tetrachloride in place of chloroform gives salicylic acid.



Phenol **Sodium phenoxide** **Salicylicacid**

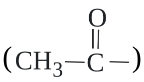
6. Esterification

Similar to alcohols, phenols react with carboxylic acids to give esters.



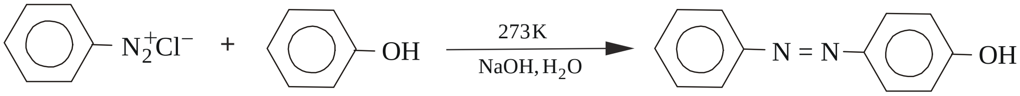
2-Hydroxybenzoic acid **Ethanoic acid** **Acetyl salicylic acid**

This reaction is an acetylation reaction as the H of –OH the phenol is replaced by the


acetyl ($CH_3-\overset{O}{\overset{||}{C}}-$) group.

7. Coupling Reaction

Phenols react with aromatic diazonium salts in slightly alkaline conditions to give *azo* compounds. These *azo* compounds are brightly coloured and are used as *azo dyes*.



Benzenediazonium chloride **Phenol** **orange solid** ***p*-Phenylazophenol (*p*-Hydroxyazobenzene)**

Uses

1. Phenol is used as a disinfectant.
2. It is also used in the synthesis of polymers.
3. Phenols are used in the synthesis of many organic compounds.
4. Substituted phenols are used in dyeing and tanning industries.

Intext Questions 28.2

1. How will you convert aniline to phenol?

   ....

2. What is the starting material in Dow's process?

   ....

3. Arrange the following in the increasing order of their acidity:

   Phenol, 2-Methylphenol, 2-Chlorophenol

   ....

4. How will you prepare salicylic acid from phenol?

   ....

5. What is an azo dye?

   ....

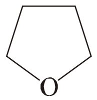
28.3 Ethers

Ethers are organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups. Thus, ethers can be represented as $R-O-R'$ where R and R' may be alkyl or aryl groups. When the two substituent groups (R and R') are identical, then the ether is called a **symmetrical ether,** otherwise if these two groups are different, then the ether is known as an **unsymmetrical ether.**

$CH_3CH_2 - O - CH_2CH_3$ — **A symmetricalether**

$CH_3 - O - CH_2CH_3$ — **An unsymmetrical ether**

The oxygen atom of the ether can also be part of a ring, in which case the ether is known as a **cyclic ether**. Tetrahydrofuran is one such cyclic ether which is used as a solvent.



Tetrahydrofuran (THF)

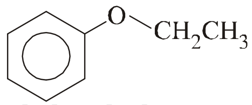
Ethers are commonly used as solvents for organic reactions. The symmetrical ether shown above is diethyl ether and is commonly also referred to simply as *ether* because of its wide use as a solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years.

28.3.1 Nomenclature of Ethers

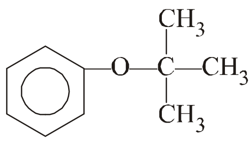
Common names of ethers are arrived by alphabetically naming the two groups attached to the oxygen followed by the word ether. The common names for some ethers are given below :

$CH_3OCH_2CH_3$
Ethyl methyl ether

$CH_3CH_2OCH_2CH_3$
Diethyl ether



Ethyl phenyl ether



***tert*-Butyl phenyl ether**

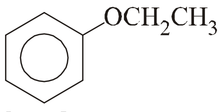
$Cl - CH_2 - O - CH_3$
Chloromethyl methyl ether

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane* and the smaller alkyl group is treated as an *alkoxy* substituent on this alkane. For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.

$CH_3OCH_2CH_3$
Ethyl methyl ether

The remaining portion , *i.e.*, $-OCH_3$ part in this case, is called the methoxy substituent. Hence, the above ether is called **methoxyethane.** Some more examples of IUPAC names of ethers are given below :

$CH_3CH_2OCH_2CH_3$
Ethoxy ethane



Ethoxybenzene

$CH_3O\overset{1}{C}H_2\overset{2}{C}H_2OCH_3$
1, 2-Dimethoxyethane

28.3.2 General Methods of Preparation

You have already studied under the reactions of alcohols that ethers can be obtained by the dehydration of alcohols. Ethers can also be prepared by Williamson synthesis which is explained below :

Williamson Synthesis : It involves the reaction of a metal alkoxide with a primary alkyl halide. The metal alkoxide is prepared by adding sodium or potassium metal or sodium hydride (NaH) to the alcohol.

$$< ROH + Na \longrightarrow \underset{\textbf{Metal alkoxide}}{RO^{-}Na^{+}} + \frac{1}{2}H_2 >$$

$$< ROH + NaH \longrightarrow \underset{\textbf{Metal alkoxide}}{RO^{-}Na^{+}} + H_2 >$$

$$< \underset{\substack{\textbf{Metal}\\\textbf{alkoxide}}}{RO^{-}Na^{+}} + \underset{\textbf{Alkyl halide}}{R'-X} \longrightarrow \underset{\textbf{Ether}}{R-O-R'} + NaX >$$

$$\underset{\textbf{propan-1-ol}}{CH_3CH_2CH_2OH} + NaH \longrightarrow \underset{\textbf{Sodium propoxide}}{CH_3CH_2CH_2ONa} \xrightarrow{CH_3CH_2I} \underset{\substack{\textbf{1-Ethoxypropane}\\\textbf{(Ethyl propyl ether)}}}{CH_3CH_2CH_2OCH_2CH_3} + NaI$$

Williamson synthesis involves the displacement of the halide ion by the alkoxide ion.

28.3.3 Sturcture and Properties of Ethers

Ethers have geometry similar to water and alcohols. The oxygen atom is sp^3 hybridised. There are two lone pairs of electrons present on the oxygen atom as is shown in Fig. 28.6.

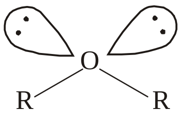


Fig. 28.6 : *Geometry of an ether molecule*

Note that the ether molecule has a bent structure. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar is nature (Fig. 28.7). Ethers, thus, act as polar solvents.

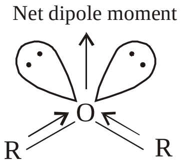
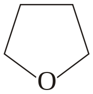
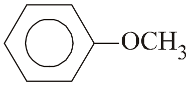


Fig. 28.7 : *Polar ether molecule*

Since ethers do not have a hydrogen atom linked to the oxygen atom, they cannot form hydrogen bonds amongst their own molecules. Due to the absence of hydrogen bonding, they have lower boiling points as compared to alcohols having similar molecular masses. The boiling boints of some ethers are listed in Table 28.5.

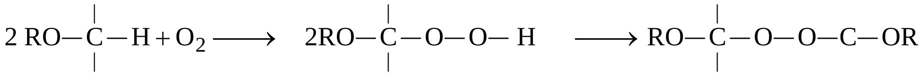
Table 28.5 : Boiling points of some common ethers

Ether	Boiling point (K)
CH_3OCH_3	248.1
$CH_3OCH_2CH_3$	283.8
$CH_3CH_2OCH_2CH_3$	307.6
$CH_3OCH_2CH_2OCH_3$	356
	338.4
	431.3

28.3.4 Reactions of Ethers

Ethers are normally unreactive in nature. Their unreactivity makes them good solvents. However, they show some reactions which are discussed below :

1. Reaction with Oxygen : Ethers slowly react with oxygen to form hydroperoxides and peroxides.



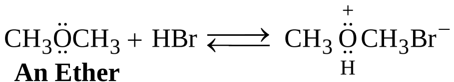
$$2\,RO-\overset{|}{\underset{|}{C}}-H+O_2 \longrightarrow 2RO-\overset{|}{\underset{|}{C}}-O-O-H \longrightarrow RO-\overset{|}{\underset{|}{C}}-O-O-C-OR$$

Ether **A hydroperoxide of ether** **A peroxide of ether**

Peroxides have a tendency to explode. Therefore, one should be very careful in handling ethers which may have been stored for sometime because they may contain some peroxide.

2. Reaction wtih Acids

Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature.



$$CH_3\ddot{\underset{..}{O}}CH_3 + HBr \rightleftharpoons CH_3\overset{+}{\underset{H}{\ddot{O}}}CH_3Br^-$$

An Ether **An oxonium salt**

3. Acidic Cleavage

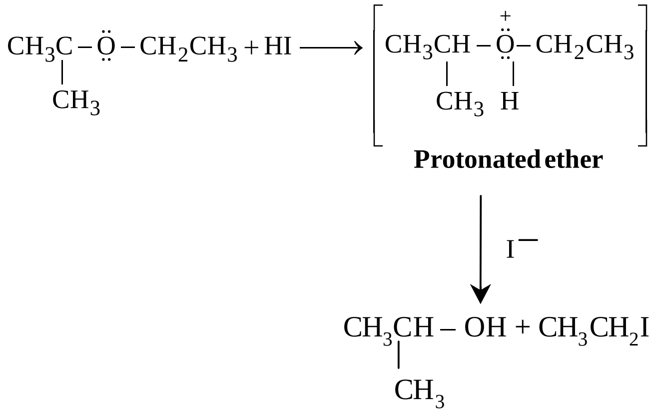
Heating dialkyl ethers with strong acids such as HI, HBr or H_2SO_4 leads to their cleavage.

$$\underset{\textbf{Ethoxyethane}}{CH_3CH_2OCH_2CH_3} + HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3CH_2Br} + \underset{\textbf{Ethanol}}{CH_3CH_2OH}$$

The alcohol formed further reacts with additional HBr to give bromoethane. Hence,

$$CH_3CH_2OCH_2CH_3 + 2HBr \longrightarrow 2CH_3CH_2Br + H_2O$$

In case of ethers having primary or secondary alkyl groups, the nucleophile (Br^- or I^-) attacks the less hindered alkyl group. Thus, in case of the following unsymmetrical ether, the products contain alkyl halide formed by the attack of the halide ion on the less hindered primary alkyl group, *i.e.*, ethyl group.



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{..}{\ddot{O}}-CH_2CH_3+HI\longrightarrow\left[CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{\overset{+}{\ddot{O}}}}-CH_2CH_3\right]$$

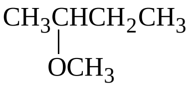
Protonated ether

$$\Big\downarrow I^-$$

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH+CH_3CH_2I$$

Intext Questions 28.3

1. What are the IUPAC names of the following ethers ?

(i) 

$CH_3\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH_2CH_3$

(ii) CH_3-O-CH_3

....

2. (i) How will you prepare methyl propyl ether using Williamson synthesis ?

(ii) What is the IUPAC name of methyl propyl ether ?

....

3. Why should you be careful in using old stock of ethers.

....

4. Why are ethers good solvents ?

....

5. What is tetrahydrofuran ? Give its structure and use.

....

What You Have Learnt?

In this lesson, you have learnt that

- Alcohols can be classified as primary, secondary or tertiary.
- Alcohols can be monohydric, dihydric or polyhydric.

- Alcohols can be prepared by the following general methods :

  – Hydrolysis of haloalkanes

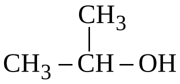
  – Hydration of alkenes

  – Reduction of carbonyl compounds

  – From aldehydes and ketones using Grignard reagents
- Alcohols behave both as weak acids and weak bases.
- Alcohols can be converted to alkyl halides, alkenes, ethers, aldehydes, ketones, carboxylic acids and esters.
- In the laboratory, phenols can be prepared from arenediazonium salts and sodium benzene sulphonate. Their industrial preparation is done by Dow's process and from cumene hydroperoxide.
- Similar to alcohols, phenols can also behave both as acids and bases.
- Typical reactions of phenols being electrophilic substitution reactions such as halogenation, sulphonation, nitration, etc.
- Phenols undergo oxidation and also exhibit Reimer Tiemann reaction. They react with aromatic diazonium salts to give azo dyes.
- Ethers can be symmetrical or unsymmetrical.
- Ethers can be prepared by Williamson synthesis.
- Dialkyl ethers are cleaved on heating with strong acids .

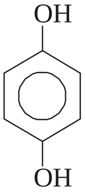
Terminal Exercise

1. Give the IUPAC names of the following compounds :

(i) 

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

(ii) $C_6H_5OCH_2CH_3$

(iii) 

2. Compare the boiling points of ethyl alcohol and dimethyl ether. Which one has higher boiling point and why ?

3. Which ester would give ethanol and methanol on reduction?

4. Complete the following reactions :

(i) $CH_3CH_2CH_2Cl + NaOH\ (aq.) \longrightarrow$ ....

(ii) $CH_3CHO \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4,\ ether}$ ....

(iii) $CH_3OH + Na \longrightarrow$ ....

5. How is ethanol prepared using fermentation?
6. What is Lucas test? What is its use?
7. Which reagent is used for oxidising primary alcohols to aldehydes?
8. Why are phenols more acidic than alcohols? Explain.
9. Why are ethers polar in nature?

Answers to Intext Questions

28.1

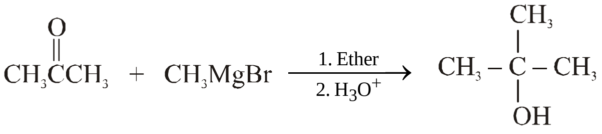
1. (i) 2-Methylpentan-2-ol

   (ii) 2-Ethylbut-2-en-1-ol

   (iii) 1, 4-Pentanediol

2. By reduction with $NaBH_4$ or $LiAlH_4$

3.



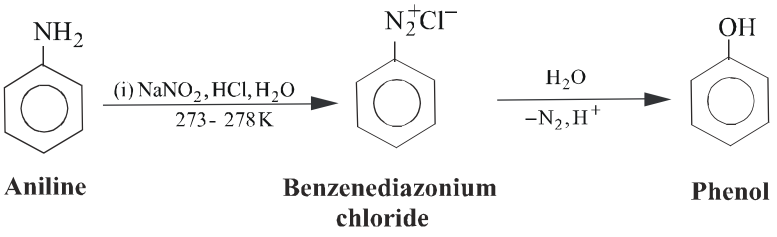
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ Ether} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

4. (i) Hexanoic Acid

   (ii) Hexanal

28.2

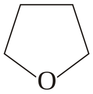
1.



2. Chlorobenzene
3. 2-Methylphenol < Phenol < 2-Chlorophenol
4. By Kolbe reaction
5. Azo dyes are azo compounds formed by the reaction of phenols with aromatic diazonium salts. They are brightly coloured.

28.3

1. (i) 2-Methoxybutane
   (ii) Methoxymethane
2. (i) $CH_3CH_2CH_2O^- + CH_3Br \longrightarrow CH_3CH_2 - O - CH_3 + Br^-$
   (ii) Methoxypropane
3. They may explode due to the presence of peroxides.
4. Because they are unreactive in nature.
5. It is a cyclic ether.



It is used as a solvent.