



12086CH11

Objectives

After studying this Unit, you will be able to

- name alcohols, phenols and ethers according to the IUPAC system of nomenclature;
- discuss the reactions involved in the preparation of alcohols from alkenes, aldehydes, ketones and carboxylic acids;
- discuss the reactions involved in the preparation of phenols from haloarenes, benzene sulphonic acids, diazonium salts and cumene;
- discuss the reactions for preparation of ethers from (i) alcohols and (ii) alkyl halides and sodium alkoxides/aryloxides;
- correlate physical properties of alcohols, phenols and ethers with their structures;
- discuss chemical reactions of the three classes of compounds on the basis of their functional groups.

Unit

11

Alcohols, Phenols and Ethers

Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.

You have learnt that substitution of one or more hydrogen atom(s) from a hydrocarbon by another atom or a group of atoms result in the formation of an entirely new compound having altogether different properties and applications. **Alcohols** and **phenols** are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by $-OH$ group. These classes of compounds find wide applications in industry as well as in day-to-day life. For instance, have you ever noticed that ordinary spirit used for polishing wooden furniture is chiefly a compound containing hydroxyl group, ethanol. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing $-OH$ groups. Just think of life without paper; no note-books, books, newspapers, currency notes, cheques, certificates, etc. The magazines carrying beautiful photographs and interesting stories would disappear from our life. It would have been really a different world.

An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s), of an aliphatic system (CH_3OH) while a phenol contains $-OH$ group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group ($R-O/Ar-O$) yields another class of compounds known as 'ethers', for example, CH_3OCH_3 (dimethyl ether). You may also visualise ethers as compounds formed by

substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

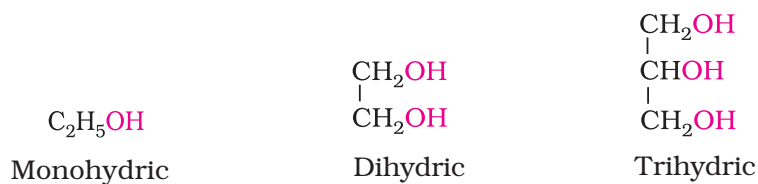
In this unit, we shall discuss the chemistry of three classes of compounds, namely — alcohols, phenols and ethers.

11.1 Classification

The classification of compounds makes their study systematic and hence simpler. Therefore, let us first learn how are alcohols, phenols and ethers classified?

11.1.1 Alcohols— Mono, Di, Tri or Polyhydric alcohols

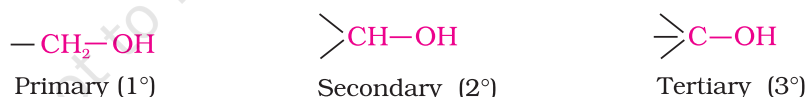
Alcohols and phenols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:



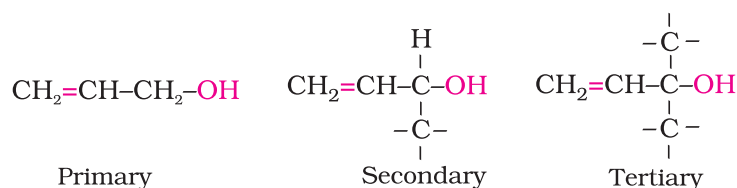
Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

(i) *Compounds containing C_{sp^3} -OH bond:* In this class of alcohols, the -OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:

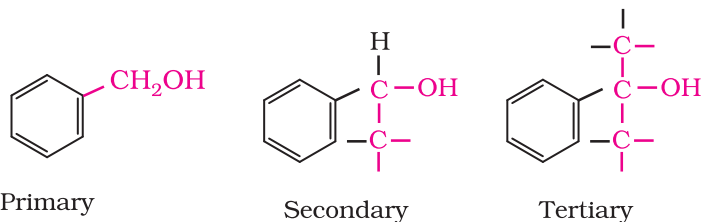
Primary, secondary and tertiary alcohols: In these three types of alcohols, the -OH group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:



Allylic alcohols: In these alcohols, the -OH group is attached to a sp^3 hybridised carbon adjacent to the carbon-carbon double bond, that is to an allylic carbon. For example



Benzylic alcohols: In these alcohols, the -OH group is attached to a sp^3 -hybridised carbon atom next to an aromatic ring. For example.

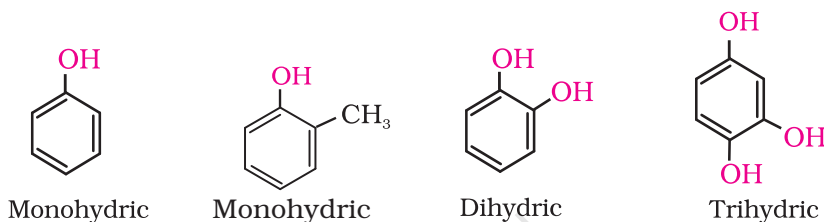


Allylic and benzylic alcohols may be primary, secondary or tertiary.

(ii) *Compounds containing C_{sp^2} -OH bond:* These alcohols contain —OH group bonded to a carbon-carbon double bond, i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

Vinylic alcohol: $CH_2 = CH - OH$

11.1.2 Phenols— Mono, Di and trihydric phenols

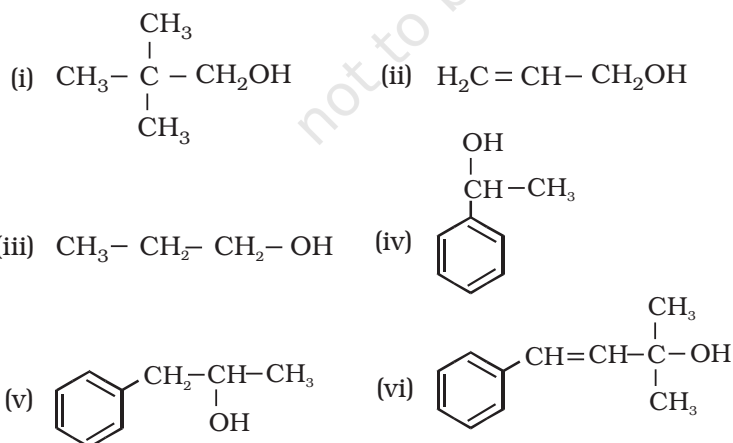


11.1.3 Ethers

Ethers are classified as **simple** or **symmetrical**, if the alkyl or aryl groups attached to the oxygen atom are the same, and **mixed** or **unsymmetrical**, if the two groups are different. Diethyl ether, $C_2H_5OC_2H_5$, is a symmetrical ether whereas $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$ are unsymmetrical ethers.

Intext Questions

11.1 Classify the following as primary, secondary and tertiary alcohols:



11.2 Identify allylic alcohols in the above examples.

11.2 Nomenclature

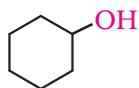
(a) Alcohols: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, CH_3OH is methyl alcohol.

According to IUPAC system (Unit 12, Class XI), the name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'. The position of substituents are indicated by numerals. For this, the longest carbon chain (parent chain) is numbered starting at the end nearest to the hydroxyl group. The positions of the -OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached. For naming polyhydric alcohols, the 'e' of alkane is retained and the ending 'ol' is added. The number of -OH groups is indicated by adding the multiplicative prefix, di, tri, etc., before 'ol'. The positions of -OH groups are indicated by appropriate locants, e.g., HO-CH₂-CH₂-OH is named as ethane-1, 2-diol. Table 11.1 gives common and IUPAC names of a few alcohols as examples.

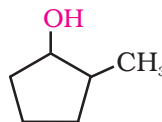
Table 11.1: Common and IUPAC Names of Some Alcohols

Compound	Common name	IUPAC name
CH ₃ - OH	Methyl alcohol	Methanol
CH ₃ - CH ₂ - CH ₂ - OH	<i>n</i> -Propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array}$	Isopropyl alcohol	Propan-2-ol
CH ₃ - CH ₂ - CH ₂ - CH ₂ - OH	<i>n</i> -Butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{OH} \end{array}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
HO-H ₂ C-CH ₂ -OH	Ethylene glycol	Ethane-1,2-diol
$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Glycerol	Propane -1, 2, 3-triol

Cyclic alcohols are named using the prefix cyclo and considering the -OH group attached to C-1.

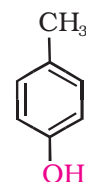
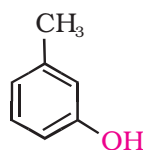
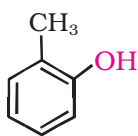
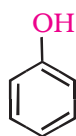


Cyclohexanol



2-Methylcyclopentanol

(b) Phenols: The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name. As structure of phenol involves a benzene ring, in its substituted compounds the terms *ortho* (1,2- disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.



Common name
IUPAC name

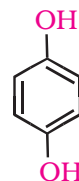
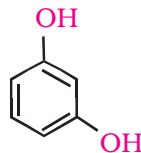
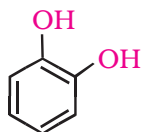
Phenol
Phenol

o-Cresol
2-Methylphenol

m-Cresol
3-Methylphenol

p-Cresol
4-Methylphenol

Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- and 1, 4-benzenediol.



Common name
IUPAC name

Catechol
Benzene-1,2-diol

Resorcinol
Benzene-1,3-diol

Hydroquinone or quinol
Benzene-1,4-diol

(c) Ethers: Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. For example, $\text{CH}_3\text{OC}_2\text{H}_5$ is ethylmethyl ether.

Table 11.2: Common and IUPAC Names of Some Ethers

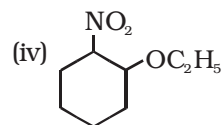
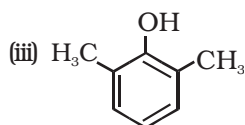
Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6 - \text{CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether.

According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-OR$ or $-OAr$ group, where R and Ar represent alkyl and aryl groups, respectively. The larger (R) group is chosen as the parent hydrocarbon. The names of a few ethers are given as examples in Table 11.2.

Example 11.1

Give IUPAC names of the following compounds:

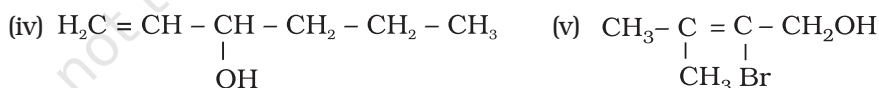
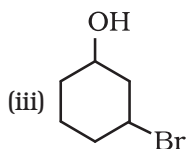


Solution

- (i) 4-Chloro-2,3-dimethylpentan-1-ol (ii) 2-Ethoxypropane
 (iii) 2,6-Dimethylphenol (iv) 1-Ethoxy-2-nitrocyclohexane

Intext Question

11.3 Name the following compounds according to IUPAC system.



11.3 Structures of Functional Groups

In alcohols, the oxygen of the $-OH$ group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. Fig. 11.1 depicts structural aspects of methanol, phenol and methoxymethane.

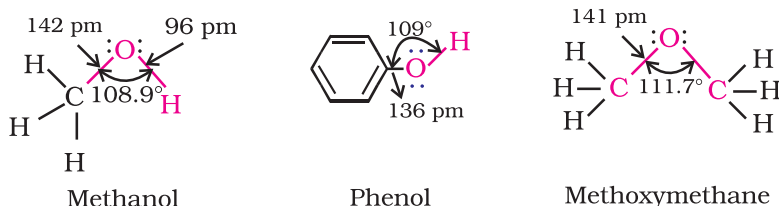


Fig. 11.1: Structures of methanol, phenol and methoxymethane

The bond angle $\text{C}-\text{O}-\text{H}$ in alcohols is slightly less than the tetrahedral angle ($109^\circ-28'$). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the $-\text{OH}$ group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring (Section 11.4.4) and (ii) sp^2 hybridised state of carbon to which oxygen is attached.

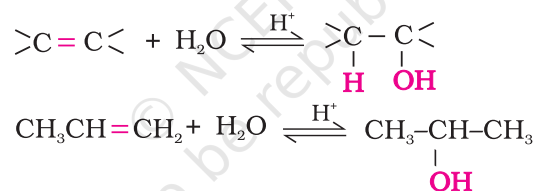
In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky ($-\text{R}$) groups. The $\text{C}-\text{O}$ bond length (141 pm) is almost the same as in alcohols.

11.4.1 Preparation of Alcohols

Alcohols are prepared by the following methods:

1. From alkenes

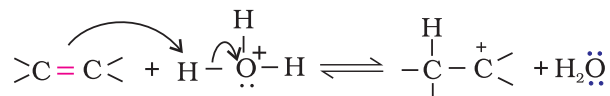
- (i) *By acid catalysed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule (Unit 13, Class XI).



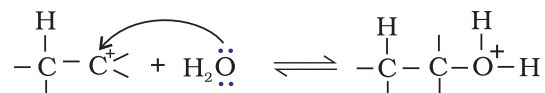
Mechanism

The mechanism of the reaction involves the following three steps:

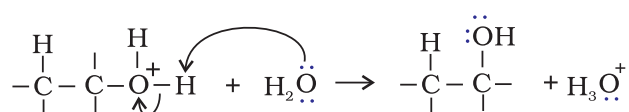
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



Step 2: Nucleophilic attack of water on carbocation.

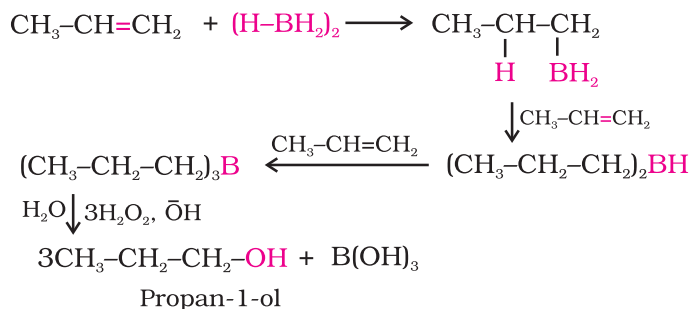


Step 3: Deprotonation to form an alcohol.



Hydroboration - oxidation was first reported by H.C. Brown in 1959. For his studies on boron containing organic compounds, Brown shared the 1979 Nobel prize in Chemistry with G. Wittig.

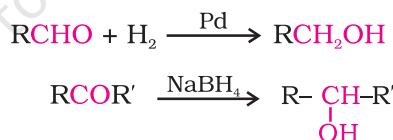
- (ii) *By hydroboration-oxidation:* Diborane (BH₃)₂ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



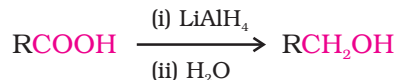
The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the *sp*² carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

2. From carbonyl compounds

- (i) *By reduction of aldehydes and ketones:* Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is a finely divided metal such as platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride (NaBH₄) or lithium aluminium hydride (LiAlH₄). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



- (ii) *By reduction of carboxylic acids and esters:* Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agent.



However, LiAlH₄ is an expensive reagent, and therefore, used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters (Section 11.4.4), followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

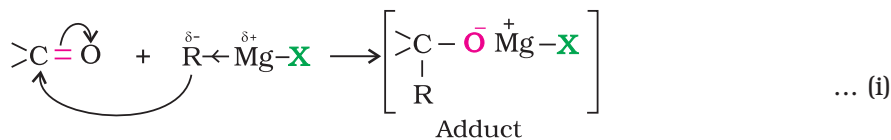


The numbers in front of the reagents along the arrow indicate that the second reagent is added only when the reaction with first is complete.

3. From Grignard reagents

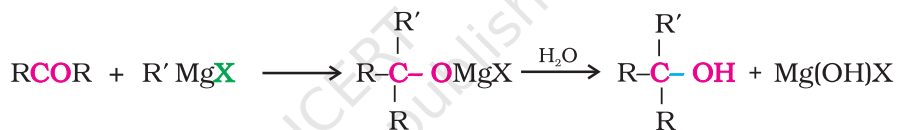
Alcohols are produced by the reaction of Grignard reagents (Unit 10, Class XII) with aldehydes and ketones.

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



The reaction of Grignard reagents with methanal produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols.

The overall reactions using different aldehydes and ketones are as follows:

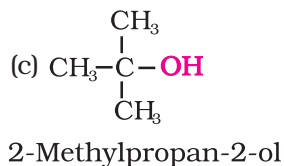
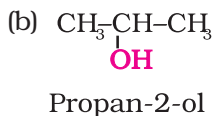
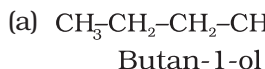


You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

Give the structures and IUPAC names of the products expected from the following reactions:

Example 11.2

- Catalytic reduction of butanal.
- Hydration of propene in the presence of dilute sulphuric acid.
- Reaction of propanone with methylmagnesium bromide followed by hydrolysis.



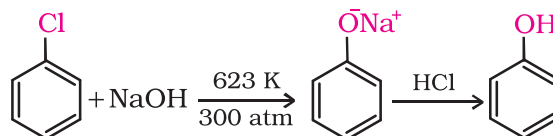
Solution

11.4.2 Preparation of Phenols

Phenol, also known as carboic acid, was first isolated in the early nineteenth century from coal tar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives by any of the following methods:

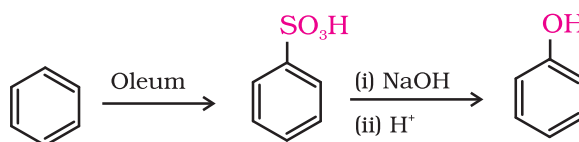
1. From haloarenes

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced (Unit 10, Class XII).



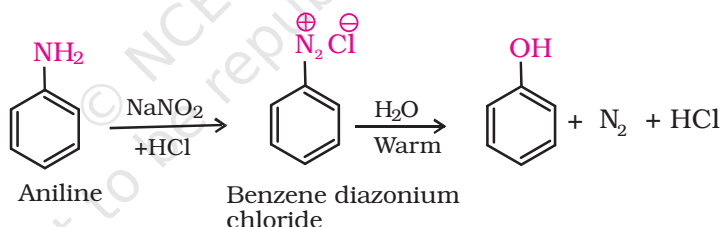
2. From benzenesulphonic acid

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol.



3. From diazonium salts

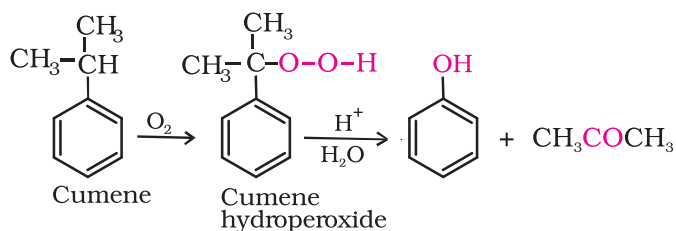
A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids (Unit 13, Class XII).



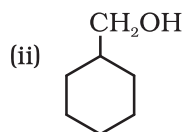
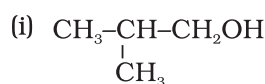
Most of the worldwide production of phenol is from cumene.

4. From cumene

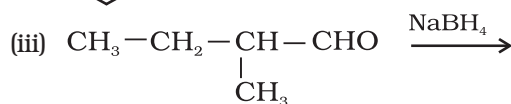
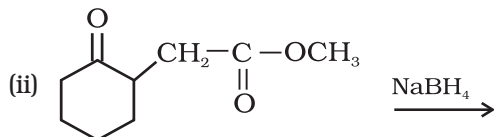
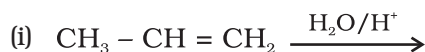
Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.



11.4 Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



11.5 Write structures of the products of the following reactions:



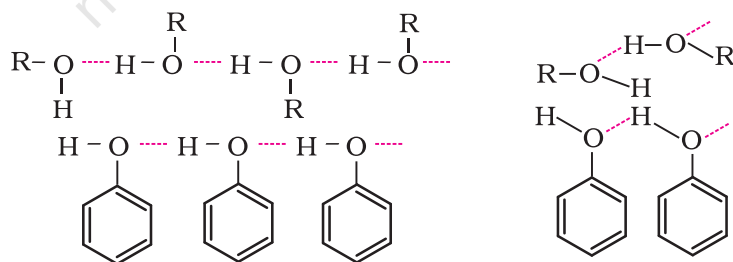
11.4.3 Physical Properties

Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

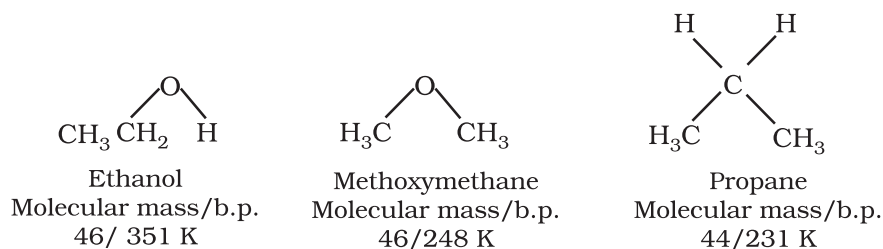
Boiling Points

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



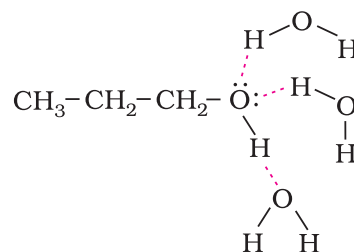
It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.



The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.

Solubility

Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups. Several of the lower molecular mass alcohols are miscible with water in all proportions.



Example 11.3

Arrange the following sets of compounds in order of their increasing boiling points:

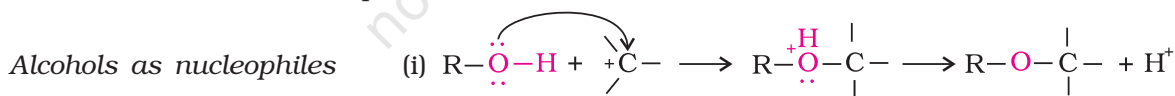
- (a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.
 (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Solution

- (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.
 (b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

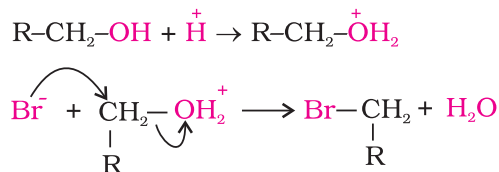
11.4.4 Chemical Reactions

Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O-H is broken when alcohols react as nucleophiles.



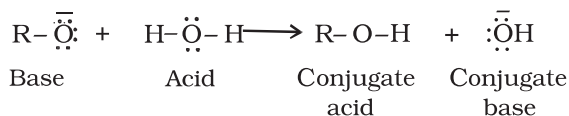
- (ii) The bond between C-O is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles



Based on the cleavage of O-H and C-O bonds, the reactions of alcohols and phenols may be divided into two groups:

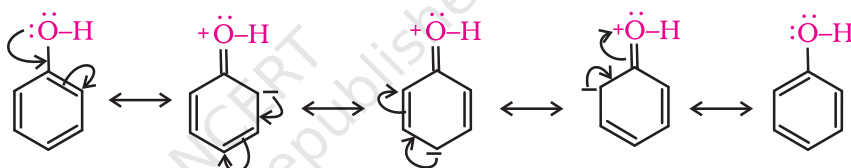
Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

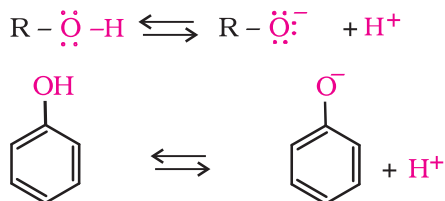
Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

(iii) *Acidity of phenols:* The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of -OH group to be positive.



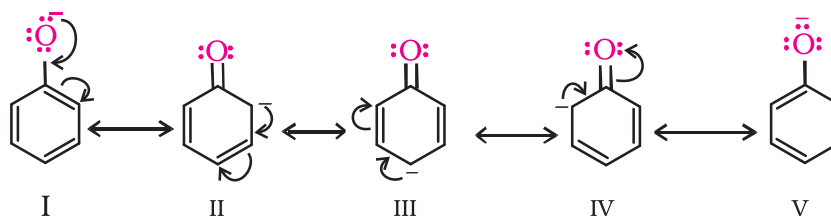
The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how a compound in which hydroxyl group attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group.

The ionisation of an alcohol and a phenol takes place as follows:



Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which -OH is attached, electron density decreases on oxygen. This increases the polarity of O-H bond and results in an increase in ionisation of phenols than that of alcohols. Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes

phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.



In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion when substituent is at *ortho* or *para* position. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

The greater the pK_a value, the weaker the acid.

Table 11.3: pK_a Values of some Phenols and Ethanol

Compound	Formula	pK_a
<i>o</i> -Nitrophenol	$o\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.2
<i>m</i> -Nitrophenol	$m\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	8.3
<i>p</i> -Nitrophenol	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-OH}$	7.1
Phenol	$\text{C}_6\text{H}_5\text{-OH}$	10.0
<i>o</i> -Cresol	$o\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
<i>m</i> -Cresol	$m\text{-CH}_3\text{C}_6\text{H}_4\text{-OH}$	10.1
<i>p</i> -Cresol	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{-OH}$	10.2
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

Arrange the following compounds in increasing order of their acid strength: [Example 11.4](#)

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol. [Solution](#)

2. Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.