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
 (i) alkenes (ii) aldehydes, ketones and carboxylic acids;
- discuss the reactions involved in the preparation of phenols from (i) haloarenes (ii) benzene sulphonic acids (iii) diazonium salts and (iv) cumene;
- discuss the reactions for preparation of ethers from (i) alcohols and (ii) alkyl hardes and sodium alkorida on oxides;
- correlate prosteal properties of alcohols, phenols and ethers van 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 altorather cherent properties and applications. Accounts and **phenols** are formed when a hydrocen atom in a hydrocarbon, aliphatic and aromatic espectively is eplaced by –OH group. These charges of compounds in a wide applications in industry as well as in flay to-day life. For instance, have you erected that ordinary spirit used for polishing 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 (CH₃OH) while a phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C₆H₅OH).

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



Common name IUPAC name Phenol o-Cresol Phenol 2-Methy

o-Cresol m 2-Methylphenol 3-

m-Cresol 3-Methylphenol *p*-Cresol 4-Methylphenol

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





OH

OH

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 in italding the word 'ether' at the end. For example, $CH_3OC_2H_2$ is chymethyl ether.

Table 11.2: Common and IUPAC Nap Some Ethers

Compound	Спітіл-пате	IUPAC name
CH ₃ OCH ₃	Dimethyl einer	Methoxymethane
C ₂ H ₅ OC ₃ H ₅	Dienvether	Ethoxyethane
CH ₃ OCh ₂ CH ₂ CH ₃	Methyl n-propyl ether	1-Methoxypropane
C ₆ H ₅ OCH ₃	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6 - CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
$CH_3O-CH-CH_3$	Methyl isopropyl ether	2-Methoxypropane
ĊH ₃		
$\begin{array}{c} \mathrm{C_6H_5-O-CH_2-CH_2-CH-CH_3}\\ \mathrm{I}\\ \mathrm{CH_3} \end{array}$	Phenyl isopentyl ether	3- Methylbutoxybenzene
CH_3 - O - CH_2 - CH_2 - OCH_3	—	1,2-Dimethoxyethane
H_3C CH_3 OC_2H_5	—	2-Ethoxy- -1,1-dimethylcyclohexane

319 Alcohols, Phenols and Ethers



Alcohols and phenols consist of two parts, an alkyl/aryl group and a 11.4.3 Physical hydroxyl group. The properties of alcohols and phenois are chiefly due to the hydroxyl group. The nature of alk and aryl groups simply **Properties** modify these properties.

Boiling Points

Boiling Points The boiling points of alcohols and phenols increase with increase in the number of tablor atoms (increase in van der Waals forces). In alcohols, Devicting points decrease with increase of branching in carbon chain because of dec cue 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.

325 Alcohols, Phenols and Ethers

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

$$R- \frac{\ddot{O}}{\dot{O}} + H- \dot{O} - H \longrightarrow R- O-H + : \frac{\ddot{O}}{\dot{O}}H$$

Base Acid Conjugate Conjugate
acid base

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 indicities 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

Preview

- (ii) *Halogenation:* On treating phenol with bromine, different reaction products are formed under different experimental conditions.
 - (a) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as FeBr_3 (Unit 10, Class XII), which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of -OH group attached to the benzene ring.

(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.

