## Class XII Chemistry Chapter 10 ALCOHOLS, PHENOLS AND ETHERS

- 1. Alcohols are compounds that have a hydroxyl group ( OH) attached to a saturated carbon atom. Enols are compounds that have a hydroxyl group attached to an unsaturated carbon atom of a double bond. The saturated carbon can be alkyl, alkenyl, alkynyl, cycloalkyl, or benzyl. If, on the other hand, a hydroxyl group is attached to a benzene ring. Phenols are the name given to these compounds.
- 2. The alcohols are further classified as monohydric (containing one OH group), dihydric (containing two OH groups), and trihydric (containing three OH groups) (containing three OH groups).
- 3. Alcohols are classified as 1°, 2° and 3°.
- 4. -OH group is attached to  $sp^3$  hybridized carbon. Alcohols further may bemonohydric, dihydric and polyhydric on the basis of OH group.
- 5. Classification:

СН.—ОН	Methanol	
0113 011	Wiethanoi	
R—CH <sub>2</sub> —OH	1° Alcohol	Primary
R I R—CH—OH	2° Alcohol	Secondary
R R C H R	3° Alcohol	Tertiary
R—O—R	Symmetrical Ether	
R—O—R'	Unsymmetrical Ether	

6. **Phenols:** Compounds containing – OH group bound directly to benzene ring.



7. **Structure:** Oxygen atom is  $sp^3$  hybridised and tetrahedral geometry of hybrid atomic orbitals ROH bond angle depends upon the R group. R – O – H angle forCH<sub>3</sub> – OH is 108.9°.



## 9. General Methods of Preparation:

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(i) Acid catalysed hydration of alkenes:

$$CH_3 - CH = CH_2 + H_2O - \frac{dil.H_2SO_4}{CH_3 - CH - CH_3}$$

#### (ii) Hydroboration oxidation:

$$3CH_3 - CH = CH_2 + \frac{1}{2}B_2H_6 \xrightarrow{D.E} (CH_3 - CH_2 - CH_2)_3B \xrightarrow{OH} H_2O_2$$

$$CH_3 - CH_2 - CH_2OH + H_3BO_3$$

## (iii) From carbonyl compounds with Grignard's reagent :



Formaldehyde gives 1° alcohol and ketones gives tertiary alcohol.

(iv) By reduction of carbonyl compounds :

$$RCHO + 2[H] \xrightarrow{Pd} RCH_2OH$$

$$H C = O + 2[H] \xrightarrow{NaBH_4} H CH_2OH$$

$$R C = O + 2[H] \xrightarrow{NaBH_4} R CHOH$$

(v) By reduction of esters with  $LiAlH_4$  or  $Na/C_2H_5OH$ :

$$R - C - OR' + 4[H] \xrightarrow{\text{LiAlH}_4} R - CH_2OH + R' - OH$$

(vi) By hydrolysis of esters :

$$R - C - O - R' + H_2O \xleftarrow{conc} R - C - OH + R' - OH$$

(vii) From alkyl halides :

$$R - X + KOH (aq) \rightarrow R - OH + KX$$

(viii) By reduction of acids and their derivatives :

$$R - COOH \longrightarrow RCH_2OH$$

$$R - COCl + 2H_2 \xrightarrow{Ni} R.CH_2OH + HCl$$

(ix) From 1° amines :

$$R - NH_2 \xrightarrow{NaNO_2 + HCl} ROH + H_2O + N_2$$

## **Physical Properties**

## **Boiling point**

The boiling points of alcohols and phenols rise as the number of carbon atoms increases (increase in van der Waals forces). The boiling point of alcohols decreases as branching increases (decrease in Van der Waals forces due to decrease in surfacearea). In alcohols and phenols, the -OH group contains a hydrogen atom that is bonded to a electronegative oxygen atom. As a result, it is capable of forming intermolecular hydrogen bonds with greater strength than amine.



Alcohols and phenols have higher boiling points than other classes of compounds, such as hydrocarbons, ethers, and haloalkanes/haloarenes, amines with comparablemolecular masses, due to the presence of strong

intermolecular hydrogen bonding.

Their boiling points are lower than those of carboxylic acid, which has a stronger hydrogen bond. Boiling points for isomeric alcohols decrease as branching increases due to a decrease in van der Waals forces as size decreases. The boiling point sequence is primary alcohol > secondary alcohol > tertiary alcohol.

Due to lower dipole moment and the absence of H-bonding, the boiling point of ethers is very low and comparable to that of alkanes of comparable molecular mass.

## **Solubility**

Alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules. Solubility decreases as the size of the hydrophobic group increases (R). Higher concentrations of alcohol are insoluble. Because of the decrease in surface area of the non-polar hydrocarbon part, branching increases solubility.

n-butylalcohol < isobutylalcohol < sec-butylalcohol < tert-butylalcohol



## **Common Phenols and Aromatic Ethers**







Anisole

Phenetole





Picric Acid



Salicylic Acid







Catechol

Resocinol

Hydroquinone

## **Preparation of Phenols**



## **Dow's Process**

It is an industrial method which is used for the preparation of phenol. It takes place through benzene mechanism.

Example:



better nuc

н⊕

OH



Example:



## Distillation of phenolic acids with soda lime

Example:



# **Grignard reagent**

Example:



#### NAME REACTIONS



4. Williamson synthesis: Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide is called Williamson synthesis.

 $R-X + R^{1} - O - Na \longrightarrow R - O - R^{1} + NaX$  $CH_3I + CH_3CH_2ONa \longrightarrow CH_3O.CH_2 - CH_3 + Nal$ ONa  $CH_3CH_2 - I + \bigcirc + Nal$ 

Both simple and mixed ether can be produced.

Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN<sup>2</sup> or SN<sup>1</sup> mechanism.

#### **MECHANISMS**

1. Hydration of Alkene :



*Mechanism* 

The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of  $H_2O^+$ .

 $H_{2}O + H^{+} \rightarrow H_{3}O^{+}$ 

$$>C = C < + H - O^{+} - H \implies - C < + H_{2}O^{+}$$

Step 2: Nucleophilic attack of water on carbocation.

Step 3: Deprotonation to form an alcohol.



#### 2. Dehydration Reaction



# Chemical Reactions of Ethers Cleavage by HBr and HI

$$R \longrightarrow O \longrightarrow R' \xrightarrow{excess HX} R \longrightarrow X + R' \longrightarrow X$$

$$Ar \longrightarrow O \longrightarrow R \xrightarrow{Excess HX} (X = Br, I) \longrightarrow Ar \longrightarrow OH + R \longrightarrow X$$

$$Ar = Aromatic Ring \xrightarrow{Excess HX} Ar \longrightarrow OH + R \longrightarrow X$$

**Auto-oxidation** 



**Preparation of epoxide** 



# **Base-promoted cyclization of halohydrins**



X = Cl, Br, I, OTs, etc.

**Examples** 



(i) Despite the fact that oxygen is more electronegative than sulfur, alcohols are weaker acids than thiols. RO<sup>-</sup>, the conjugate base of alcohol, is more basic than RS<sup>-</sup> because the negative charge in RO<sup>-</sup> is placed on smaller oxygen atoms, resulting in higher charge density. However, because the RS<sup>-</sup> negative charge is dispersed on larger sulphur, it is a poor base and its conjugate acid is more acidic.

(ii) Due to the +I effect of the alkyl group, all alcohols (except CH<sub>3</sub>OH) are weaker than water CH<sub>3</sub>OH is slightly more powerful than H<sub>2</sub>O. Because of the electron withdrawing benzene ring and the resonance stabilized phenolic ion, phenols are stronger than alcohol. Because alkoxide ions, the conjugate base of alcohol, lack resonance, they are less stable and more basic. Phenol is less stable than carboxylicacid, which has a strong electron-drawing carbonyl group and more stable, resonating structure.

