Alcohols

B.Sc. Part I (Hons.)

Paper : I C (Organic chemistry)

Group B

-by Dr. Manju Kumari
Maharaja College.

Monohydric Alcohol.

Methods of preparation of monohydric alcohols :

(i) Addition of water to alkenes → **Hydration of alkenes** : Most of the alkenes are absorbed in conc. H_2SO_4 to give alkyl hydrogen sulphates which on hydrolysis from alcohols.

$$R-CH=CH_2 + H_2SO_4 \rightarrow R-\underset{\displaystyle OSO_3H}{\underset{|}{C}}H-CH_3$$

$$\xrightarrow{HOH} R-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3$$

Secondary alcohol

It is not possible to prepare primary alcohol by this method (except ethyl alcohol).

(iv) **Hydroboration-Oxidation :** This method is very useful for the preparation of primary alcohols.

$$6RCH=CH_2 + B_2H_6 \rightarrow 2(R-CH_2-CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 6R-CH_2-CH_2OH$$

Nucleophilic substitution :

(i) **From alkyl halides :** Hydrolysis of alkyl halides with aqueous NaOH or KOH yields alcohols.

$$R-X + NaOH \xrightarrow[\Delta]{H_2O} R-OH + NaX$$

$$C_2H_5-Br + NaOH \xrightarrow[\Delta]{H_2O} C_2H_5-OH + NaBr.$$

Reduction :

(i) Catalytic hydrogenation :

$$R-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow[\text{Pressure}]{Ni} R-CH_2-OH \text{ (Pr. alcohol)}$$

$$R-\overset{O}{\overset{\|}{C}}-R' + H_2 \xrightarrow[\text{Pressure}]{Ni} R-\underset{R'}{\overset{|}{CH}}-OH \text{ (Sec. Alcohol)}$$

(ii) Reduction with $LiAlH_4$ and $NaBH_4$:

$LiAlH_4$ is widely used for the reduction of aldehydes, ketones, acids, acid chlorides and esters into alcohols. The solvent used for the reaction is generally dry ether, THF or dichloromethane.

$$R-CHO \xrightarrow{LiAlH_4} R-CH_2OH$$

$$R-COOH \xrightarrow{LiAlH_4} R-CH_2OH$$

$$R-COOC_2H_5 \xrightarrow{LiAlH_4} R-CH_2OH + C_2H_5OH$$

$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{LiAlH_4} R-\underset{R'}{\underset{|}{C}}H-OH$$

$NaBH_4$ is a milder ~~reduction~~ reducing agent and does not reduce acids and acid derivatives. However, it reduces aldehydes and ketones into corresponding alcohols.

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaBH_4} R-CH_2-OH$$

$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{NaBH_4} R-\overset{OH}{\overset{|}{C}}H-R'$$

Physical Properties :

(i) Boiling point of compounds :—

compound →	H_2O	CH_4	CH_3OH
M.Wt	18	16	32
bp °C	100	−164	65

(ii) Sulubility : Low molecular weight alcohols are water soluble, owing to their ability to form hydrogen bond with water. As molecular weight increases, however, water solubility decreases.

compound	Mol. Wt.	m.p. (°C)	bp (°C)	water Solubility
CH_3OH	32	−94	65	S
CH_3CH_2OH	46	−117	78·5	S
$CH_3CH_2CH_2OH$	60	−127	97	S
$CH_3CH_2CH_2CH_2OH$	74	−90	118	7.5g / 100ml.

Chemical Reactions:

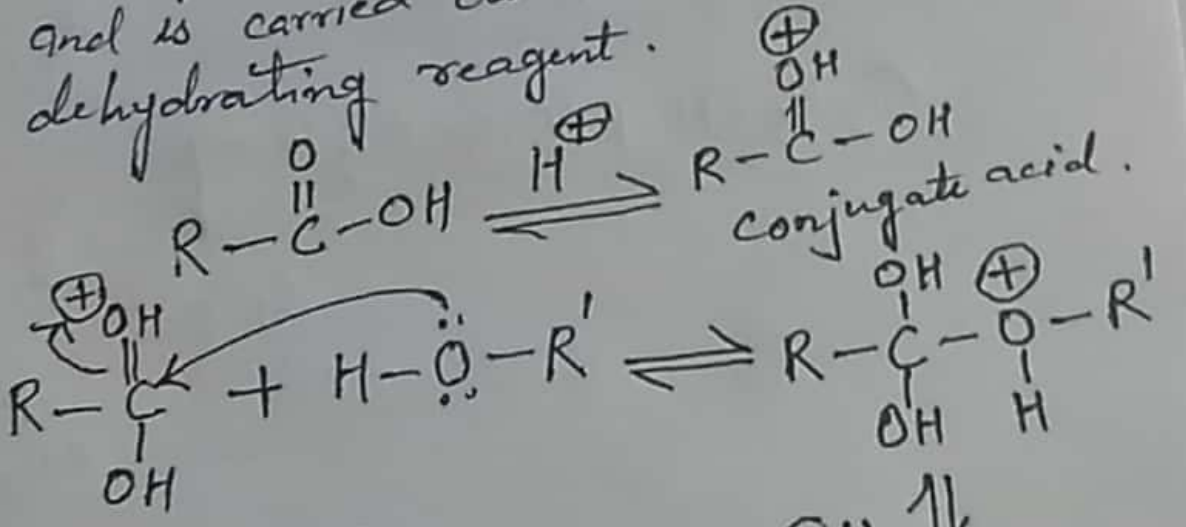
Reaction with carboxylic acids:

Esterification

Alcohols react with acids in the presence of catalyst (Conc. H_2SO_4) to form esters.

$$R-OH + R'COOH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} R-O-\overset{O}{\overset{\|}{C}}-R' + H_2O$$

The esterification is a reversible process and is carried out in the presence of dehydrating reagent.



The reaction is acid catalysed, the function of the strong acid is to convert carboxylic acid into its conjugate acid.

Reaction with Acid chloride and acid anhydride : Acetylation.

With acid chloride and acid anhydride alcohols form esters :

$$R-OH + R'COCl \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-R'$$

$$CH_3COCl + C_2H_5OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

$$R-OH + \begin{matrix} R'-CO \\ R'-CO \end{matrix}\!\!>O \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-R' + R'COOH$$

$$C_2H_5OH + (CH_3CO)_2O \longrightarrow C_2H_5-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH.$$

(To be continued....)