ALCOHOLS

(Part II)

CHEMICAL PROPERTIES OF ALCOHOLS

- Alcohols acts both as nucleophiles as well as electrophiles.
- The bond between O-H is broken when alcohols react as nucleophiles and the bond between C-O is broken when they react as electrophiles.
- The chemical properties of any given aliphatic alcohol depend on the nature of the alkyl group and on the properties of the hydroxyl group.
- Based on the cleavage of O-H and C-OH bonds, the reactions of alcohols may be divided into two groups.

(A) Reactions involving cleavage of O-H bond

(B) Reaction involving fission of R—OH bond (cleavage of C—O bond)

During cleavage of C-O bond Alcohols show following order of reactivity.

Tertiary alcohol> secondary alcohol> Primary alcohol

and in case of O-H bond cleavage order of reactivity changes to CH_3OH> Primary alcohol> Secondary alcohol> Tertiary alcohol

(A)Reactions involving cleavage of O-H bond :

1. **Acylation of alcohol:** When alcohol reacts with acyl halide and anhydride substitution of hydrogen atom by acyl group is known as acylation of alcohols

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$$

$$C_2H_5OH + CH_3COOH \longrightarrow C_2H_5COOC_2H_5 + H_2O$$

$$C_2H_5OH + CH_3COCl \longrightarrow CH_3COOC_2H_5 + HCl$$

B)Reaction involving fission of R—OH bond

The reactions involving R – OH bond with cleavage of C – O bond are as follows;

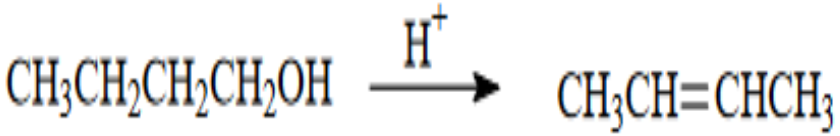
$$C_2H_5OH + SOCl2 \longrightarrow C_2H_5Cl + SO_2 + HCl$$

$$C_2H_5OH + HNH2 \longrightarrow C_2H_5NH_2 + H_2O$$

1. Dehydration (alkene formation):

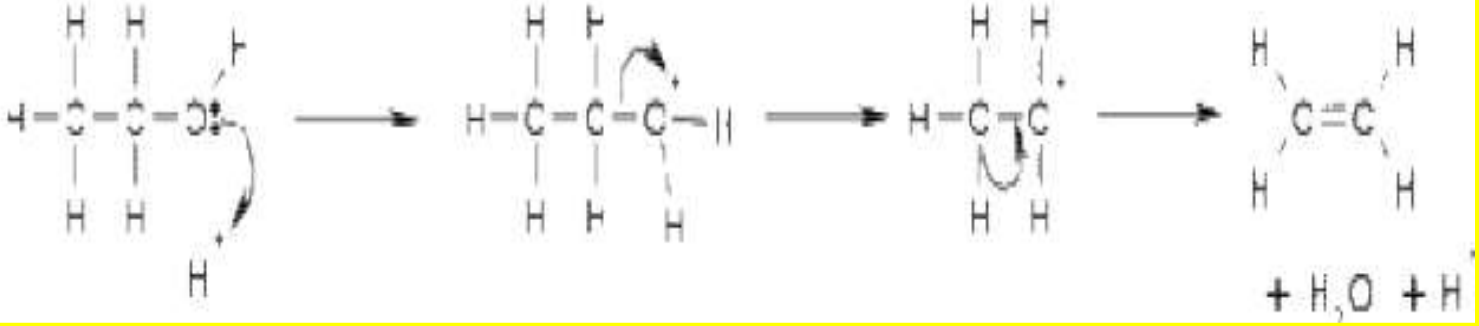
Alcohols on treating with a protic acid (Con. H_2SO_4 or H_3PO_4, or catalysts such as anhydrous $ZnCl_2$ or Al_2O_3) undergo dehydration to form unsaturated Hydrocarbon. In this reaction the OH and an H groups removes from an adjacent carbons. Since water is removed from the alcohol, this reaction is known as a dehydration reaction (or an elimination reaction).

The conditions for dehydrating alcohols depend closely on the structure of individual alcohols. For **primary alcohols**, the conditions required are conc. H_2SO_4 and temperature of 170°C.



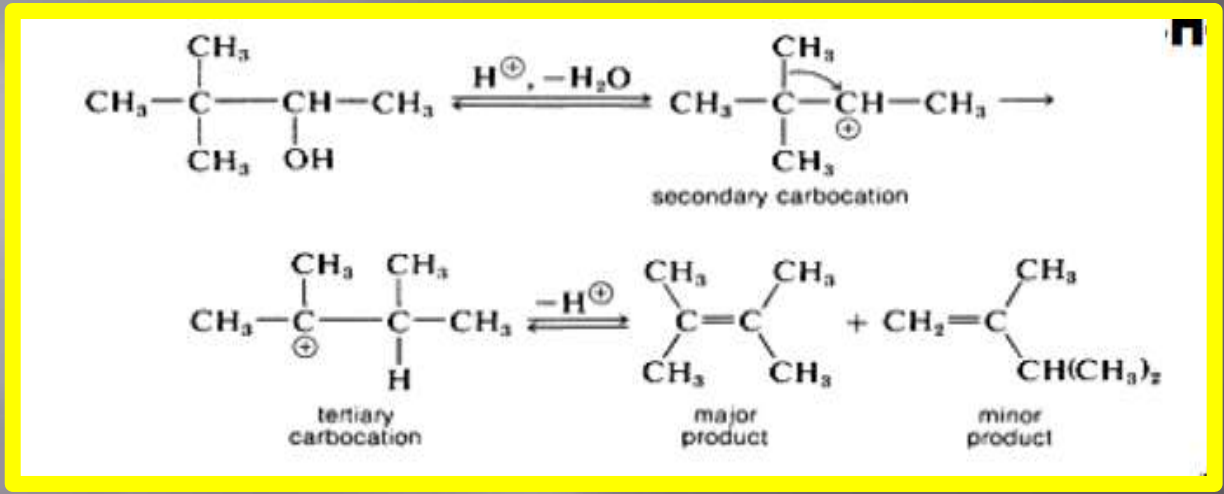
Dehydration of 2º and3º alcohols containing more than three carbon atoms will give a mixture of alkenes, the major product can be determined from **Saytzeff's Rule:** When an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond i.e., the major product is that contains the higher number of alkyl groups attached to the C=C bond.

e.g.



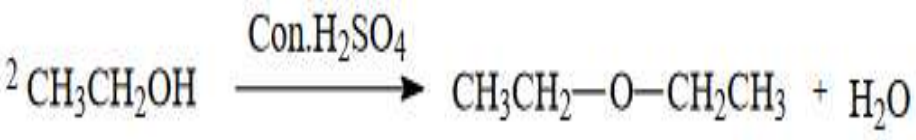
Rearrangement of the alkyl groups of alcohols is very common in dehydration, particularly in the presence of strong acids, which are conducive to carbocation formation. Typical examples showing both methyl and hydrogen migration follow.

Mechanism:



Intermolecular dehydration (forming ether):

When the dehydration is carried out at 140° C with an excess of alcohol, ether will be formed. This reaction removes a molecule of water from two alcohol molecules, causing the two "R" groups to become attached to an oxygen atom, forming an ether functional group:

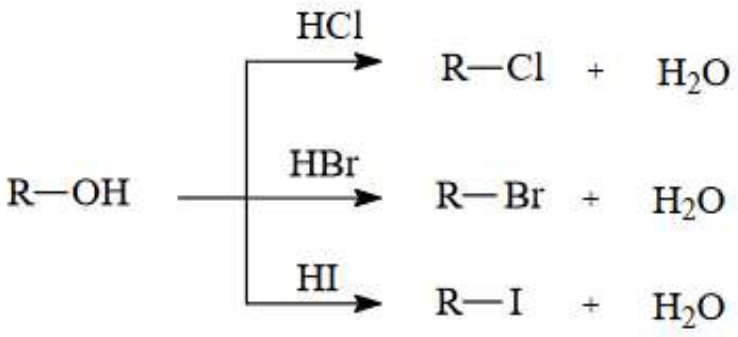


2 . **Halogenation**:

Alcohols can be converted to alkyl halides using one of three reactions:

a) Reaction with hydrogen halides:

Respective alkyl halides are formed by reacting with the appropriate hydrogen halide, HCl for chlorination, HBr for bromination and HI for iodination. The reaction involves the initial protonation of the hydroxyl group of the alcohol. This improves the leaving group ability of the hydroxyl group.

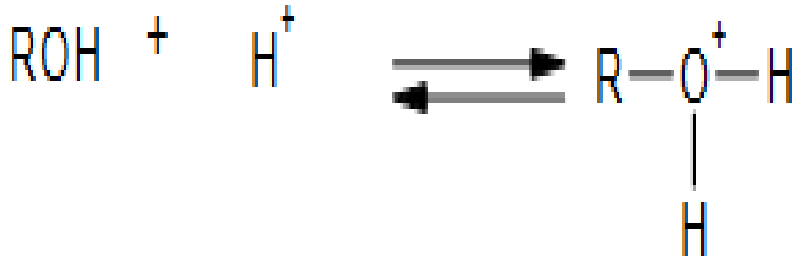


Mechanism:

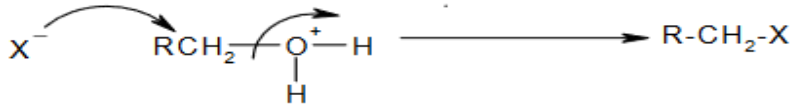
- Step1: Protonation of the alcohols:

The alcohol acts as a weak base and accepts the proton donated by the hydrogen halide.

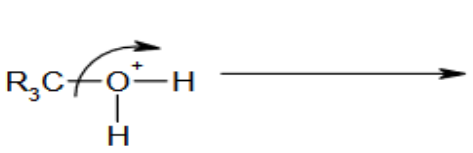
- Step 2: Removal of a water molecule and formation of halide through SN2 mechanism / SN1 mechanism as:



(i) For primary and secondary alcohols, it is a S_N2 reaction.



(ii) For tertiary alcohols, it is a S_N1 reaction.



(b) Substitution Reactions:

Alcohols give substitution reaction by reacting with reagents Like phosphorus halides(PCl_5,PCl_3), HCl or $SOCl_2$. These Reagents acts as Nucleophile and replace OH group with Halogen group(X).

Then the chloride will act as the nucleophile in a second step and displace the oxygen from the carbinol carbon.

$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + SO_2 + HCl$$

$$C_2H_5OH + HNH_2 \longrightarrow C_2H_5NH_2 + H_2O$$

(c) Reaction with phosphorus halides :

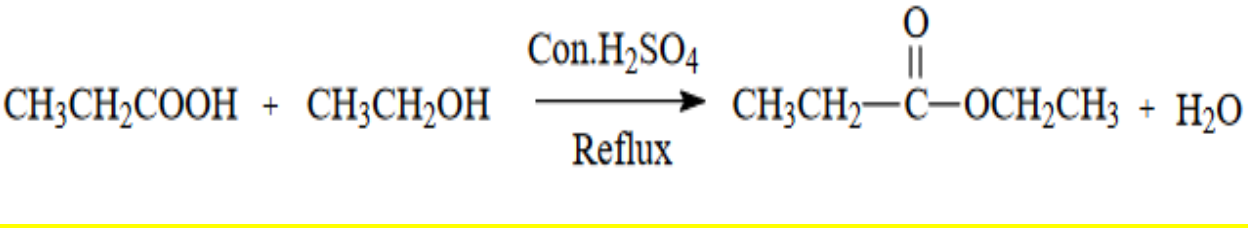
Alcohols will react with phosphorus tribromide or phosphorus pentabromide to form alkyl bromides.

$$3\,C_2H_5OH + PCl_5 \longrightarrow 3C_2H_5Cl + H_3PO_4$$

$$C_2H_5OH + PCl_3 \longrightarrow C_2H_5Cl + POCl + HCl$$

3. Esterification:

- Alcohol reacts with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride is reversible, and therefore, water is removed as soon as it is formed. Esterification takes place much faster in the presence of a catalyst such as conc. H_2SO_4.



- Alcohols can also react with acid chlorides and acid anhydrides to form esters. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation.

Reactivity

Distinction between methanol and ethanol

Methanol and ethanol are distinguished by reacting with iodine in the presence of NaOH, which lead to the formation of yellow crystals of iodoform that indicates that alcohol is ethanol while methanol does not form yellow crystals with iodine.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + NaI + H_2O$$

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No yellow ppt}$$

Distinction between 1º , 2º & 3º alcohol (Lucas Test)

$$R\text{-}OH + HCl \xrightarrow[immediatly]{ZnCl_2} R\text{-}Cl + H_2O$$

Primary alkyl halide

$$(R)_2CH\text{-}OH + HCl \xrightarrow[Heat]{ZnCl_2} (R)_2CH\text{-}Cl + H_2O$$

Secondary alkyl halide

$$(R)_3C\text{-}OH + HCl \xrightarrow[5\text{–}10min]{ZnCl_2} (R)_3C\text{-}Cl + H_2O$$

Tertiary alkyl halide

Dihydric alcohols preparation:

Dihydric alcohols are prepared by following different methods:

From ethylene:

(b) With O_2 in presence of Ag :

$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + \tfrac{1}{2}O_2 \xrightarrow[Ag\ 200\_400\ ^0C]{catalyst} \text{(epoxide)} \xrightarrow[dil.HCl]{H_2O} \begin{matrix}CH_2—OH\\ |\\ CH_2—OH\end{matrix}$$

(c) With HOCl followed by hydrolysis:

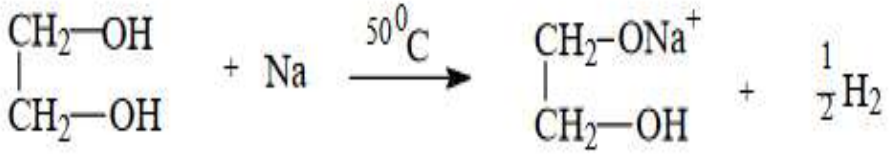
$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + HOCl \longrightarrow \begin{matrix}CH_2—OH\\ |\\ CH_2—Cl\end{matrix} \xrightarrow{NaHCO_3} \begin{matrix}CH_2—OH\\ |\\ CH_2—OH\end{matrix} + NaCl + CO_2$$

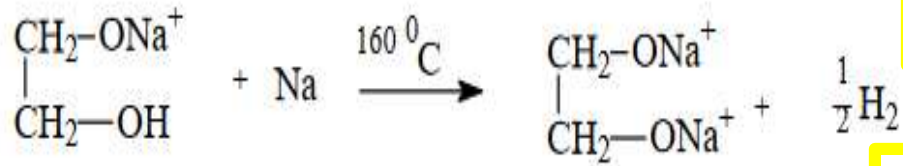
CHEMICAL REACTIONS OF VICINAL GLYCOLS

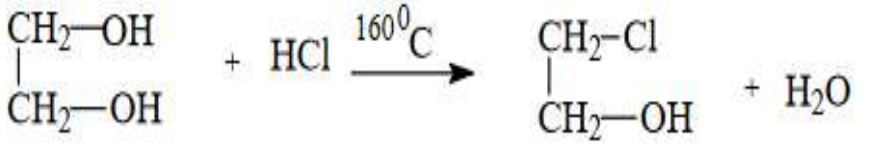
Glycerol molecule is made up of two 1° alcohol groups joined together. It reacts with Na metal at 50°C to form mono and dialkoxide at elevated temperature.

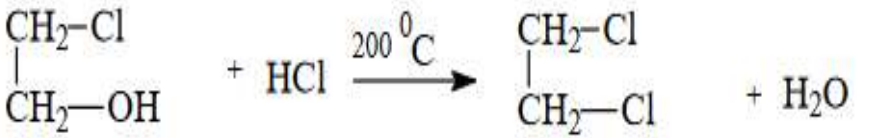
Ethylene dichloride is formed in two steps at high temperature

Ethylene dihalides are formed upon reaction with PBr_3







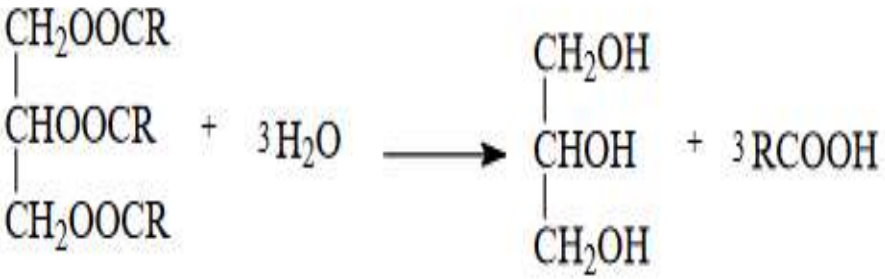


TRIHYDRIC ALCOHOL PREPARATION

Glycerol can be synthesized by following different methods:

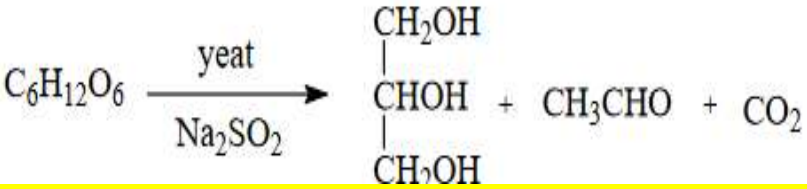
1.From fats and oil:

On hydrolysis of fats and oils, glycerol and higher fatty acids are formed



2 . By fermentation of sugars:

Alcoholic fermentation of sugar in the presence of sodium sulphite gives good yield of glycerol.



Importance and Use of Alcohols

- Alcohols are important for its use in medicine as an antiseptic and disinfectant.
- These are applied to skin to disinfect it before needle stick and before surgery.
- These are used (especially methanol) as solvent for fats, oils, paints and varnishes.
- These are used as antifreeze, denaturing agents, as well as fuel in some areas.
- Moreover in pharmaceutical preparations and as preservative for biological specimen.