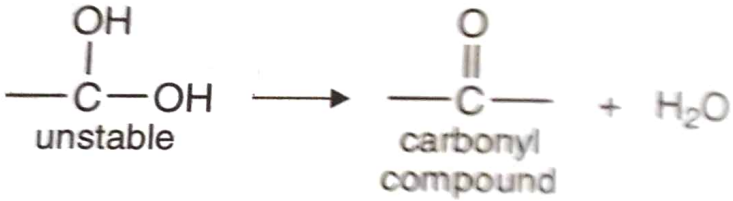
Compounds which contain more than one –OH group are called **Polyhydric**. They are further classified according to the number of –OH groups present in the

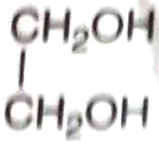
DIHYDRIC ALCOHOLS (DIOLS)

Compounds which contain two –OH groups on different carbons are called **Dihydric Alcohols**. **Diols**. Compounds with two –OH groups on one carbon are seldom encountered they are unstable and undergo spontaneous decomposition to give the corresponding compound and water. Diols were commonly known as **Glycols**, since they have (Greek, *glycys* = sweet).

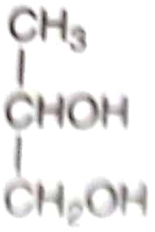


NOMENCLATURE

Diols have both common and IUPAC names. The IUPAC names are obtained by adding *diol* to the name of the parent alkane. Numbers are used to indicate the position of the groups. For example,

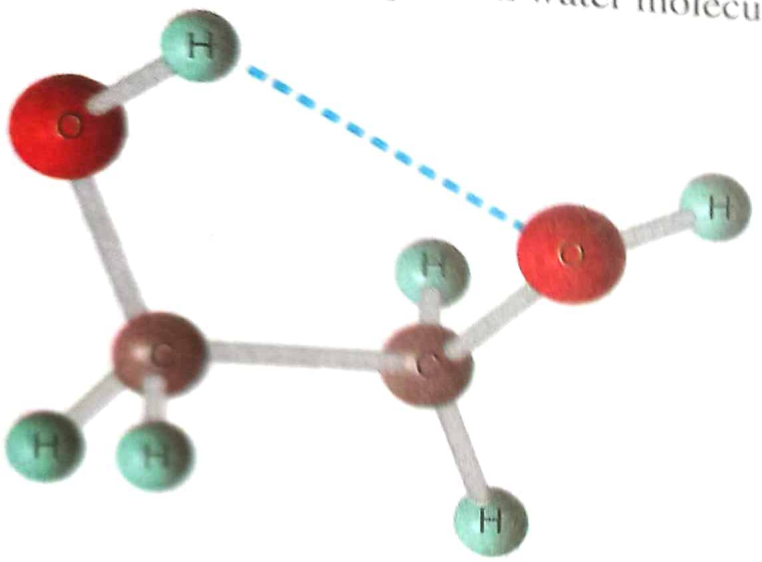


1,2-Ethanediol
(Ethylene glycol)



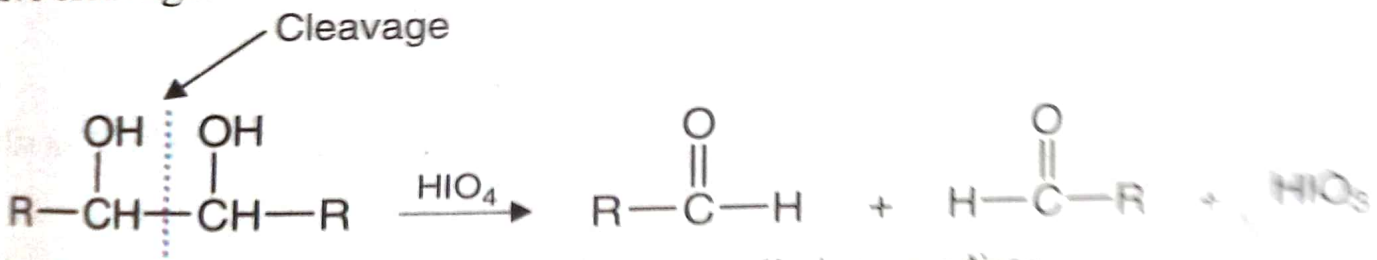
1,2-Propanediol
(Propylene glycol)

...which are colorless, viscous liquids. They are soluble in water. Their boiling points are ... than those of monohydric alcohols of similar molecular weight. For example, the b... ethylene glycol (MW = 62) is 197°C while that of 1-propanol (MW = 60) is 97°C. T... the presence of two –OH groups in the molecule gives rise to extensive hydrogen bon... explains their high viscosity, because the molecules of liquid diol being associat... bonds, cannot move freely relative to each other. The high solubility of diols is due to ... form hydrogen bonds at both –OH groups with water molecules.

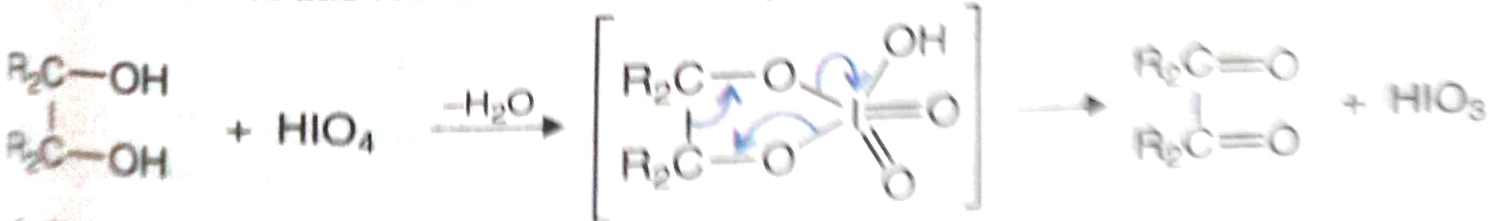


Ethylene glycol is a highly viscous liquid. This is because the molecules also undergo intramolecular hydrogen bonding

Diols give the same reactions as monohydric alcohols at the two –OH groups separately, alt... the second of these groups reacts under more vigorous conditions. Thus they undergo ester form... halide formation, oxidation etc., twice over. However, when oxidized with periodic acid (HIO_4)... undergo oxidation by cleavage to form aldehydes or ketones. Monohydric alcohols do not ... such oxidative cleavage.

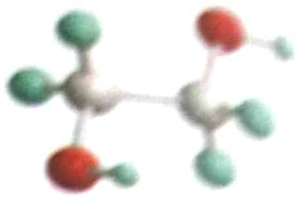


The **mechanism** of this reaction involves a cyclic intermediate.



Diols do not undergo oxidative cleavage as above.

ETHYLENE GLYCOL, 1,2-Ethanediol, $HO-CH_2-CH_2-OH$



Ethylene glycol is the most important member of the class. It is often referred to as Glycol.

Preparation. It is prepared as follows :

(1) By oxidation of ethylene with cold dilute potassium permanganate solution.

$$\underset{\text{Ethylene}}{CH_2=CH_2} + (H_2O + O) \xrightarrow[KMnO_4]{\text{Cold}} \underset{\text{Ethylene glycol}}{CH_2(OH)-CH_2(OH)}$$

(2) By oxidation of ethylene with osmium tetroxide in the presence of sodium bisulphite.

$$\underset{\text{Ethylene}}{CH_2=CH_2} + (H_2O + O) \xrightarrow[NaHSO_3]{OsO_4} \underset{\text{Ethylene glycol}}{CH_2(OH)-CH_2(OH)}$$

(3) By hydrolysis of 1,2-dibromoethane with aqueous sodium carbonate solution.

$$\underset{\text{1,2-Dibromoethane}}{CH_2Br-CH_2Br} + 2Na_2CO_3 + 2H_2O \longrightarrow \underset{\text{Ethylene glycol}}{CH_2OH-CH_2OH} + 2NaHCO_3 + 2NaBr$$

(4) By hydrolysis of ethylene chlorohydrin with sodium bicarbonate.

$$2\,\underset{\text{Ethylene chlorohydrin}}{CH_2(OH)-CH_2Cl} + NaHCO_3 \longrightarrow 2\,\underset{\text{Ethylene glycol}}{CH_2(OH)-CH_2(OH)} + NaCl + CO_2$$

Ethylene chlorohydrin is made by passing ethylene into aqueous hypochlorous acid ($H_2O + Cl_2 \longrightarrow HOCl + HCl$).

$$\underset{\text{Ethylene}}{CH_2=CH_2} + HOCl \longrightarrow \underset{\text{Ethylene chlorohydrin}}{CH_2(OH)-CH_2Cl}$$

(5) By hydrolysis of ethylene oxide with H_2O at 200°C under pressure or with dilute H_2SO_4 at 60°C.

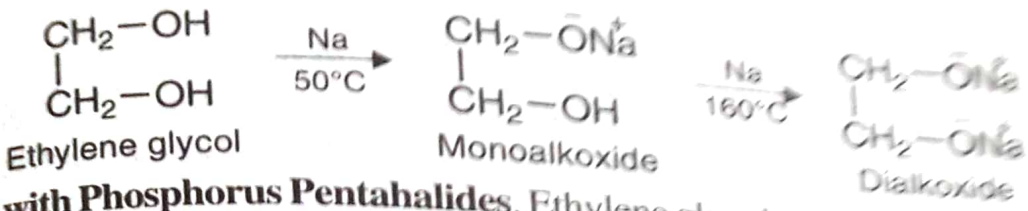
$$\underset{\text{Ethylene oxide}}{CH_2(O)CH_2} + H_2O \xrightarrow[60^\circ C]{H^+} \underset{\text{Ethylene glycol}}{CH_2(OH)-CH_2(OH)}$$

Ethylene oxide is made by passing a mixture of ethylene and oxygen over heated silver at 300°C.

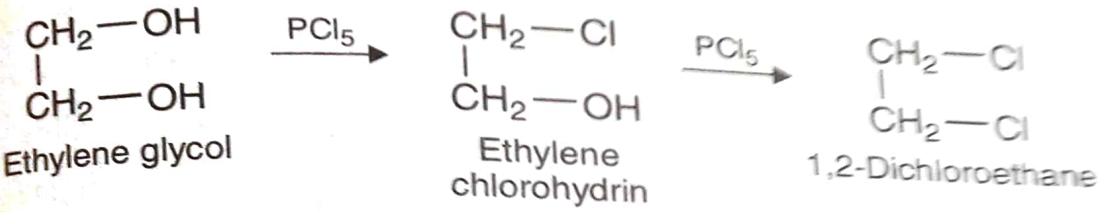
$$CH_2=CH_2 + O_2 \xrightarrow{Ag} CH_2(O)CH_2$$

...ecause, Ethylene glycol molecule contains two primary –OH groups. In chemical reactions ...ever, those of primary alcohols twice over. Generally, one –OH group is attacked completely ...e other reacts. More vigorous conditions are sometimes needed for reaction of the second ...OH groups.

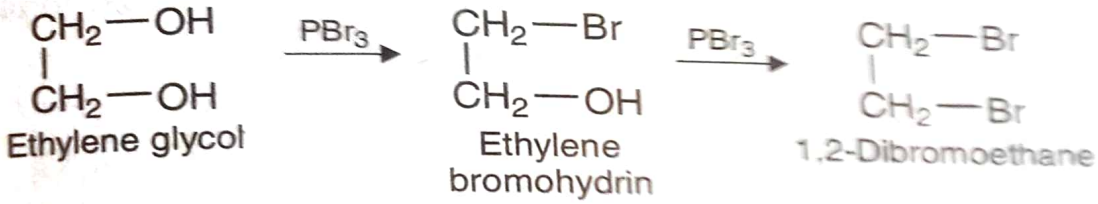
Reaction with Sodium. Ethylene glycol reacts with sodium at 50°C to form monoalkoxide and ...ide when temperature is raised.



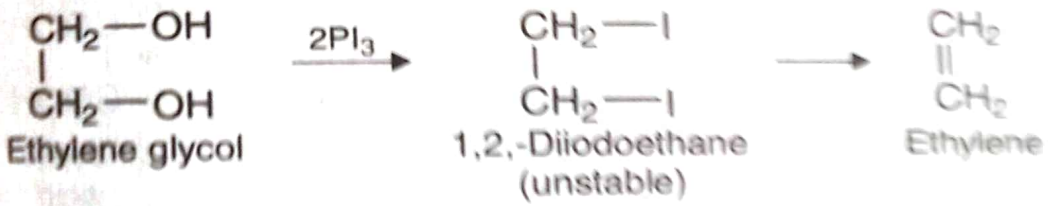
(2) **Reaction with Phosphorus Pentahalides.** Ethylene glycol reacts with PCl_5 first to form ethylene ...rohydrin and then 1,2-dichloroethane. PBr_5 reacts in the same way.



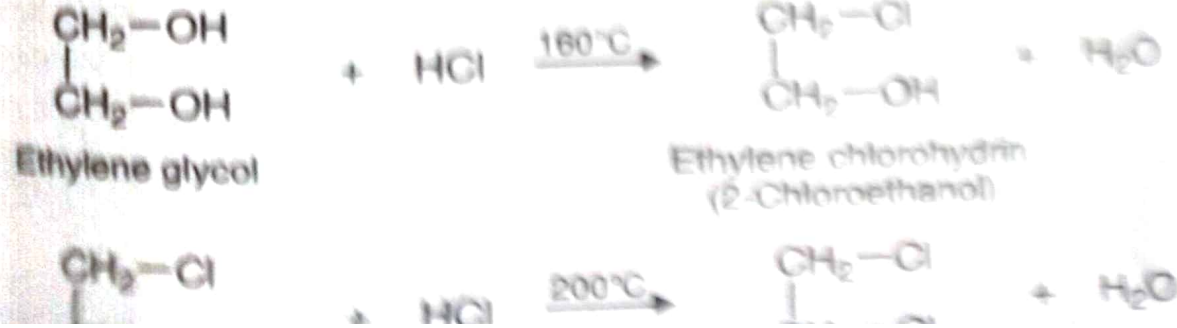
(3) **Reaction with Phosphorus Trihalides.** Ethylene glycol reacts with PBr_3 or PCl_3 to form the ...responding dihalides.

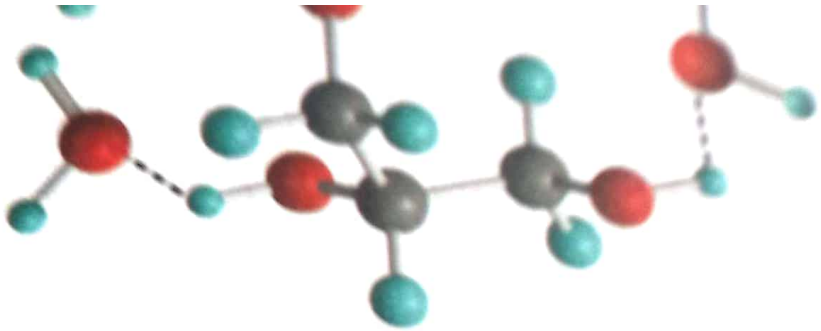


Ethylene glycol reacts with phosphorus triiodide to form 1,2-diiodoethane which is unstable and ...composes to form ethylene.



(4) **Reaction with Hydrogen Chloride.** Ethylene glycol reacts with HCl in two steps first forming ...ylene chlorohydrin at 160°C and then at 200°C to yield 1,2-dichloroethane

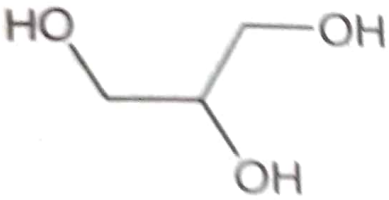


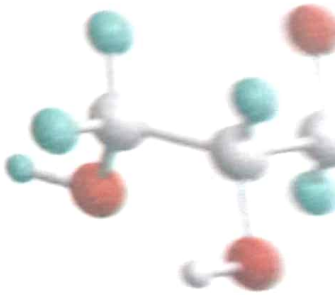


Glycerol is highly soluble in water. This is because it also forms hydrogen bonds with water molecules (Intermolecular hydrogen bonding

Phenols give many reactions of the primary and secondary –OH groups which they contain. We give the simple reactions of –OH groups in triplicate. The only important member of the glycerol or 1,2,3-propanetriol.

GLYCEROL, *1,2,3-Propanetriol*, $HOCH_2–CH(OH)–CH_2OH$

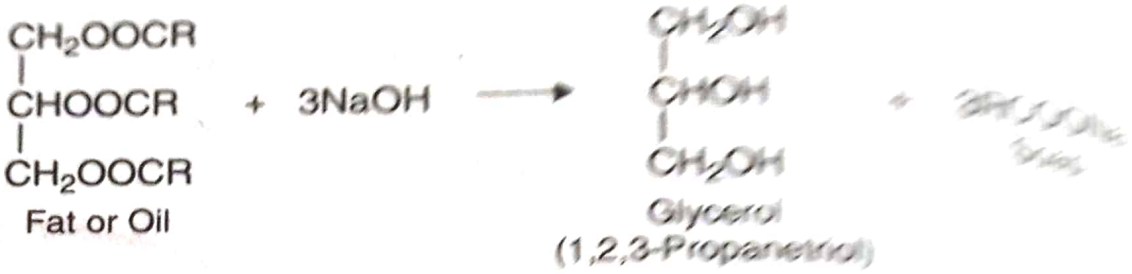




Glycerol or 1,2,3-propanetriol is the most important trihydric alcohol. It was formerly known as *Glycerine*. Glycerol is found in all natural fats and oils as glyceryl esters of long-chain carboxylic acids.

Manufacture. Glycerol is manufactured

(1) **From Fats and Oils.** Natural oils and fats are triesters of glycerol and long-chain acids (mainly palmitic, stearic, and oleic acids). On hydrolysis with alkali, the fat or oil gives glycerol and the salts of the long-chain acids which are called soaps.



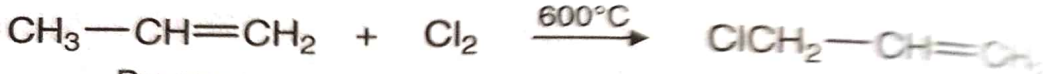
Fat or Oil

Glycerol
(1,2,3-Propanetriol)

In the above equation, R is 9 to 17 carbons. The hydrolysis of fats and oils is used in soap manufacture, and glycerol is obtained as a by-product. This is still a source of glycerol.

(2) **From Propene.** Large quantities of glycerol are obtained as a by-product in the manufacture of soap. However, this supply is not sufficient. Today much of glycerol is manufactured from propene obtained by the catalytic cracking of petroleum. Following four steps are involved.

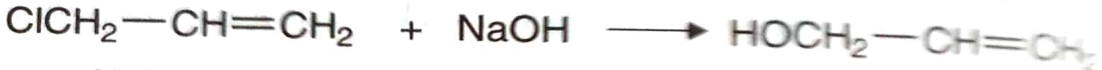
Step 1. Propene is treated with Cl_2 at 600°C to give allyl chloride.



Propene

Allyl chloride

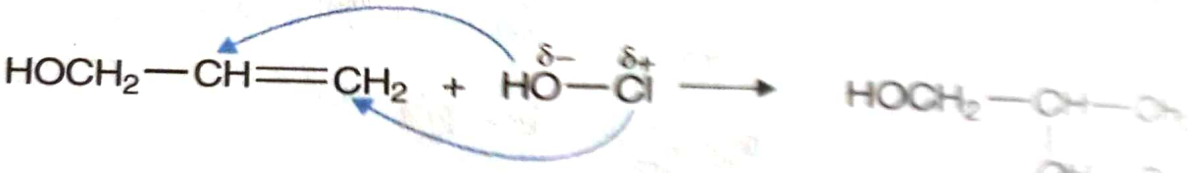
Step 2. Allyl chloride is treated with dil. NaOH to give allyl alcohol.



Allyl chloride

Allyl alcohol

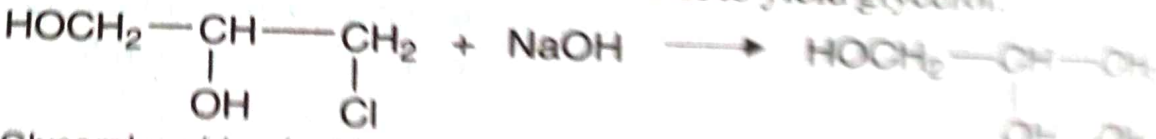
Step 3. Allyl alcohol is treated with dilute hypochlorous acid to give a chlorohydrin. The addition of HOCl to the carbon-carbon double bond takes place according to the Markovnikov rule.



Allyl alcohol

Glycerol α-chlorohydrin

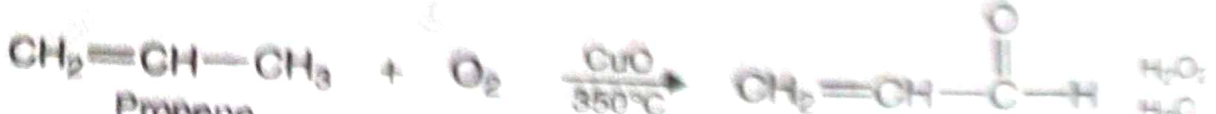
Step 4. The chlorohydrin is treated with dil. NaOH to yield glycerol.



Glycerol α-chlorohydrin

Glycerol

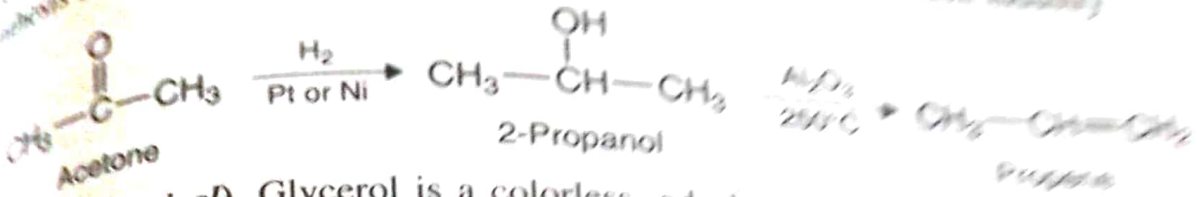
Alternative Method. Propene may be oxidized with oxygen (air) in the presence of Cu_2O at 350°C to give acrolein. Acrolein is then treated with hydrogen peroxide (H_2O_2) followed by reduction (H_2O) to produce glycerol.



Propene

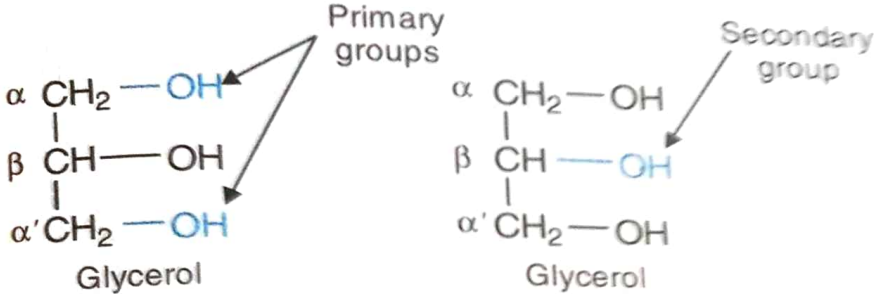
Acrolein

country like India where petroleum is not found in abundance, propene required for the carbon may also be obtained from acetone of the wood distillation industry.



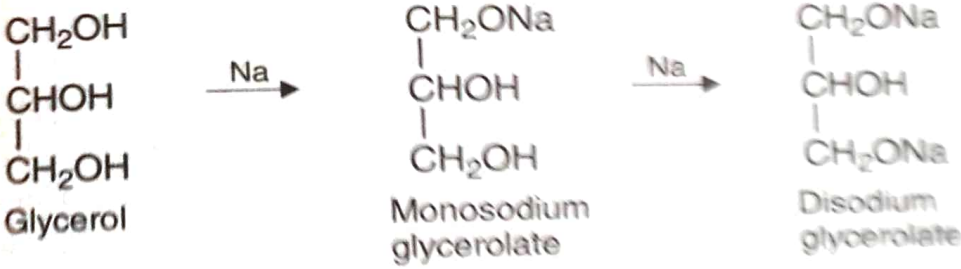
Properties (*Physical*). Glycerol is a colorless, odorless sweet-tasting and syrupy liquid. It is nontoxic. Glycerol is soluble in water and ethanol, but insoluble in ether. It is hygroscopic. It absorbs moisture from air.

(*Chemical*). Glycerol molecule contains two primary –OH groups and one secondary –OH group. It undergoes many of the reactions to be expected of these types of alcohols. The carbon atoms in glycerol are indicated as α, β, and α′.

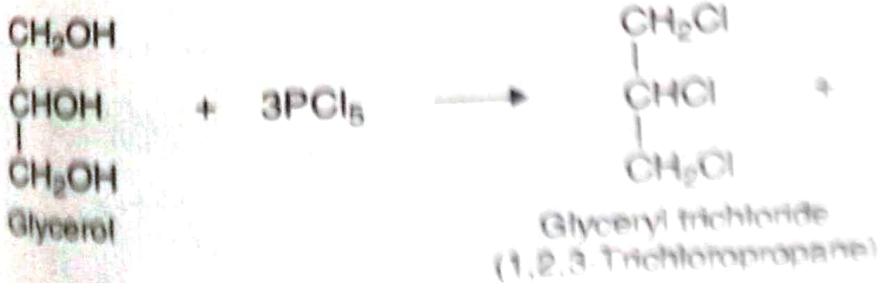


In general, the two primary –OH groups are more reactive than the secondary –OH group. Some of the reactions that are characteristic of monohydroxy compounds are modified to a certain extent by the presence of three –OH groups.

(1) **Reaction with Sodium.** When glycerol is treated with sodium at room temperature, one of the primary –OH groups is attacked to form monosodium glycerolate. At higher temperatures, the second primary –OH group is also attacked to give disodium glycerolate. The secondary –OH group does not react at all.

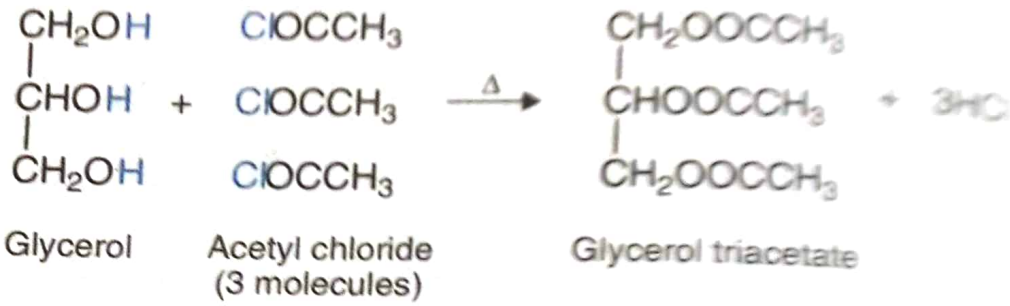


(2) **Reaction with PCl_5.** Glycerol reacts with PCl_5 to form glyceryl trichloride. All these –OH groups are replaced by Cl atoms.



(3) **Reaction with Carboxylic Acids.** Glycerol reacts with monocarboxylic acids to form mono-, di- and triesters depending on the amount of acid used. For example, glycerol reacts with a mixture of formic acid and acetic anhydride to give the following three esters.

(8) **Reaction with Acetyl Chloride.** Glycerol reacts with acetyl chloride (or acetic anhydride) to form glyceryl triacetate.



(9) **Oxidation.** The two primary alcohol groups in glycerol are capable of being oxidized to aldehyde and then the carboxyl group. The secondary alcohol group can be oxidized to keto group. Thus glycerol can give rise to a variety of oxidation products depending on the strength of oxidizing agent (Fig. 16.2).