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TOPIC – GLYCEROL

B.Sc – HONOURS

PART – 2

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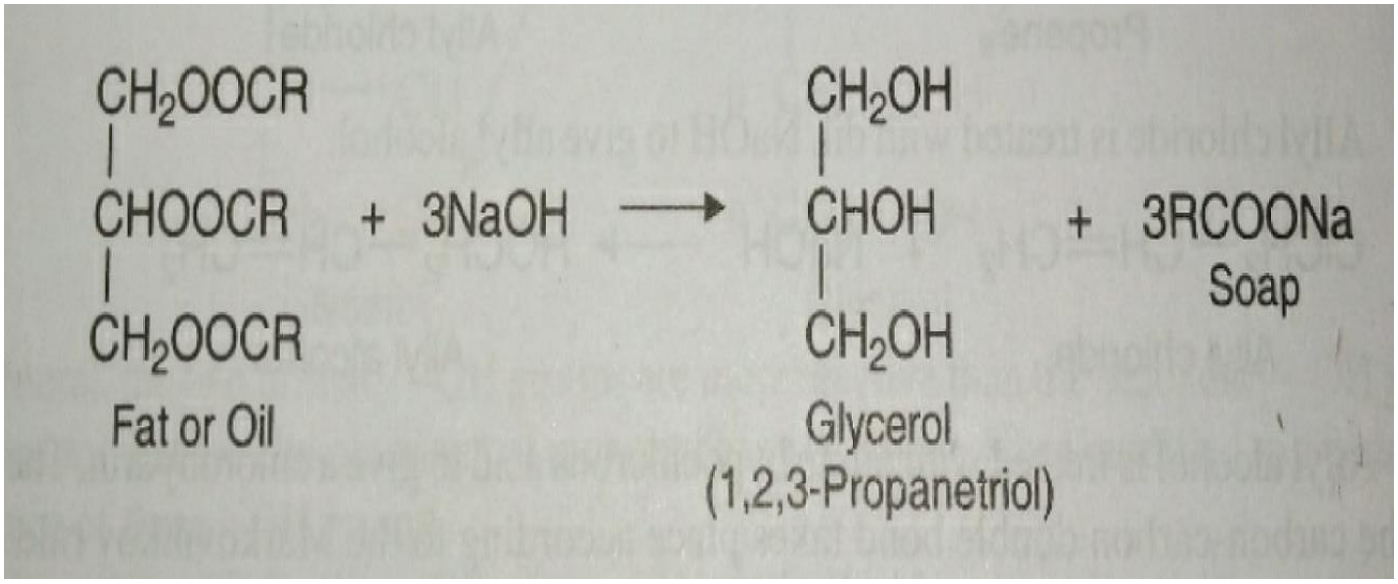
INTRODUCTION

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

Glycerol is the simplest trihydric alcohol (triol). The name glycerol or glycerine was originally derived from the word glyceros, meaning sweet. Its IUPAC name is 1,2,3-propanetriol since glycerol could be considered as trihydroxy derivative of propane.

Manufacture. Glycerol can be prepared industrially by the following methods.

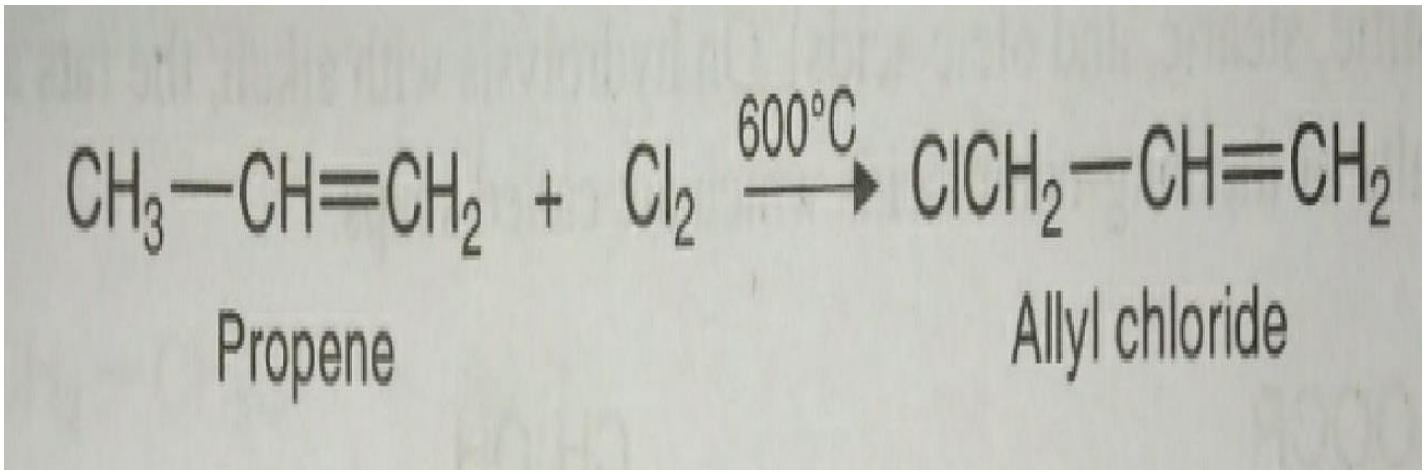
(1) From Fats and Oils. Natural oils and fats are triesters of glycerol and long-chain carboxylic acids (mainly palmitic, stearic, and oleic acids). On hydrolysis with alkali, the fats and oils produce glycerol and the salts of the long-chain acids which are called soaps.



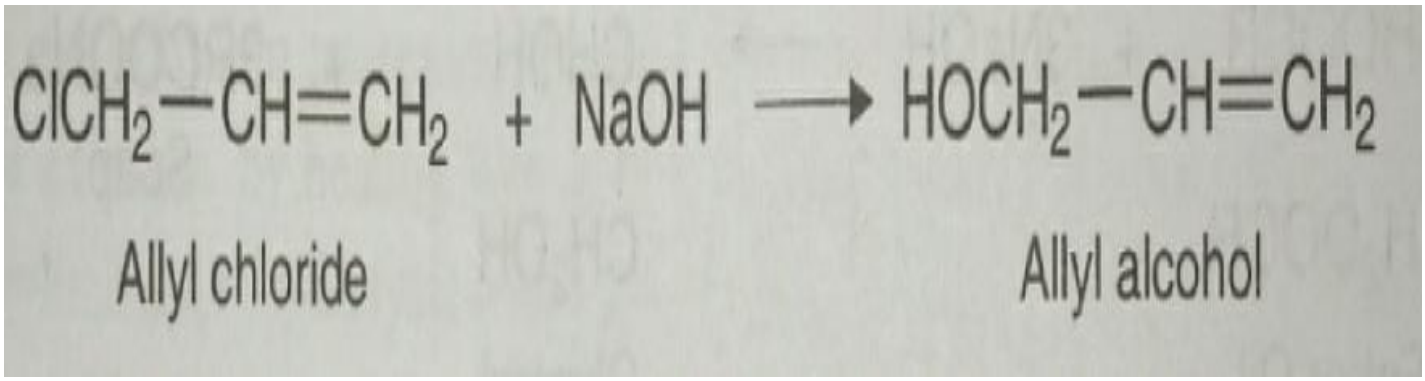
In the above equation, R is 9 to 17 carbons. The hydrolysis of fats and oils is carried originally for soap manufacture, and glycerol is obtained as a by-product. This is still a commercial source of glycerol.

(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 :

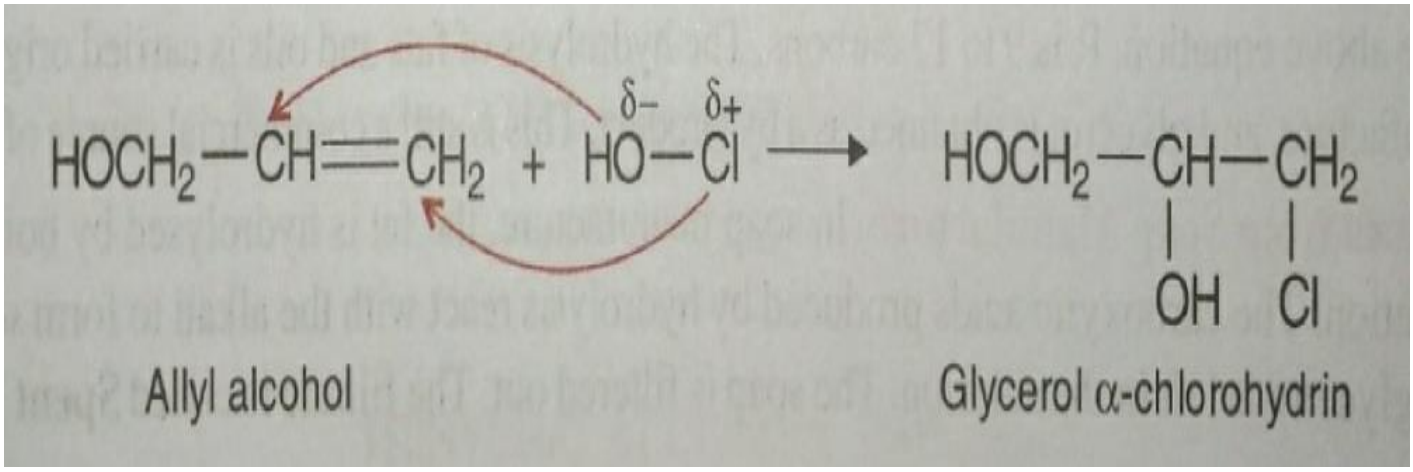
Step 1. Propene is treated with Cl_2 at 600°C to give allyl chloride.



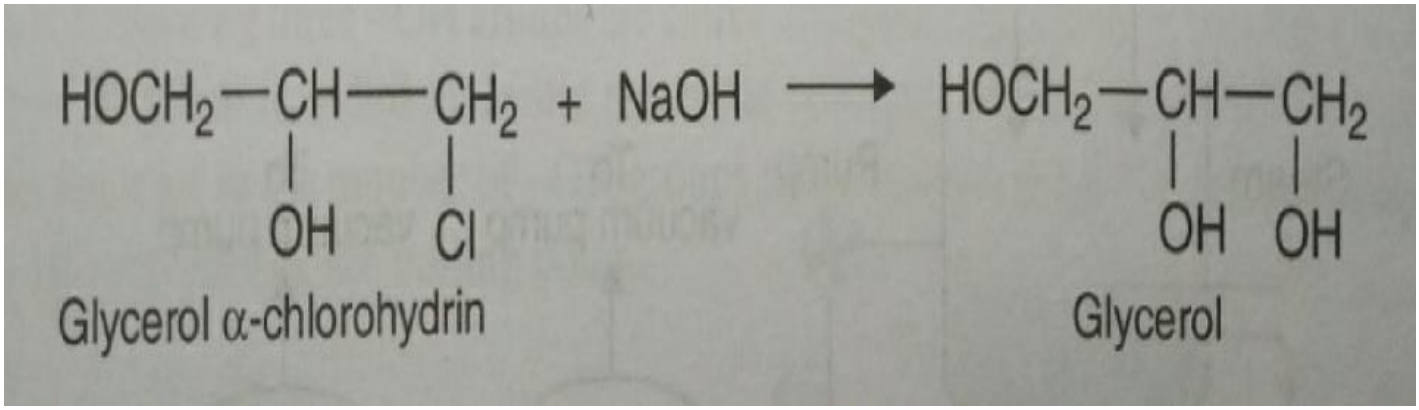
Step 2. Allyl chloride is treated with dil. NaOH to give allyl alcohol.



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.



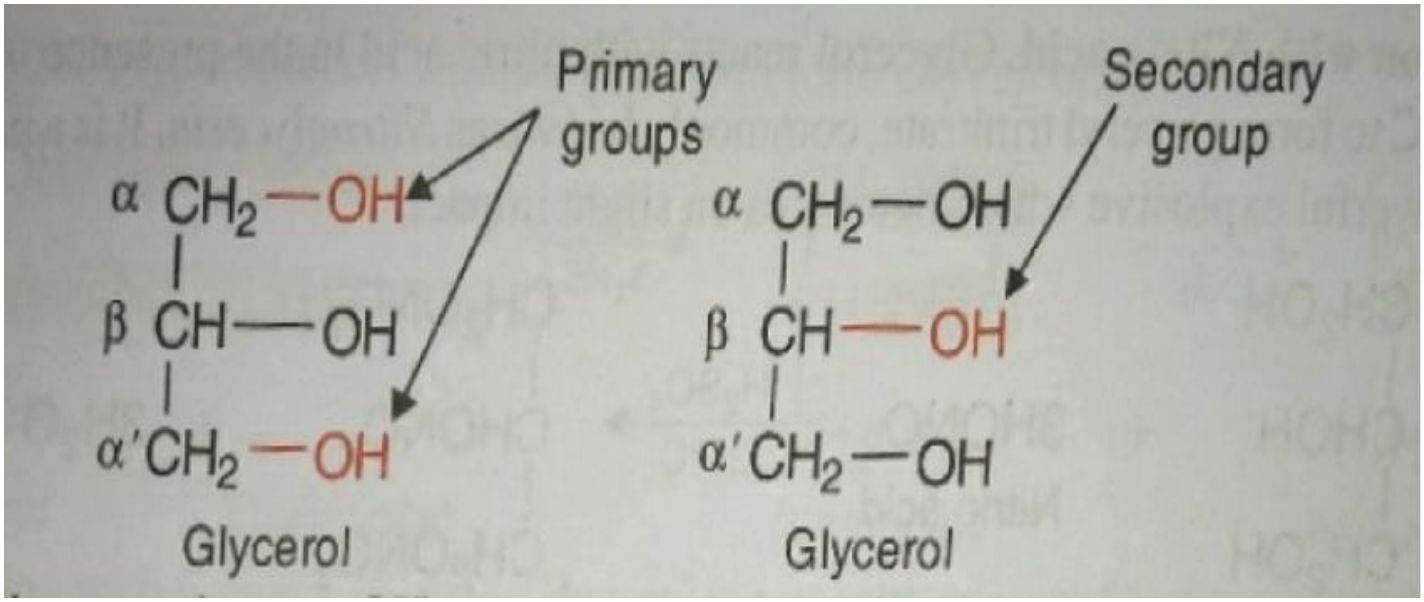
Step 4. The chlorohydrin is treated with dil. NaOH to yield glycerol.



Properties (Physical). Glycerol is a colorless, odorless sweet-tasting and syrupy liquid, bp 290°C. It is nontoxic. Glycerol is soluble in water and ethanol, but insoluble in ether. It is hygroscopic, that is, it absorbs moisture from air.

(Chemical). Glycerol molecule contains two primary -OH groups and one secondary -OH group. It

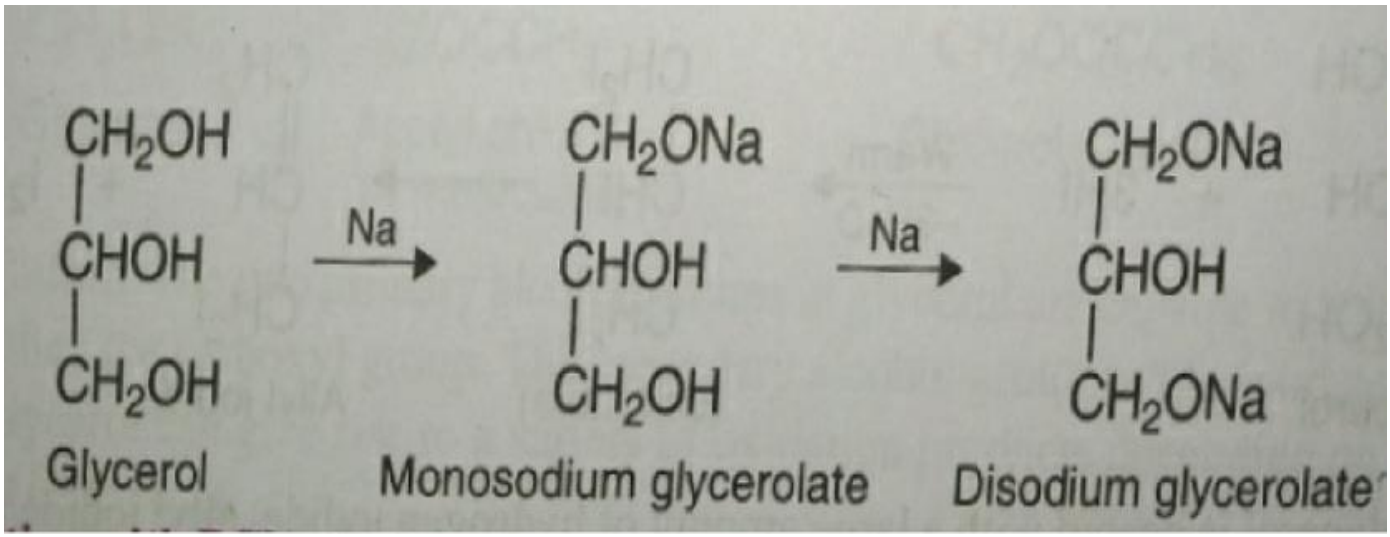
undergoes many of the reactions to be expected of these types of alcohols. The carbon atoms in glycerol are indicated as α, β, and β:



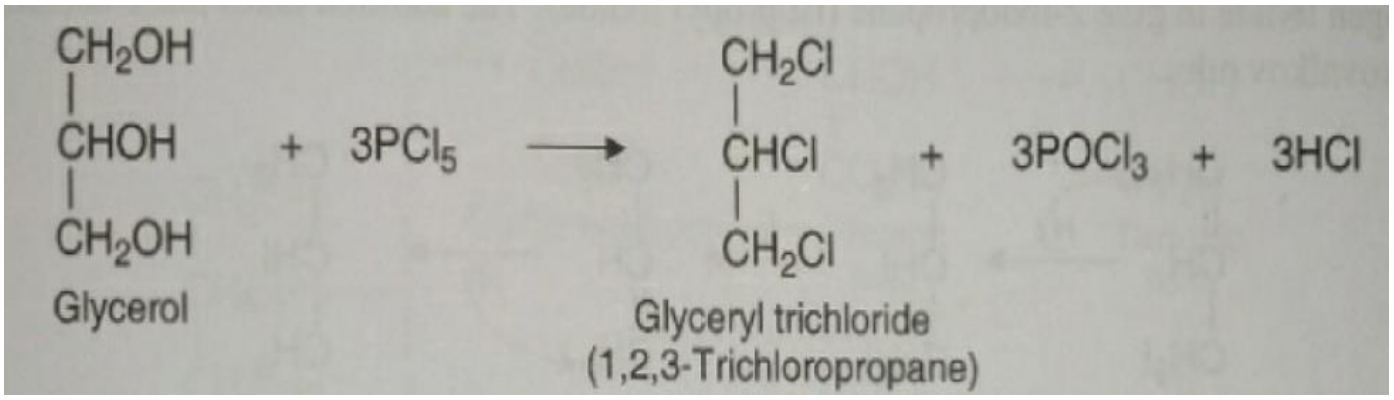
In general, the two primary - OH groups are more reactive than the secondary -OH group. Some of the reactions that are characteristic of monohydroxy compounds are modified to a certain extent by the presence of three -OH groups.

(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.

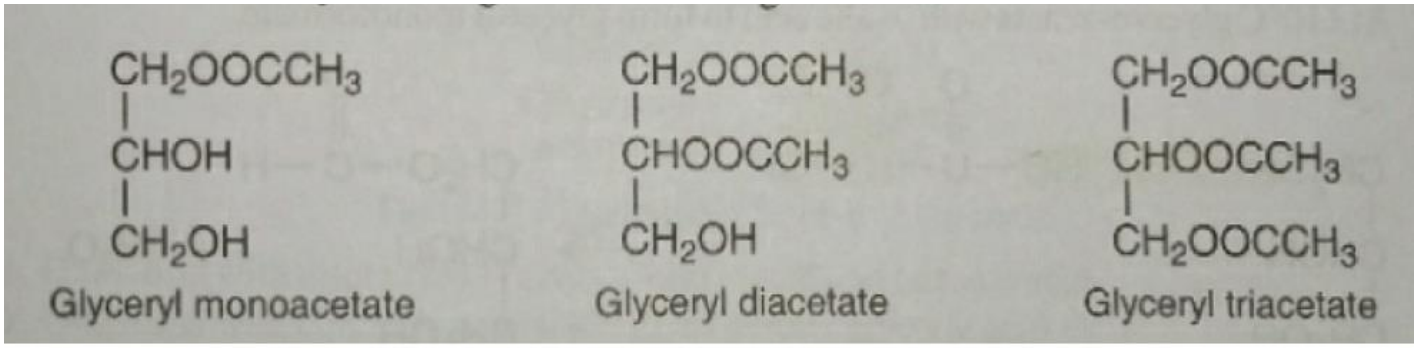


(2) Reaction with PCl_5 Glycerol reacts with PCl_5 to form trichloride. All these –OH groups are replaced by Cl atoms.

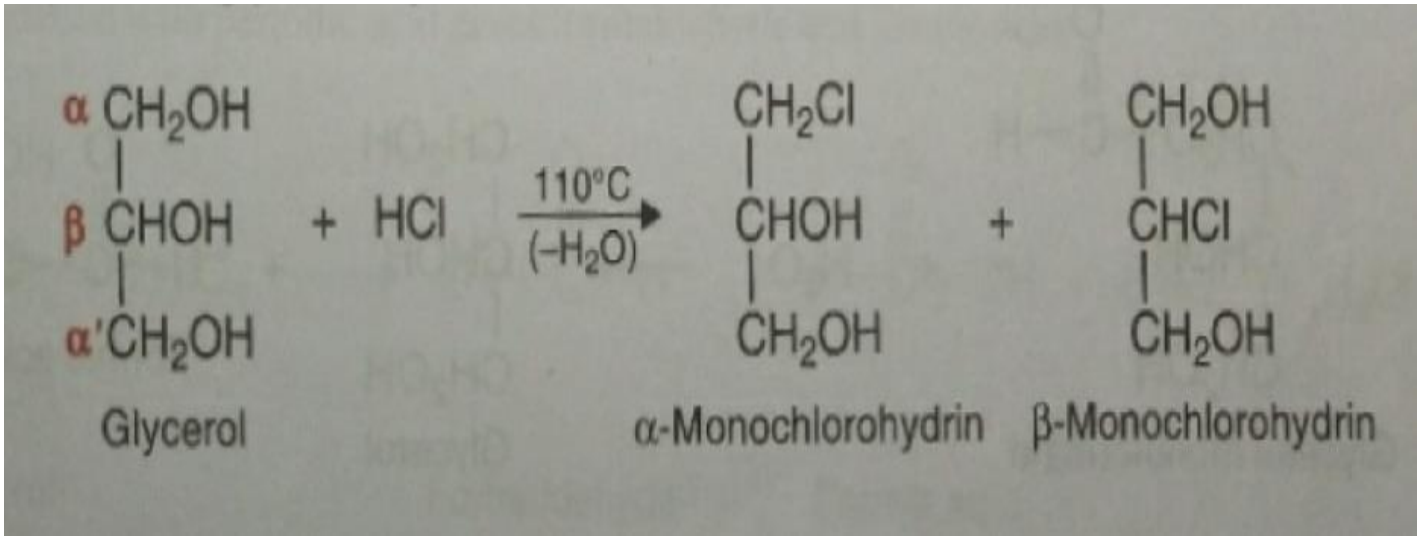


(3) Reaction with Carboxylic acids. Glycerol reacts with monocarboxylic acids to form mono-, di-, and triesters depending on the amount of acid used. For

example, glycerol reacts with a mixture of acetic acid and acetic anhydride to give the following three esters :

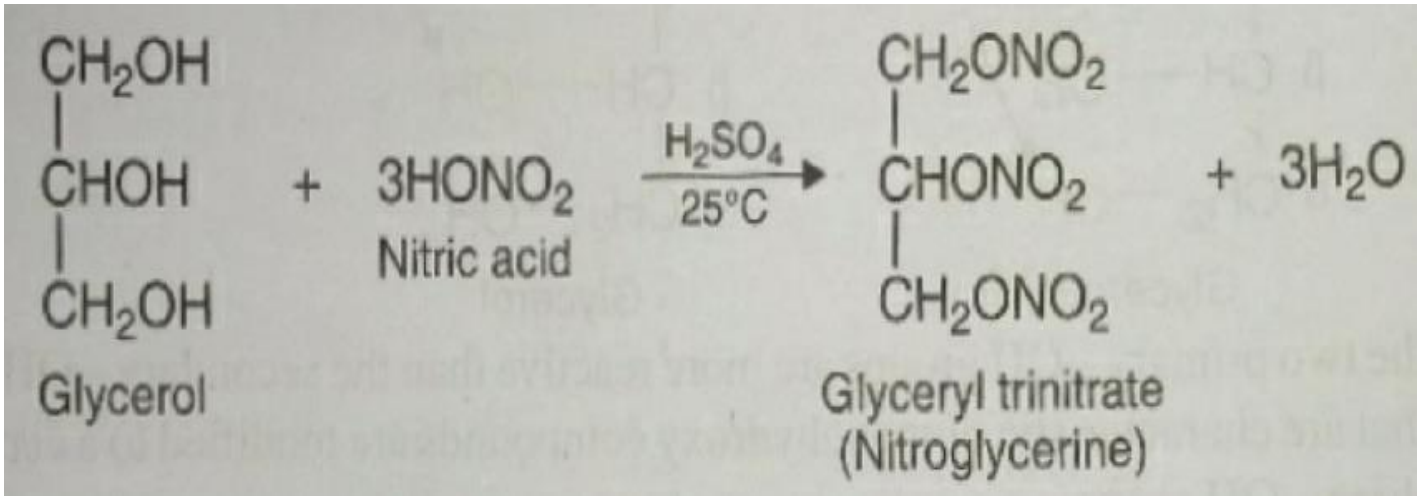


(4) Reaction with Hydrogen chloride. When HCl is passed into glycerol at 110°C, both α- and β-glycerol monochlorohydrins are formed. If the reaction is carried for a long time, glycerol α, α -dichlorohydrin and glycerol α. β-dichlorohydrin are formed.



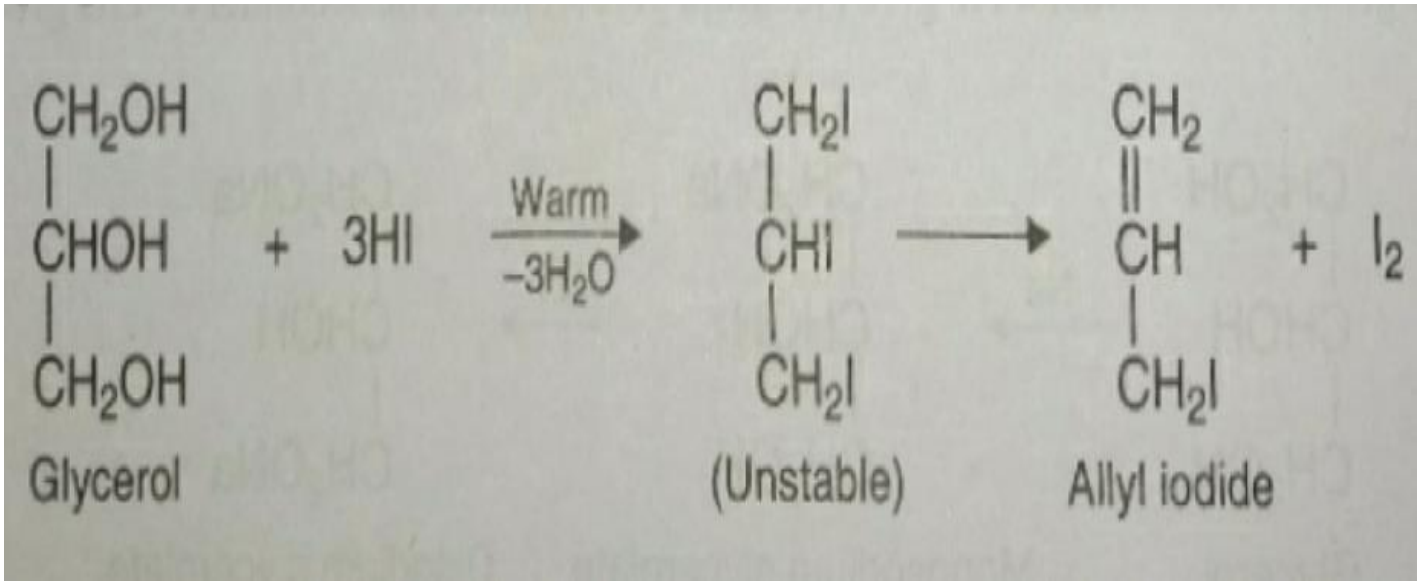
(5) Reaction with Nitric acid. Glycerol reacts with nitric acid in the presence of sulfuric acid (catalyst),

at 25°C to form glyceryl trinitrate, commonly known as Nitroglycerin. It is a pale yellow oily liquid. It is a powerful explosive which detonates on slight impact.

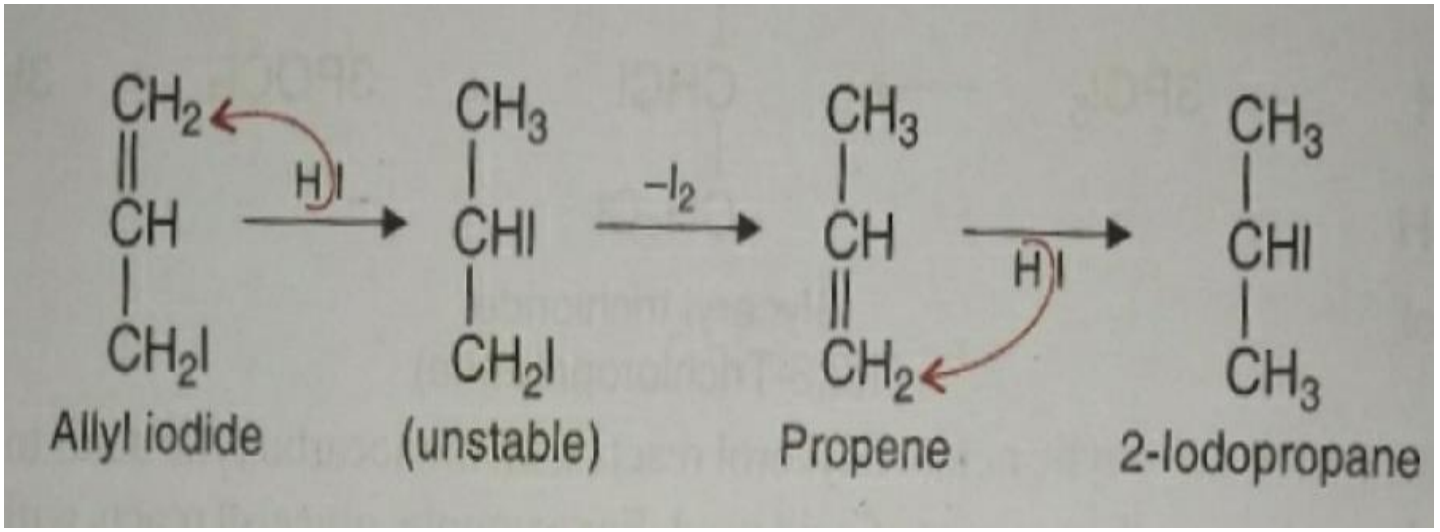


(6) Reaction with Hydrogen iodide. Glycerol reacts with hydrogen iodide in two ways:

(a) When glycerol is warmed with a small amount of hydrogen iodide, it gives 1,2,3-triiodopropane. This is unstable and splits out a molecule of iodine to yield allyl iodide.

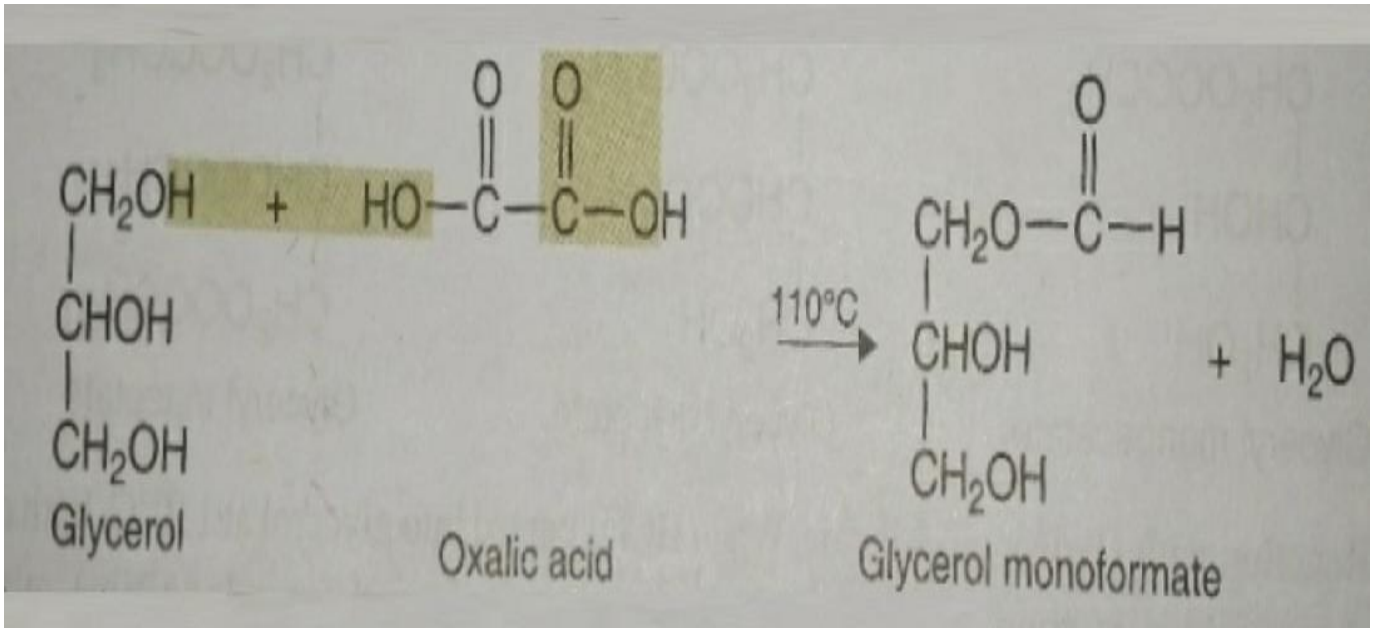


(b) When glycerol is heated with a large amount of hydrogen iodide, allyl iodide first produced as above is reduced to propene. In the presence of excess hydrogen iodide, propene adds a molecule to of hydrogen iodide to give 2-iodopropane (isopropyl iodide). The-addition takes place according to the Markovnikov rule.

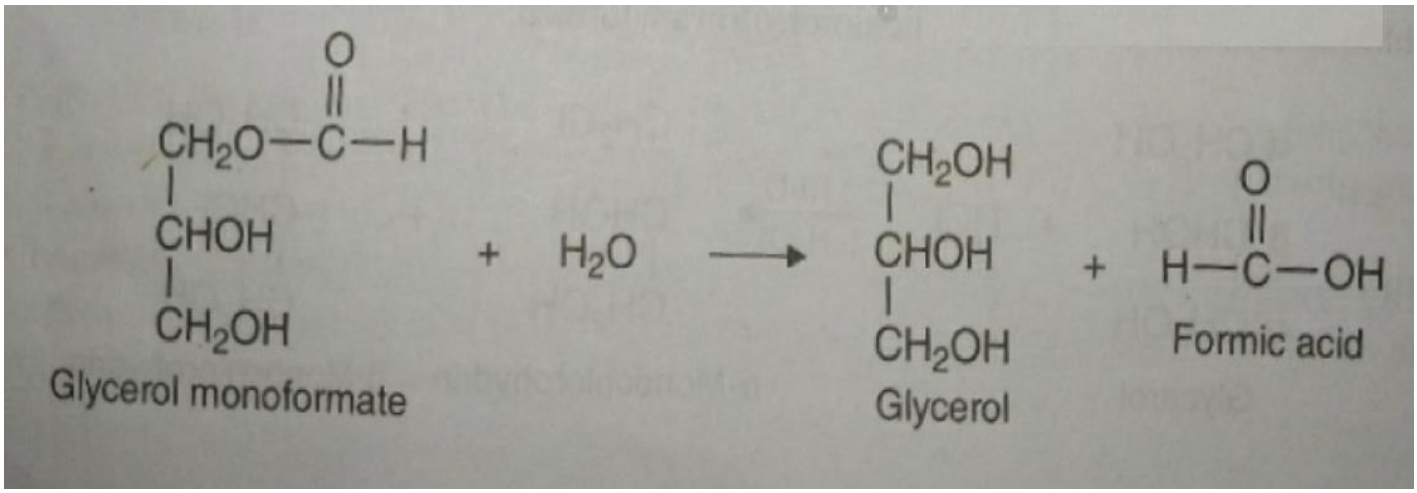


(7) Reaction with Oxalic acid. Glycerol reacts with oxalic acid in two ways :

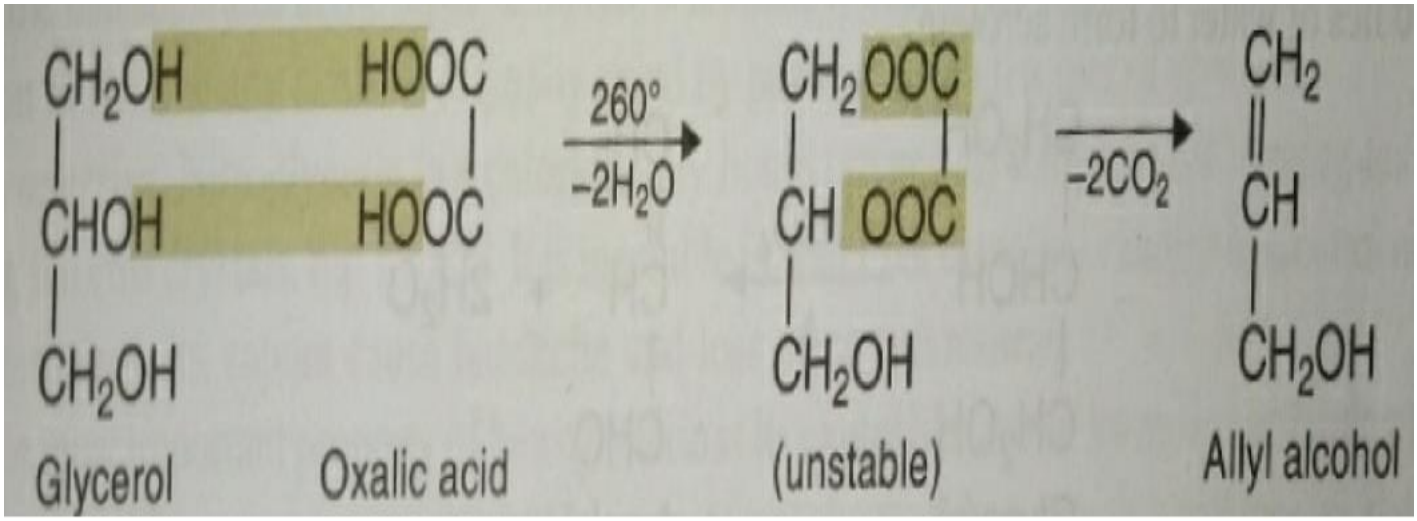
(a) At 110°C glycerol reacts with oxalic acid to form glycerol monoformate.



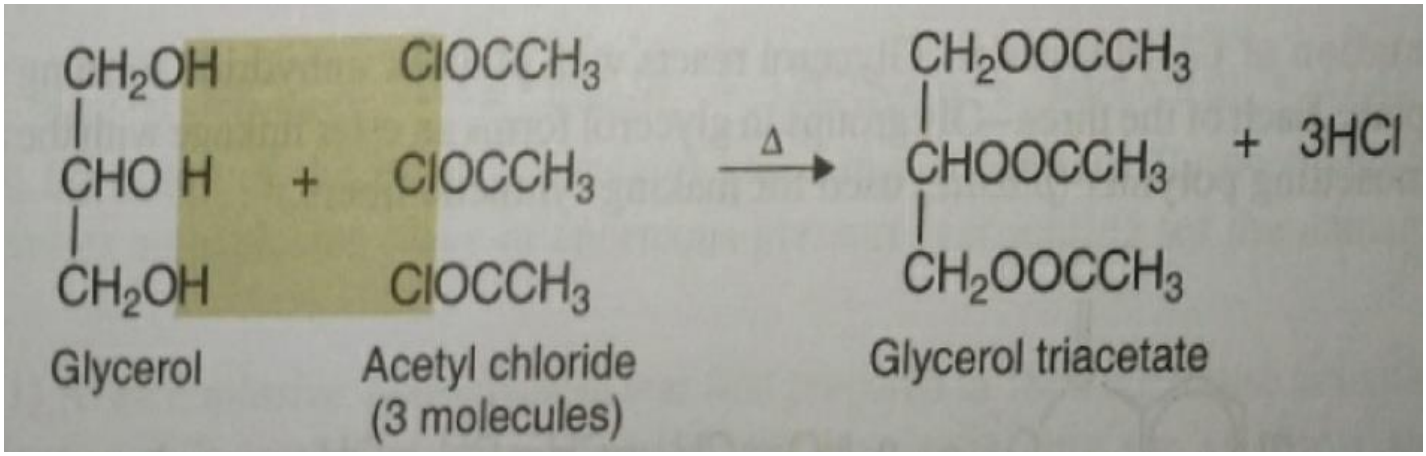
Glycerol monoformate on hydrolysis gives formic acid and glycerol is regenerated.



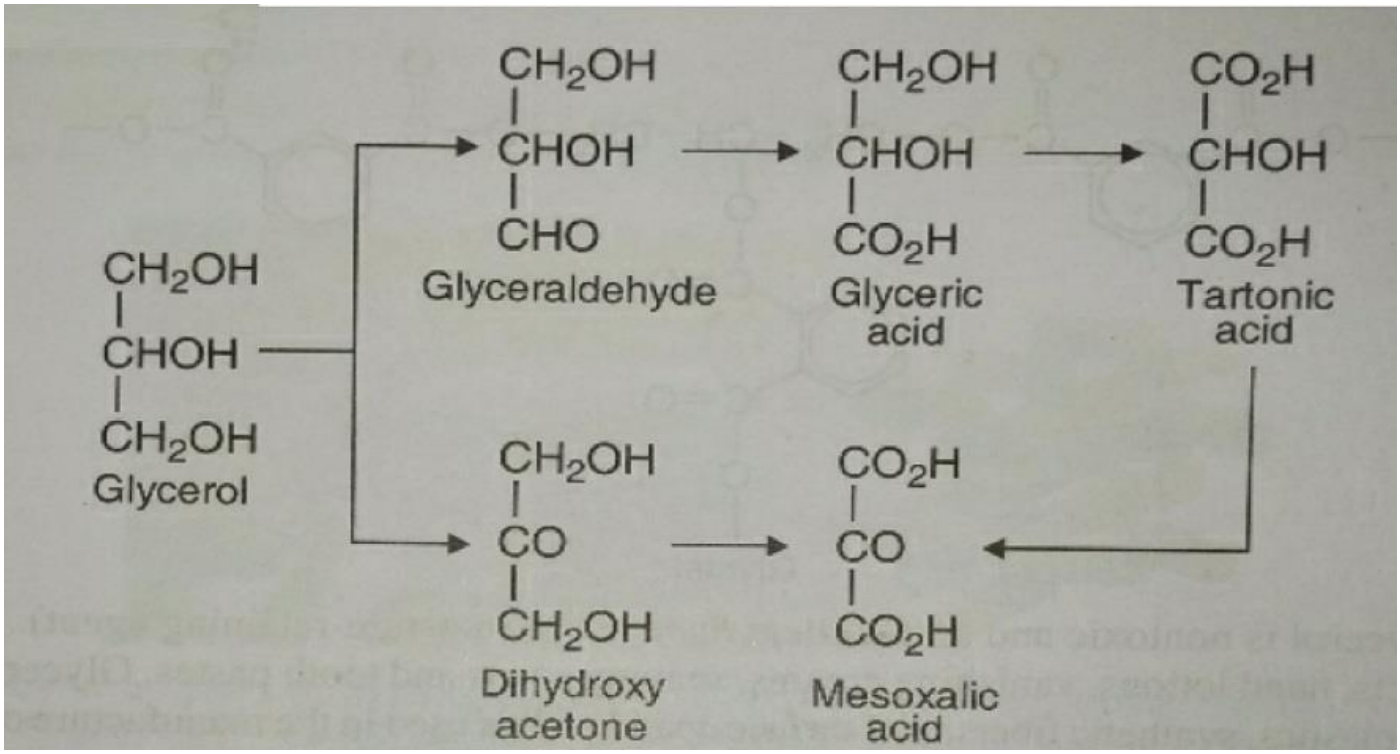
(b) At 260°C glycerol reacts with oxalic acid to form allyl alcohol.



(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 the aldehyde and then the carboxyl group. The secondary alcohol group can be oxidized to the carbonyl group. Thus glycerol can give rise to a variety of oxidation products depending on the nature of the oxidizing agent



Oxidation products of Glycerol.

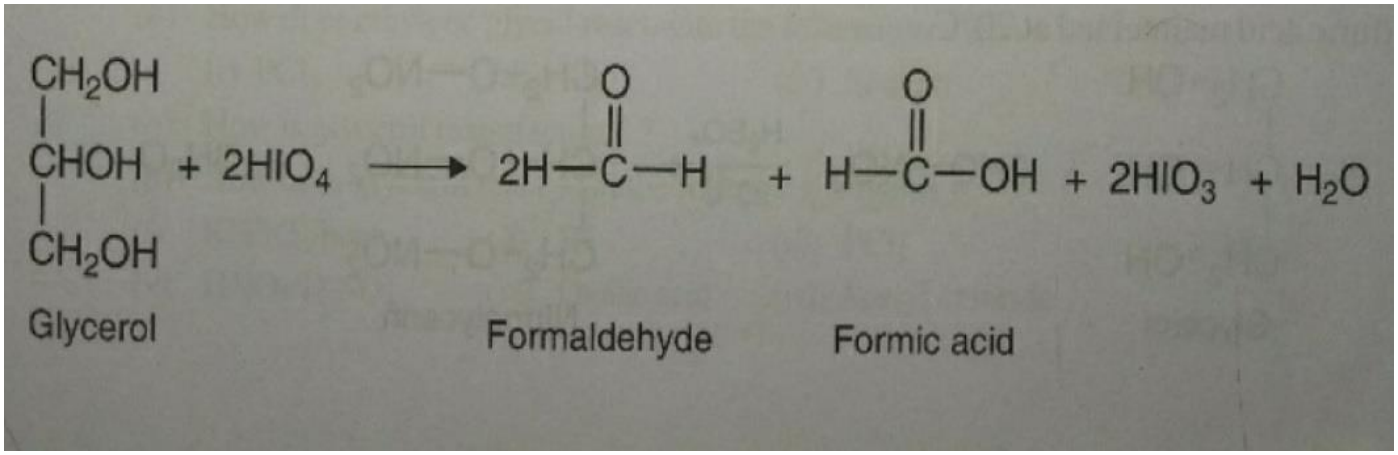
(a) Oxidation with dilute HNO_3 gives glyceric acid and tartonic acid.

(b) Oxidation with concentrated HNO_3 gives mainly glyceric acid.

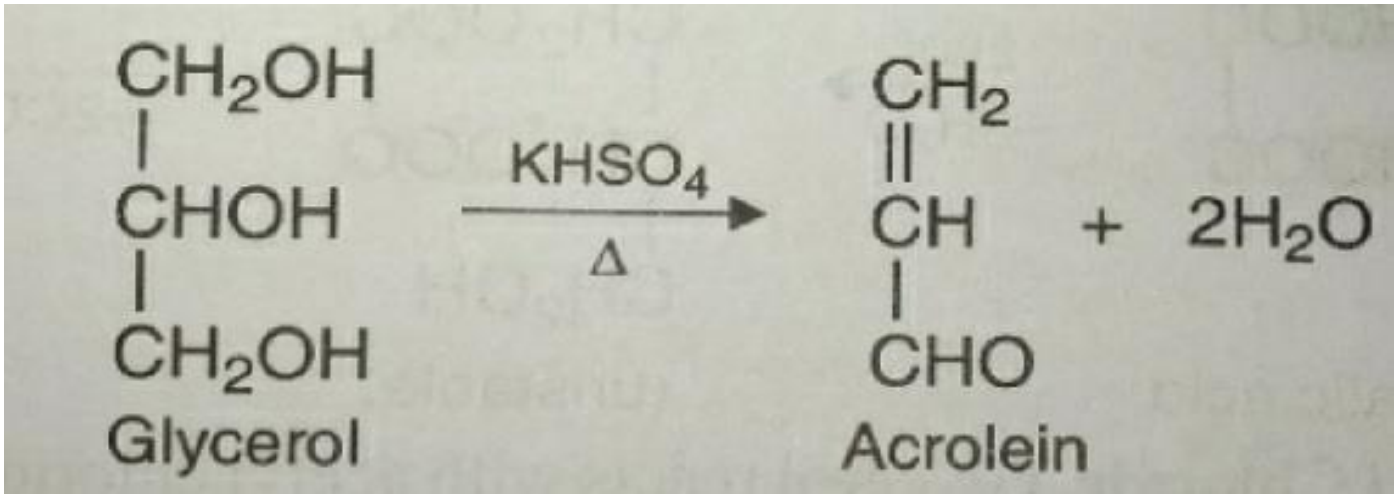
(c) Oxidation with bismuth nitrate gives mainly mesoxalic acid.

(d) Oxidation with bromine water, sodium hypobromite, or Fenton's reagent ($FeSO_4+H_2O_2$), gives a mixture of glyceraldehyde and dihydroxyacetone.

(e) Oxidation with periodic acid gives formaldehyde and formic acid.



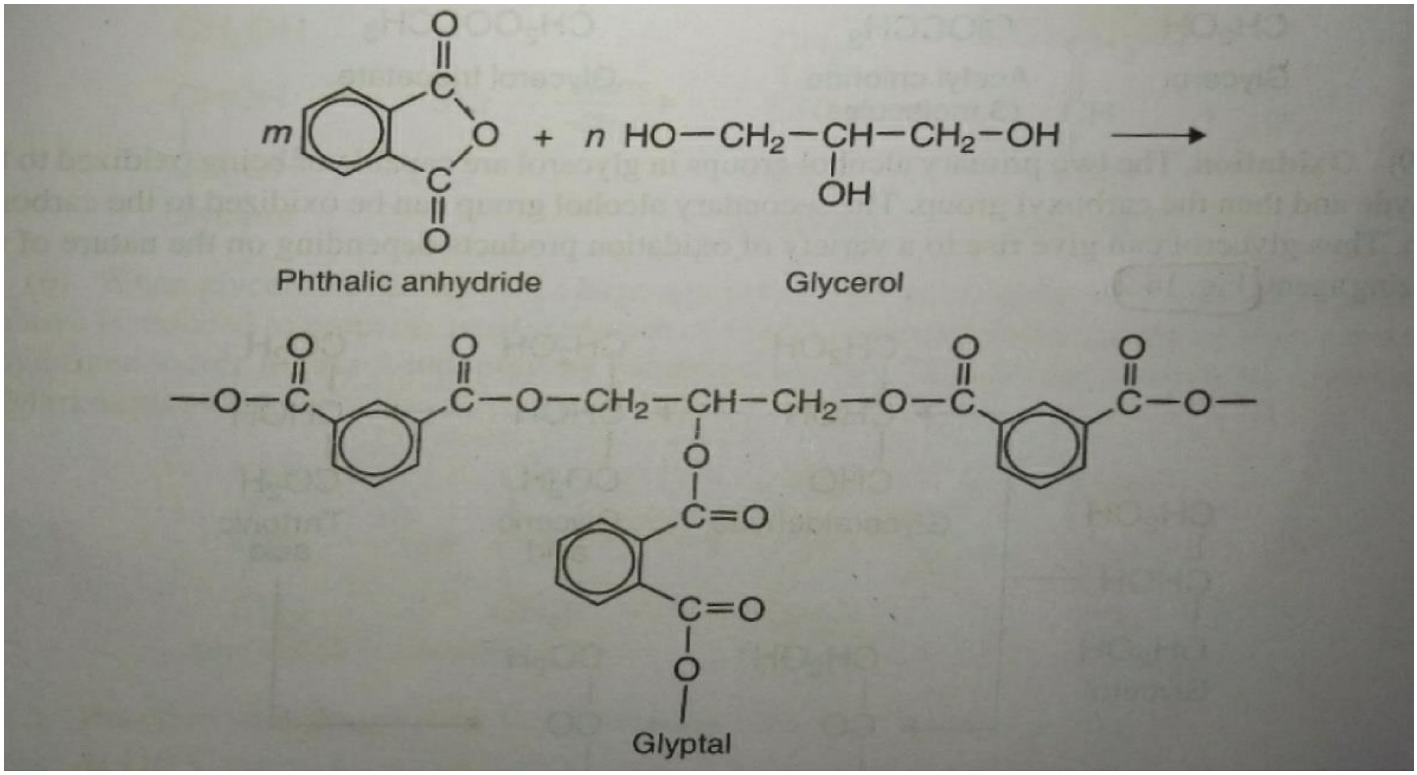
(10) Dehydration. When heated alone or with potassium hydrogen sulphate, glycerol eliminates two molecules of water to form acrolein.



This reaction is often used as a qualitative test for the presence of glycerol, since acrolein is

easily detected on account of its peculiar odor.

(11) Formation of Glyptal resins. Glycerol reacts with phthalic anhydride forming polyesters known as glyptals. Each of the three -OH groups in glycerol forms an ester linkage with the anhydride, giving a thermosetting polymer (plastic) used for making synthetic fibers.


m
+ n HO—CH2—CH—CH2—OH
OH
Phthalic anhydride
Glycerol
—O—C
C—O—CH2—CH—CH2—O—C
C—O—
C=O
C=O
O
Glyptal