

ALCOHOL

CONTENTS:

- 1.1 Objectives
- 1.2 Introduction
- 1.3 Classification of alcohols
- 1.4 Nomenclature of alcohols
- 1.5 Methods of preparation of alcohols
- 1.6 Acidic nature of alcohols
- 1.7 Chemical reactions of alcohols
- 1.8 Dihydric alcohols
- 1.9 Methods of preparation
- 1.10 Physical properties of dihydric alcohols
- 1.11 Chemical reactions of vicinal glycols
- 1.12 Trihydric alcohols
- 1.13 Methods of preparation
- 1.14 Chemical reactions
- 1.15 Summary

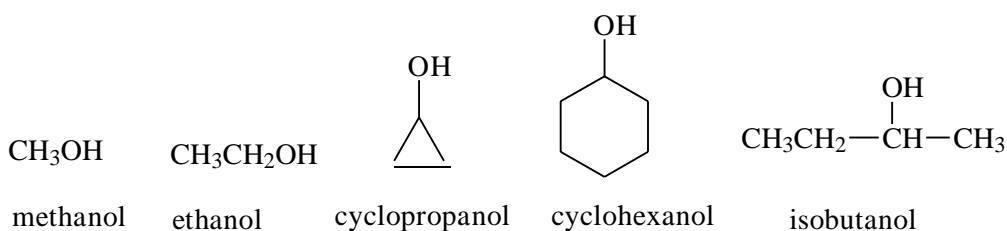
ORGANIC CHEMISTRY

1.1 OBJECTIVES

Objectives of this unit are to study the alcohols, their structures, nomenclature, and classification on the basis of number of –OH groups present like monohydric alcohol, dihydric and polyhydric alcohols. Classification on the basis of nature of carbon attached with –OH group like primary, secondary and tertiary alcohols. This unit also aims on methods of preparation of alcohols with their physical and chemical properties, acidic and basic characters. Chemical reactions of alcohols like Acid-catalyzed dehydration etc, Study on chemical properties of dihydric and polyhydric alcohols have also been aimed in this unit

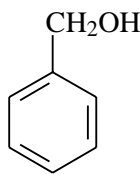
1.2 INTRODUCTION

Alcohols are organic compounds in which one or more hydrogen atoms from hydrocarbon have been replaced by hydroxyl (-OH) group. They are some of the most common and useful compounds in nature, in industry, and around the house. The general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$, where $n=1, 2, 3$, etc. The saturated carbon chain is often designated by the symbol R, so that ROH can represent any alcohol in the homologous series. Alcohols can be viewed as organic analogues of water in which one hydrogen atom is replaced by an alkyl group. The simplest and most commonly used alcohols are methanol and ethanol. They occur widely in nature and have many industrial and pharmaceutical applications.

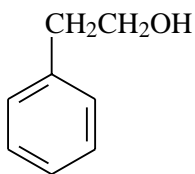


Aromatic compounds, which contain a hydroxy group on a side chain, behave like alcohols are called aromatic alcohol. In these alcohols, the —OH group is attached to a sp^3 hybridized carbon atom next to an aromatic ring.

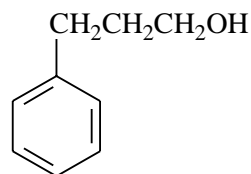
ORGANIC CHEMISTRY



benzyl alcohol



2- phenyl ethanol

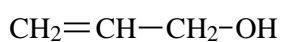


3- phenyl propanol

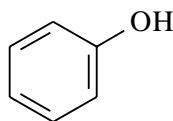
In some alcohols, the —OH group is attached to a sp^3 hybridized carbon next to the carbon-carbon double bond that is to an allylic carbon are known as allylic alcohols. In some alcohols —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols. Allylic and benzylic alcohols may be primary, secondary or tertiary in nature.



vinylic alcohol



allylic alcohol



phenol

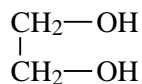
1.3 CLASSIFICATION OF ALCOHOLS

Alcohols are classified into following types on the basis of number of —OH groups present in the molecule and nature of carbon attached with —OH group as follow:

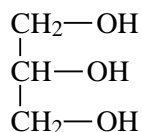
(a) **Monohydric Alcohols:** These compounds contain only one —OH group.



(b) **Dihydric Alcohols:** These contain two —OH groups.



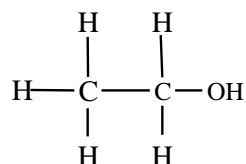
(c) **Trihydric Alcohols:** These contain three —OH groups.



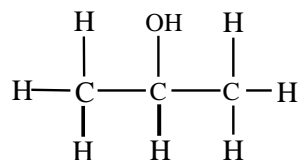
ORGANIC CHEMISTRY

On the basis of nature of carbon atom attached with -OH group the monohydric Alcohols can be further classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bound to the hydroxyl-bearing carbon.

(a) **Primary alcohol (1° alcohol):** A primary alcohol has one alkyl group attached to the carbon bound to the -OH, *i.e.*, a compound in which the hydroxyl group is bounded to a primary carbon. Primary alcohols have the group $-\text{CH}_2\text{OH}$, where the carbon atom with the alcoholic hydroxyl group has at least two additional hydrogens attached to that carbon. Primary alcohol has -OH group bonded to a carbon which is bonded to one other carbon:

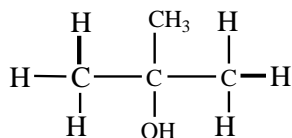


(b) **Secondary alcohol (2° alcohol):** A secondary alcohol has two alkyl group attached to the carbon bound to the -OH, *i.e.*, the hydroxyl group is bounded to a secondary carbon. Secondary alcohols have the group $-\text{CHOH}$, where the carbon atom with the alcoholic hydroxyl group has only **one** additional H atom attached to it. There are two R groups (R stands for any other organic chain or group), and the alcoholic hydroxyl group is attached to a secondary carbon. Secondary alcohol has -OH group bonded to a carbon which is bonded to two other carbon:

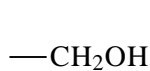


(c) **Tertiary alcohol (3° alcohol):** A tertiary alcohol has three alkyl group attached to the carbon bound to the -OH, *i.e.*, the hydroxyl group is bounded to a tertiary carbon. Tertiary alcohols have the group $-\text{COH}$, where the carbon atom with the alcoholic hydroxyl group has no additional H atoms attached to it.

ORGANIC CHEMISTRY



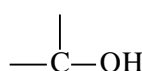
If we replace hydrogen with a $-\text{OH}$ group we get the following groups for three alcohols:



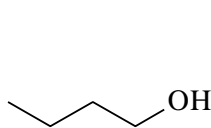
primary alcohol



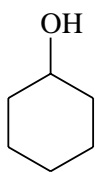
secondary alcohol



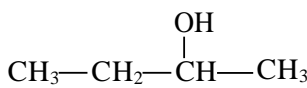
tertiary alcohol



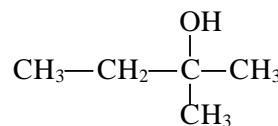
primary alcohol



secondary alcohol



secondary alcohol



tertiary alcohol

1.4 NOMENCLATURE OF ALCOHOLS

According to the IUPAC system of nomenclature, alcohols are called alkanols. They are named as the derivatives of the corresponding alkane in which the $-e$ of the alkane is replaced by $-ol$. The IUPAC have come up with a set of rules that are used to name any alcohol regardless of its complexity. These rules are summarized as follows:

Step 1. Name the longest continuous chain to which the hydroxyl ($-\text{OH}$) group is attached. Count the number of carbon atoms and identify the corresponding alkane. The name for this chain is obtained by dropping the final $-e$ from the name of the hydrocarbon parent name and adding the ending $-ol$.

Step 2. Number the longest chain to give the lowest possible number to the carbon bearing the hydroxyl group.

Step 3. Locate the position of the hydroxyl group by the number of the carbon to which it is attached.

Step 4. Number the any other substituents according to their position on the chain.

ORGANIC CHEMISTRY

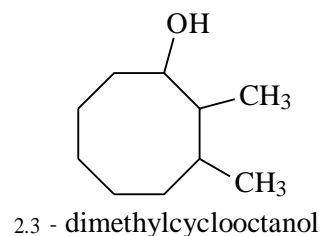
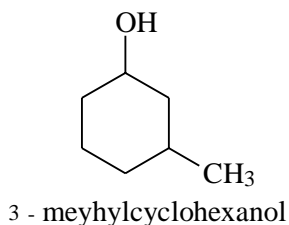
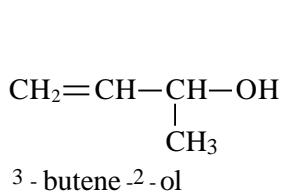
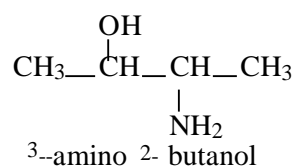
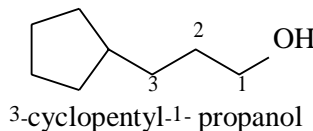
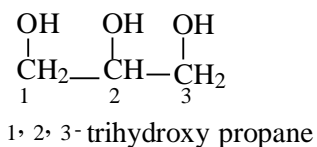
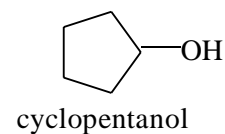
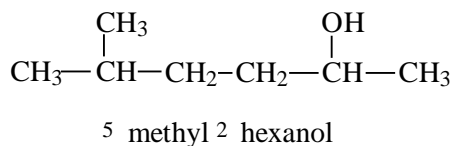
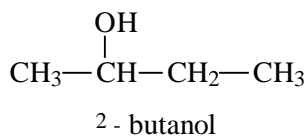
Step 5. Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

Step 6. If there are more than one –OH group do not remove the –e from the suffix, but add a di- or tri- prefix to the –ol suffix.

Step 7. Identify and locate the other branches on the chain so that they are named alphabetically and their carbon number is hyphenated onto the front of the name.

viz;	Alcohols	Common name	IUPAC name
	CH ₃ OH	Methyl alcohol	Methanol
	CH ₃ CH ₂ OH	Ethyl alcohol	Ethanol
	CH ₃ CH ₂ CH ₂ OH	n-Propyl alcohol	1-Propanol
	CH ₃ CHOHCH ₃	Isopropyl alcohol	2-Propanol
	CH ₃ (CH ₂) ₂ CH ₂ OH	n-Butyl alcohol	1-Butanol
	CH ₃ (CH ₂) ₃ CH ₂ OH	n-Pentyl alcohol	1-Pentanol

Other examples:

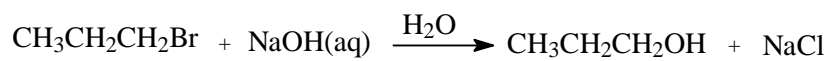
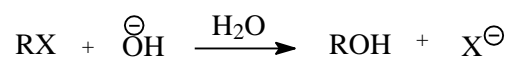


ORGANIC CHEMISTRY

1.5 METHOD OF PREPARATION OF ALCOHOLS

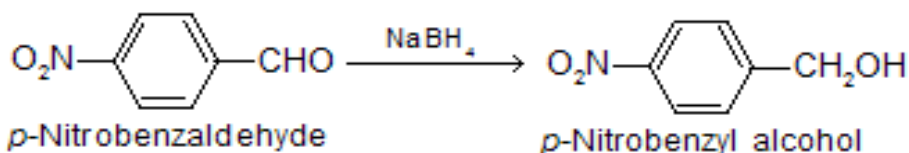
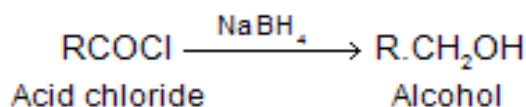
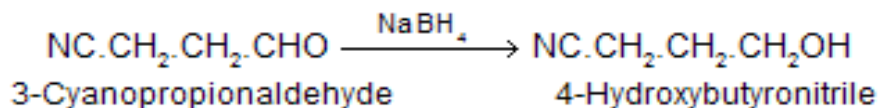
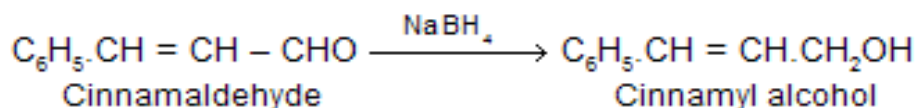
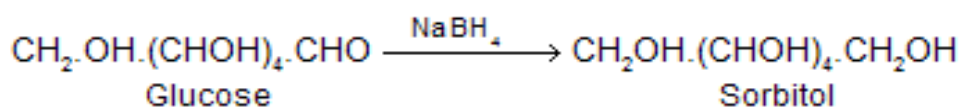
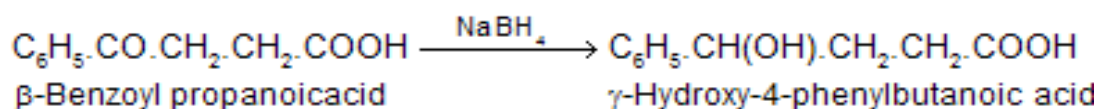
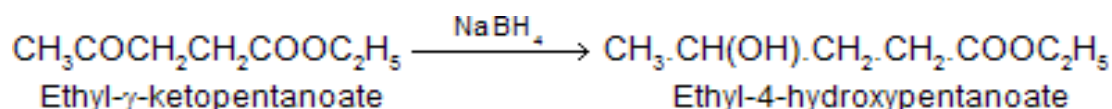
The following methods are used for the preparation of alcohols:

- 1. Hydrolysis of haloalkanes:** Haloalkanes can be converted to corresponding alcohols using aqueous NaOH, KOH or Ca (OH)₂. With this method primary and secondary alcohols are formed from a primary and secondary halogenoalkane. This is a type of nucleophilic substitution reaction (S_N). This reaction is useful only with reactants that do not undergo E₂ elimination readily.



ORGANIC CHEMISTRY

2. Reduction of carbonyl compounds: Carbonyl compounds (which contain -C=O group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols. Aldehydes give primary alcohols while ketones yield secondary alcohols, either by catalytic hydrogenation or by use of chemical reducing agents like lithium aluminum hydride, LiAlH_4 . Carboxylic acids and esters also give primary alcohols on reduction with hydride reagents such as LiAlH_4 and sodium borohydride



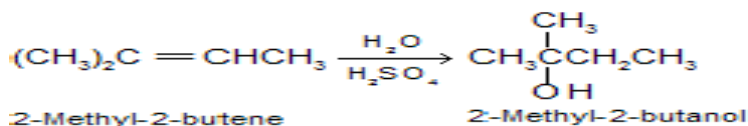
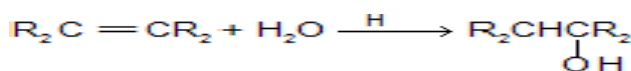
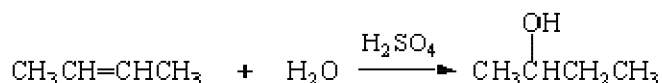
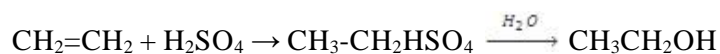
(NaBH_4). NaBH_4 does not reduce carbon-carbon double bonds, not even those conjugated with carbonyl groups, and is thus useful for the reduction of such unsaturated carbonyl compounds to unsaturated alcohols.

In the above reactions it is observed that only the carbonyl group is reduced and the other functional groups remain unaffected. Highly selective behavior of

ORGANIC CHEMISTRY

NaBH_4 makes it the preferred reagent for the reduction of carbonyl groups in sensitive polyfunctional group containing compounds.

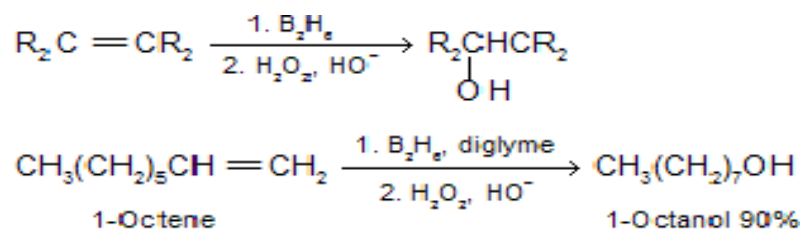
- 3. From hydration of alkenes:** Hydration i.e.s addition of H^+ and OH^- across a $\text{C}=\text{C}$ double bond to give alcohols. This is an electrophilic addition of H_2O to the alkene. Alcohols can be prepared by adding water to an alkene in the presence of a strong acid such as conc. H_2SO_4 . Because these reactions follow Markovnikov's rule, the product of the reaction is often a highly substituted 2° or 3° alcohol.



Ease of preparation is tert. > sec. > prim alcohol; ease of dehydration follows same sequence.

- 4. Oxidation of organoboranes:** When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained. Hydroboration followed by oxidation will produce an alcohol. Since BH_3 has three hydrogens, above addition can occur three times to give trialkyl borane. This is oxidized to alcohol by hydrogen peroxide (H_2O_2) in the presence of aqueous sodium hydroxide. The overall reaction is addition of water across the double bond opposite to that of Markovnikov's rule and the reaction is regioselective producing the least substituted alcohol.

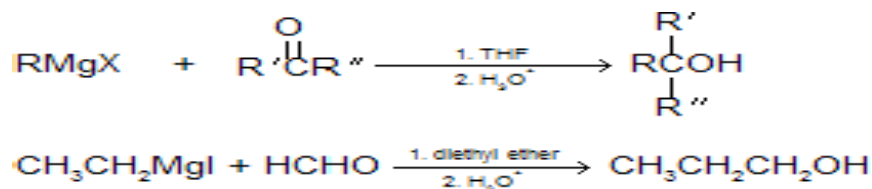
ORGANIC CHEMISTRY



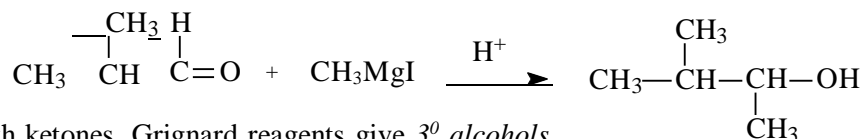
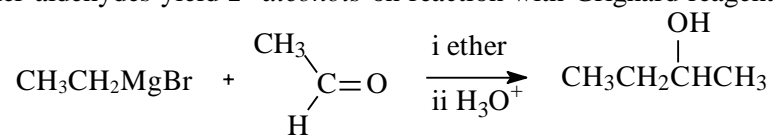
Except ethyl alcohol no other primary alcohol can be obtained by this method, however hydroboration of terminal alkenes gives primary alcohols.

5. **From Grignard reagents** – Alcohol can easily be prepared by using Grignard (RMgX) reagent as follow:

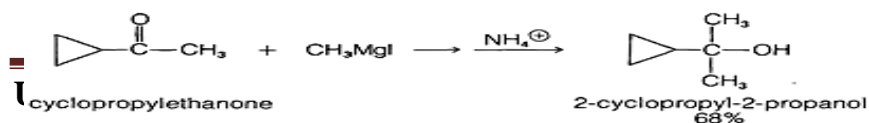
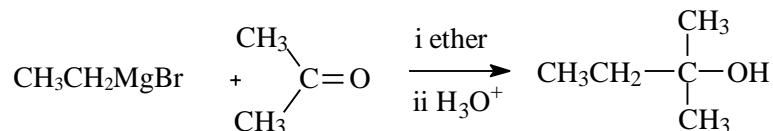
(a) **By reaction with aldehydes & ketones:** The reaction of Grignard reagents with formaldehyde produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols. In this method alcohol is prepared with the formation of new carbon-carbon bonds.



All other aldehydes yield 2^o alcohols on reaction with Grignard reagents.

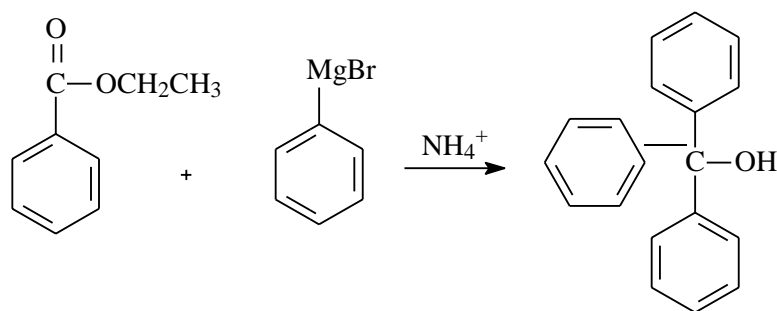
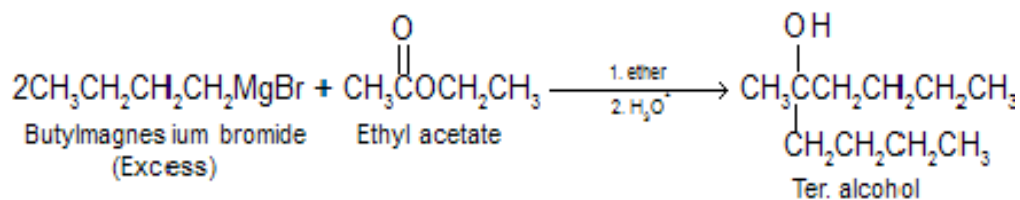
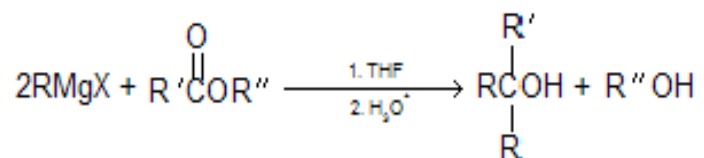


With ketones, Grignard reagents give 3^o alcohols.

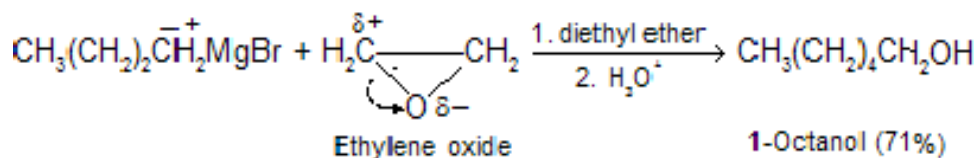
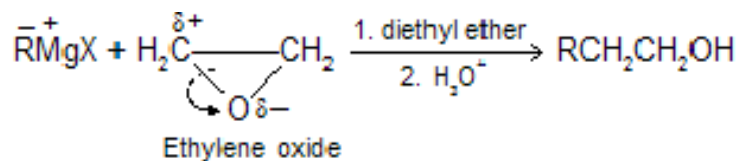
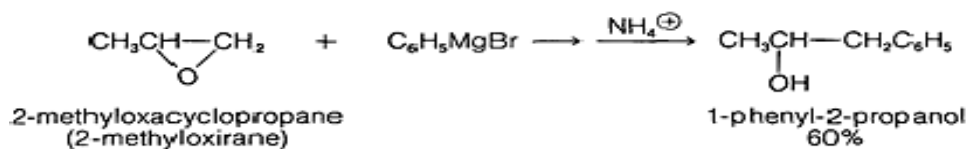


ORGANIC CHEMISTRY

(b) **By reaction with esters:** Produces tertiary alcohols in which two of the substituents on the hydroxyl-bearing carbon are derived from the Grignard reagent.

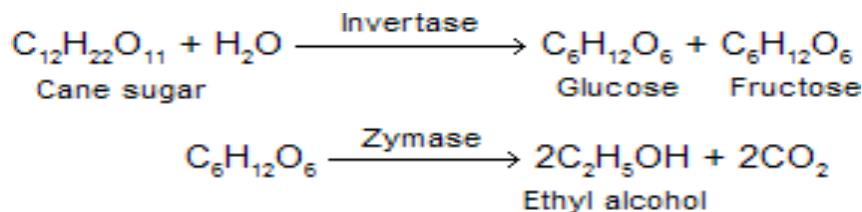


(c) **By reaction with epoxides:** Grignard reagents react with epoxide to yield primary alcohols containing two or more carbon atoms.



ORGANIC CHEMISTRY

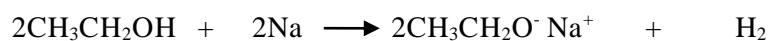
5. Fermentation: Ethanol is prepared on a large scale using fermentation process. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes. Yeast converts the reactant glucose or fructose into ethanol and carbon dioxide in presence of zymase enzyme.



1.6 ACIDIC NATURE OF ALCOHOLS

Alcohols can act as Brønsted acids as well as Lewis's base due to donation of proton and presence of unpaired electron on oxygen respectively. Alcohols are very weak acids because the alkyl group pushes electrons towards the —OH group, so that the oxygen does not strongly attract the electrons in the —OH bond. Furthermore, once a RO^- ion is formed, it cannot be stabilized by the delocalization of the charge. Thus, alcohols react only to a very slight extent with alkali, but will react with very electropositive metals under anhydrous conditions to give alkoxide with the general formula $\text{RO}^- \text{M}^+$.

Example: Reaction of ethanol with sodium



Addition of water will regenerate the alcohol readily.

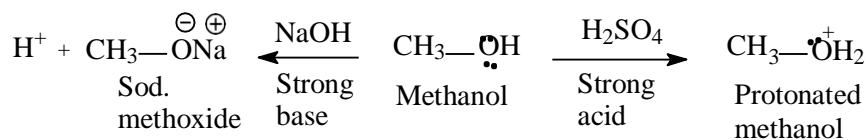


The reaction is much slower than the reaction of water with sodium. Alcohols tend to be slightly less acidic ($\text{pK}_a = 15$) compared to water ($\text{pK}_a = 14$). The higher the pK_a value the lower is the acid strength. The reaction of alcohol with sodium can be used to deposit the excess sodium in the laboratory. Even alcohols are neutral to litmus and do not react with alkali like NaOH but contain active hydrogen atom so reacts with Na or K metal.

ORGANIC CHEMISTRY



Reactivity of alcohol towards metal: $1^\circ > 2^\circ > 3^\circ$ alcohol. An electron-releasing group ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$) increases electron density on oxygen tend to decrease the polarity of O-H bond. For example, with methanol:



(i) The lower alcohols are colorless liquids with a characteristic smell and a burning taste. The higher members (with more than 12 carbons) are colorless wax like solids.

(ii) Because of hydrogen bonding, alcohols tend to have higher boiling points than comparable hydrocarbons and ethers of similar molecular weight. Alcohols exists associated molecules due to the association of molecules in the liquid phase through strong intermolecular hydrogen bond between hydrogen atom of one molecule and oxygen atom of another molecule. The oxygen-hydrogen bond is polar because oxygen is much more electronegative than hydrogen. The lowers members have low boiling points. With the increase in molecular weight, the boiling points keep on increasing gradually. For example, the boiling point of butyl alcohol is 118°C whereas the boiling point of the isomeric diethyl ether is 36°C .

(iii) Solubility: The general rule in solubility is “*like dissolves like.*” The hydroxyl group generally makes the alcohol molecule polar and therefore more likely to be soluble in water. Hydrogen bonding also has an effect on water solubility. The OH groups of an alcohol can hydrogen bond with water, and so this portion of the alcohol is hydrophilic. On the other hand, the alkyl chain in an alcohol is similar to hydrophobic molecules like hydrocarbon that do not mix with water. Compounds like alcohols that have hydrophilic and hydrophobic regions are called ambiphilic (or amphiphilic). The water solubility of a given alcohol depends on whether the hydrophilic OH or the hydrophobic alkyl chain dominates. Alcohols with shorter carbon chains (CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) are usually more soluble than those with longer carbon chains because the increasing size of the nonpolar chain disrupts the hydrogen bonding network. Formation of hydrogen bonds with water will increase their

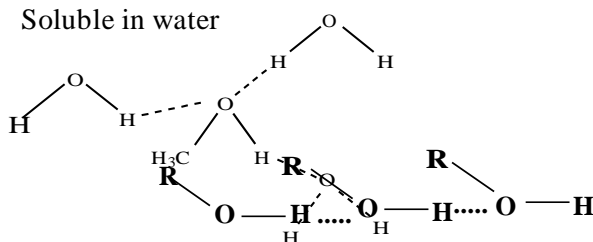
ORGANIC CHEMISTRY

solubility. That is why alcohols are much more soluble in water than their corresponding alkanes, aromatic hydrocarbons, alkyl halides or aryl halides. Amongst isomeric alcohols, the solubility increases with branching.

(iv) The B.P. and M.P. will also increase with carbon chain length. The longer the alcohols carbon chain, the better the chance that the alcohol will be a solid at room temperature. Alcohols show higher boiling points than alkane and ethers of similar mass due to hydrogen bonding. Since there is not any possibility of hydrogen bonding in ether, the forces between the ether molecules are much weaker and can be much more easily vaporized.

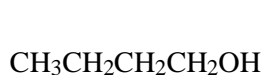


Soluble in water



Insoluble in water

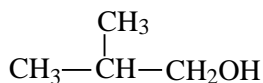
Comparison of boiling points among isomeric alcohols



1-butanol

B.P. 118°C

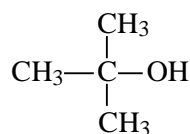
M.Wt = 74



2-methyl 1-propanol

B.P. 108°C

M.Wt = 74



2-methyl 2-propanol

B.P. 83°C

M.Wt = 74

(v) The viscosity of small alcohols is much higher than the viscosity of alkanes.

(vi) Generally alcohols are lighter than water, i.e., less dense than water. Density of alcohols increases with molecular mass.

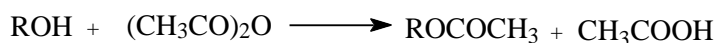
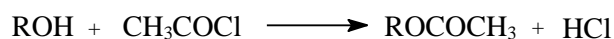
ORGANIC CHEMISTRY

1.7 CHEMICAL REACTIONS OF ALCOHOLS

Alcohols act 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

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

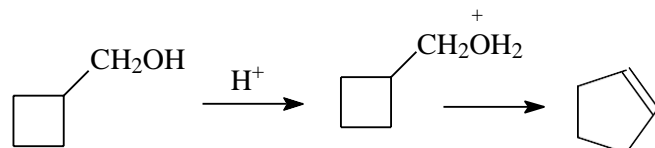
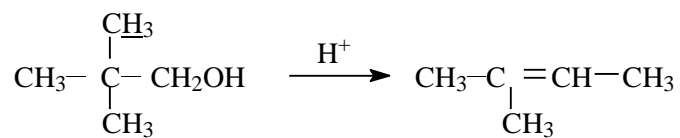
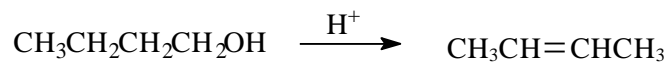
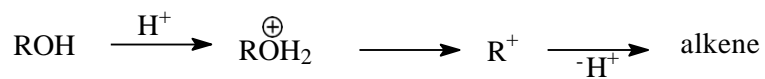


(B) Reaction involving fission of R—OH bond (cleavage of C—O bond): The reactions involving R—OH bond with cleavage of C—O bond are as follow

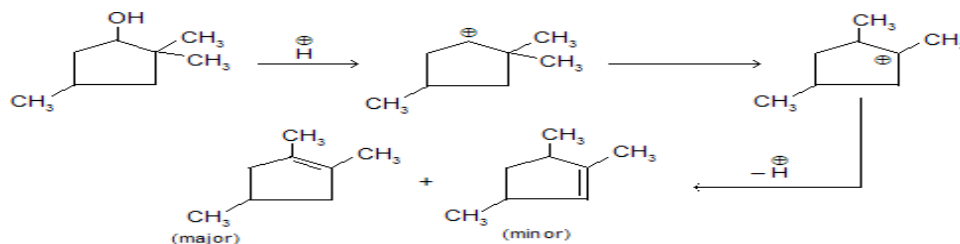
1. Dehydration: (a) Intramolecular dehydration (forming alkene): Alcohols undergo dehydration to form unsaturated hydrocarbon on treating with a protic acid e.g., conc. H_2SO_4 or H_3PO_4 , or catalysts such as anhydrous ZnCl_2 or Al_2O_3 . In this reaction the OH and an H group removes from an adjacent carbon. Since water is removed from the alcohol, this reaction is known as a **dehydration reaction** (or an *elimination reaction*). Secondary and tertiary alcohols are dehydrated under much milder conditions. The conditions for dehydrating alcohols depend closely on the structure of individual alcohols.

For primary alcohols, the conditions required are conc. sulphuric acid and temperature of 170°C .

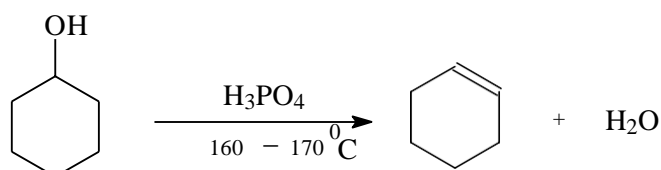
ORGANIC CHEMISTRY



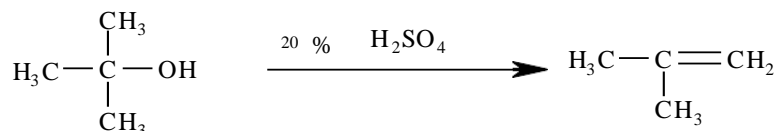
In smaller ring always ring expansion takes place due to molecular strain and they tend to convert to high stability with large ring.



Secondary alcohols dehydrate under milder conditions than primary alcohols.



Tertiary alcohols dehydrate under even milder conditions.

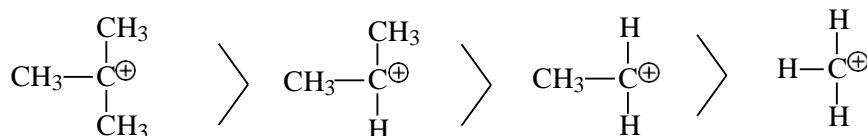


ORGANIC CHEMISTRY

The main function of the acid is to transform the poor leaving group —OH into the very good leaving group —OH₂. The order of the relative ease of dehydration of alcohols is: 3° > 2° > 1°

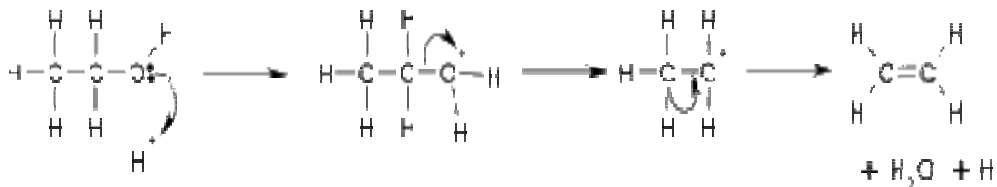
Tertiary carbocations are most stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

The order of stability of the carbocations is:



Dehydration of secondary and tertiary alcohols containing more than three carbon atoms will give a mixture of alkenes, the major product can be determined from Saytzeff's Rule:

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.

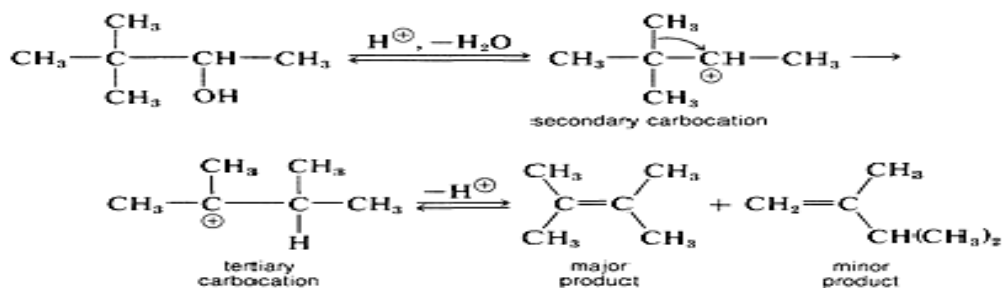


Rearrangement of the alkyl

groups of alcohols are 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:

ORGANIC CHEMISTRY



(b)

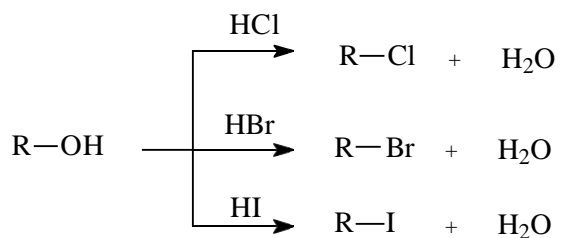
Intermolecular dehydration (forming ether):

When the dehydration is carried out at a temperature of 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:

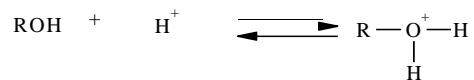
(a) Reaction with hydrogen halides: Respective alkyl halides are formed by reacting with the appropriate hydrogen halide, HCl for chlorination, HBr for bromination, and HI for iodination. The reaction involves the initial protonation of the hydroxyl group of the alcohol. This improves the leaving group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



Mechanism:

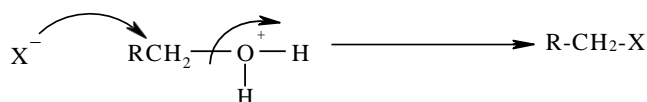
Step1: Protonation of the alcohols: The alcohol acts as a weak base and accepts the proton donated by the hydrogen halide.

ORGANIC CHEMISTRY

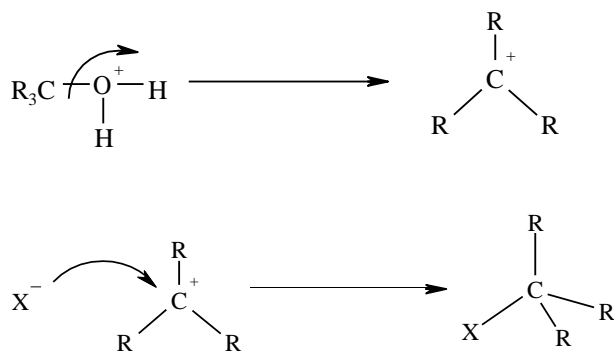


Step 2: Removal of a water molecule and formation of halide through $\text{S}_{\text{N}}2$ mechanism/
 $\text{S}_{\text{N}}1$ mechanism as:

(i) For primary and secondary alcohols, it is a $\text{S}_{\text{N}}2$ reaction.



(ii) For tertiary alcohols, it is a $\text{S}_{\text{N}}1$ reaction.



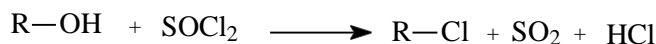
(iii) Rate of the reaction for 1° , 2° and 3° alcohols:

The order of rates of reaction:



The rate can be shown by the turbidity in the aqueous layer since the chloroalkane formed is immiscible with water.

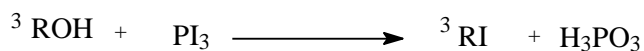
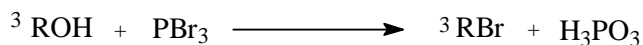
(b) Reaction with thionyl chloride, SOCl_2 : Alcohols will react with thionyl chloride to produce alkyl halides. The reaction involves a nucleophilic attack of the alcohol on a SOCl_2 molecule displacing one of the chlorides. Then the chloride will act as the nucleophile in a second step and displace the oxygen from the carbinol carbon.



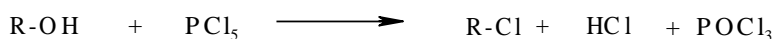
ORGANIC CHEMISTRY

(c) Reaction with phosphorus halides

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

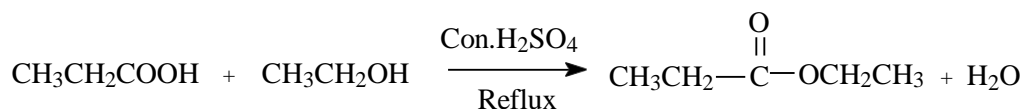


The mechanism is very similar to the thionyl chloride reaction. The alcohol acts as the nucleophile and displaces a halide ion from the PX_3 or the PX_5 .



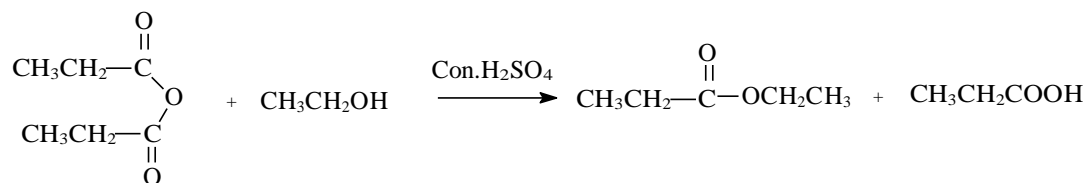
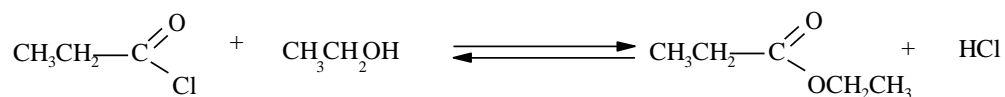
3. Esterification: Alcohol reacts with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride is reversible, and therefore, water is removed as soon as it is formed. Esterification takes place much faster in the presence of a catalyst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

Example :



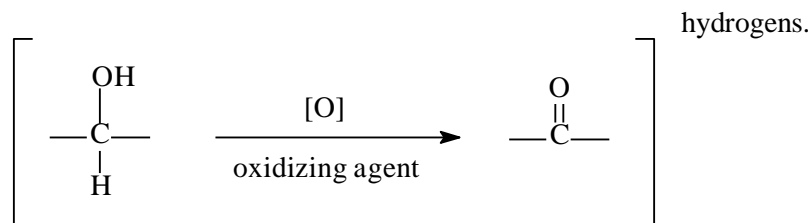
Alcohols can also react with acid chlorides and acid anhydrides to form esters. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation.

Example:

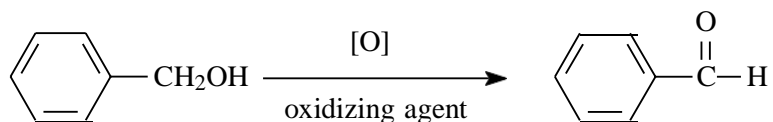
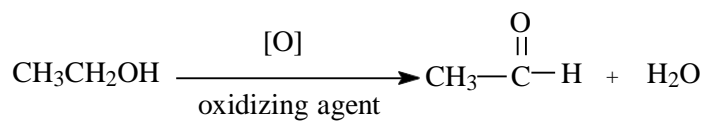
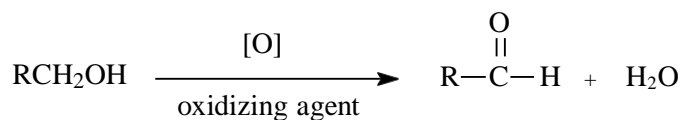


ORGANIC CHEMISTRY

3. Oxidation: Alcohols can be oxidized by various oxidizing agents to aldehyde, ketones or carboxylic acids. Oxidation is the gain of oxygens and /or the loss of

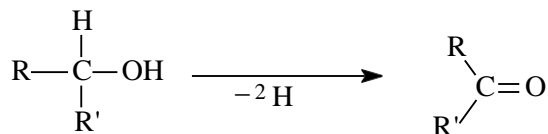


(a) 1^o alcohol oxidizes readily, first to an aldehyde, then to a carboxylic acid. These two oxidation steps make sense because the primary alcohol functional group has two C-H bonds that can be broken. Primary or secondary alcohols can be oxidized to produce compounds containing the carbonyl group (a carbon-oxygen double bond, C=O). Strong oxidizing agents such as hot alkaline KMnO₄ or CrO₃ in H₂SO₄ will oxidize primary alcohols right past the aldehyde to the salt of the carboxylic acid in which the acid may be precipitated by acidification. The alcohol, aldehyde and acid retain the same number of carbon atoms.



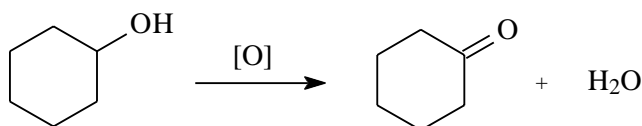
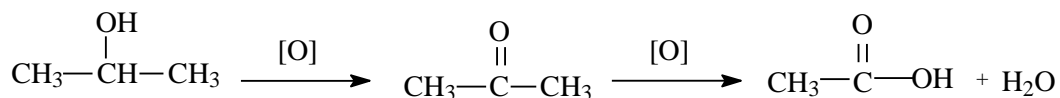
(b) 2^o alcohol has only one C-H bond that can be broken, so it can only oxidize once, to a ketone, which cannot be oxidized any further:

ORGANIC CHEMISTRY

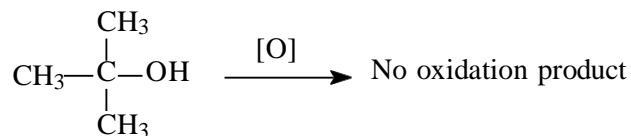


3^o alcohol

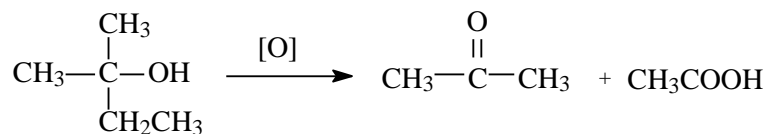
Ketone



(c). 3^o alcohol has no C-H bonds that can be broken, so it is not oxidized, no matter how strong the oxidizing agent because it would involve the breakage of the high energy C—C bonds in the alcohol molecule.



In acidic solutions, 3^o alcohols can be oxidized to give a mixture of ketone and acid, both with fewer carbon atoms than the alcohol.

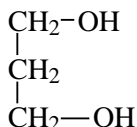
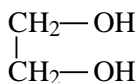


Characterization of the oxidation products of alcohols is a means of distinguishing between primary, secondary and tertiary alcohols.

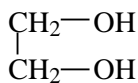
ORGANIC CHEMISTRY

1.8 DIHYDRIC ALCOHOLS

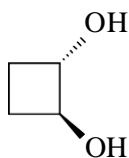
These compounds contain two hydroxyl (–OH) groups in a molecule. These are dihydroxy components of alkanes. Their general formula is $C_nH_{2n+2}O_2$. The simplest and most important dihydric alcohol is ethylene glycol. They are classified as $\alpha, \beta, \gamma, \dots$ glycols, according to the relative position of two hydroxyl groups. α is 1, 2 glycol, β is 1, 3 glycol.



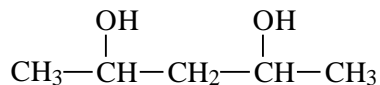
Nomenclature: For naming polyhydric alcohols, the name of the alkane is retained and the ending -e is not dropped but add a di- or tri- prefix to the -ol suffix. Thus dihydric alcohols are named as alkane diols and trihydric alcohols are named as alkene triols.



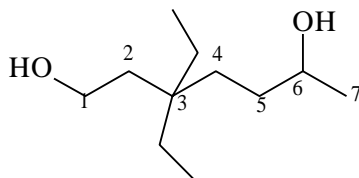
eth - 1,2 - diol



trans - 1,2 - cyclobutanediol



2,4 - pentadienol



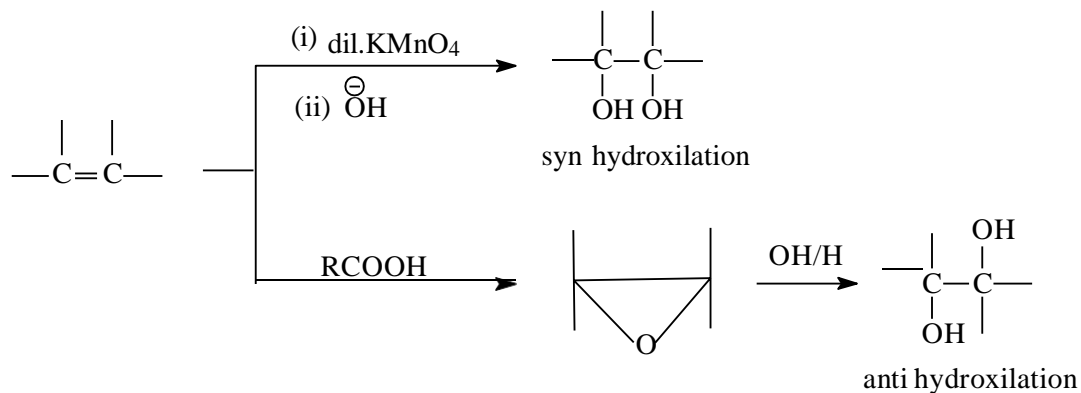
3,3 - diethyl - 1,6 - heptanediol

1.9 METHODS OF PREPARATION

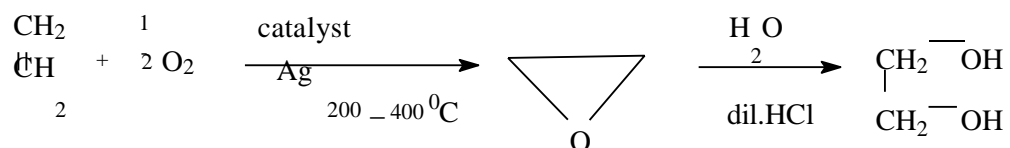
Dihydric alcohols are prepared by following different methods:

From ethylene: (a) through icy dilute alkaline solution of Bayer's reagent.

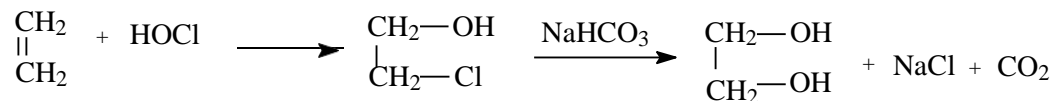
ORGANIC CHEMISTRY



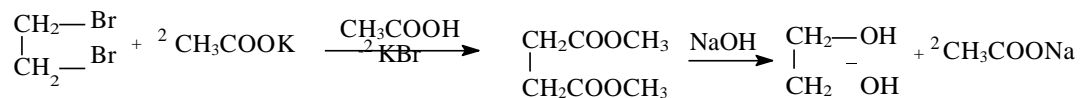
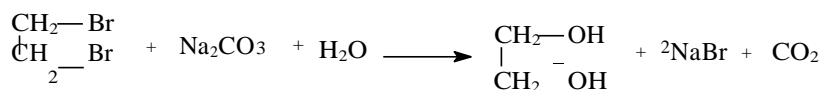
(b) With O₂ in presence of Ag :



(c) With HOCl followed by hydrolysis:



From 1, 2 dibromo ethane :



1.10 PHYSICAL PROPERTIES OF DIHYDRIC ALCOHOL

Dihydric alcohol viz; glycerol exhibits the following physical properties:

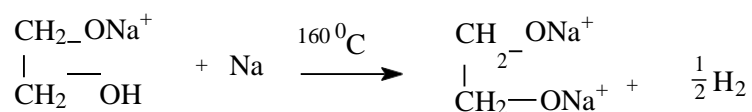
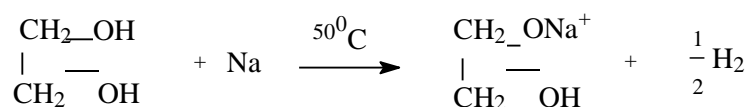
ORGANIC CHEMISTRY

- (i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is 197°C . melting point -11.5°C
- (ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.
- (iii) It is toxic as methanol when taken orally.
- (iv) It is widely used as a solvent and as an antifreeze agent.

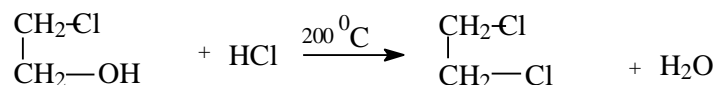
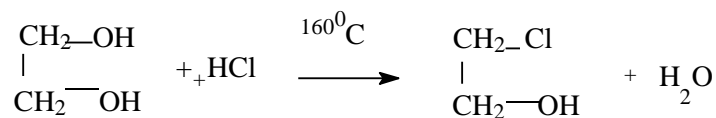
1.11 CHEMICAL REACTIONS OF VICINAL GLYCOLS

Glycerol molecule is made up of two 1° alcohol groups joined together its chemical reactions are, therefore those of 1° alcohols twice over viz;

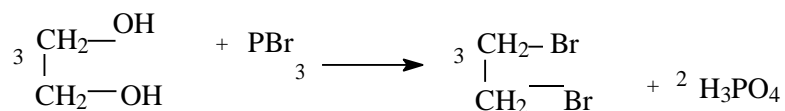
1. Action of Sodium: It reacts with Na at 50°C to form to form mono and dialkoxide at elevated temperature.



2. Reaction with HCl: Ethylene dichloride is formed in two successive steps at elevated temperature



3. Action with phosphorus halides : ethylene dihalides are formed as follow:

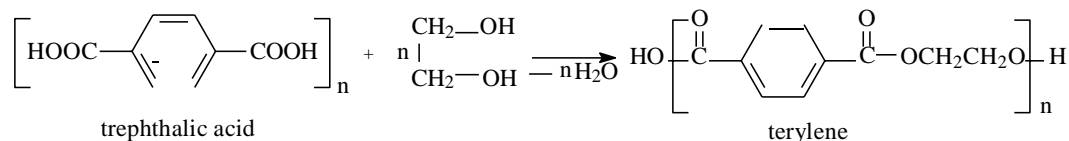
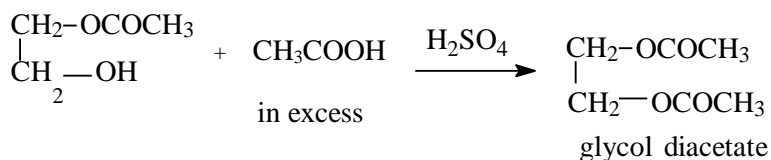
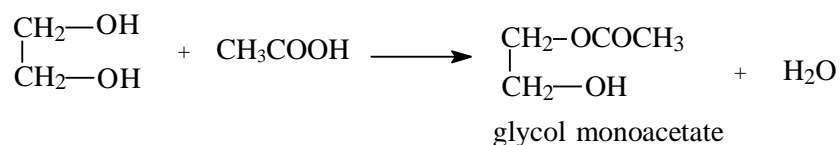


ORGANIC CHEMISTRY

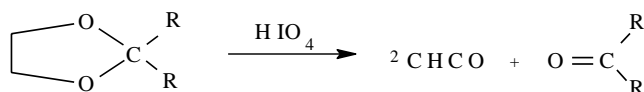
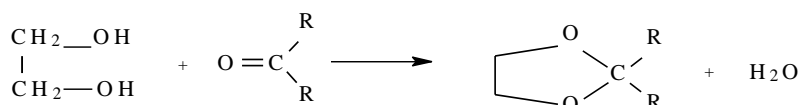
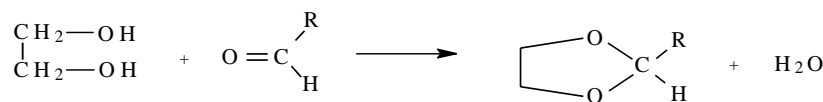
PI₃ produce ethylene diiodide which is unstable and split into I₂ and ethylene



4. Reaction with carboxylic acid: Gives diester depending upon the amount of glycol and acid taken:

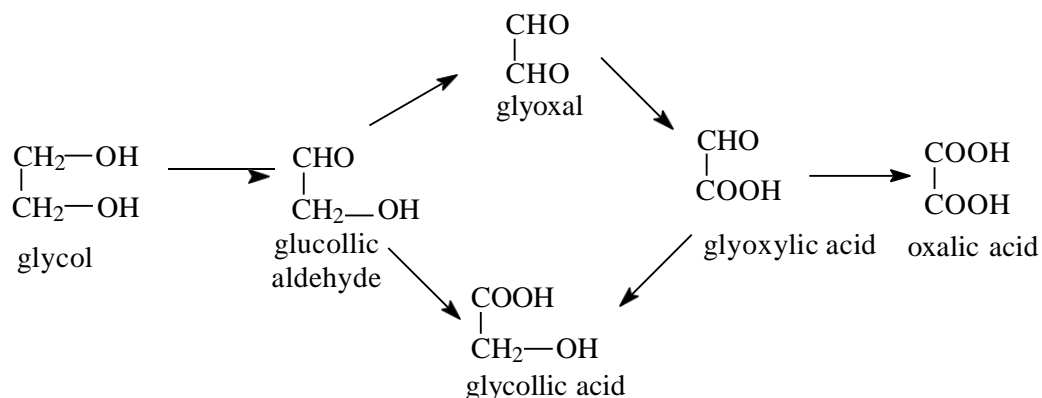


5. Reaction with aldehyde and ketones: Glycol reacts with aldehyde and ketones in presence of p- toluene sulphonic acid to give cyclic acetals/ketals which further may give ketone/aldehyde while treating with HIO₄. This reaction thus can be useful to protect carbonyl group.

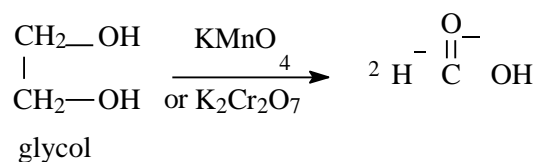


ORGANIC CHEMISTRY

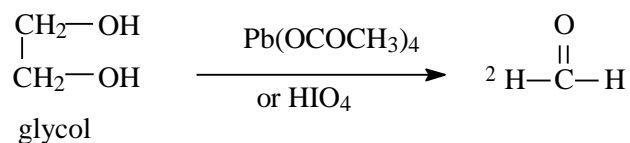
6. (i) The oxidation of ethylene glycol with HNO_3 to yields a number of substance as follow:



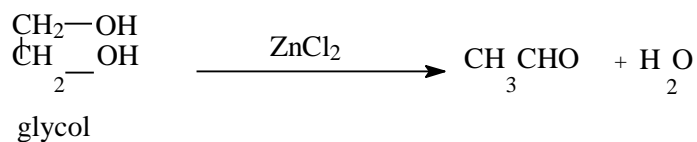
- (ii) Oxidation with KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ to form formic acid:



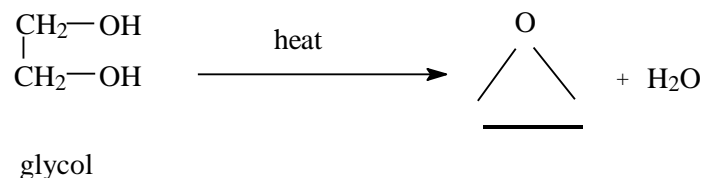
- (iii) Oxidation with $\text{Pb}(\text{OCOCH}_3)_4$ or HIO_4 glycol gives formaldehyde.



7. Dehydration: (i) Heating with ZnCl_2 glycol gives acetaldehyde

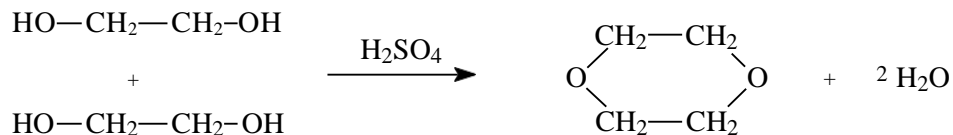


- (ii) When heated alone at 500°C , it gives ethylene oxide.



- (iii) Dioxane is obtained when glycol is heated with conc. H_2SO_4 .

ORGANIC CHEMISTRY

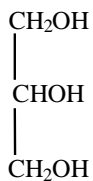


Uses of ethylene glycol:-

1. It is used as antifreeze substance which prevents the freezing of water in car radiators in cold countries.
2. Due it has a high viscosity, so it is used in the hydrolic break, printing ink ball, pen inks, organic solvents.
3. Used in the manufacture of Dacron, dioxane etc.
4. As a solvent and as a preservative.
5. As a cooling agent in aeroplanes.
6. As an explosive in the form of dinitrate.
7. Large amounts of ethylene glycol are converted to polymers (such as polyethylene glycol) used in the manufacture of dacron fibers, photographic films and cassette tapes.

1.12 TRIHYDRIC ALCOHOL

It is a triol. The introduction of third -OH group in diol molecule raises the b.p. about 100°C, increase viscosity and make the alcohol sweeter. Viz; glycerol



It is designated as prop-1, 2, 3-triol in IUPAC nomenclature. It may be considered as derivative of propane, obtained by replacement of three hydrogen atoms from different

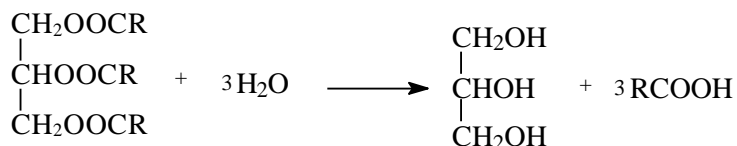
ORGANIC CHEMISTRY

carbon atoms by three hydroxyl group. In industry, it's known as glycerin. It occurs as glycosides in almost all animal and vegetable oils and fats.

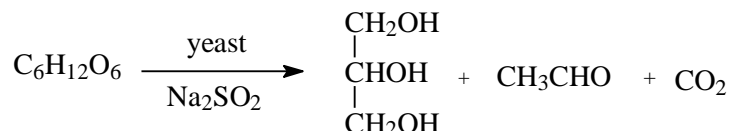
1.13 METHODS OF PREPARATION

Glycerol can be synthesized by following different methods:

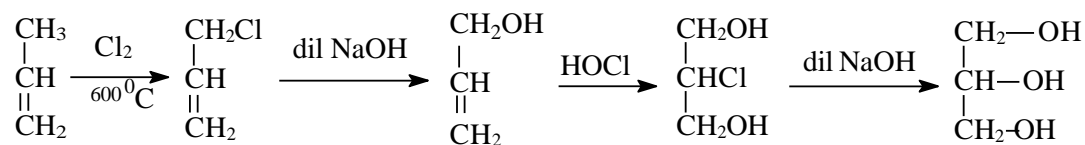
1. **From fats and oil:** On hydrolysis of fats and oils, glycerol and higher fatty acids are formed.



2. **By fermentation of sugars:** Alcoholic fermentation of sugar in the presence of sodium sulphite gives good yield of glycerol.



3. **Synthesis (from propene):** Today much of glycerol is obtained from propene.

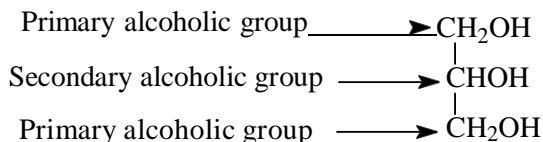


Physical properties: Glycerol is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-oxic in nature. It is soluble in water and ethyl alcohol but insoluble in ether. It has high boiling point, i.e., 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding purified in the lab by reduced pressure distillation or vacuum distillation.

1.14 CHEMICAL REACTIONS

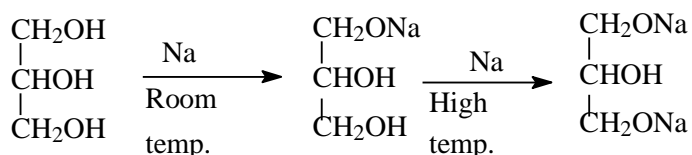
Glycerol molecule contains two 1^o – OH groups and one 2^o – OH group. Thus, it shows characteristics of both primary and secondary alcohols.

ORGANIC CHEMISTRY

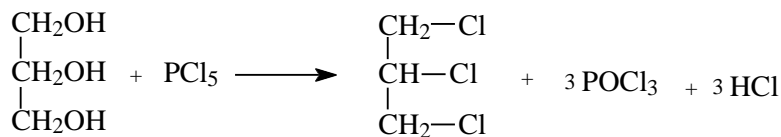


In general, 1° - OH groups are more reactive than 2° - OH group.

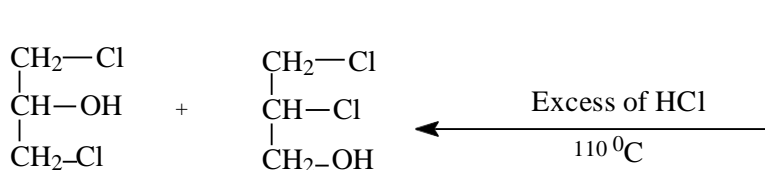
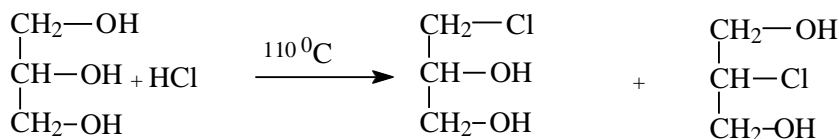
- Reaction with sodium: Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked, Sodium forms monosodium glycerolate at room temperature and disodium glycerolate at higher temperature.



- Reaction with PCl_5 : All three OH groups are replaced by Cl atoms.



- Reaction with HCl or HBr: When HCl is passed into glycerol at 110°C , both, α or β glycerol monochlorohydrins are formed. If the HCl gas is passed for sufficient time, glycerol α, α' dichlorohydrin and glycerol, α, β - dichlorohydrin are formed.

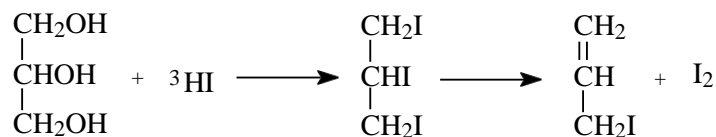


Same reactions occur with HBr.

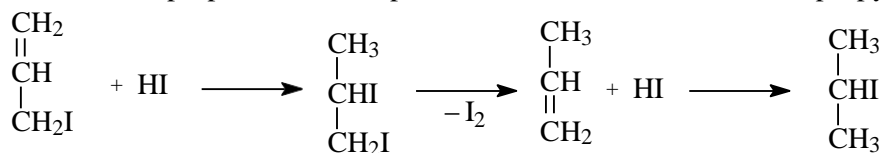
- Reaction with HI: Glycerol reacts with HI in two ways:
 - When glycerol is warmed with a small amount of hydrogen iodide, allyl iodide is

ORGANIC CHEMISTRY

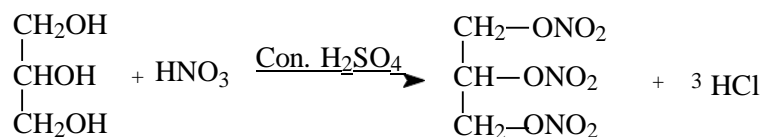
formed. First triiodide is formed but due to large size of iodine atom I_2 comes out from product.



(b) When glycerol is heated with a large amount of HI, the allyl iodide first formed is reduced to propene, which in presence of excess of HI forms iso-propyl iodide.

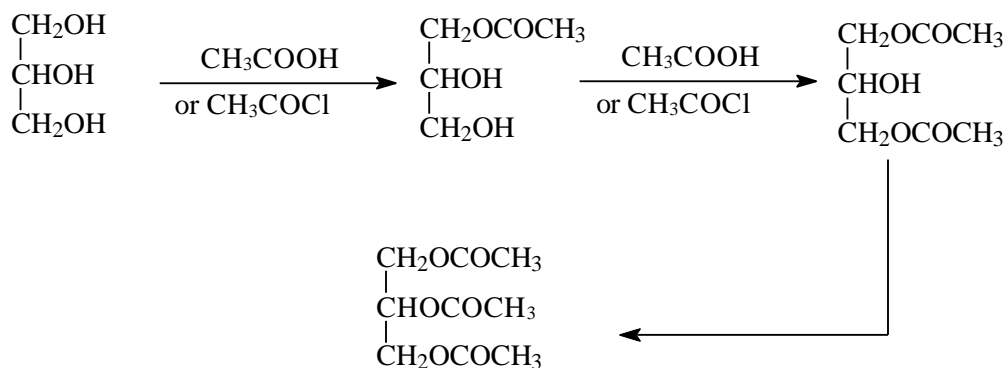


5. Reaction with HNO_3 : When one part of glycerol in a thin stream is added to three times conc. HNO_3 and five parts of concentrated sulphuric acid, nitro-glycerine (glyceryl trinitrate) is formed.



Glyceryl trinitrate is a yellow oily liquid. It is poisonous and causes headache. It explodes violently when heated rapidly or subjected to sudden shock. It becomes a safer explosive when absorbed on kieselguhr. In this form, it is known as **dynamite**. Dynamite was discovered by Alfred Nobel in 1867.

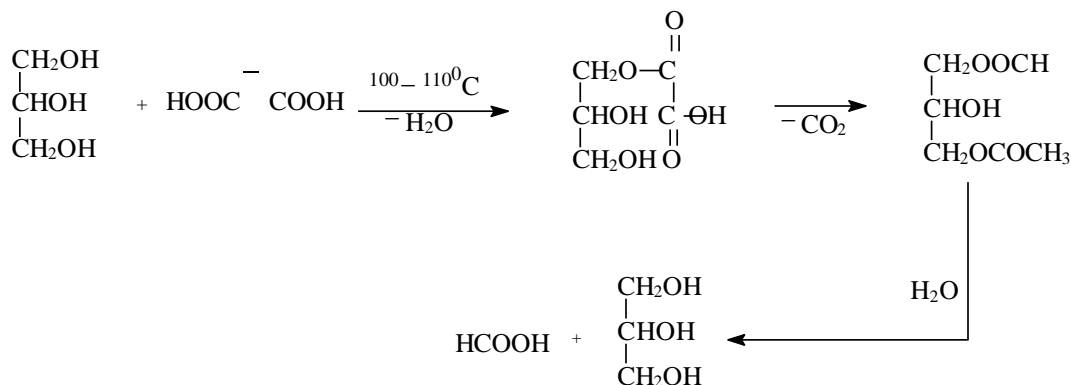
6. Reaction with acetic acid, acetic anhydride or acetyl chloride: Mono-, di- and tri-esters are formed.



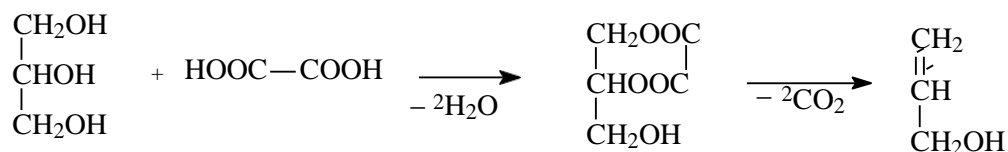
ORGANIC CHEMISTRY

7. **Reaction with oxalic acid:** Different products are formed under different conditions.

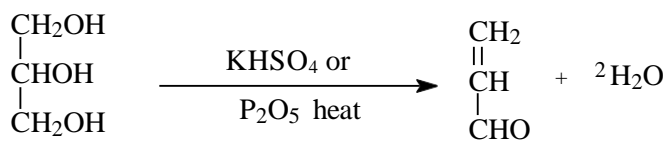
(a) At 100⁰C and with excess of oxalic acid, formic acid is formed



(b) At 260⁰C allyl alcohol is formed

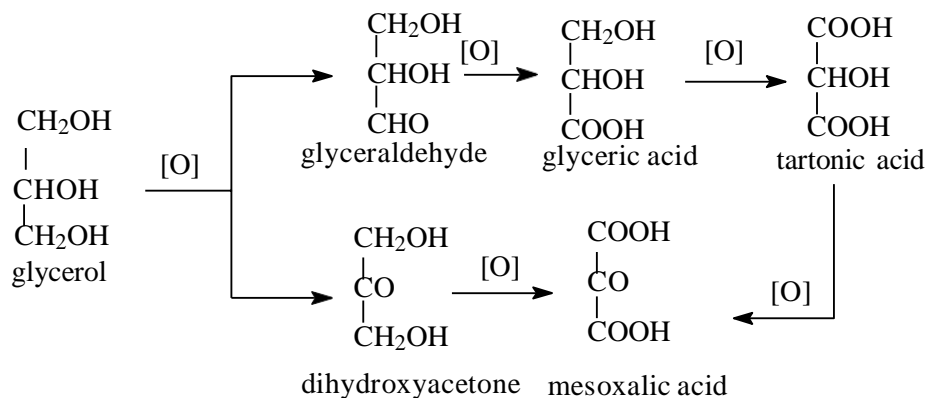


8. Dehydration: Glycerol when heated alone or with dehydrating agents such as potassium hydrogen sulphate or phosphorus pentoxide or conc. sulphuric acid, acrolein or acrylaldehyde is formed which has a characteristic bad smell. This reaction can be used as a test of glycerol.



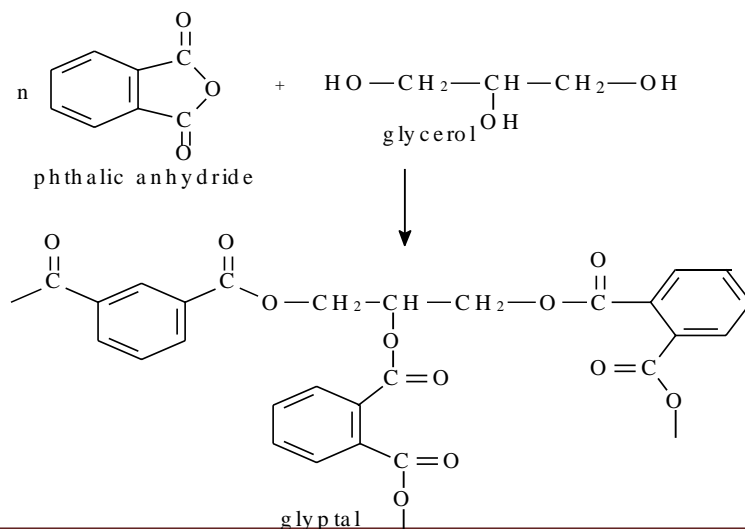
9. Oxidation: Glycerol gives different oxidation products depending on the nature of oxidizing agent. The following products may be obtained during oxidation of glycerol.

ORGANIC CHEMISTRY



- (a) Dilute HNO_3 gives mainly glyceric acid.
- (b) Conc. HNO_3 oxidises glycerol into glyceric acid and tartronic acid.
- (c) Bismuth nitrate gives mainly meso oxalic acid.
- (d) Fenton's reagent ($\text{H}_2\text{O}_2 + \text{FeSO}_4$) or NaOBr or Br_2 - water in presence of Na_2CO_3 oxidises glycerol into a mixture of glyceraldehyde and dihydroxy acetone (or glycerose).

10. Formation of resin: Glycerol reacts with phthalic anhydride forming polyesters known as glyptals. Each of the three $-\text{OH}$ groups in glycerol forms an ester linkage with the anhydride, giving a thermosetting polymer (plastic) used for making synthetic fibers.



ORGANIC CHEMISTRY

Uses: Glycerol is used: Glycerol is used as a sweetening agent in confectionery, beverages and medicines being non-toxic in nature. It is used as antifreeze in automobile radiators, in the preparation of good quality of soap, hand lotions, shaving creams, tooth pastes and cosmetics and as a lubricant in watches and preservative.

1.15 SUMMARY

In this unit we have learnt that: Alcohols are compounds in which a hydrogen of alkane has been replaced by an –OH group and are classified as monohydric, dihydric, trihydric or polyhydric on the basis of –OH group present. The monohydric alcohols can be classified into 1°, 2° and 3° alcohols. In IUPAC name alcohols are designated as alkanol by replacing ‘e’ with –ol from the corresponding alkane. This unit also describes the methods of preparation of alcohols by using different methods like; hydrolysis of halogenoalkanes, hydration of alkene, reduction of aldehydes and ketones using Grignard reagents (RMgX), LiAlH₄, NaBH₄, by fermentation of carbohydrates etc. The amphoteric nature of alcohols has also been described in this unit. As an acid, it ionizes to form an alkoxide ion (RO⁻) and hydrogen ion, H⁺ in the presence of a base, while in presence of an acid, the alcohol may function as a base and can accept a proton. This unit makes the readers aware about methods of preparation, physical properties and chemical reactions along with applications of dihydric alcohol glycol and trihydric alcohol glycerol.