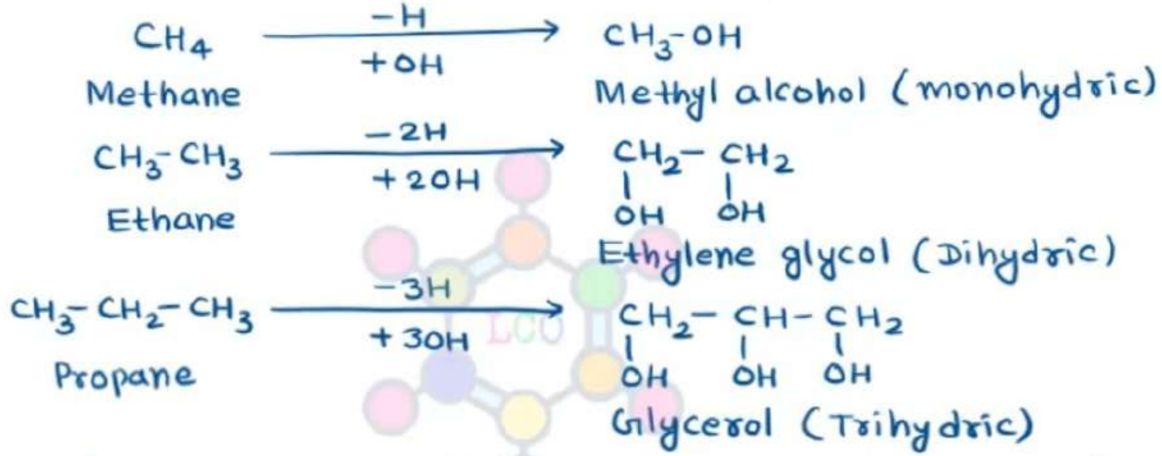
→ Alcohols: →

- Introduction:-

- Alcohols are derivatives of aliphatic hydrocarbons in which one or more hydrogen atoms are replaced by the corresponding number of hydroxyl groups (-OH).



$$CH_4 \xrightarrow[+OH]{-H} CH_3-OH$$

Methane — Methyl alcohol (monohydric)

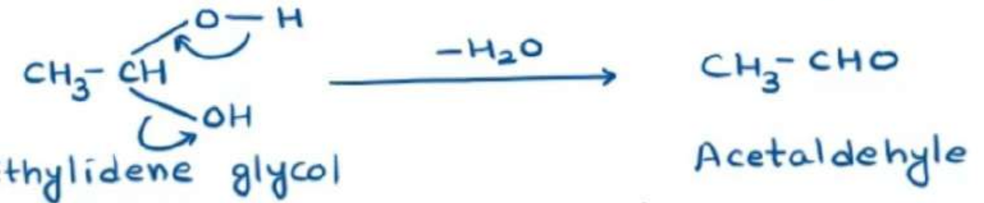
$$CH_3-CH_3 \xrightarrow[+2OH]{-2H} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

Ethane — Ethylene glycol (Dihydric)

$$CH_3-CH_2-CH_3 \xrightarrow[+3OH]{-3H} \underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

Propane — Glycerol (Trihydric)

- If two or more hydroxyl groups are attached to same carbon atom then the compound is unstable and converted into carbonyl compound by elimination of water molecule.



$$CH_3-CH(OH)(O-H) \xrightarrow{-H_2O} CH_3-CHO$$

Ethylidene glycol — Acetaldehyle

- Alcohol may also regarded as alkyl derivative of water in which one hydrogen of water is replaced by an alkyl group.

$$H-O-H \xrightarrow[+R]{-H} R-O-H$$

- Water and alcohol both have sp^3 hybridised O-atom but C–O–H bond angle in alcohol is 108·9° which is larger than that in water (104·5°). because the alkyl group is much larger in size than the hydrogen atom.

→ Classification:-

- The R group in the alcohol may be an alkyl, alkenyl, alkynl, aryl and halogen substituents
- An alcohol may be cyclic or acyclic.
- Alcohols can be classified in three different ways as follows-

Ⓐ classification on the basis of hydrocarbon moiety:-

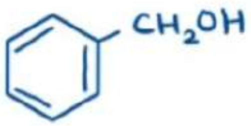
① Aliphatic alcohols:- –OH linked with aliphatic carbon chain.

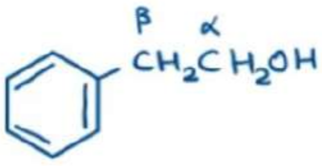
CH_3-OH Methanol

CH_3-CH_2-OH Ethanol

$CH_3-CH_2-CH_2-CH_2-OH$ Butanol

② Aromatic alcohols:- –OH linked with side chain of an aromatic hydrocarbon.


Benzyl alcohol

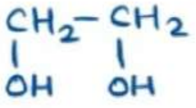

β-phenylethyl alcohol

Ⓑ Classification on the basis of number of hydroxyl groups:-

① Monohydric alcohols:- one -OH group.

CH_3-OH Methyl alcohol or methanol (monohydric alcohol)

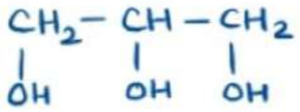
② Dihydric alcohols:- two -OH groups.



$$\underset{OH}{CH_2}-\underset{OH}{CH_2}$$

Ethylene glycol or Ethane-1,2-diol (Dihydric alcohol)

③ Trihydric alcohols:- three -OH groups.

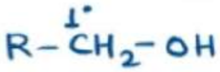


$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

Glycerol or propane-1,2,3-triol (Trihydric alcohol)

Ⓒ Classification on the basis of nature of carbon atom attached with hydroxyl group.

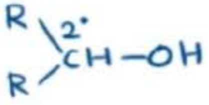
① Primary (1°) alcohols:- hydroxyl group attached with primary (1°) carbon.



$$R-\overset{1^\circ}{C}H_2-OH$$

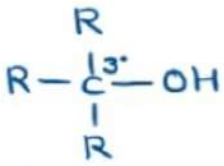
primary (1°) alcohol

② Secondary (2°) alcohols:- hydroxyl group attached with secondary (2°) carbon.



secondary (2°) alcohol

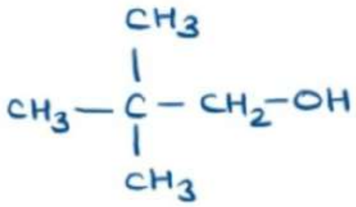
③ Tertiary (3°) alcohols :- hydroxyl group attached with tertiary (3°) carbon.


$$R-\overset{R}{\underset{R}{\overset{|3^\circ}{C}}}-OH$$ tertiary (3°) alcohol

- Alternatively, a primary alcohol contains a monovalent $-CH_2OH$ group; a secondary alcohol contains a divalent $>CHOH$ group and a tertiary alcohol contain a trivalent $\rightarrow C-OH$ group.
- Primary alcohols may also be named by writing the suffix n (normal), iso, neo etc., which indicate the type of branching in R group.

$CH_3-CH_2-CH_2-CH_2-OH$ n-butyl alcohol (straight chain)


$(CH_3)_2CH-CH_2-OH$ Isobutyl alcohol (Branched chain)


$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-OH$$ Neopentyl alcohol (Branched chain)

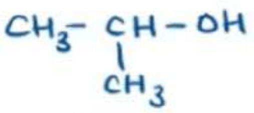
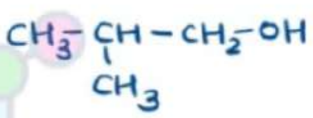
→ Monohydric alcohols :-

→ Nomenclature :-

- Three methods have been developed for nomenclature of monohydric alcohols.

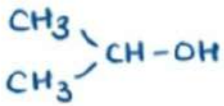
① The common name system :-

- In this system, suffix 'alcohol' is used after the common name of the alkyl group.

CH_3-OH	Methyl alcohol	CH_3-CH_2-OH	Ethyl alcohol
$CH_2=CH-OH$	Allyl alcohol	$C_6H_5-CH_2-OH$	Benzyl alcohol
 $CH_3-\underset{\vert}{\underset{CH_3}{CH}}-OH$	Isopropyl alcohol	 $CH_3-\underset{\vert}{\underset{CH_3}{CH}}-CH_2-OH$	Isobutyl alcohol

② The carbinol system :-

- All alcohols may be regarded as the derivatives of methyl alcohol, which is commonly known as carbinol (carbine alcohol).
- The name of all the substituents attached to the carbon atom bearing the -OH group are written in alphabetical order before the suffix carbinol and the whole name is written as one word.

CH_3-OH	Carbinol	CH_3-CH_2-OH	Methylcarbinol
 $\begin{matrix}CH_3\\CH_3\end{matrix}>CH-OH$	Dimethylcarbinol	$(C_6H_5)_3-C-OH$	Triphenylcarbinol

③ The IUPAC system:-

- In this system, the suffix -e in the name of hydrocarbon is replaced by suffix -ol.

$$\text{Alkane} \xrightarrow[+ol]{-e} \text{Alkanol}$$

- Some important rules of this system are as follows-

(i) The longest chain of the carbon atom bearing -OH group is first selected and the compound is considered as derivative of this hydrocarbon. The remaining groups are considered as substituent.

(ii) The carbon atoms of the logenst chain so selected are numbered from one end to the other in such a way that carbon atom bearing -OH is assigned the lowest number. These numbers indicate the positions of the substituent including -OH group.

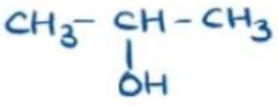
(iii) Finally, the name of alcohol is written as one word by writing the name of substituents in alphabetical order and the position of substituent is shown by numbers. The number and name are separated by putting a hyphen between them.

Example:-

CH_3-OH Metanol

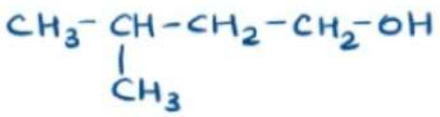
$C_6H_5-CH_2-CH_2-OH$ 2-phenylethanol

$CH_2=CH-CH_2OH$ 2-propen-1-ol or 2-propenol



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

2-propanol



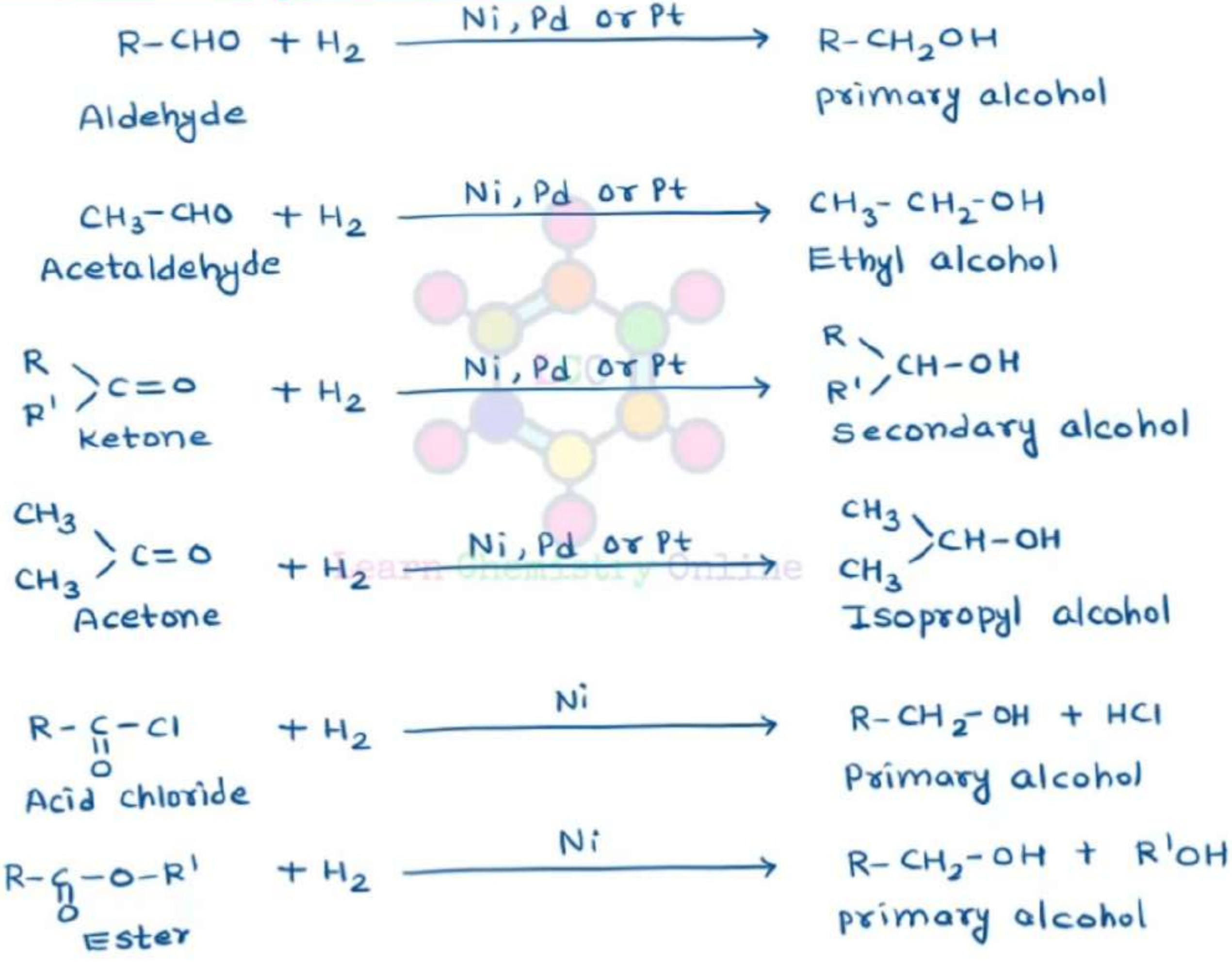
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-OH$$

3-Methyl-1-butonol or 3-Methylbutanol

→ Monohydric alcohols:-

→ Methods of formation by reduction of aldehyde, ketone, carboxylic acids and esters.

1. Catalytic hydrogenation of carbonyl compounds:-



$$\underset{\text{Aldehyde}}{R-CHO} + H_2 \xrightarrow{Ni,\ Pd\ or\ Pt} \underset{\text{primary alcohol}}{R-CH_2OH}$$

$$\underset{\text{Acetaldehyde}}{CH_3-CHO} + H_2 \xrightarrow{Ni,\ Pd\ or\ Pt} \underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}$$

$$\underset{\text{ketone}}{\begin{matrix} R \\ R' \end{matrix}\!\!>C=O} + H_2 \xrightarrow{Ni,\ Pd\ or\ Pt} \underset{\text{secondary alcohol}}{\begin{matrix} R \\ R' \end{matrix}\!\!>CH-OH}$$

$$\underset{\text{Acetone}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O} + H_2 \xrightarrow{Ni,\ Pd\ or\ Pt} \underset{\text{Isopropyl alcohol}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-OH}$$

$$\underset{\text{Acid chloride}}{R-\underset{\underset{O}{\|}}{C}-Cl} + H_2 \xrightarrow{Ni} \underset{\text{Primary alcohol}}{R-CH_2-OH} + HCl$$

$$\underset{\text{Ester}}{R-\underset{\underset{O}{\|}}{C}-O-R'} + H_2 \xrightarrow{Ni} \underset{\text{primary alcohol}}{R-CH_2-OH} + R'OH$$

- Since hydrogenation of carbon carbon double bond is a easier process, saturation of c=c double bond always takes place with hydrogenation of carbonyl group in unsaturated aldehydes and Ketones.

$$CH_3CH=CHCHO \xrightarrow{H_2/Ni} CH_3-CH_2-CH_2-CH_2-OH$$

Crotonialdehyde n-Butyl alcohol

2. Reduction of carbonyl compounds with complex metal hydrides:-

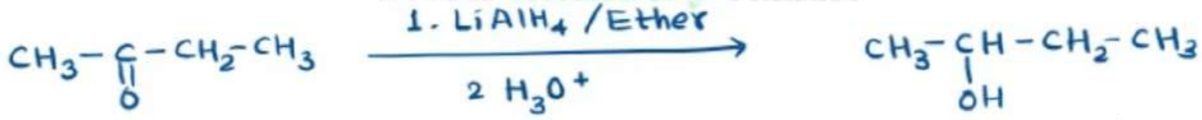
(a) Reduction of carbonyl compounds with $LiAlH_4$:-

- Lithium aluminium hydride is a versatile reducing agent. It is highly sensitive to moisture, therefore, used in nonhydroxylic solvents.

(i) Reduction of aldehyde and Ketone:-

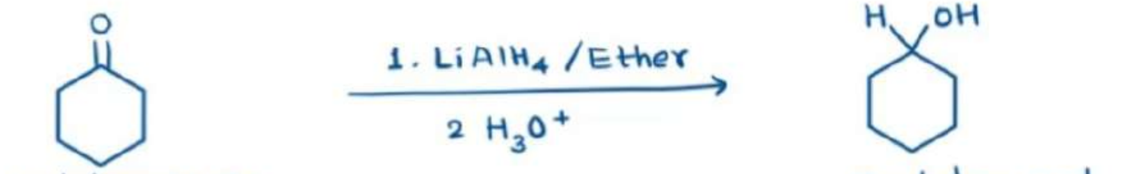
$$CH_3(CH_2)_4CHO \xrightarrow[2\ H_3O^+]{1.\ LiAlH_4/Ether} CH_3(CH_2)_4CH_2OH$$

1-Hexanal 1-Hexanol



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow[2\ H_3O^+]{1.\ LiAlH_4/Ether} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$$

But-2-one Butan-2-ol



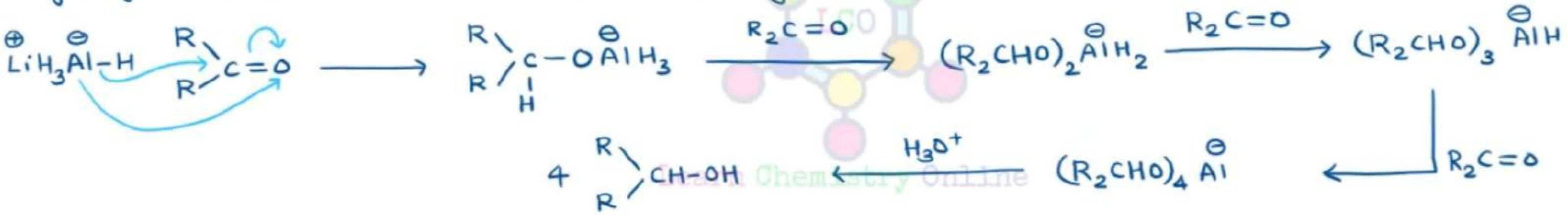
cyclohexanone Cyclohexanol

- Reduction of aldehyde is faster than that of Ketones. It is due to less steric interaction in aldehyde.
- Lithium aluminium hydride is a very useful reagent for conversion of unsaturated carbonyl compounds into unsaturated alcohols. because it does not reduce carbon-carbon double bond.

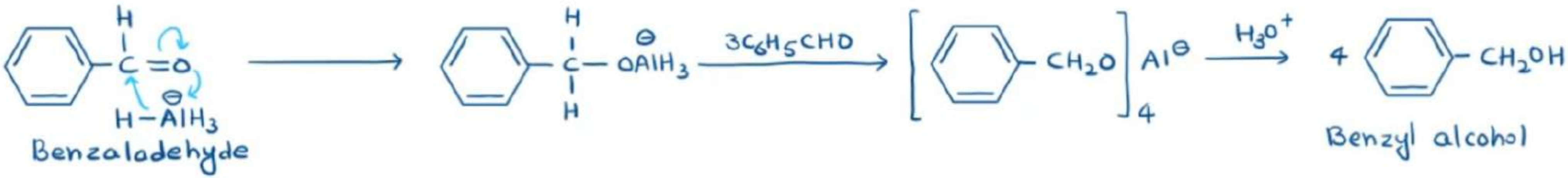
$$\underset{\text{Crotonialdehyde}}{CH_3-CH=CH-CHO} \xrightarrow{LiAlH4} \underset{\text{Crotyl alcohol}}{CH_3-CH=CH-CH_2-OH}$$

→ Mechanism:-

- The Aluminium hydride complex ion, $[AlH_4]^-$, is acts as hydride ion donor and all the four hydrogen atoms of anion are succesively transfer to the carbonyl carbon.



- The mechanism of reduction of Benzaldehyde



- First is fastest and the rate decreases in the succesive steps because −I effect of alkoxy groups opposes the transfer of hydride ion.

(ii) Reduction of carboxylic acids and their derivatives:-

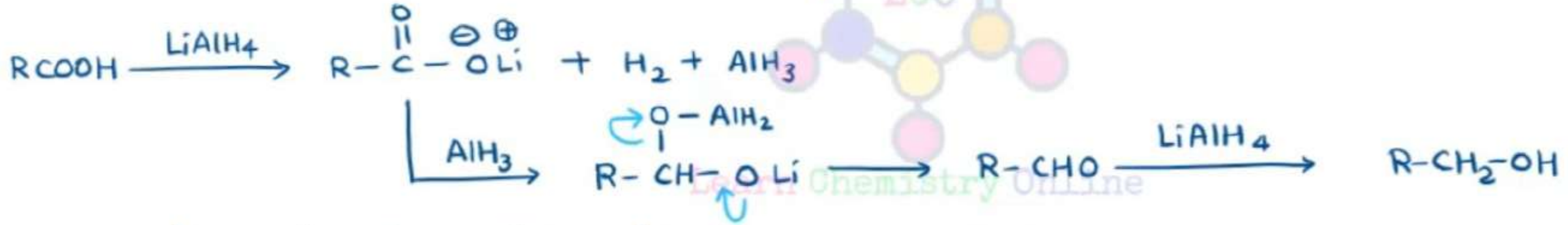
- The reactivity order of carboxylic acids and their derivatives towards $LiAlH_4$ is as follows -

$$R-\underset{\overset{\|}{O}}{C}-Cl > R-\underset{\overset{\|}{O}}{C}-O-R > R-\underset{\overset{\|}{O}}{C}-NH_2 > R-CN > (RCO)_2O$$

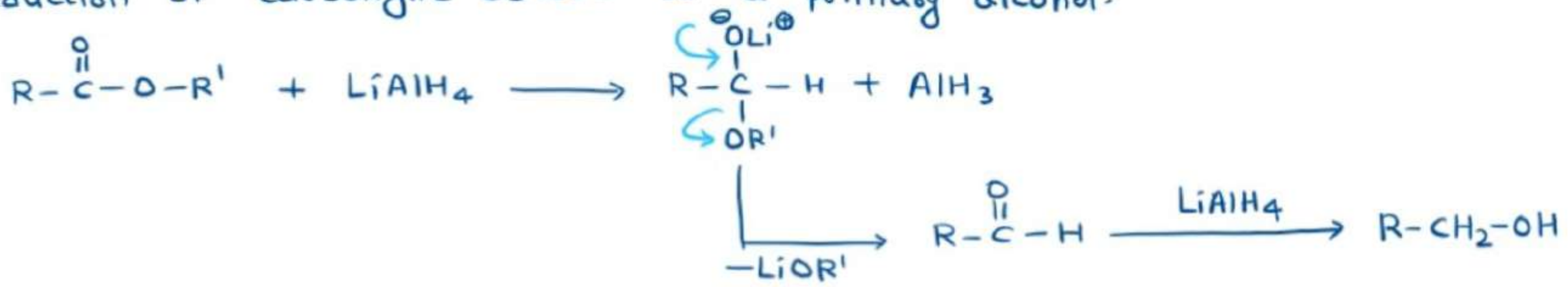
$$4\,RCOOH + 8\,LiAlH_4 \xrightarrow[-4H_2]{} (RCH_2O)_4AlLi \xrightarrow[H_3O^+]{} 4\,RCH_2OH$$

Mechanism:-

(i) Reduction of carboxylic acid to primary alcohol.

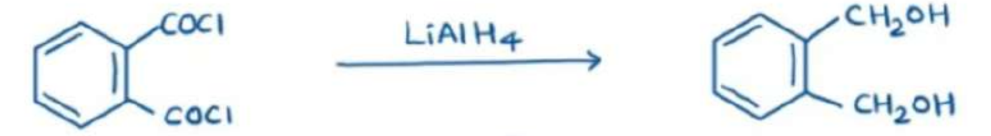


(ii) Reduction of carboxylic esters to a primary alcohol.

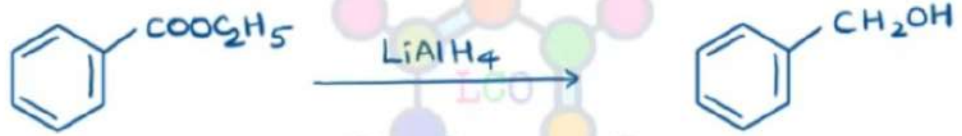


- Some other reactions are -

$$\underset{\text{propanoic acid}}{CH_3-CH_2-COOH} \xrightarrow{LiAlH_4} \underset{\text{1- propanol}}{CH_3-CH_2-CH_2-OH}$$



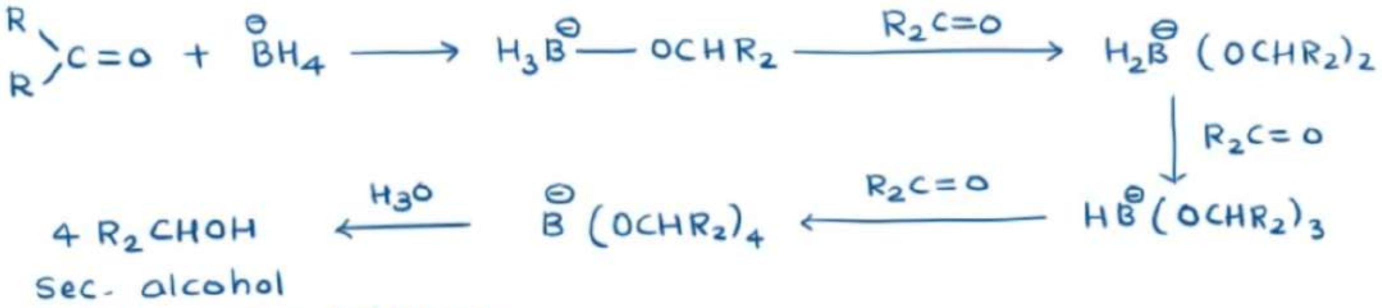
Phthaloyl chloride 1,2- Benzenedimethanol



Ethyl benzoate Benzyl alcohol

(b) Reduction of aldehydes and Ketones with $NaBH_4$:-

- Sodium borohydride is more selective than $LiAlH_4$ as reducing agent and reduces aldehyde and Ketone to corresponding alcohols.
- other functional groups such as halogen, cyano, amido and alkoxycarbonyl group remain unaffected.
- It does not reduce C=C bonds, not even those which are conjugated with carbonyl group.
- The mechanism of reduction by $NaBH_4$ is similar to $LiAlH_4$.



$$R_2C=O + \overset{\ominus}{B}H_4 \longrightarrow H_3\overset{\ominus}{B}-OCHR_2 \xrightarrow{R_2C=O} H_2\overset{\ominus}{B}(OCHR_2)_2 \xrightarrow{R_2C=O} H\overset{\ominus}{B}(OCHR_2)_3 \xrightarrow{R_2C=O} \overset{\ominus}{B}(OCHR_2)_4 \xrightarrow{H_3O} 4\,R_2CHOH$$

Sec. alcohol

- Advantages of $NaBH_4$ over $LiAlH_4$:-

Although $NaBH_4$ is less powerful reducing agent than $LiAlH_4$, it has following advantages –

- It can be used in protic solvents.
- It is an important reagent for the reduction of unsaturated carbonyl compounds to unsaturated alcohols.

3. Reduction of carbonyl compounds with sodium metal and ethanol:-

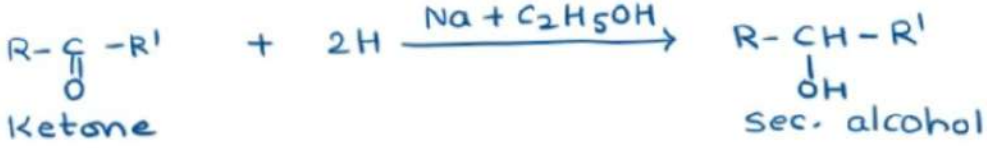
(a) Classical method:-

$$R-CHO + 2H \xrightarrow{Na + C_2H_5OH} R-CH_2-OH$$

Aldehyde → primary alcohol

$$CH_3-CH_2-CH_2-CHO + 2H \xrightarrow{Na + C_2H_5OH} CH_3-CH_2-CH_2-CH_2-OH$$

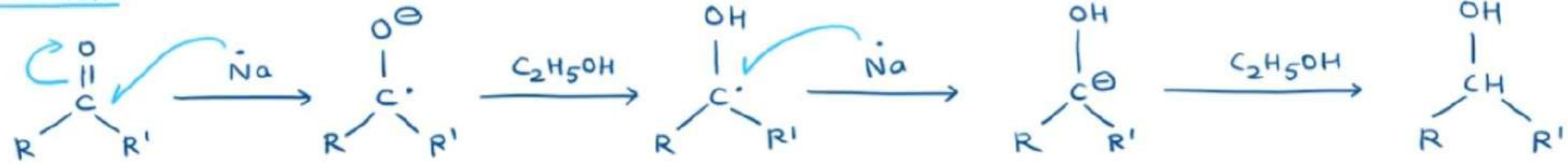
Butanal → Butan-1-ol



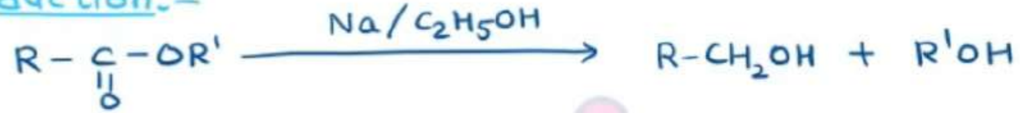
$$R-\underset{\underset{O}{\|}}{C}-R' + 2H \xrightarrow{Na + C_2H_5OH} R-\underset{\underset{OH}{|}}{CH}-R'$$

Ketone → Sec. alcohol

Mechanism:-



(b) Bouveault-Blanc reduction:-

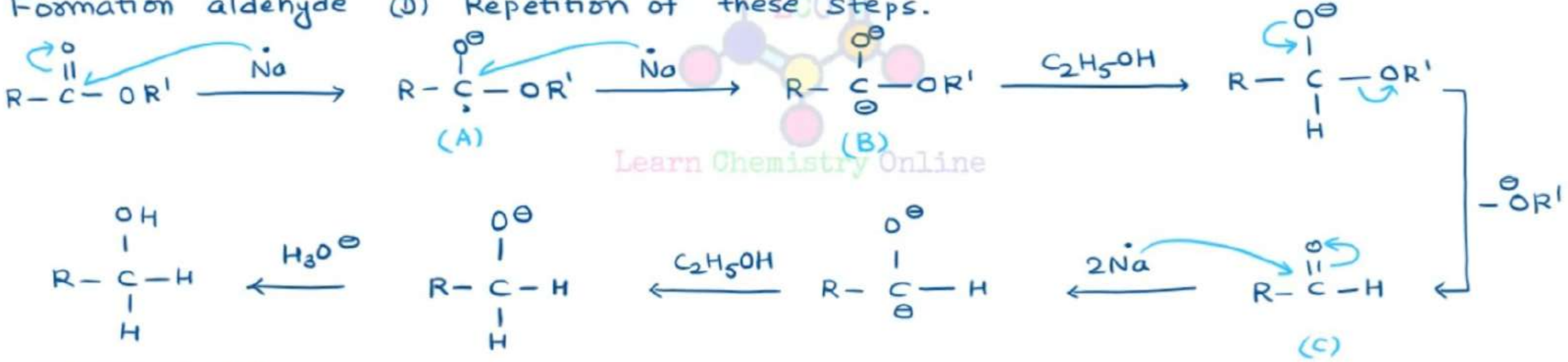


$$R-\underset{\overset{\|}{O}}{C}-OR' \xrightarrow{Na/C_2H_5OH} R-CH_2OH + R'OH$$

Mechanism:-

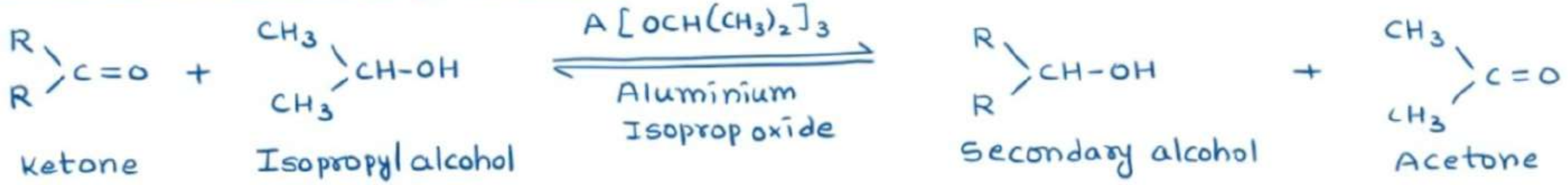
(A) Formation of radical anion (B) Formation of divalent anion

(C) Formation aldehyde (D) Repetition of these steps.

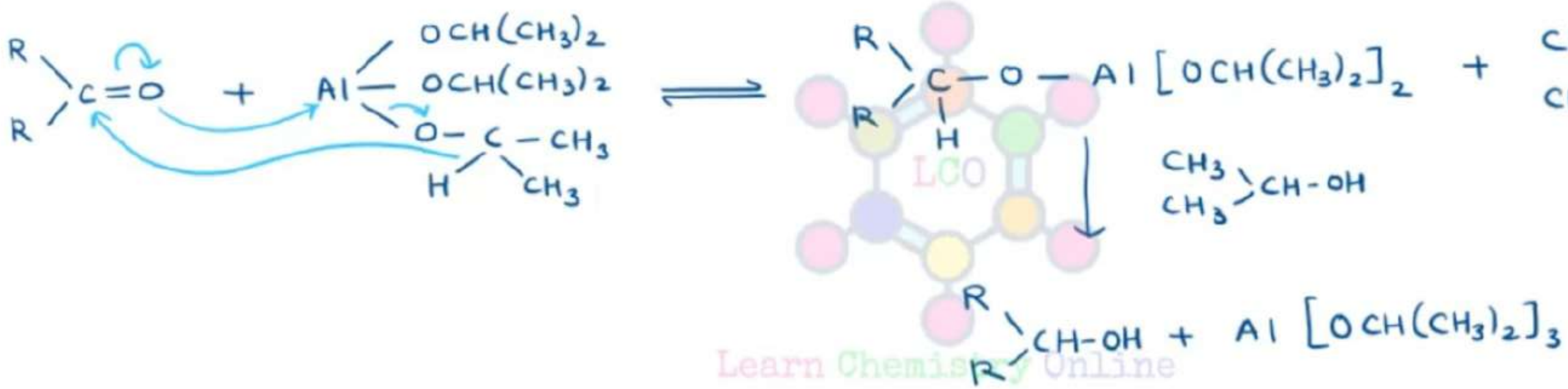


primary alcohol

4. Meerwein - Ponndroff - verley reduction:-



Mechanism:-



- Acetone is removed from reaction mixture by distillation.

→ Monohydric alcohols:→

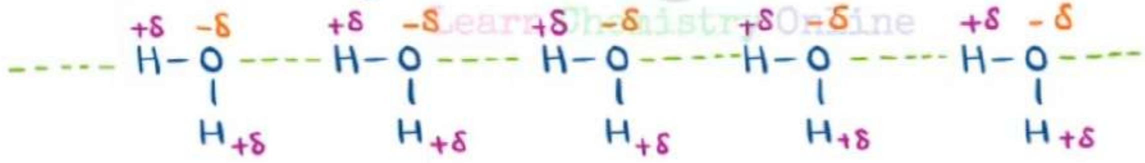
→ Physical properties:→

1 Physical state:→

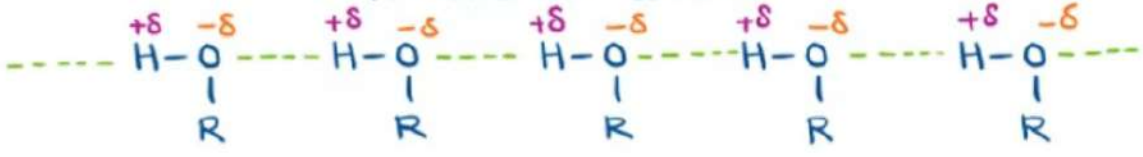
- The lower alcohols are colourless liquids with characteristic smell and burning taste while the alcohols having more than twelve carbon atoms are solids.

2. Hydrogen bonding:-

- When hydrogen, with a partial positive charge, is attracted towards the electron cloud of the electronegative atom of the same or different molecule, a weak bond is formed. This type of bond is called hydrogen bond.
- Hydrogen bond is the most powerful kind of dipole-dipole attraction.
- Hydrogen bond is weaker than normal covalent bond and the hydrogen bond energy is only 12.5 – 42 KJ mol^{-1}.
- Hydrogen bond is represented by dotted line.



H-bond in water

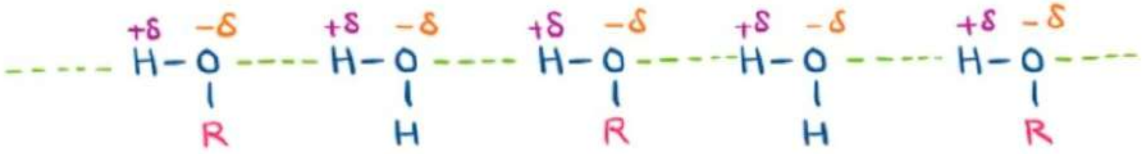


H-bond in alcohol

- There are two types of hydrogen bonds:-

(i) Intermolecular hydrogen bond:-

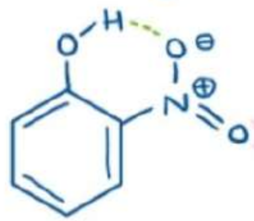
- This bond formed between atoms of two or more molecules, resulting in their association.



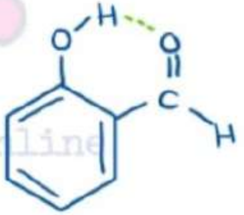
Intermolecular H-bond between water and alcohol.

(ii) Intramolecular hydrogen bond:-

- This bond formed between two atoms of same molecule. As a result five membered or six membered chelate ring is formed.



o-nitrophenol



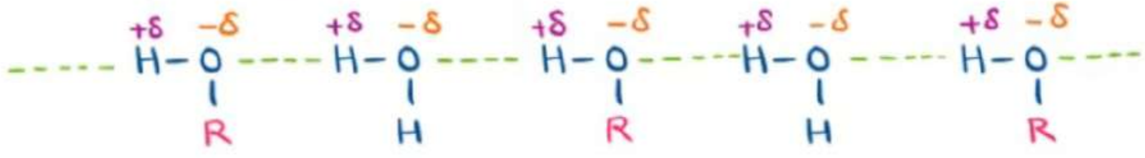
Salicylaldehyde

→ Conditions for Intramolecular hydrogen bonding:-

1. The molecule must have two groups in such a way that one group contains H-atom linked to a highly electronegative atom and the other group also contains an electronegative atom.
2. The molecule must be planar.
3. The H-bond must lead to formation of five or six membered ring.

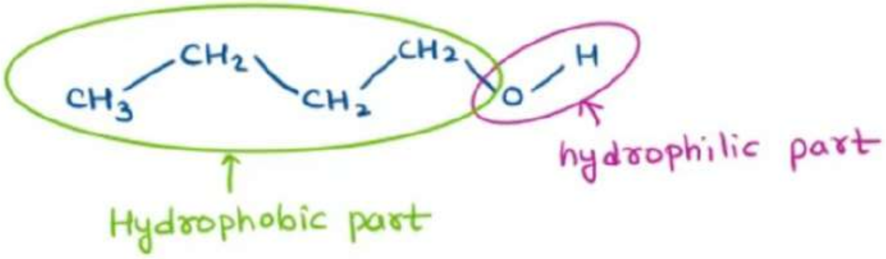
3. Solubility :-

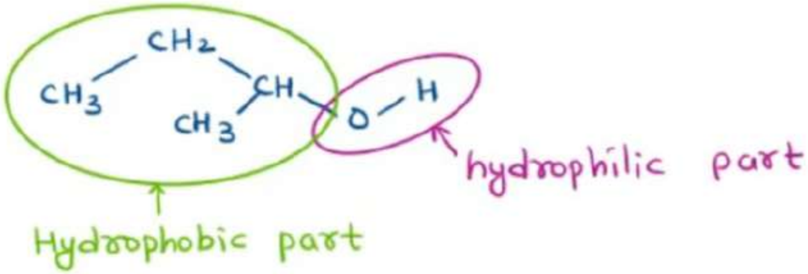
- The lower alcohols are easily miscible with water due to formation of intermolecular hydrogen bond between molecules of alcohol and water.



Intermolecular H-bond between water and alcohol.

- With the increase in the number of carbon atoms, the water solubility decreases. This is due to fact that alcohols have both hydrophilic (due to -OH) and hydrophobic (due to carbon chain) moieties. Thus with increase in the molecular weight hydrophobic character of alcohols increases. This reduces water solubility.
- Among Isomeric alcohols, the solubility increases with the increase in branching. This is due to decrease in relative volume of hydrophobic portion.





4. Boiling and melting point of alcohols:-

- The b.p and m.p. of alcohols are higher than hydrocarbons of comparable molecular weights. It is due to presence of intermolecular H-bond in alcohols which cause association of molecules.
- The b.p. and m.p. of alcohols increases with increase in number of carbon atoms. This is due to increase in Van der Waals attractions.
- In case of isomeric alcohols, the boiling point decreases with increase in branching. because Van der Waals attraction decreases with increasing branching.

→ Monohydric alcohols:→

→ Acidic nature:→

- As the $-OH$ group of alcohols contains lone pair of electrons on oxygen atom, they are expected to behave as base. But alcohols behave as weak acids.
- The slight acidic character of alcohols can be explained on the basis of the fact that the hydrogen atom is attached to highly electronegative oxygen atom, which attracts the electron pair of the $O-H$ bond towards itself. Due to this attraction there is a tendency for the loss of hydrogen as a proton.
- In other words, the acidic character of alcohol is due to the ability of oxygen atom to accomodate negative charge after the loss of a proton.
- Due to acidic character, alcohols react with strong electropositive metals to evolve H_2.

$$R-O-H + M \longrightarrow R-\overset{\ominus}{O}\overset{\oplus}{M} + \frac{1}{2}H_2 \quad (M = Na, K \text{ etc.})$$

- Alcohols also show acidic characters when reacts with grignard reagent. Alcohols replace weakly acidic hydrcarbon part of grignard reagent

$$R-O-H + \overset{\ominus}{R'}\overset{\oplus}{Mg}X \longrightarrow R'-H + R\overset{\ominus}{O}\overset{\oplus}{Mg}X$$

- Alcohols are stronger acids than terminal alkynes but weaker than water.

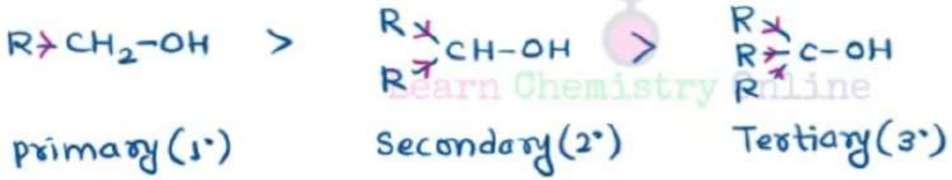
  This is due to fact that alkoxides are converted into alcohols when treated with water.

$$R\overset{\ominus}{O}\overset{\oplus}{Na} + \underset{\text{Strong acid}}{H_2O} \longrightarrow \underset{\text{Weak acid}}{R-OH} + \overset{\oplus}{Na}\overset{\ominus}{O}H$$

- This reaction shows that water is a better proton donor (i.e. stronger acid) than alcohol. Also this reaction shows that alkoxide ion is better proton acceptor than hydroxide ion. i.e. Sodium ethoxide is a stronger base than sodium hydroxide.
- Acetylides are decomposed by alcohols to liberate acetylene.

$$R-C\equiv\overset{\ominus}{C}\overset{\oplus}{M} + \underset{\text{acid}}{\underset{\text{Strong}}{R-OH}} \longrightarrow \underset{\text{acid}}{\underset{\text{weak}}{R-C\equiv CH}} + R\overset{\ominus}{O}\overset{\oplus}{M}$$

- The main structural feature that makes them weaker acid than water is the presence of electron releasing (+I) alkyl group which tends to increase the negative charge on oxygen. This makes the alkoxide ion less stable than hydroxide ion.
- The acid strength of various types of alcohol is



$$R\rightarrow CH_2-OH > R_2CH-OH > R_3C-OH$$

primary (1°) Secondary (2°) Tertiary (3°)

→ Monohydric alcohols :-

→ Chemical Reactions :→

1. Reaction with electropositive metals (Acidic character) :→

- Alcohols react with electropositive metal to evolve hydrogen gas and show acidic nature.

$$R-O-H + M \longrightarrow R-\overset{\ominus}{O}\overset{\oplus}{M} + \frac{1}{2}H_2 \quad (M = Na, K\ etc.)$$

2. Reaction with carboxylic acids : Esterification :-

- Alcohols react with carboxylic acid in the presence of H_2SO_4 to give ester. (reversible)

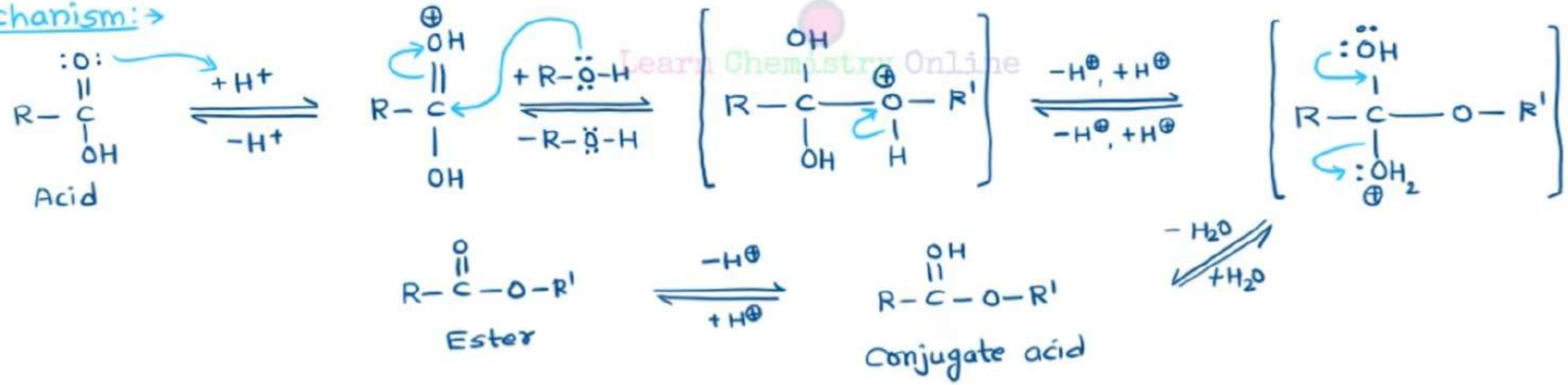
$$C_2H_5OH + CH_3COOH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

Ethyl acetate

$$C_2H_5OH + ClCH_2COOH \overset{H^+}{\rightleftharpoons} ClCH_2COOC_2H_5 + H_2O$$

Chloroacetic acid — Ethyl chloroacetate

→ Mechanism :→

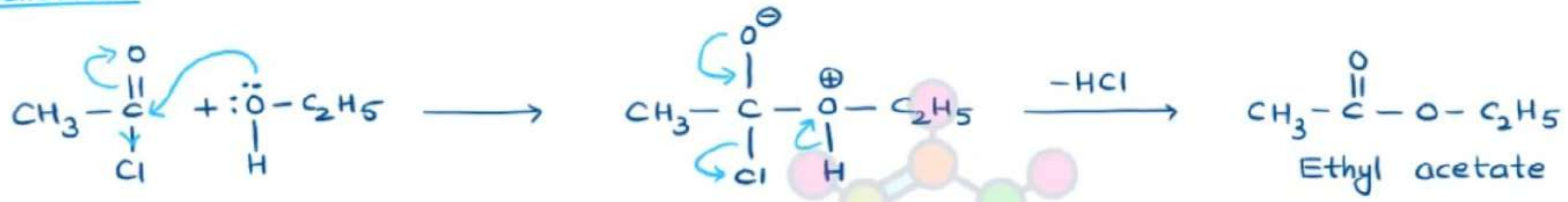


3. Reaction with acid chloride or acetic anhydride : Acetylation or acylation:-

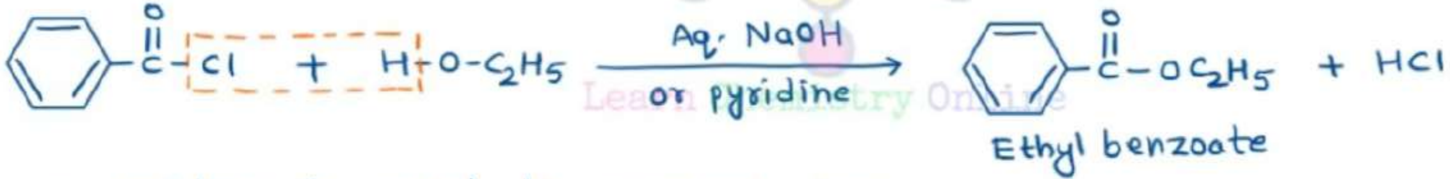
(a) Reaction with acetyl chloride:-

$$\underset{\text{Acetyl chloride}}{CH_3-CO-\boxed{Cl + H}-O-C_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3-COOC_2H_5} + HCl$$

Mechanism:-

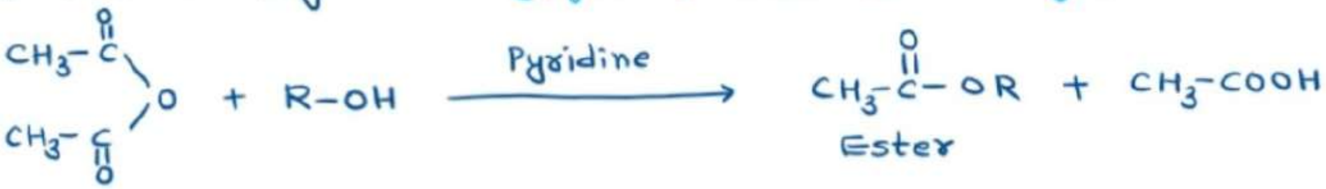


- The reaction of alcohols with benzoyl chloride in presence of aq. NaOH or pyridine is a benzoylation reaction and called Schotten- Baumann reaction.



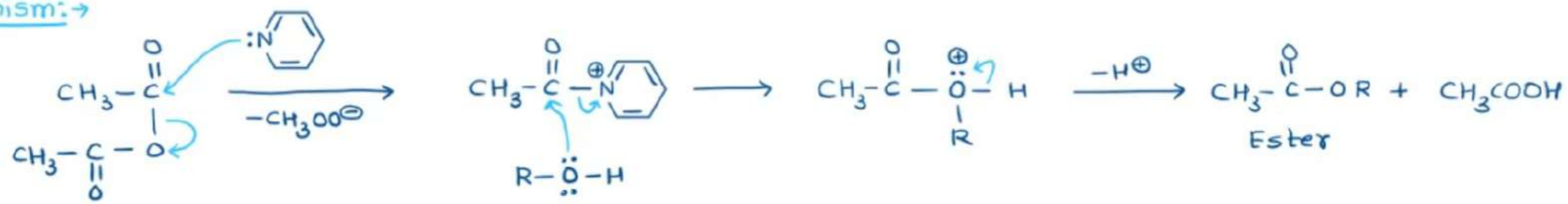
✲ Aq. NaOH or pyridine is used to remove HCl.

(b) Reaction with acetic anhydride:- (pyridine used as catalyst)



$$(CH_3CO)_2O + R-OH \xrightarrow{\text{Pyridine}} \underset{\text{Ester}}{CH_3-\overset{O}{\overset{\|}{C}}-OR} + CH_3-COOH$$

Mechanism:→



4. Reaction with hydrogen halide:-

- Gaseous HCl or HBr, reacts with alcohol to form alkyl chlorides or alkyl bromides.

$$C_2H_5-OH + HBr \overset{\Delta}{\rightleftharpoons} C_2H_5Br + H_2O$$

- Since reaction is reversible, a dehydrating agent such as anhydrous zinc chloride or anhydrous aluminium chloride has to be added to supress the reverse process.
- The reactivity order of alcohols is 3° > 2° > 1°
- This reaction is completed through S_N1 and S_N2 mechanism.

5. Reaction with concentrated H_2SO_4 : Dehydration:-

- Alcohols on heating with conc. H_2SO_4 undergo dehydration to form alkene. (β-elimination)

$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \xrightarrow{\Delta} >C=C< + H_2O$$

- Reactivity order 3° > 2° > 1° (on the basis of stability of carbocation)

Mechanism:- dehydration of alcohols into alkenes involved following steps:-

Step-I Formation of oxonium salt

$$CH_3-CH_2-\ddot{O}-H + \overset{\oplus}{H} \longrightarrow CH_3-CH_2-\overset{\oplus}{\ddot{O}}(H)-H \text{ (oxonium salt)}$$

Step-II Formation of carbocation by loss of water

$$CH_3-CH_2-\overset{\oplus}{\ddot{O}}(H)-H \longrightarrow CH_3-\overset{\oplus}{C}H_2 + H_2O$$

Step III Elimination of proton from carbocation to form alkene.

$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}^{\oplus} \longrightarrow \underset{\text{Ethene}}{CH_2=CH_2} + H^{\oplus}$$

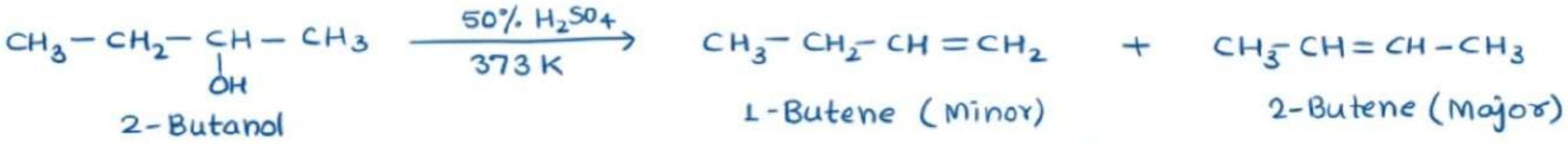
- Some examples of dehydration reactions are-

(a) When n-butyl alcohol is heated with conc. H_2SO_4 at 443 K, 2-butene is formed.

$$\underset{\text{n-Butyl alcohol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[443\,K]{75\%\ H_2SO_4} \underset{\text{2-Butene}}{CH_3-CH=CH-CH_3} + H_2O$$

- In this reaction, 1° carbocation is converted into 2° carbocation to increase stability. so 2-Butene is formed as major product and 1-Butene is formed as minor product

(b) Dehydration of secondary and tertiary alcohols containing four or more carbon atoms yields a mixture of two alkenes. e.g.



$$CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[373\,K]{50\%\ H_2SO_4} CH_3-CH_2-CH=CH_2 + CH_3-CH=CH-CH_3$$

2-Butanol   1-Butene (Minor)   2-Butene (Major)

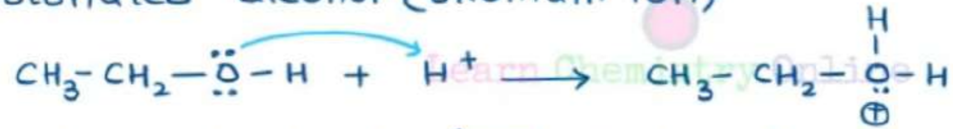
- The alkene produced as the major product as per Saytzeff rule which states that the alkene which has greater number of substituents across the double is preferbly formed. Thus, in the above example, 2-butene, containing two alkyl groups is the major product.

(c) Dehydration of alcohols to ethers:-

$$CH_3-CH_2-OH + HO-CH_2-CH_3 \xrightarrow[413\,K]{Conc.\ H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O$$

Mechanism:-

1. Formation of protonated alcohol (oxonium ion)



$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow CH_3-CH_2-\underset{\oplus}{\overset{H}{\overset{|}{\ddot{O}}}}-H$$

2. Elimination of water molecule to form carbocation

$$CH_3-CH_2-\underset{\oplus}{\overset{H}{\overset{|}{\ddot{O}}}}-H \longrightarrow CH_3-\overset{\oplus}{C}H_2 + H_2O$$

3. Attact of carbocation on another alcohol molecule to form oxonium ion.

$$\overset{\oplus}{CH_3CH_2} + :\underset{H}{\underset{|}{\ddot{O}}}-CH_2-CH_3 \longrightarrow CH_3CH_2-\underset{\oplus}{\overset{H}{\overset{|}{\ddot{O}}}}-CH_2CH_3$$

4. Oxonium ion loses a proton to form an ether:-

$$CH_3-CH_2-\overset{H}{\underset{\oplus}{\ddot{O}}}-CH_2-CH_3 \xrightarrow{-H^{\oplus}} \underset{\text{Ether}}{CH_3-CH_2-O-CH_2-CH_3} + H^{\oplus}$$

(d) Dehydration of alcohols using alumina

$$CH_3-CH_2-OH \xrightarrow[623K]{Al_2O_3} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

$$2\ CH_3-CH_2-OH \xrightarrow[573\ k]{Al_2O_3} \underset{\text{Diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3} + H_2O$$

→ Monohydric alcohols:→

- Chemical reactions:→

6. Oxidation:-

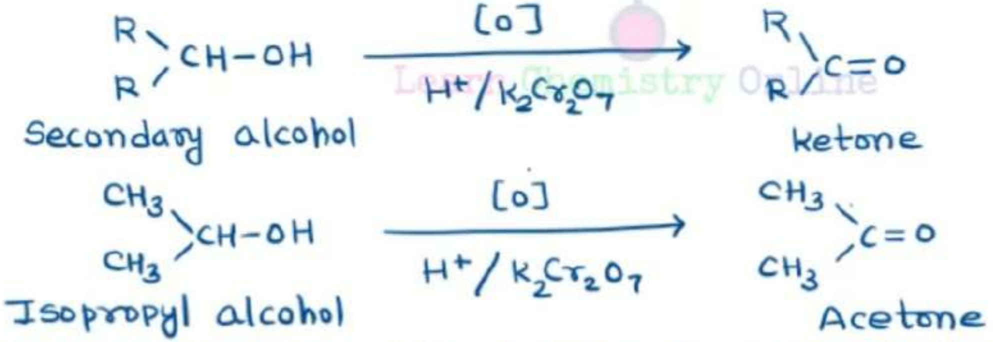
- Different alcohols give different products on oxidation. Thus oxidation of alcohols can be used to distinguish between primary, secondary and tertiary alcohols.

(a) Primary alcohols:-

$$\underset{\text{Primary alcohol}}{R-CH_2-OH} \xrightarrow[H^+/K_2Cr_2O_7]{[O]} \underset{\text{Aldehyde}}{R-CHO} \xrightarrow[H^+/K_2Cr_2O_7]{[O]} \underset{\text{Carboxylic acid}}{R-COOH}$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow[H^+/K_2Cr_2O_7]{[O]} \underset{\text{Acetaldehyde}}{CH_3-CHO} \xrightarrow[H^+/K_2Cr_2O_7]{[O]} \underset{\text{Acetic acid}}{CH_3-COOH}$$

(b) Secondary alcohols:-



$$\underset{\text{Secondary alcohol}}{R_2CH-OH} \xrightarrow[H^+/K_2Cr_2O_7]{[O]} \underset{\text{Ketone}}{R_2C=O}$$

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CH-OH} \xrightarrow[H^+/K_2Cr_2O_7]{[O]} \underset{\text{Acetone}}{(CH_3)_2C=O}$$

- However, under drastic conditions, the ketone is converted into carboxylic containing fewer number of carbon atoms than the origional alcohol.

(c) Tertiary alcohols do not undergo oxidation but under drastic conditions, they undergo dehydration to give alkenes.

$$(CH_3)_3C-OH \xrightarrow[H^+/K_2Cr_2O_7]{\text{Oxidation}} \text{Not oxidised , forms alkene}$$

7. Dehydrogenation:-

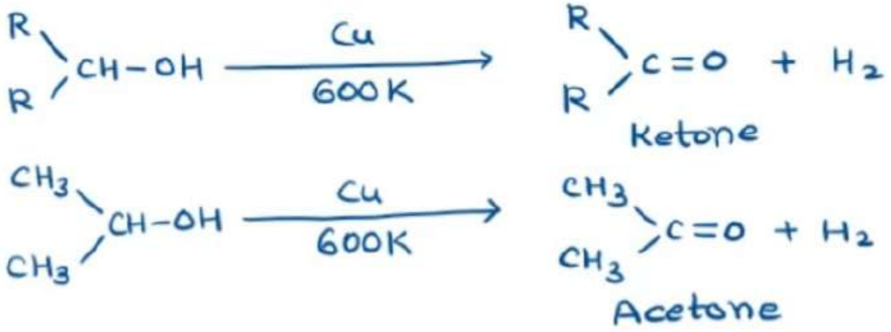
- Dehydrogenation of different alcohols give different products.

(a) Primary alcohol:-

$$\underset{\substack{\text{Alcohol}\\\text{(vapour form)}}}{R-CH_2OH} \xrightarrow[600\,K]{Cu} R-CHO + H_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow[600K]{Cu} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

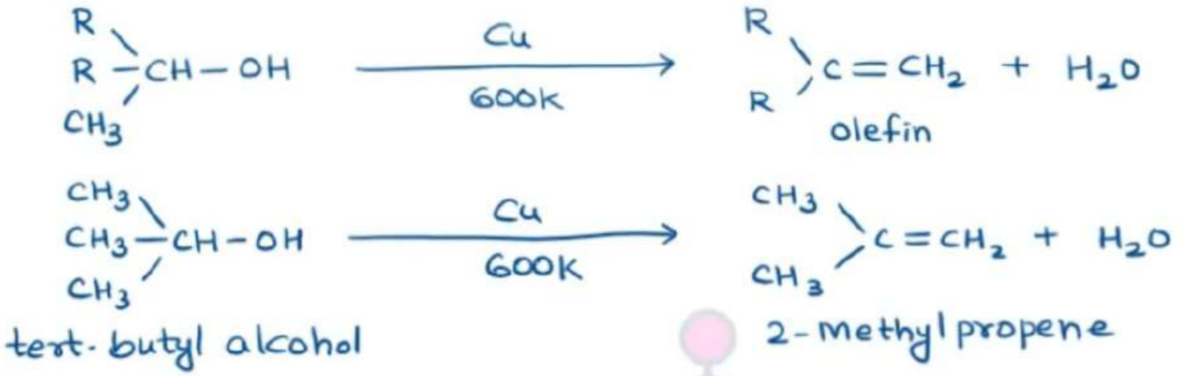
(b) Secondary alcohol:-



$$\begin{matrix}R\\R\end{matrix}\!\!>CH-OH \xrightarrow[600K]{Cu} \underset{\text{Ketone}}{\begin{matrix}R\\R\end{matrix}\!\!>C=O} + H_2$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-OH \xrightarrow[600K]{Cu} \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O} + H_2$$

(c) Tertiary alcohols :-



$$R_2(CH_3)CH-OH \xrightarrow[600K]{Cu} R_2C=CH_2 + H_2O$$

$$(CH_3)_3CH-OH \xrightarrow[600K]{Cu} (CH_3)_2C=CH_2 + H_2O$$

8. Reaction with phosphorus halide:-

$$R-OH + PCl_3 \longrightarrow R-Cl + \underset{\text{Phosphorus acid}}{H_3PO_3} + HCl$$

$$R-OH + PCl_5 \longrightarrow R-Cl + \underset{\text{Phosphoryl chloride}}{POCl_3} + HCl$$

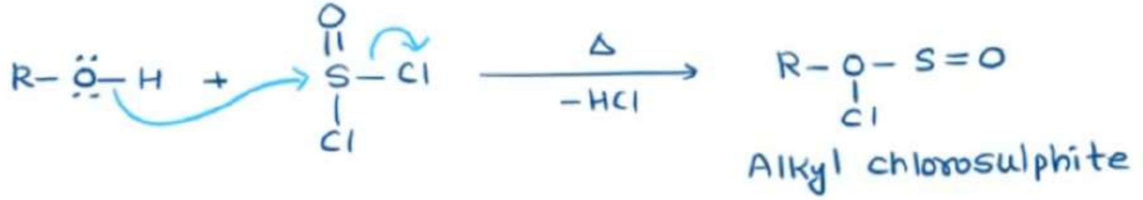
9. Reaction with thionyl chloride:-

$$R-OH + SOCl_2 \longrightarrow R-Cl + HCl\uparrow + SO_2\uparrow$$

- This procedure is best for synthesis of alkyl halides because side products are gases (SO_2 and HCl)

Mechanism:-

Step-1- Formation of chlorosulphite



Step. 2- Formation of alkyl halide

→ Distinction between primary, secondary and Tertiary alcohols :-

1. Victor Meyer's test :-

Primary alcohol

$R-CH_2-OH$

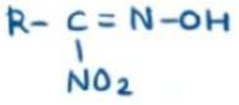
$\downarrow P+I_2$

$R-CH_2-I$

$\downarrow AgNO_3$

$R-CH_2-NO_2$

$\downarrow HNO_2$



$R-\underset{\displaystyle NO_2}{\underset{|}{C}}=N-OH$

Nitrolic acid

$\downarrow NaOH$

Blood red colour
(due to formation of
Sod. Nitrolate)

secondary alcohol

R_2CH-OH

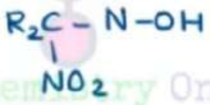
$\downarrow P+I_2$

R_2-CH-I

$\downarrow AgNO_3$

$R_2-CH-NO_2$

$\downarrow HNO_2$



$R_2\underset{\displaystyle NO_2}{\underset{|}{C}}-N-OH$

Pseudonitrole

$\downarrow NaOH$

Blue colour
(No salt formation)

Tertiary alcohol

R_3C-OH

$\downarrow P+I_2$

R_3C-I

$\downarrow AgNO_3$

R_3C-NO_2

$\downarrow HNO_2$

No reaction

$\downarrow NaOH$

Colourless
(No hydrogen attached
with 3° carbon)

2. Lucas test:-

- Lucas reagent :- An equimolar solution of conc. HCl and anhyd. $ZnCl_2$.

Primary alcohol	Secondary alcohol	Tertiary alcohol
$R-CH_2-OH$	R_2CH-OH	R_3C-OH
$\text{HCl}\Big\downarrow\text{Anhyd. }ZnCl_2$	$\text{HCl}\Big\downarrow\text{Anhyd. }ZnCl_2$	$\text{HCl}\Big\downarrow\text{Anhyd. }ZnCl_2$
No reaction	$R_2CHCl + H_2O$	$R_3CCl + H_2O$
No turbidity	Turbidity appears after five minutes	Turbiditiy appears immediately

3. Oxidation:-

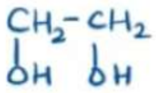
- Primary alcohol first gives aldehyde and then acids containing same no. of carbon atoms as the original alcohol.
- Secondary alcohol gives ketone containing the same no. of carbon atoms and then acids containing lesser no. of carbon atoms.
- Tertiary alcohol gives ketone containing lesser no. of carbon atom as the original alcohol and then acids containing lesser no. of carbon atom as the ketone.

4. Action of hot copper:-

- Primary alcohols give aldehyde.
- Secondary alcohols give ketone
- Tertiary alcohols give alkene.

→ Dihydric alcohols :-

- Dihydric alcohols contain two hydroxyl groups.



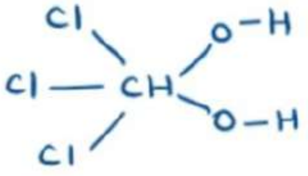
$\underset{OH}{CH_2}-\underset{OH}{CH_2}$ Ethylene glycol (Ethane-1,2-diol)

- If two hydroxyl groups are attached to the same carbon atom, loss of water molecule leading to a more stable carbonyl compound takes place.

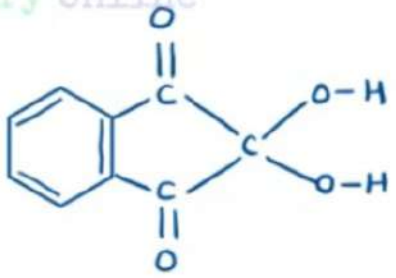
Methylene glycol

Formaldehyde

- It is, therefore, all dihydric alcohols have only one hydroxyl group attached to one carbon atom. However, few diols namely chloral hydrate, ninhydrin etc. are known and stable



chloral hydrate



Ninhydrin

→ Nomenclature: →

(i) Common name system: →

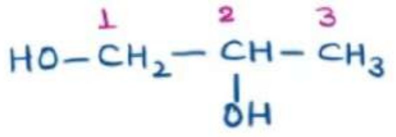
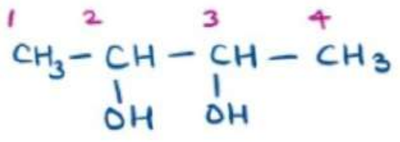
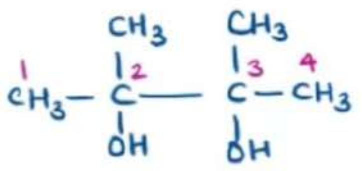
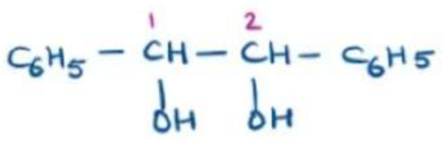
- Compounds having two hydroxyl groups attached to different carbon atoms are commonly called glycols (Greek word → Glykus → sweet).
- Word glycol is used as suffix with the name of alkylene.
- The relative positions of $-OH$ groups are represented by following greek alphabates –

1, 2 - position → α
1, 3 - position → β
1, 4 - position → γ
other position → polymethylene glycols.

(ii) IUPAC name:–

- In this system, longest straight chain of carbon atoms containing the $-OH$ groups is selected and the compound is named as the hydroxy derivative of the corresponding alkane.
- The chain is numbered in such a way that the substituents and $-OH$ groups get lowest numbers
- Suffix → diol
- Positions of $-OH$ groups are indicated by numbers, and these numbers are written b/w the name of hydrocarbon and suffix.

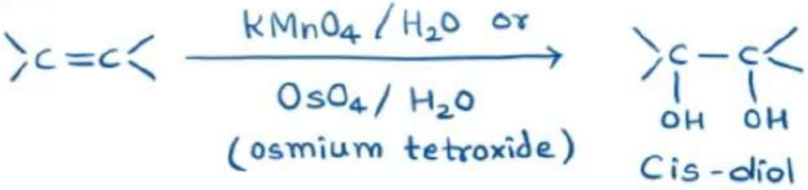
→ Examples:-

compound	IUPAC Name	Common name
$HO-\overset{1}{CH_2}-\overset{2}{CH_2}-OH$	Ethane-1,2-diol	Ethylene glycol OR 1,2- Ethylene glycol OR α- Ethylene glycol
$HO-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-OH$	Propane-1,3-diol	β- propylene glycol OR 1,3- propylene glycol OR Trimethylene glycol
 $HO-\overset{1}{CH_2}-\underset{OH}{\overset{2}{CH}}-\overset{3}{CH_3}$	propane-1,2-diol	α- propylene glycol OR 1,2- propylene glycol OR
 $\overset{1}{CH_3}-\underset{OH}{\overset{2}{CH}}-\underset{OH}{\overset{3}{CH}}-\overset{4}{CH_3}$	Butane-2,3-diol	α- Butylene glycol OR 2,3- Butylene glycol
 $\overset{1}{CH_3}-\underset{OH}{\overset{CH_3}{\overset{|}{C}^{2}}}-\underset{OH}{\overset{CH_3}{\overset{|}{C}^{3}}}-\overset{4}{CH_3}$	2,3-dimethylbutane-2,3-diol	Pinacol
 $C_6H_5-\underset{OH}{\overset{1}{CH}}-\underset{OH}{\overset{2}{CH}}-C_6H_5$	1,2-diphenylethane-1,2-diol	Hydrobenzoin

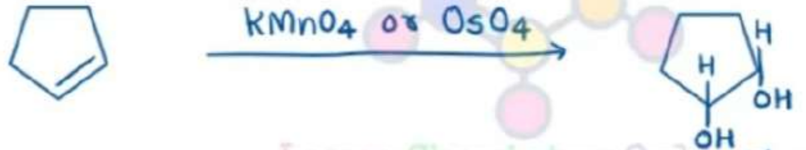
→ Dihydric alcohols :-

→ Methods of formation :→

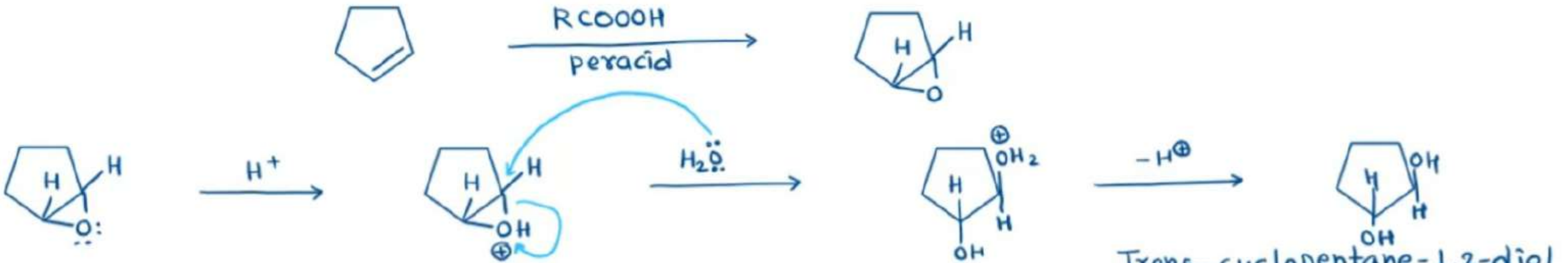
1. From alkenes : Hydroxylation:-



- The addition of these reagents to alkene is stereospecific and form cis-isomers due to formation of cyclic permanganate or osmate ester.
- The tran-diol can be synthesised by acid catalysed ring opening of epoxide which is prepared by treating alkenes with peracids.

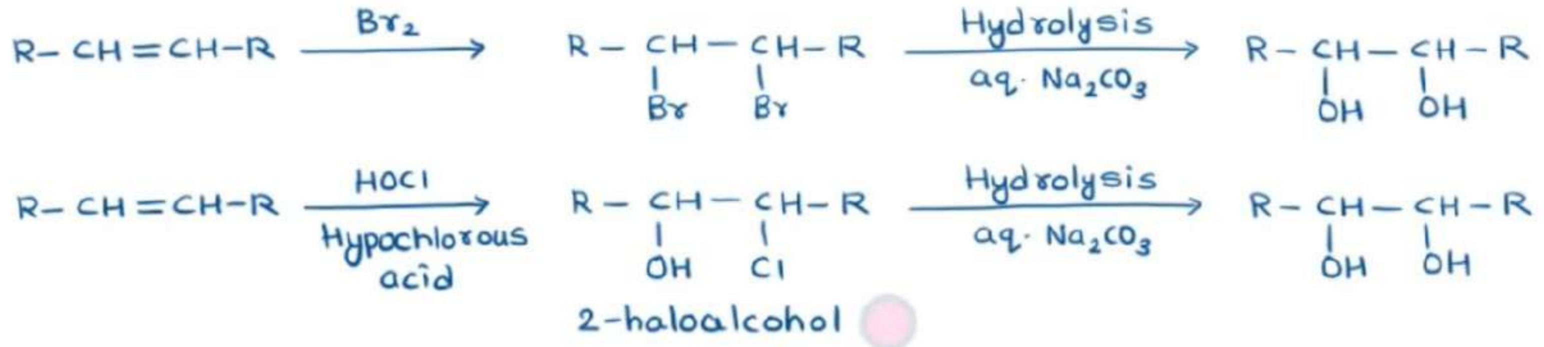


cis-cyclopentane-1,2-diol



Trans-cyclopentane-1,2-diol

2. From 1,2-dihaloalkanes and 2-haloalcohols:-

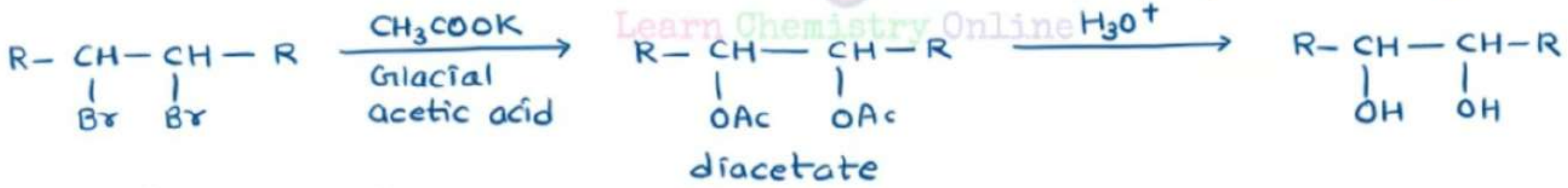


$$R-CH=CH-R \xrightarrow{Br_2} R-\underset{Br}{CH}-\underset{Br}{CH}-R \xrightarrow[aq.\ Na_2CO_3]{Hydrolysis} R-\underset{OH}{CH}-\underset{OH}{CH}-R$$

$$R-CH=CH-R \xrightarrow[\text{Hypochlorous acid}]{HOCl} R-\underset{OH}{CH}-\underset{Cl}{CH}-R \xrightarrow[aq.\ Na_2CO_3]{Hydrolysis} R-\underset{OH}{CH}-\underset{OH}{CH}-R$$

2-haloalcohol

- It may be pointed out that hydrolysis of the 2-haloalcohols should be carried out under milder conditions since in the presence of strong alkali, they undergo ring closure and form epoxides.
- Hydrolysis of dihaloalkanes also give vinyl halides as side products.
- dihydric alcohols can also prepared from dihaloalkanes through following reaction-



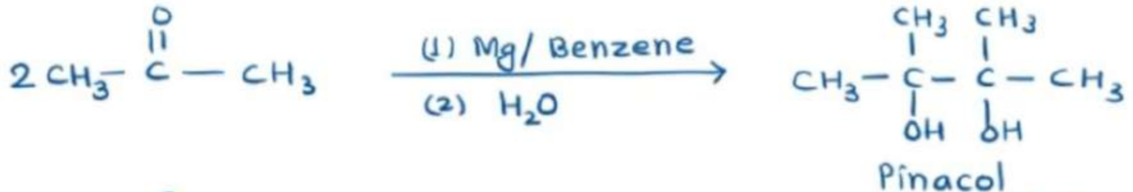
$$R-\underset{Br}{CH}-\underset{Br}{CH}-R \xrightarrow[\text{Glacial acetic acid}]{CH_3COOK} R-\underset{OAc}{CH}-\underset{OAc}{CH}-R \xrightarrow{H_3O^+} R-\underset{OH}{CH}-\underset{OH}{CH}-R$$

diacetate

3. From carbonyl compounds:-

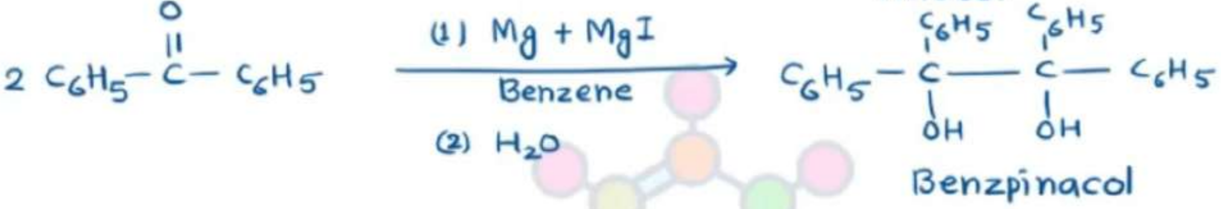
- The reduction of aldehydes and ketones normally results in the formation of primary and secondary alcohols, respectively. However they may also be reduced to 1,2-diols under specific conditions.

- These reductions are called bimolecular reductions which takes place with metal in inert solvents such as benzene, ether etc., or under alkaline conditions.



$$2\,CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[(2)\ H_2O]{(1)\ Mg/\ Benzene} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

Pinacol



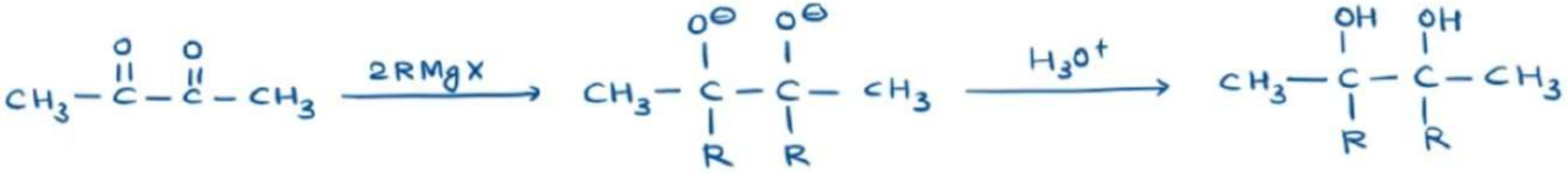
$$2\,C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow[\text{Benzene}]{(1)\ Mg + MgI} \text{(2) } H_2O \quad C_6H_5-\underset{OH}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{C_6H_5}{C}}-C_6H_5$$

Benzpinacol

Mechanism:-

$$2\,CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[(Mg)]{e^-} 2\,CH_3-\underset{CH_3}{\overset{O^\ominus}{C^\bullet}} \xrightarrow[\text{Coupling}]{\text{Radical}} CH_3-\underset{CH_3}{\overset{O^\ominus}{C}}-\underset{CH_3}{\overset{O^\ominus}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

- 1,2-Diols can also be obtained by the action of grignard reagent on 1,2-diketones.



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{2RMgX} CH_3-\underset{R}{\overset{O^\ominus}{C}}-\underset{R}{\overset{O^\ominus}{C}}-CH_3 \xrightarrow{H_3O^+} CH_3-\underset{R}{\overset{OH}{C}}-\underset{R}{\overset{OH}{C}}-CH_3$$

→ Physical properties:-

1. Solubility:-

- Dihydric alcohols are more soluble in water than monohydric alcohols due to availability of two –OH groups for intermolecular hydrogen bonding.

2. Boiling points and melting points:-

- They have higher b.p. and m.p. than monohydric alcohols of comparable molecular weights. This is due to extensive hydrogen bonding.
- Beause of high b.p. and water solubility, ethylene glycol used in automobiles as antifreeze.

3. Viscosity:-

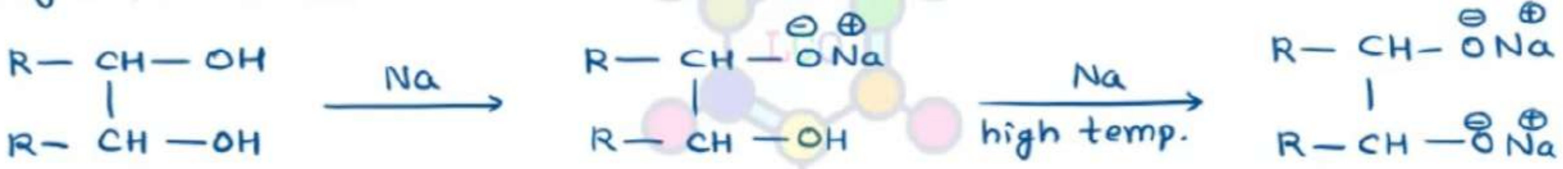
- Diols are highly viscous due to intermolecular hydrogen bonding.

→ Dihydric alcohols:-

→ Chemical reactions of vicinal glycol (1,2-diols):→

1. Reaction with electropositive metals : Acidic nature:-

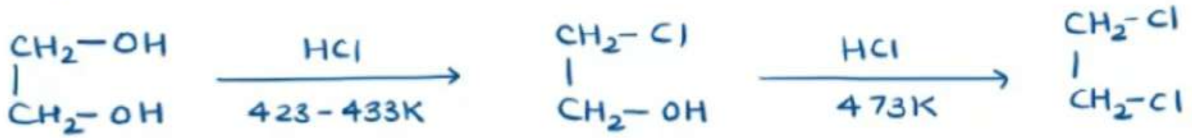
- Like monohydric alcohols, they also liberate hydrogen gas when react with electropositive metals.
- Both hydroxyl groups do not react simultaneously but react one after the other.
- After reacting one -OH group, the second reacts slowly. Because after reacting first -OH group, an alkoxide ion formed which has +I effect. This alkoxide ion makes second hydrogen less acidic.



$$\begin{array}{l} R-CH-OH \\ \quad\;\; | \\ R-CH-OH \end{array} \xrightarrow{Na} \begin{array}{l} R-CH-\overset{\ominus}{O}\overset{\oplus}{Na} \\ \quad\;\; | \\ R-CH-OH \end{array} \xrightarrow[\text{high temp.}]{Na} \begin{array}{l} R-CH-\overset{\ominus}{O}\overset{\oplus}{Na} \\ \quad\;\; | \\ R-CH-\overset{\ominus}{O}\overset{\oplus}{Na} \end{array}$$

2. Reaction with hydrogen halides:-

- Like monohydric alcohols, they react with hydrogen halides to form the corresponding dihalogen derivatives.
- The reaction takes place in two steps.



$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} \xrightarrow[423-433K]{HCl} \begin{array}{l} CH_2-Cl \\ | \\ CH_2-OH \end{array} \xrightarrow[473K]{HCl} \begin{array}{l} CH_2-Cl \\ | \\ CH_2-Cl \end{array}$$

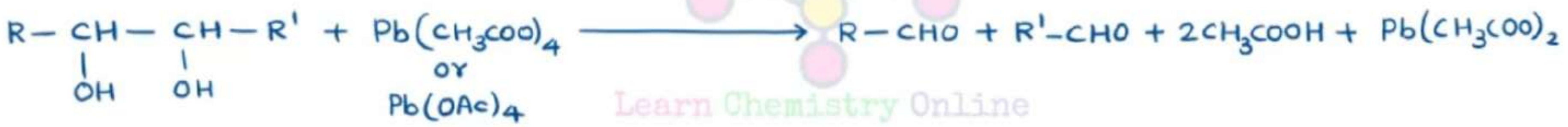
- The displacement of second hydroxyl group is more difficult than that of the first one. because replacement of an –OH group by –Cl reduces the overall electron density on the remaining oxygen due to strong –I effect of chlorine. This makes protonation of second –OH group difficult and hence required higher temp.

3. Oxidation:-

- Oxidation of glycol gives different products depending on reaction condition and type of reagents.
- The oxidation of 1,2-glycols takes place with or without carbon-carbon fission.

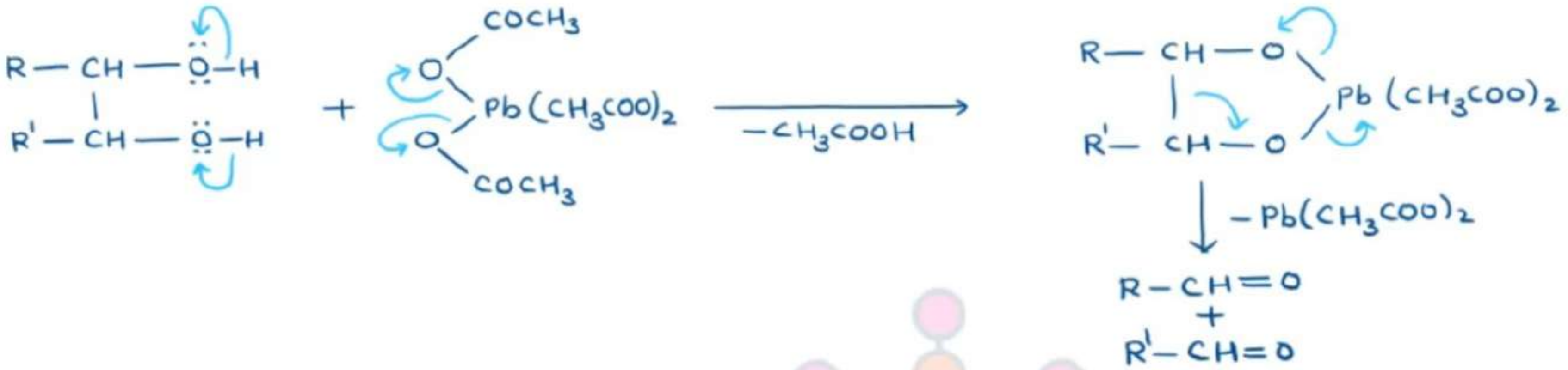
(A) oxidation involving C–C bond fission:-

(a) Oxidation with lead tetraacetate :-



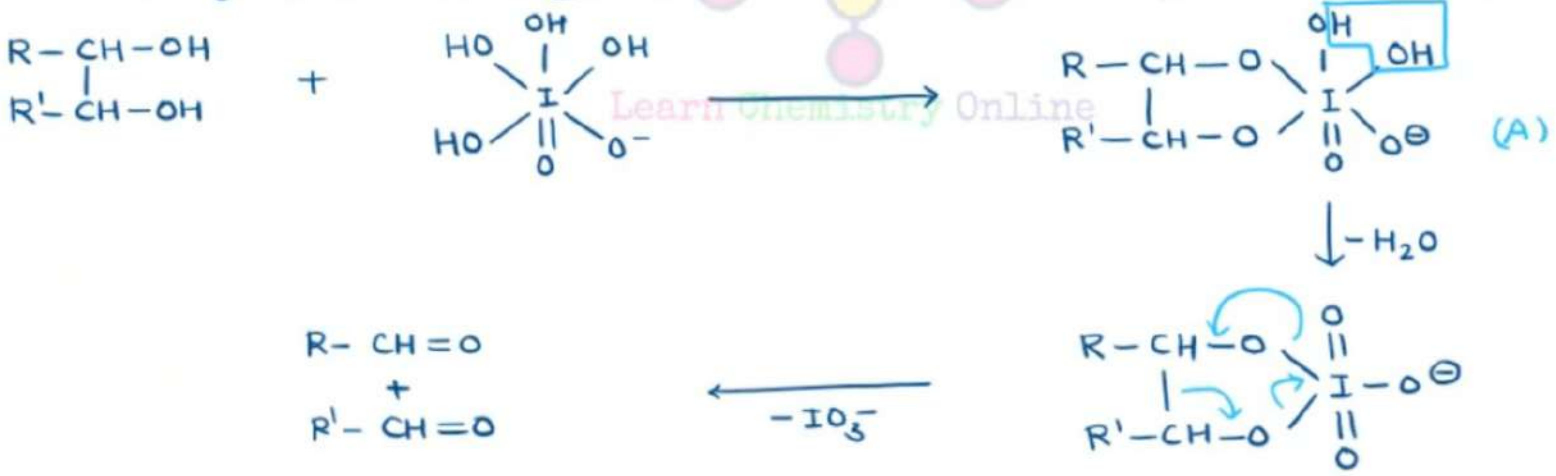
$$\underset{\displaystyle OH}{R-\underset{|}{C}H}-\underset{\displaystyle OH}{\underset{|}{C}H}-R' + \underset{\substack{\text{or}\\ Pb(OAc)_4}}{Pb(CH_3COO)_4} \longrightarrow R-CHO + R'-CHO + 2CH_3COOH + Pb(CH_3COO)_2$$

- This reaction is not only important for the formation of aldehydes, but also for locating the position of two –OH groups in the molecule as the two carbonyl carbons of the product aldehydes are original carbons bearing the hydroxyl groups.
- Mechanism:-
- A five membered cyclic ester as an intermediate is formed which undergoes on oxidation-reduction process resulting in the cleavage of carbon-carbon bond.

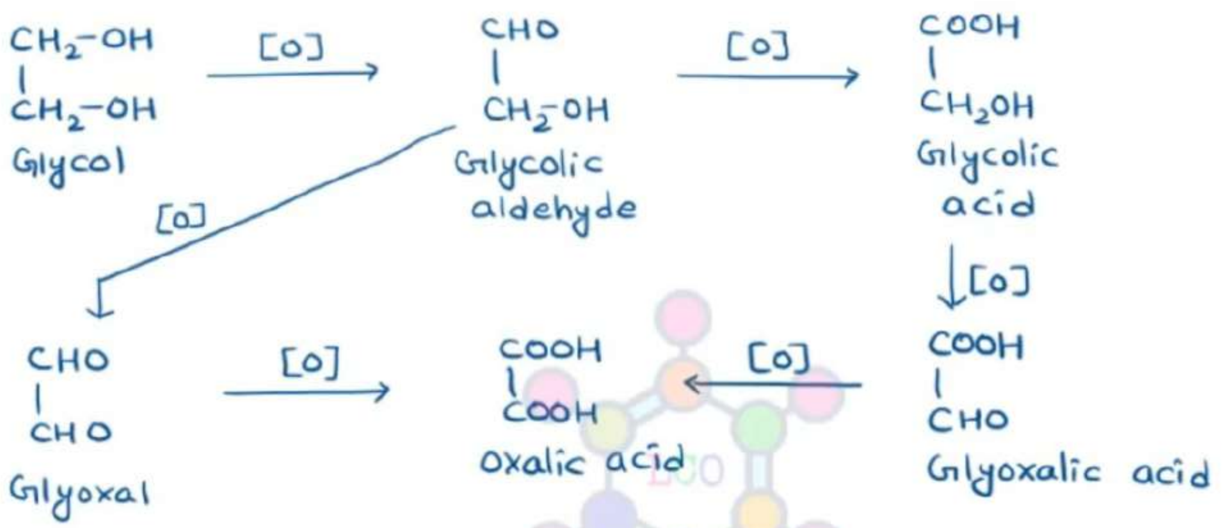


(b) oxidation with periodic acid :- (HIO_4)

– 1,2-diols also undergo c-c bond cleavage upon treatment with an aqueous solution of periodic acid, H_5IO_6 ($HIO_4 + 2H_2O$). The active species is periodate anion, $H_4IO_6^-$



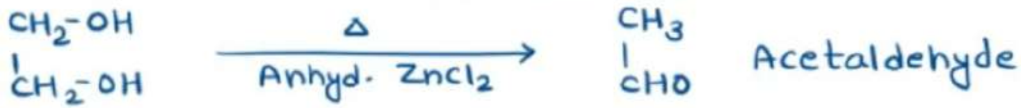
B. Oxidation in which carbon-carbon bond remains intact :-



4. Dehydration:-

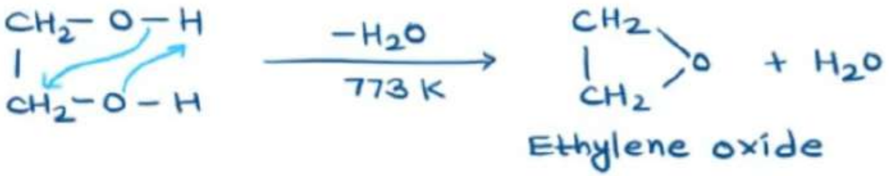
- Dehydration of 1,2-diol gives different products with different reagents

(a) When heated with anhyd $ZnCl_2$



$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[\text{Anhyd. } ZnCl_2]{\Delta} \begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \text{ Acetaldehyde}$$

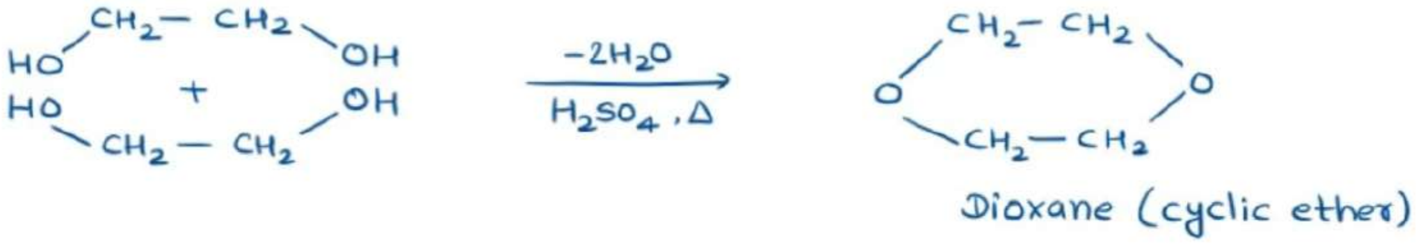
(b) When heated alone



$$\begin{matrix} CH_2-O-H \\ | \\ CH_2-O-H \end{matrix} \xrightarrow[773\,K]{-H_2O} \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>O + H_2O$$

Ethylene oxide

(c) When heated with conc. H_2SO_4 :-



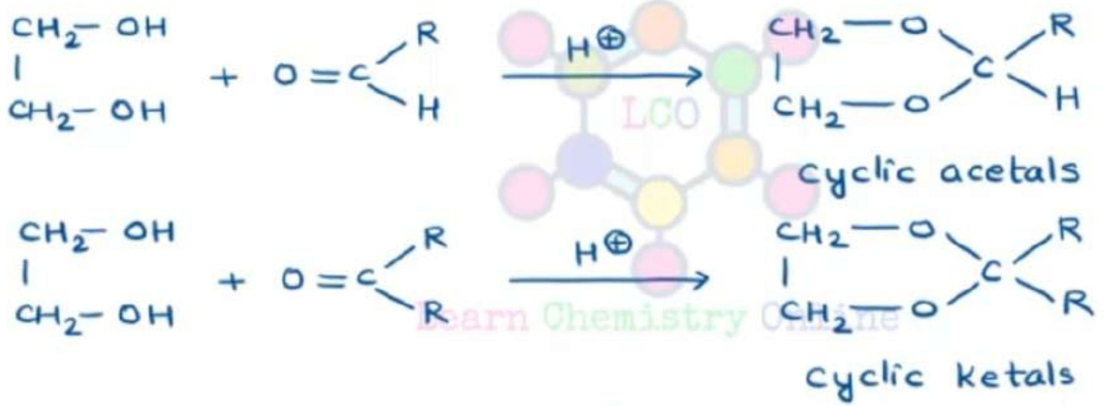
Dioxane (cyclic ether)

→ Dihydric alcohols:-

→ Chemical reactions of vicinal glycol (1,2-diols):→ (Part-2)

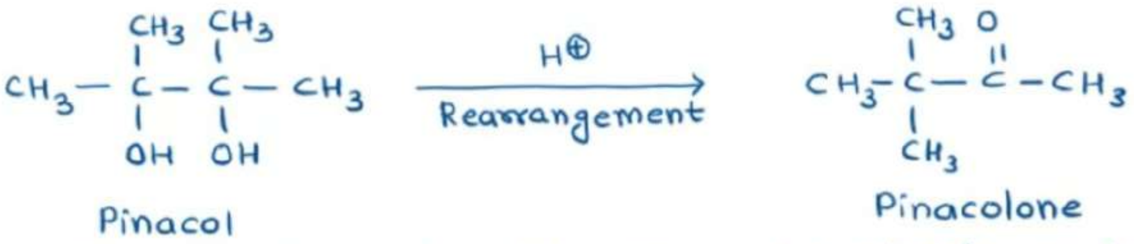
5. Formation of cyclic acetals or Ketals:-

- when an aldehyde or a ketone is treated with an alcohol in presence of an acid catalyst it forms gem-diethers called acetals and ketals, respectively. These products are formed by condensation of two -OH groups of alcohols with one molecule of carbonyl compound.
- 1,2-diols reacts with carbonyl compounds in similar manner to form cyclic acetals and ketals



- This reaction used in organic synthesis for 'protecting' the carboyl group. The carbonyl group is regenerated by acid hydrolysis.

6. Acid- catalysed rearrangement of glycols: Pinacol – Pinacolone rearrangement:-



- Similar type of reaction is observed with other 1,2-glycols and such rearrangements are collectively known as Pinacol-Pinacolone rearrangement.

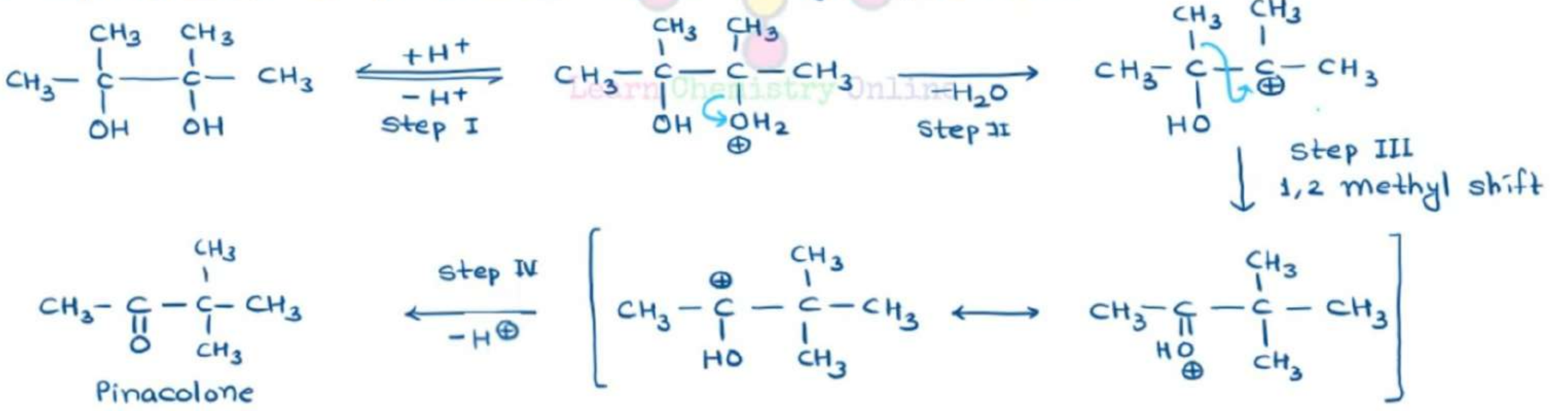
- Mechanism:-

step-I Protonation of 1,2-diol

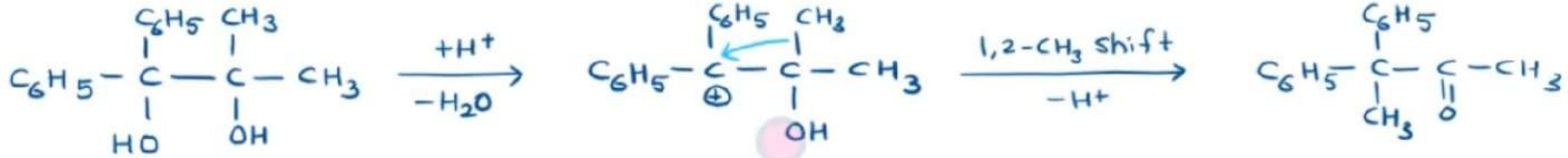
step-II Formation of carbocation by loss of water from diol

step-III Rearrangement of carbocation by 1,2-nucleophilic shift to give protonated ketone.

step-IV Deprotonation of protonated ketone to give pinacolone.



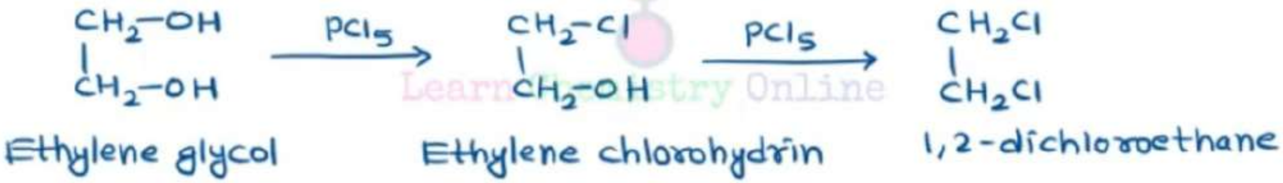
- The driving force for the migration of the methyl group is provided by the resonance stabilisation of the rearranged ion by the attached oxygen.
- In case of unsymmtrically substituted glycols, the positive charge is generated on that carbon which is best able to support it.



$$C_6H_5-\underset{HO}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-H_2O]{+H^+} C_6H_5-\underset{\oplus}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-H^+]{1,2-CH_3\ shift} C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\underset{O}{\overset{}{C}}-CH_3$$

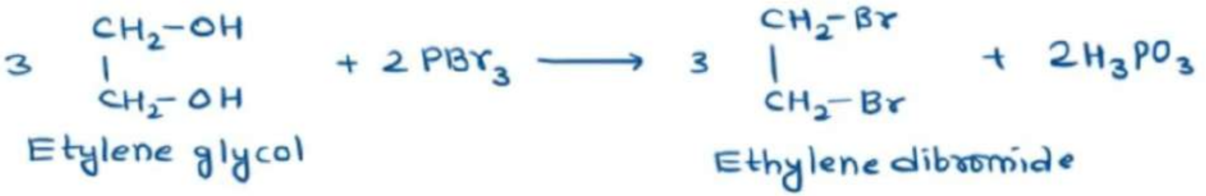
- In case of above reaction carbocation is produced on the phenylated carbon rather than on the methylated carbon because of resonance stablilisation of the former.

7. Reaction with phosphorus halide:-



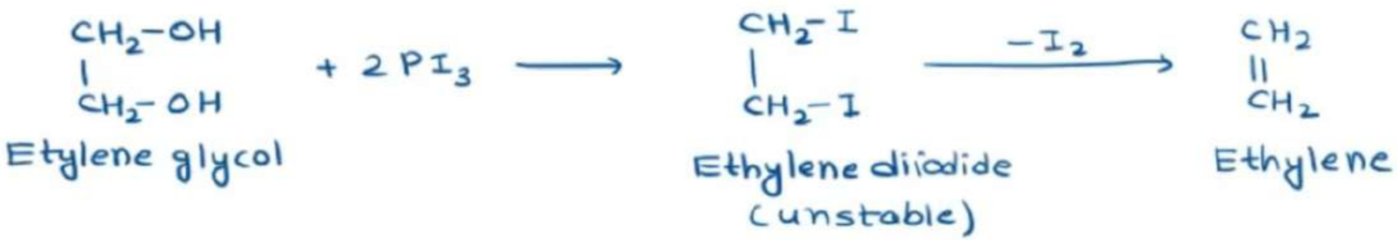
$$\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} \xrightarrow{PCl_5} \begin{matrix}CH_2-Cl\\|\\CH_2-OH\end{matrix} \xrightarrow{PCl_5} \begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$$

Ethylene glycol — Ethylene chlorohydrin — 1,2-dichloroethane

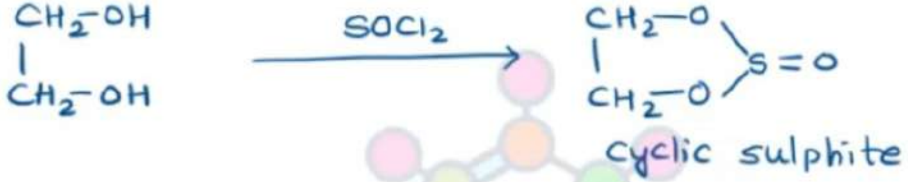


$$3\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} + 2PBr_3 \longrightarrow 3\begin{matrix}CH_2-Br\\|\\CH_2-Br\end{matrix} + 2H_3PO_3$$

Etylene glycol — Ethylene dibromide

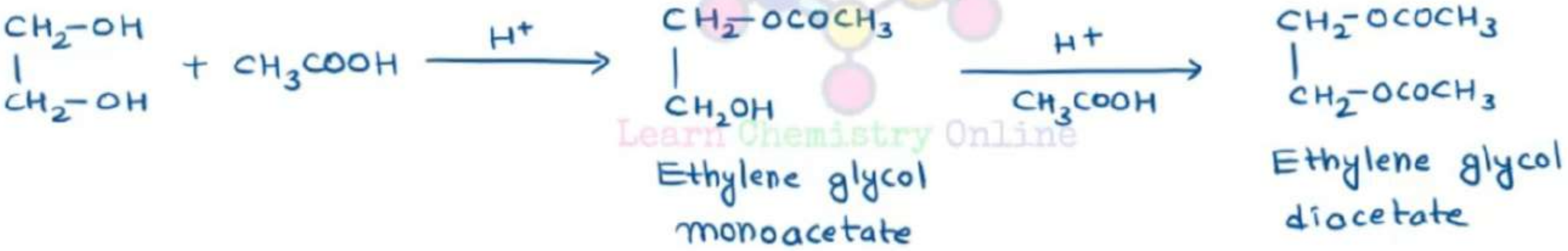


$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} + 2PI_3 \longrightarrow \begin{matrix} CH_2-I \\ | \\ CH_2-I \end{matrix} \xrightarrow{-I_2} \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}$$



$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow{SOCl_2} \begin{matrix} CH_2-O \\ | \\ CH_2-O \end{matrix} \rangle S=O$$

8. Esterification:-

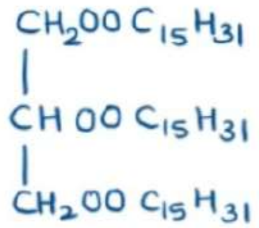


$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} + CH_3COOH \xrightarrow{H^+} \begin{matrix} CH_2-OCOCH_3 \\ | \\ CH_2OH \end{matrix} \xrightarrow[CH_3COOH]{H+} \begin{matrix} CH_2-OCOCH_3 \\ | \\ CH_2-OCOCH_3 \end{matrix}$$

→ Trihydric alcohols:-

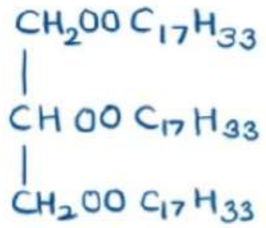
→ Introduction:-

- Trihydric alcohols contain three hydroxyl groups attached to three adjacent carbon atoms.
- General formula $C_nH_{2n-1}(OH)_3$
- The introduction of third -OH group in a diol molecule raises the boiling point by about 100K. This also increases viscosity and the makes the alcohol more sweet. The increase in boiling point is due to increase in number of -OH groups. This enhances the extent of hydrogen bonding ability (association) and consequently increases the boiling point.
- The simplest and most important trihydric alcohol is propane-1,2,3-triol commonly known as glycerol. It is also known as glycerine.
- Glycerol is found in all natural fats and oils as glyceryl esters of long chain fatty acids.
- Fatty acids present in glyceryl esters are palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$) and oleic acid ($C_{17}H_{33}COOH$). Esters of these acids are called glycerides.



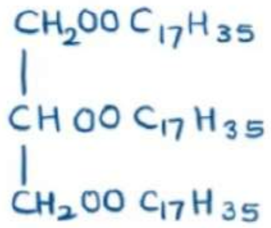
$$\begin{array}{l} CH_2OOC_{15}H_{31} \\ | \\ CH\,OOC_{15}H_{31} \\ | \\ CH_2OOC_{15}H_{31} \end{array}$$

Tripalmitin



$$\begin{array}{l} CH_2OOC_{17}H_{33} \\ | \\ CH\,OOC_{17}H_{33} \\ | \\ CH_2OOC_{17}H_{33} \end{array}$$

Triolein



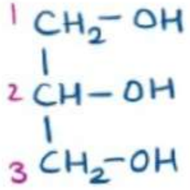
$$\begin{array}{l} CH_2OOC_{17}H_{35} \\ | \\ CH\,OOC_{17}H_{35} \\ | \\ CH_2OOC_{17}H_{35} \end{array}$$

Tristearin

→ Nomenclature :-

- IUPAC system

- Name of alkane, Positions of three -OH groups, suffix - triol



$$\begin{array}{l} {}^{1}\,CH_2-OH \\ \quad | \\ {}^{2}\,CH-OH \\ \quad | \\ {}^{3}\,CH_2-OH \end{array}$$

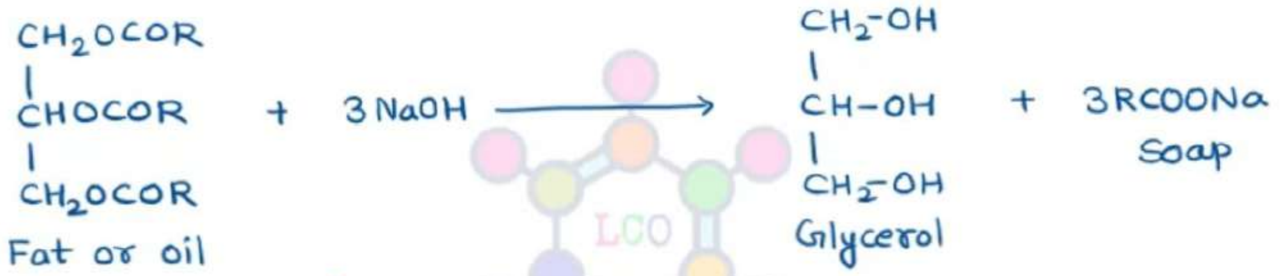
Propane-1,2,3-triol

→ Trihydric alcohols:→

- Methods of formation:-

1. From Fats and oils:- (During soap manufacture)-

- Fats and oils are triesters of glycerol and long chain fatty acids (palmitic, stearic and oleic acid) They are hydrolysed with alkali to form salt of long chain fatty acids which are also called as soaps.



$$\begin{matrix} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \\ \text{Fat or oil} \end{matrix} + 3NaOH \longrightarrow \begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \\ \text{Glycerol} \end{matrix} + \begin{matrix} 3RCOONa \\ \text{Soap} \end{matrix}$$

(i) Glycerol from the spent lye of soap industry:-

- After hydrolysis of fats and oils, soap is salted out by adding sodium chloride to the reaction mixture which is then filtered. The filtrate obtained after removing the soap is known as spent lye.
- Spent lye contains 3–5% glycerol, free alkali, some soluble soap, sodium chloride, suspended impurities and water.
- The spent lye is allowed to settle in settling tank where most of the suspended impurities settle down.
- The decanted solution is transfered to a treatment tank where it is first treated with dilute HCl to neutrilise most of free alkali and then with aluminium sulphote which precipitates

free alkali as aluminium hydroxide and soluble soap as aluminium soap. This is filtered by passing through a filter press and taken to a storage tank.

- The dilute solution is then concentrated under reduced pressure in concentration pan using low pressure steam for heating, when most of the sodium chloride separates out.
- This is filtered and the filtrate is decolourised with animal charcoal and subjected to vacuum distillation.
- Glycerol, thus obtained, is approximately 90-95% pure.

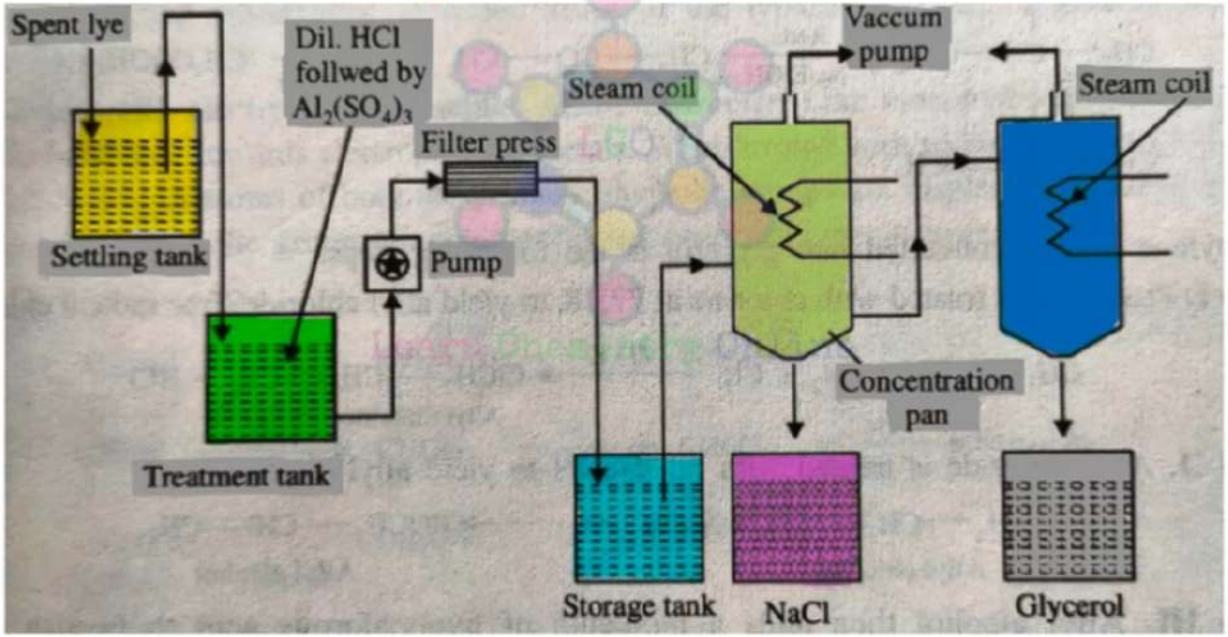
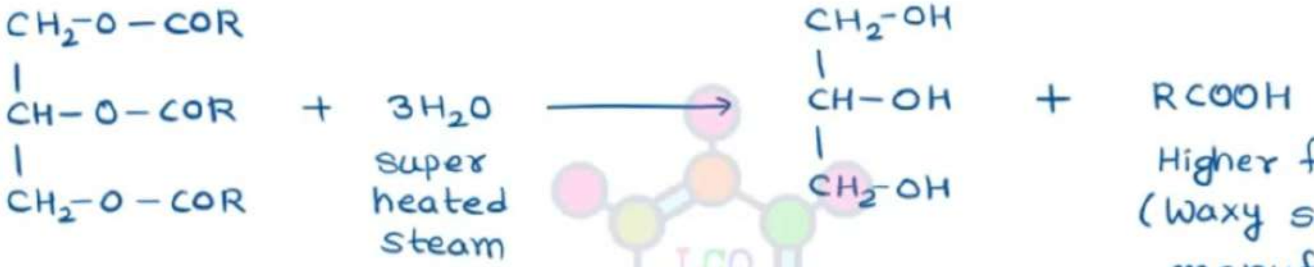


Fig:- Flowchart showing recovery of glycerol from spent lye

(ii) During candle manufacture:-

- The higher fatty acids required for the manfacture of candles are obtained by the hydrolysis of fats and oils with superheated steam using sulphuric acid as catalyst.
- These fatty acids are usually solids and are removed by filtration. The filtrate is called sweet water.



$$\begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-COR \end{array} + \underset{\text{super heated steam}}{3H_2O} \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + RCOOH$$

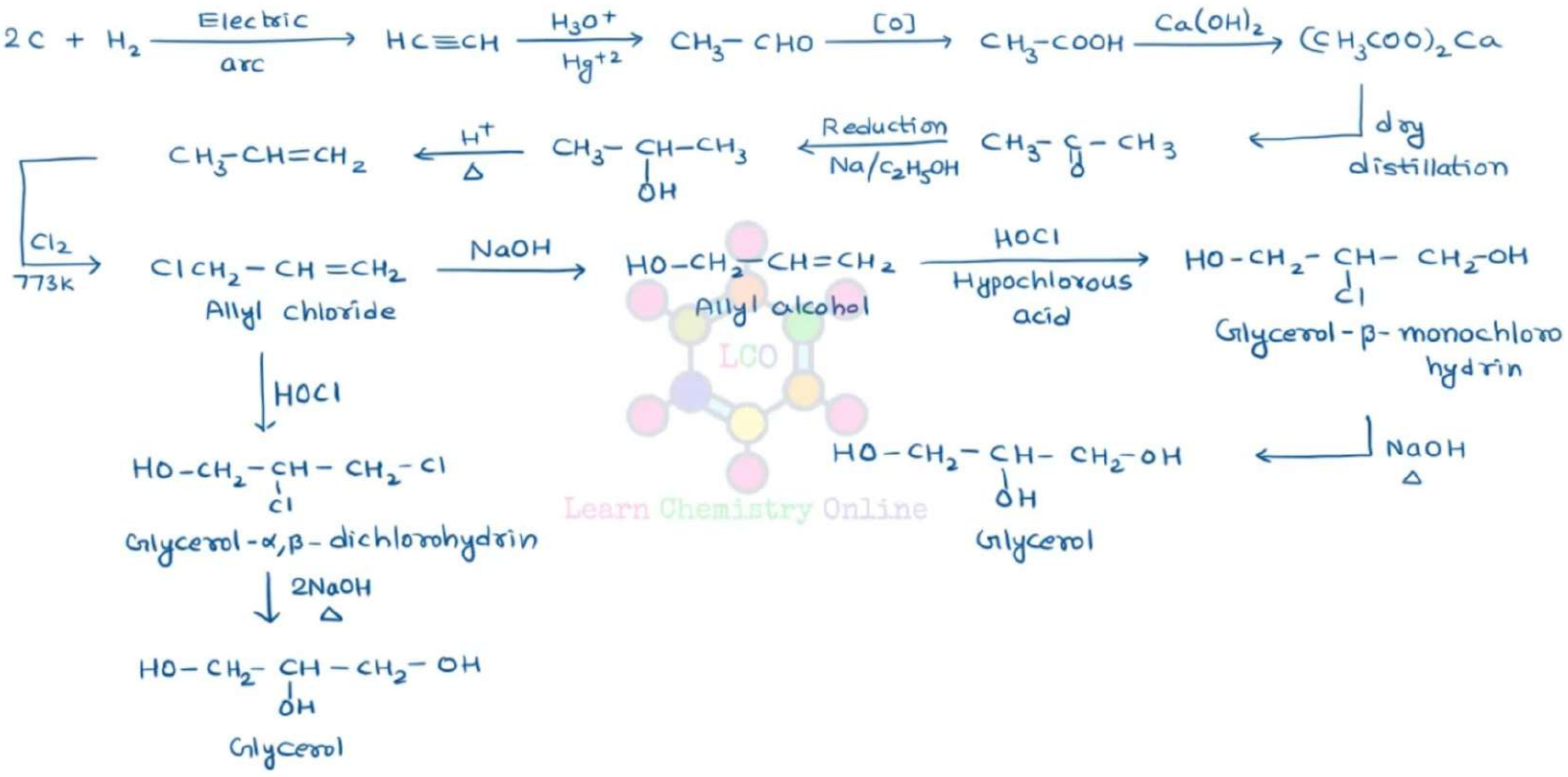
Higher fatty acids
(Waxy solids used in the manufacture of candle)

- The sweet water contains water and glycerol along with small amount of Volatile fatty acids. It is neutrilised with sodium Carbonate and subjected to steam distillation. Volatile fatty acids form non-volatile sodium salts and are left behind as residue while dilute solution of glycerol distils over.
- The dilute solution, thus obtained is concentrated under vacuum and purified.

2. By fermentation of sugars:-

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Yeast}} 2\,C_6H_{12}O_6 \xrightarrow[Na_2SO_3]{\text{Yeast}} \underset{\text{Glycerol}}{CH_2OH-CHOH-CH_2OH}$$

3. Synthesis from elements :→

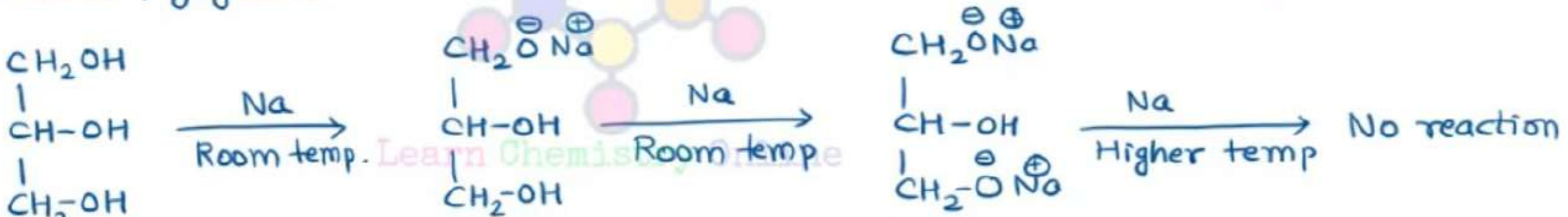


→ Trihydric alcohols:→

- Physical properties:-
- Glycerol is colourless, odourless, hygroscopic and viscous liquid.
- Boiling point → 563 K (decomposed at b.p.)
- Specific gravity is 1.265 at 293 K
- It is misible with water due to availability of three hydroxyl groups for hydrogen bonding with water.
- It is sweet in taste.
- Chemical reactions:-

1. Reaction with electropositive metals : Acidic character:-

- Like monohydric alcohols, glycerol shows acidic character towards electropositive metals.

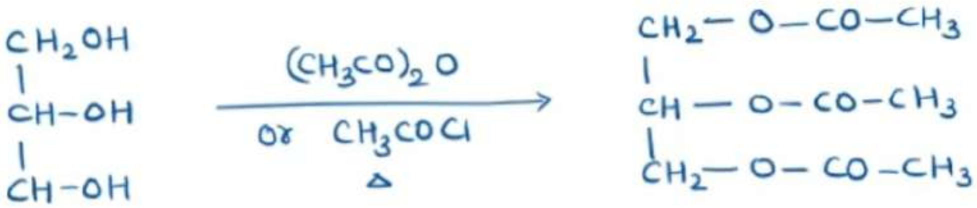


$$\begin{array}{l}CH_2OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array} \xrightarrow[\text{Room temp.}]{Na} \begin{array}{l}CH_2\overset{\ominus}{O}\overset{\oplus}{Na}\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array} \xrightarrow[\text{Room temp}]{Na} \begin{array}{l}CH_2\overset{\ominus}{O}\overset{\oplus}{Na}\\ |\\ CH-OH\\ |\\ CH_2-\overset{\ominus}{O}\overset{\oplus}{Na}\end{array} \xrightarrow[\text{Higher temp}]{Na} \text{No reaction}$$

monosodium salt

disodium salt

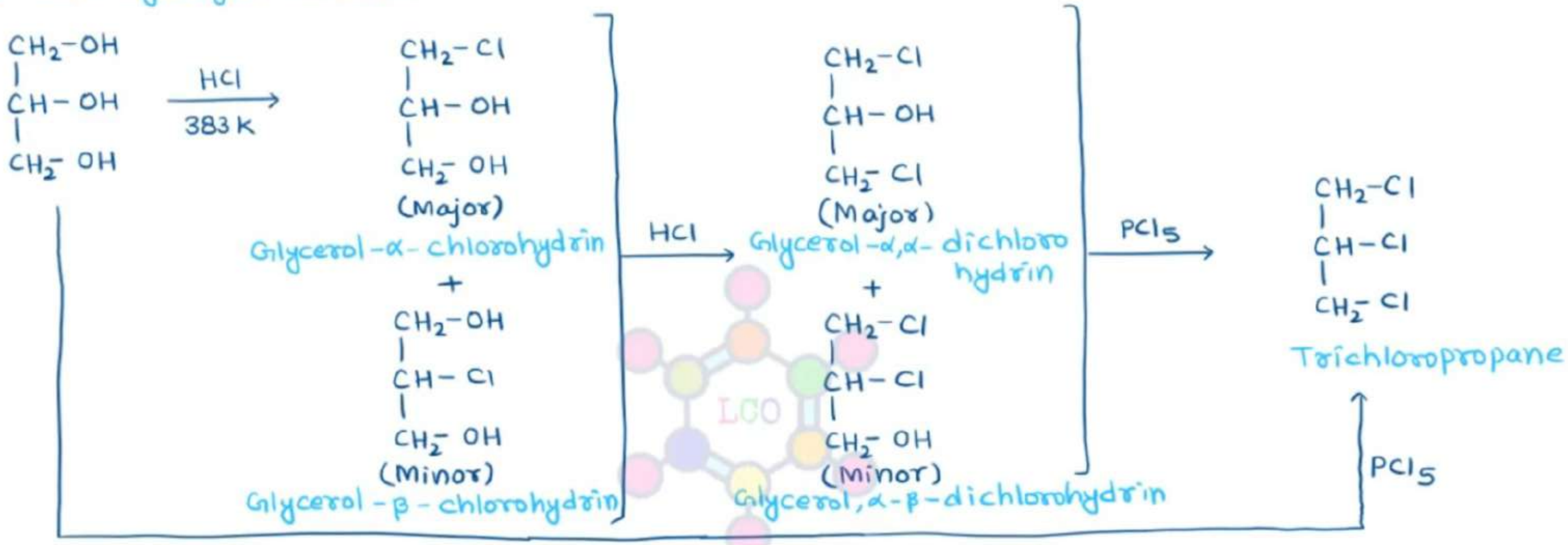
2. Esterification:-



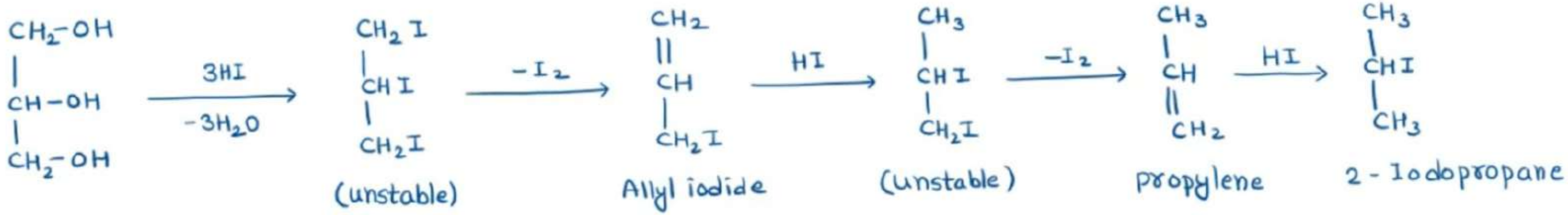
$$\begin{array}{l}CH_2OH\\ |\\ CH-OH\\ |\\ CH-OH\end{array} \xrightarrow[\text{or } CH_3COCl,\ \Delta]{(CH_3CO)_2O} \begin{array}{l}CH_2-O-CO-CH_3\\ |\\ CH-O-CO-CH_3\\ |\\ CH_2-O-CO-CH_3\end{array}$$

Glyceryl triacetate
(Triacetin)

3. Reaction with hydrogen halides:-

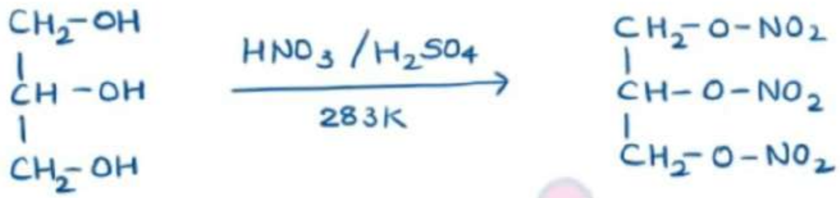


- Reaction with HI



4. Reaction with nitric acid in presence of sulphuric acid :→

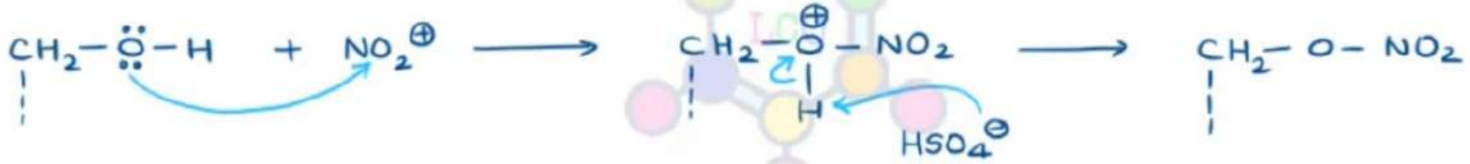
- Reaction of glycerol with conc. HNO_3 in the presence of conc. H_2SO_4 at 283 K gives glyceryl trinitrate (Trinitroglycerine, TNG) which is also called Nobel's oil.



$$\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[283K]{HNO_3/H_2SO_4} \begin{matrix} CH_2-O-NO_2 \\ | \\ CH-O-NO_2 \\ | \\ CH_2-O-NO_2 \end{matrix}$$

- Mechanism: -

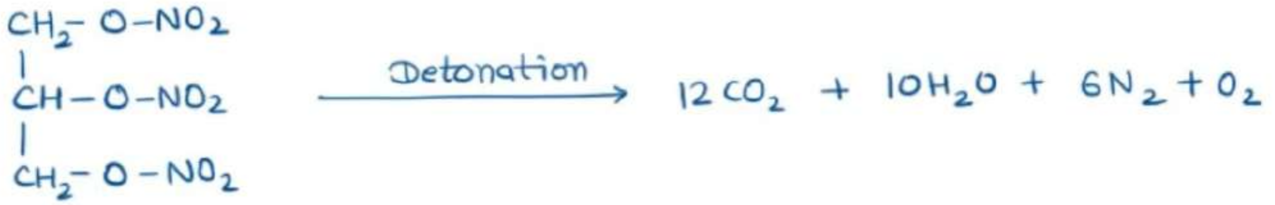
$$2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}$$



$$CH_2-\ddot{O}-H + NO_2^{\oplus} \longrightarrow CH_2-\overset{\oplus}{O}(H)-NO_2 \xrightarrow{HSO_4^{\ominus}} CH_2-O-NO_2$$

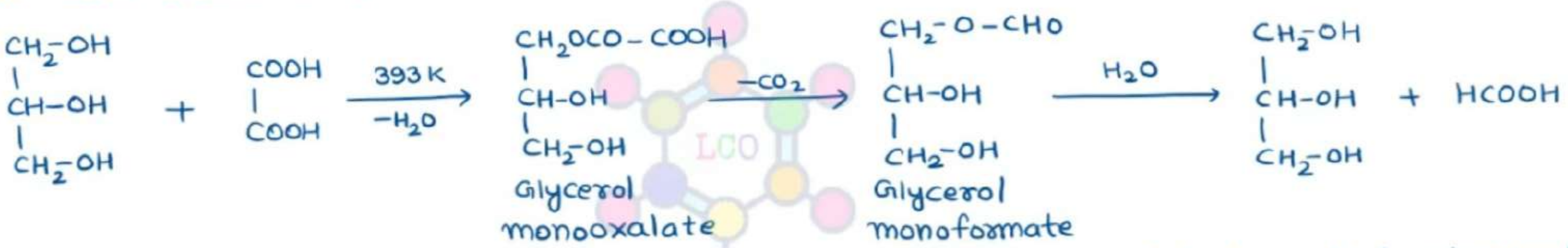
- Glyceryl trinitrate is a highly poisonous oil which explodes violently when detonated. It, was, therefore, widely used as an explosive.
- Its usefulness was, however, limited because of its high reactivity which made transportation a very hazardous task.
- Alfred Nobel discovered that when this oil is absorbed on keiselghur it could be transported easily. This form is called dynamite.
- It is outcome of the income from the patent of dynamite that the coveted Nobel prize were instituted.

- However, now-a-days dynamite is prepared by using saw-dust or wood pulp and ammonium nitrate.



$$\begin{array}{l} CH_2-O-NO_2 \\ | \\ CH-O-NO_2 \\ | \\ CH_2-O-NO_2 \end{array} \xrightarrow{\text{Detonation}} 12CO_2 + 10H_2O + 6N_2 + O_2$$

5. Reaction with oxalic acid :-



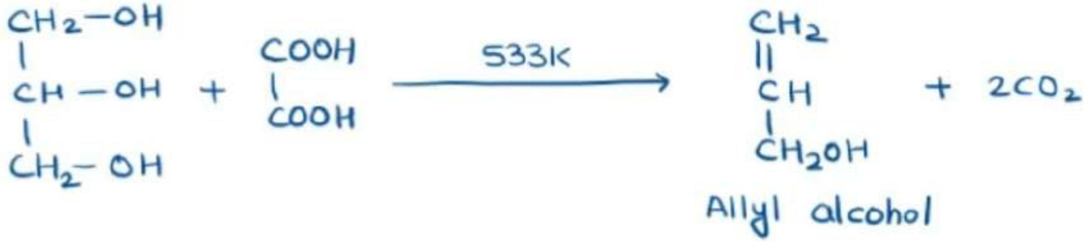
$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} \xrightarrow[-H_2O]{393\,K} \begin{array}{l} CH_2OCO-COOH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{-CO_2} \begin{array}{l} CH_2-O-CHO \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + HCOOH$$

Glycerol monooxalate

Glycerol monoformate

- This reaction is used to convert oxalic acid into formic acid in which glycerol used as catalyst

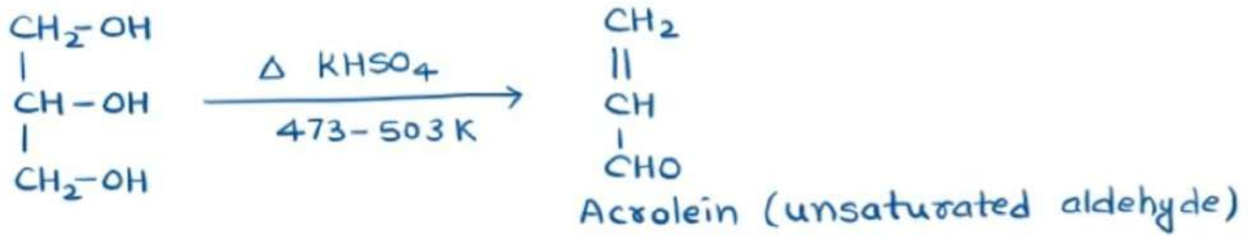
- If glycerol and oxalic acid heated at 533 K, allyl alcohol is formed.



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} \xrightarrow{533K} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} + 2CO_2$$

Allyl alcohol

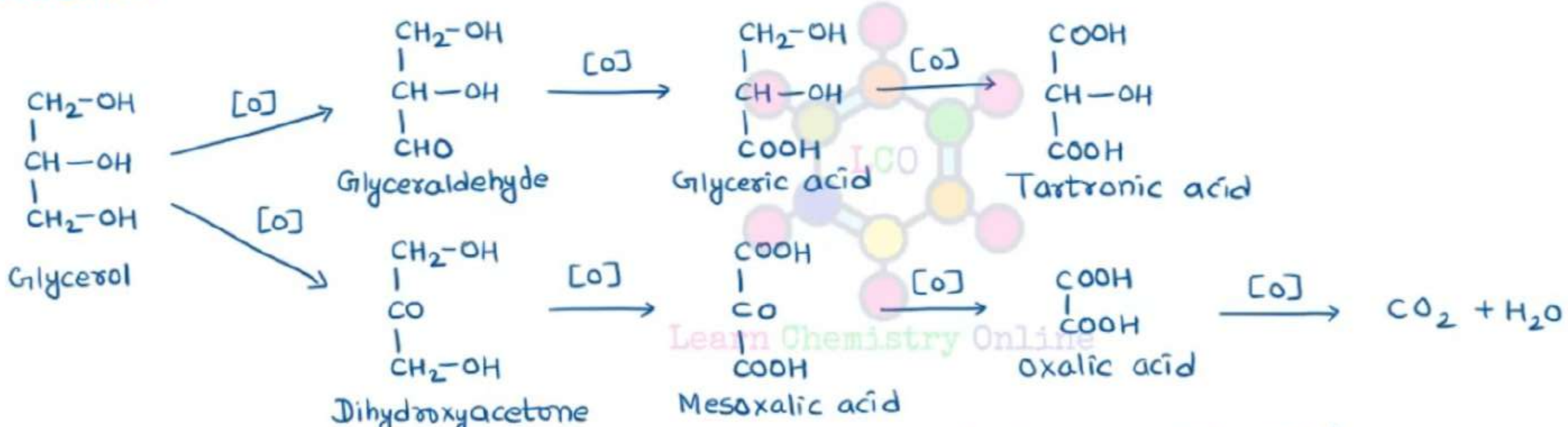
6. Reaction with potassium hydrogen sulphate: Dehydration:-



$$CH_2{-}OH{-}CH{-}OH{-}CH_2{-}OH \xrightarrow[473-503\,K]{\Delta\ KHSO_4} CH_2{=}CH{-}CHO$$

Acrolein (unsaturated aldehyde)

7. Oxidation:-



- The nature of product(s) depends upon the type of the reagent used-

(i) With bismuth nitrate, mesoxalic acid is formed.

(ii) with dil HNO_3, mixture of glyceric and tortronic acid is obtained.

(iii) With conc. HNO_3, glyceric acid is formed.

(iv) Br_2 water or Fenton's reagent ($H_2O_2 + FeSO_4$), mixture of glceraldehyde and dihydroxy acetone, called glycerose is obtained.

(v) With periodic acid, formaldehyde and formic acid are formed.

$$HOCH_2 - CHOH - CH_2OH \xrightarrow{HIO_4} HCOOH + HCHO$$

→ Uses:-

- As an antifreeze in automobile radiaters.
- In the manufactring of cough syrups, lotions etc.
- In the preparation of dynamite.
- In the preparation of glyptal which is used in the preparation of paints and laquers.