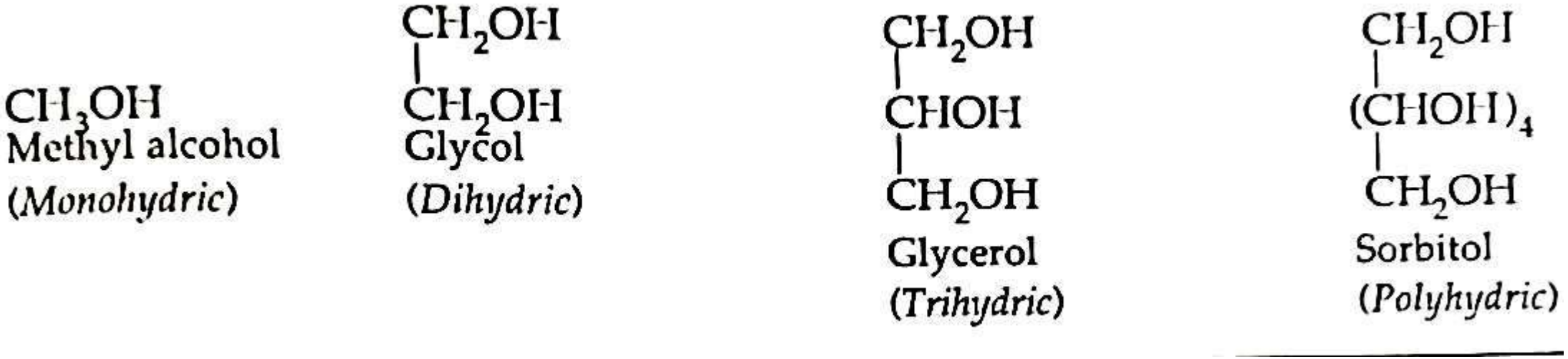
Alcohols

Hydroxy derivatives of Alkanes

Classification of Alcohols

Depending upon the number of OH groups

- **Monohydric alcohols**
- **Dihydric Alcohols**
- **Trihydric Alcohols**
- **Polyhydric Alcohols**



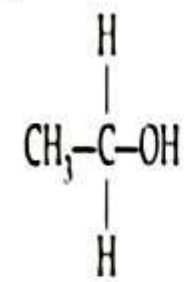
Classification of Alcohols

Depending upon the nature of carbon to which OH is attached

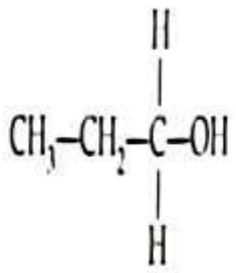
Primary Alcohols(1^o)
Characteristic group is $-CH_2OH$

Secondary Alcohols(2^o)
Characteristic group is >CHOH

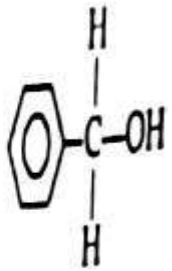
Tertiary Alcohols(3^o)
Characteristic group is



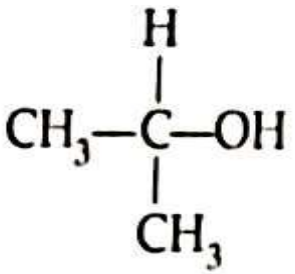
Ethyl alcohol



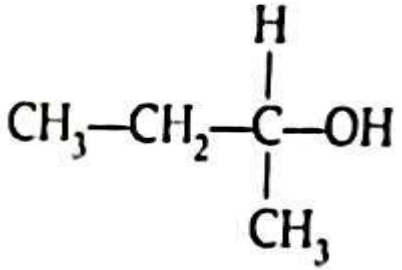
n-Propyl alcohol



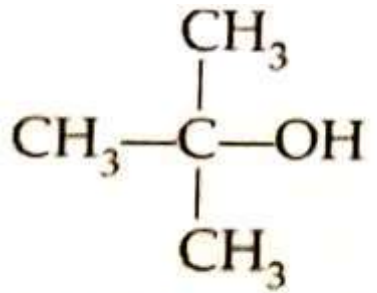
Benzyl alcohol



Isopropyl alcohol



sec. Butyl alcohol



tert. Butyl alcohol

Classification of Alcohols

Depending upon the nature of alcohol

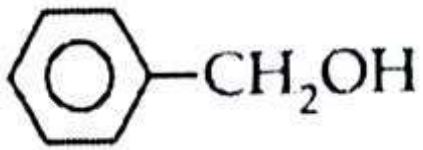
Aliphatic alcohols

CH_3OH Methyl alcohol

$CH_3CH_2CH_2OH$ n –Propyl alcohol

Aromatic alcohols

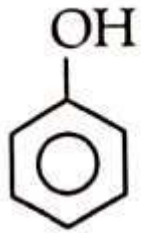
OH gp attached to side chain present on benzene



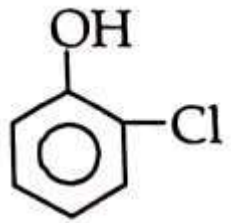
Benzyl alcohol

Phenols

OH gp attached to benzene ring directly



Phenol



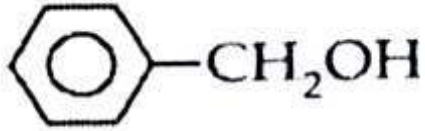
2-Chlorophenol
(*o*-Chlorophenol)

Nomenclature of monohydric alcohols

Common system
- Alkyl alcohols

CH_3OH
Methyl alcohol

$CH_3CH_2CH_2OH$
n –Propyl alcohol

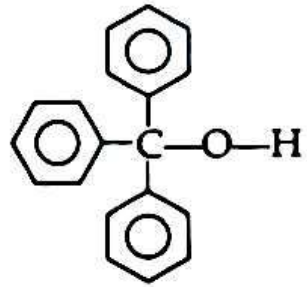

Benzyl alcohol

Carbinol system
- CH_3OH is known as carbinol

CH_3OH
Carbinol

$CH_3—CH_2OH$
Methyl carbinol

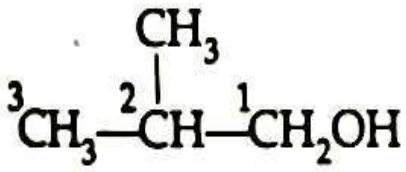

Dimethyl carbinol

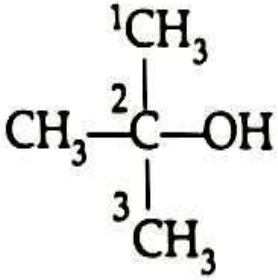

Triphenyl carbinol

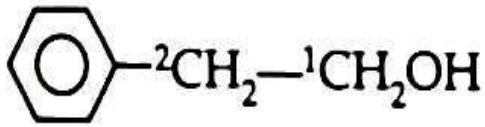
IUPAC System
- Alkanols

$CH_3—CH_2OH$
Ethanol

$^4CH_3—^3CH_2—^2CH_2—^1CH_2OH$
Butan-1-ol

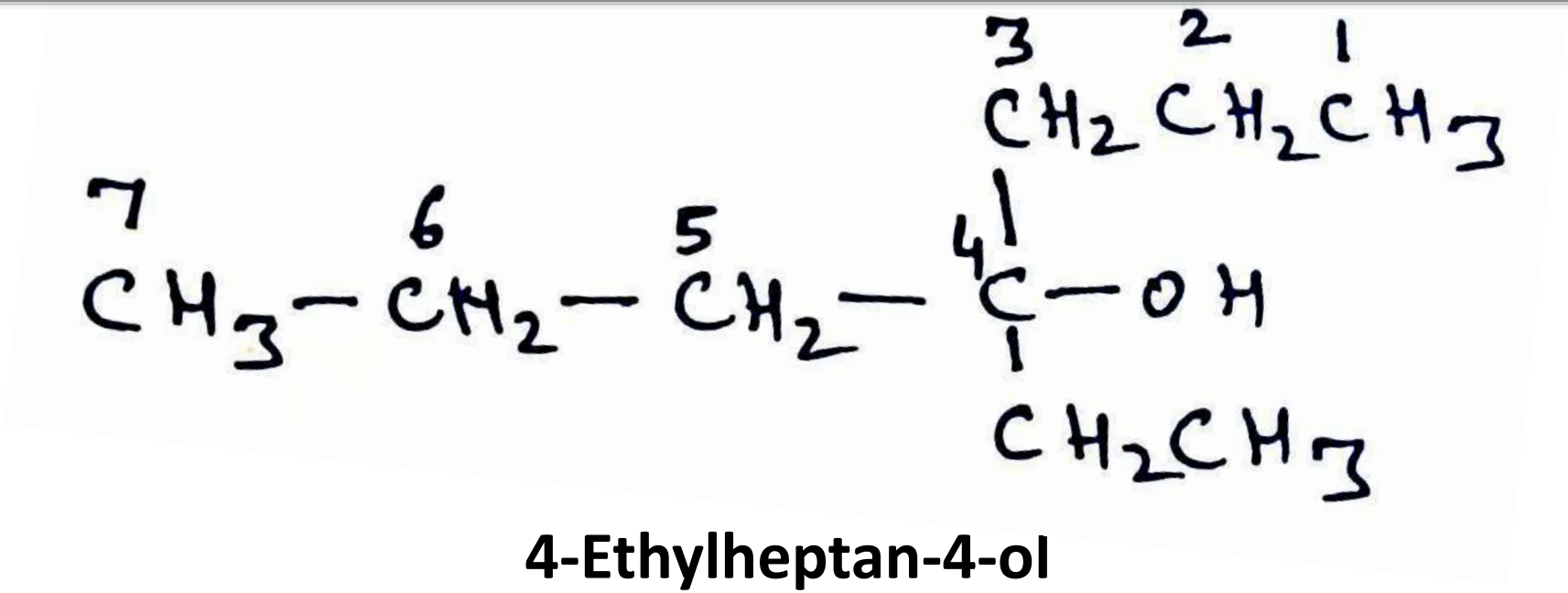

2-Methylpropan-1-ol


2-Methylpropan-2-ol

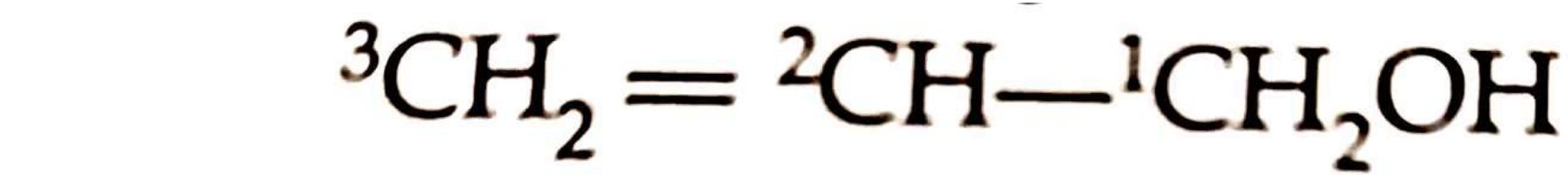

2-Phenylethan-1-ol

Nomenclature of monohydric alcohols

IUPAC System



4-Ethylheptan-4-ol



Prop-2-en-1-ol

Structural isomerism in Alcohols

1. **Chain Isomerism**

2. **Position isomerism**

3. **Functional isomerism**

- **Alcohols are functionally related to ethers**

Physical properties

❑ Boiling points

➢ Alcohols have higher boiling points as compared to ethers and alkanes of comparable molecular masses

✓ It is due to the presence of intermolecular H-bonding between alcohol molecules(Associated state)

✓ Ethyl alcohol > Dimethyl ether > Propane

(351.5 K)	(249 K)	(249 K)
46	46	44

❑ Solubility

➢ Lower members are highly soluble in water

✓ Alcohols can form hydrogen bonds with water molecules

➢ Solubility decreases from C4 to C9 alcohols

✓ Because nonpolar alkyl chain masks the polar character of –OH group

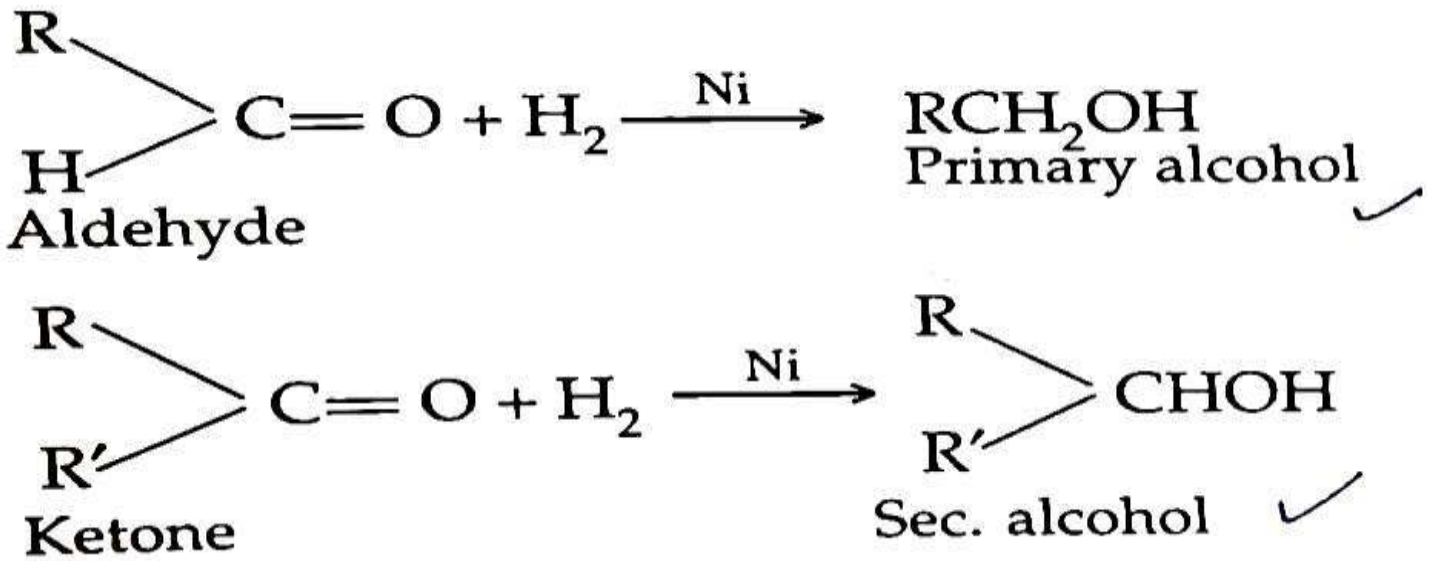
➢ Nonanol-1 is completely insoluble in water

Methods of preparation of alcohols

❑ By reduction of carbonyl compounds

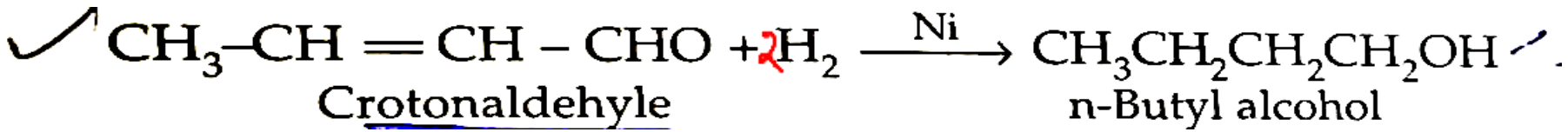
1. Reduction of aldehydes and ketones

a. By catalytic hydrogenation



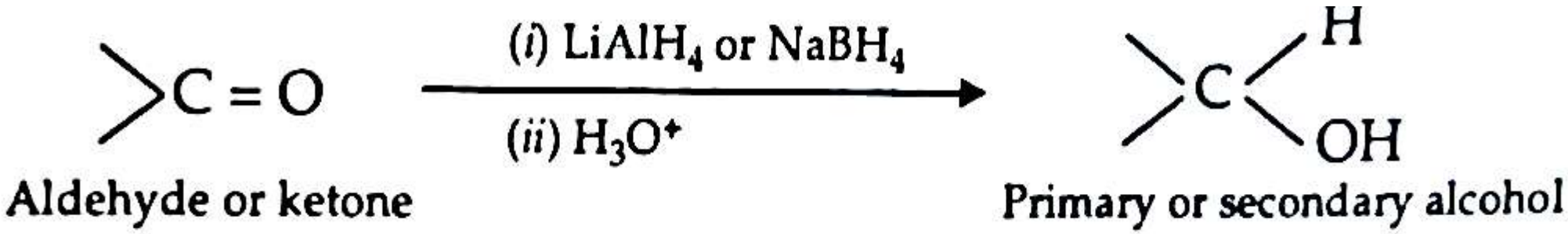
❑ Limitation

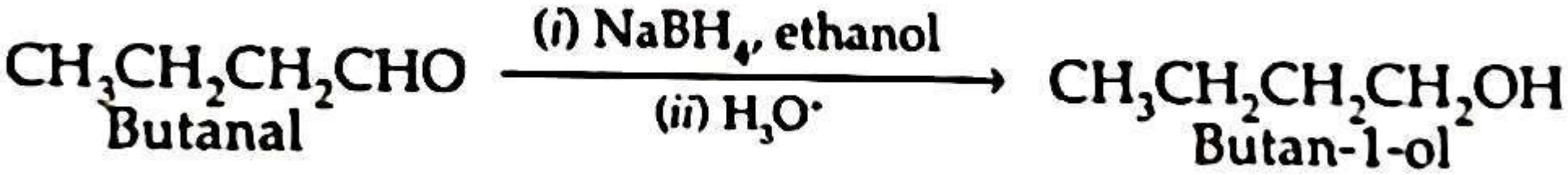
- **Selective reduction can not be done**
- **Other easily reducible groups are also reduced**

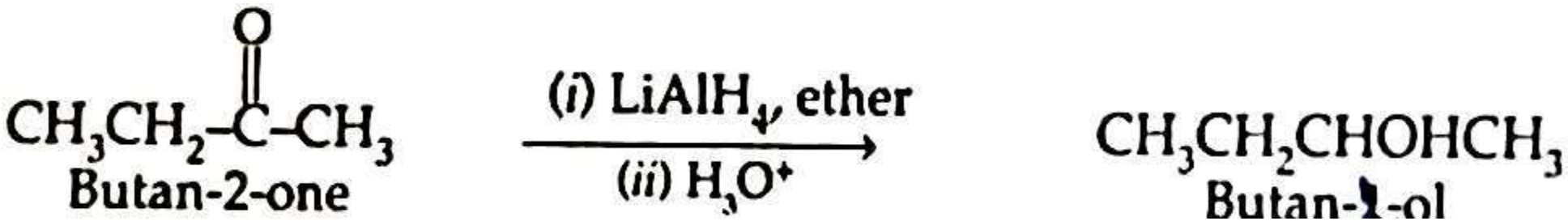


Methods of preparation of alcohols

b. Reduction with complex metal hydrides

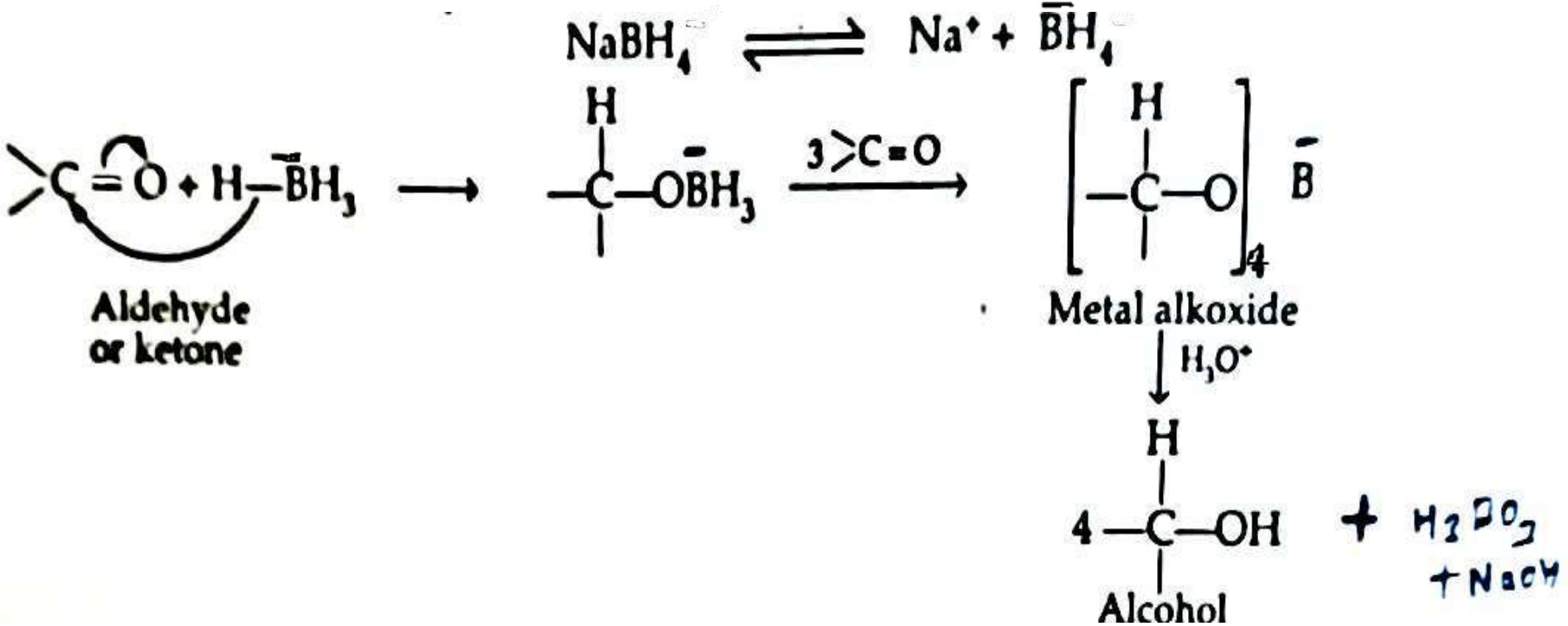






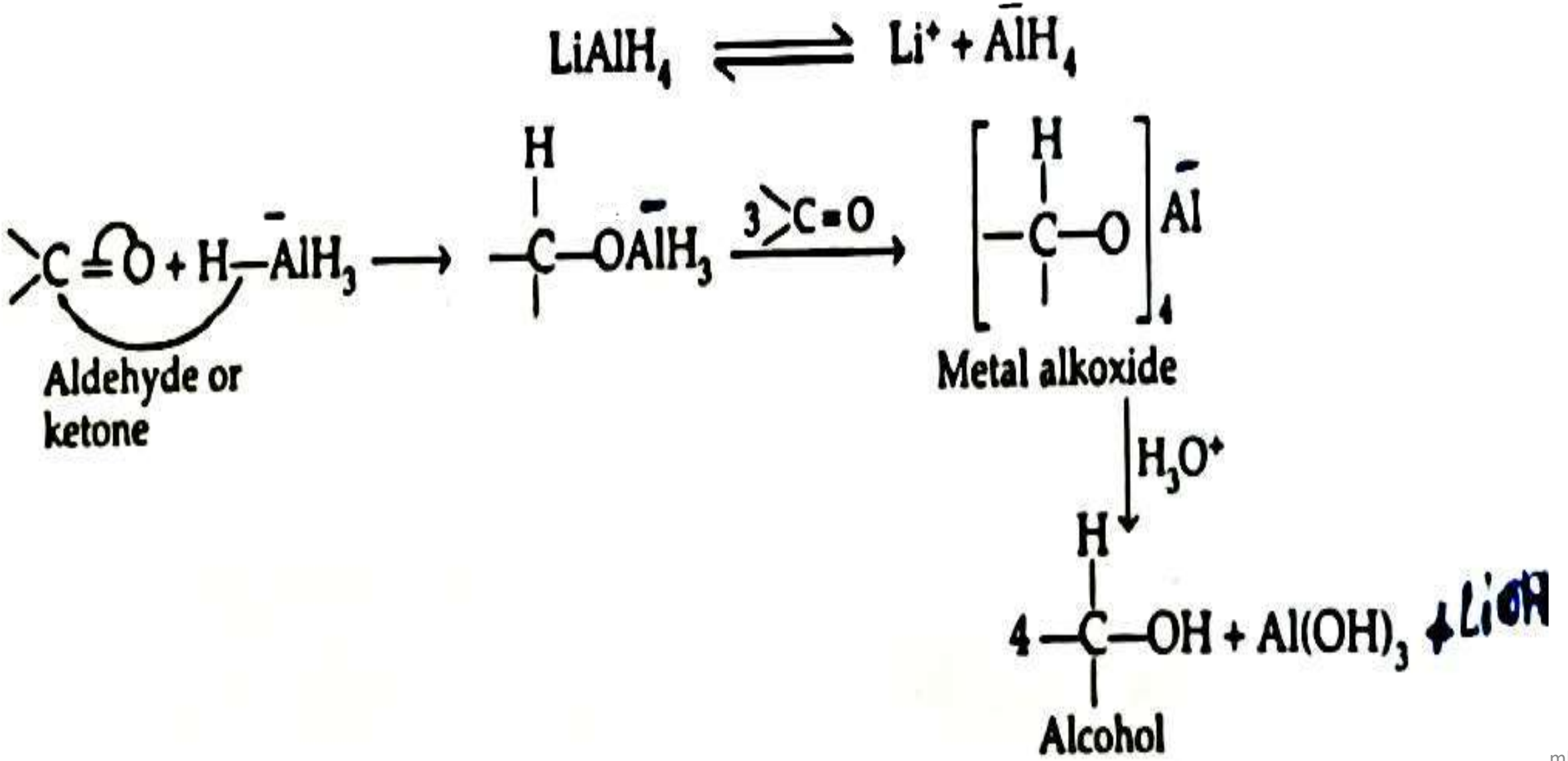
Methods of preparation of alcohols

Mechanism of reduction with Sodium borohydride



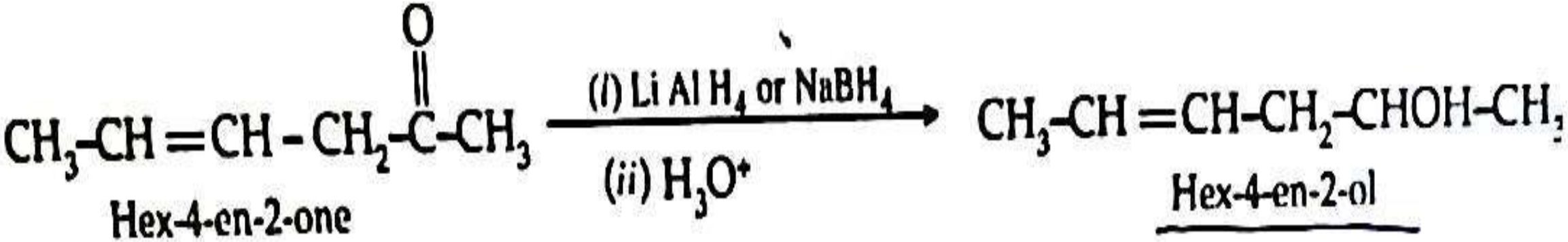
Methods of preparation of alcohols

Mechanism of reduction with Lithium Aluminium hydride



Methods of preparation of alcohols

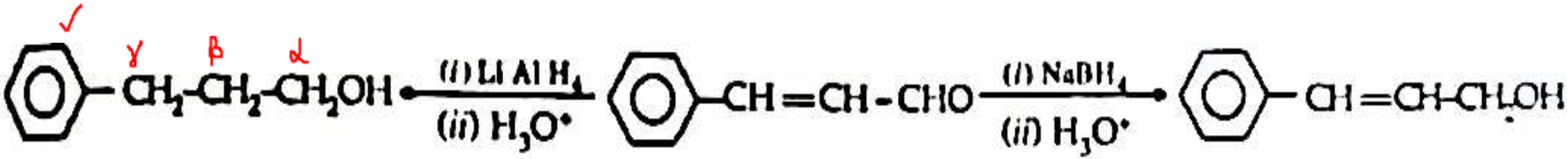
- **Selectivity**
  - **Both are selective…….Isolated double bonds are not reduced**



Hex-4-en-2-one

Hex-4-en-2-ol

  - **$NaBH_4$ is less reactive and more selective……..Conjugated double bond is not reduced by $NaBH_4$ but is reduced by $LiAlH_4$**



γ-Phenylpropyl alcohol (Carbon-carbon double bond is also reduced)

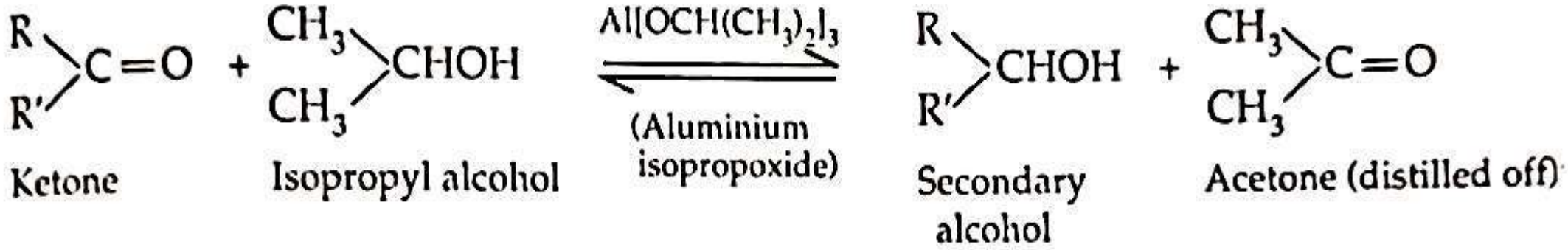
Cinnamaldehyde

Cinnamyl alcohol (Carbon-carbon double bond is not reduced)

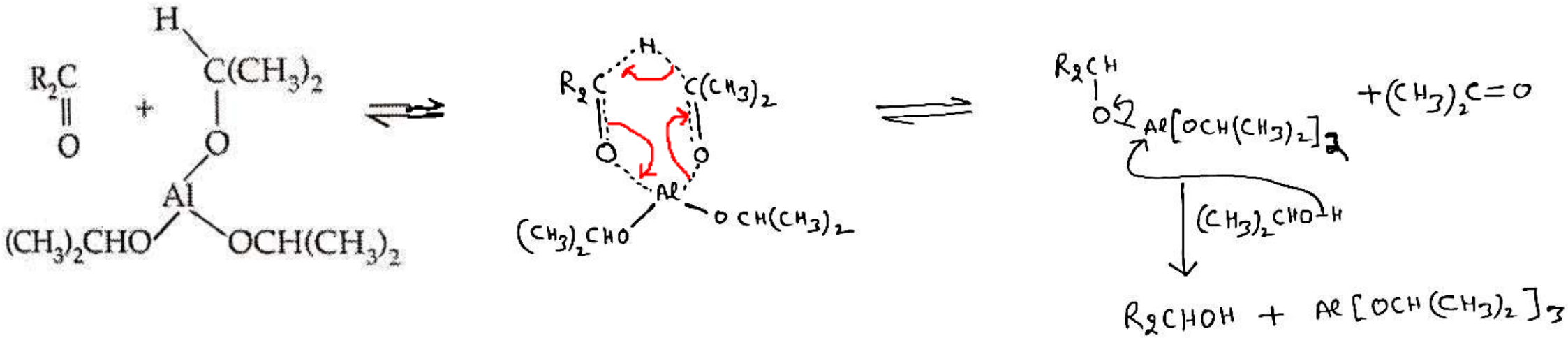
Methods of preparation of alcohols

C. Meerwein-Ponndorf-Verley Reduction

- Ketones are selectively reduced to secondary alcohols



- Mechanism

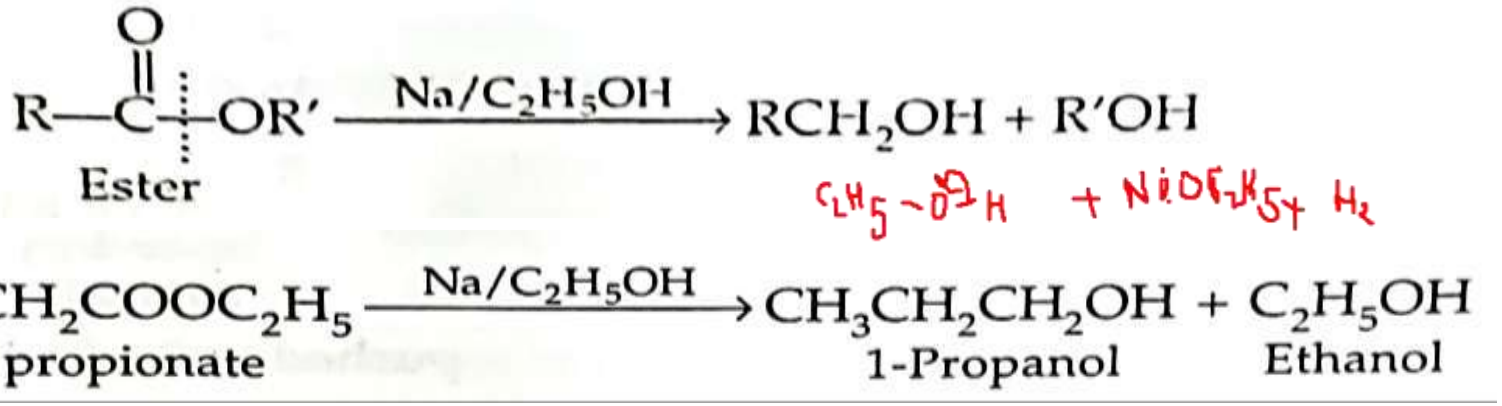


Methods of preparation of alcohols

2. By reduction of esters

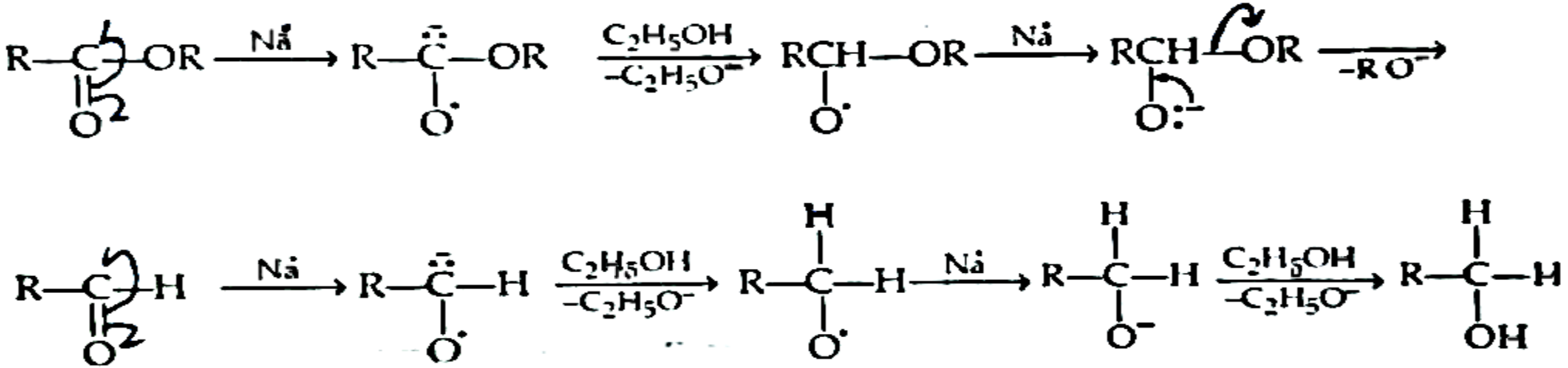
a. Bouveault-Blanc reduction

- Mixture of alcohols is formed, one from acyl group and other from alkoxyl group



❖ Mechanism

- It involves electron transfer from sodium metal and abstraction of proton from ethanol successively

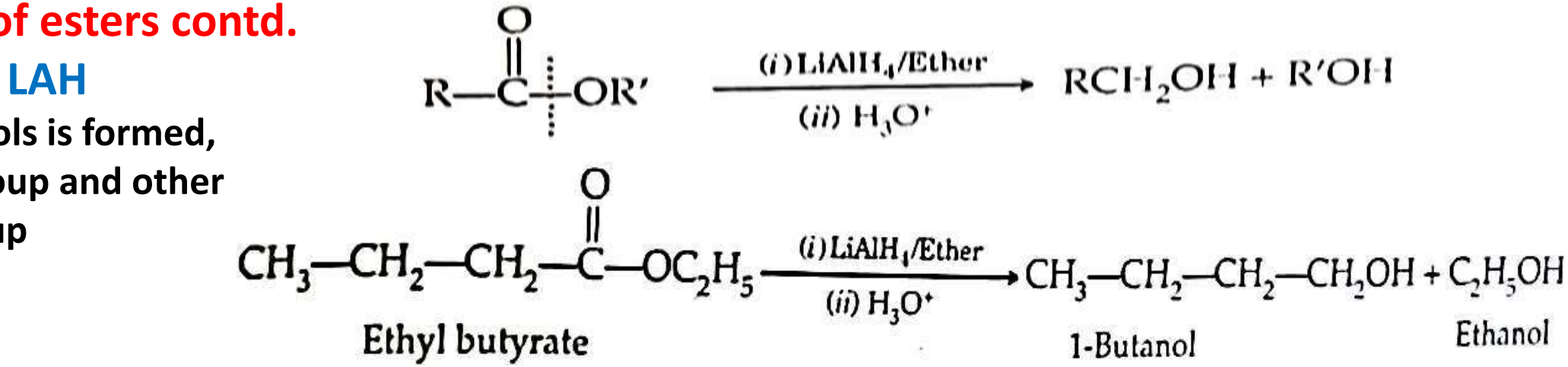


Methods of preparation of alcohols

2. By reduction of esters contd.

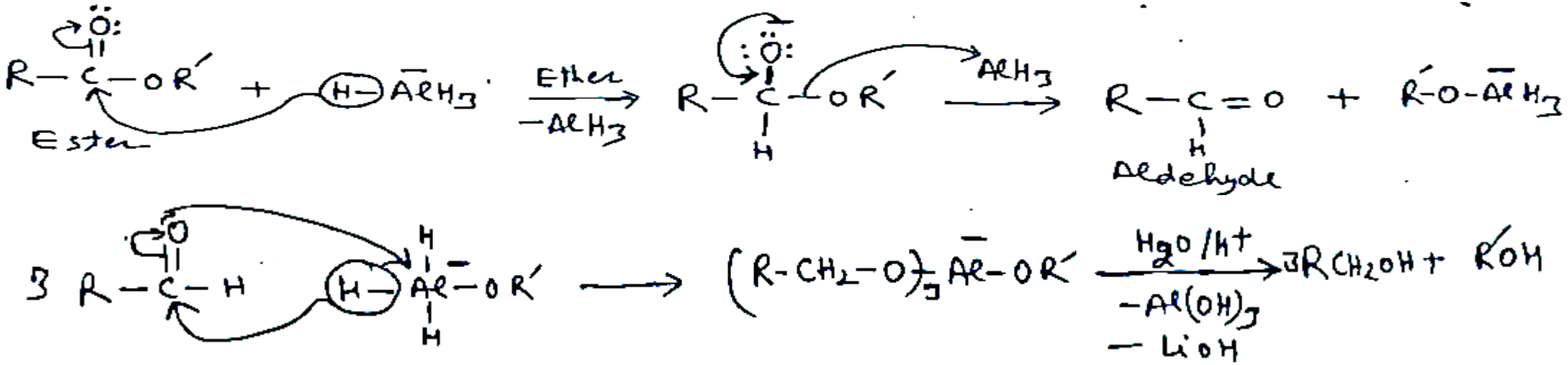
b. Reduction with LAH

- Mixture of alcohols is formed, one from acyl group and other from alkoxyl group



❖ Mechanism

- It involves attack of hydride ion on carbonyl group followed by release of alkoxide ion to give aldehyde which is further reduced to give alcohol successively

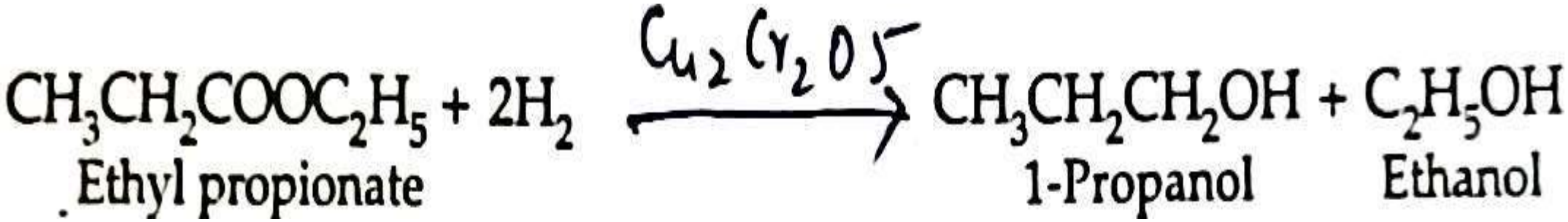


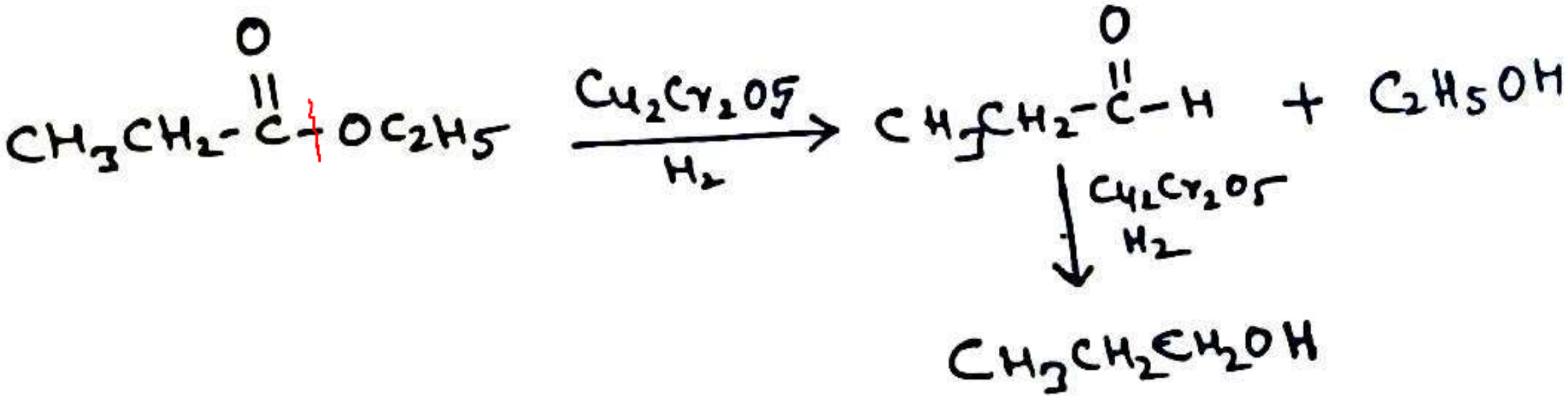
Methods of preparation of alcohols

2. By reduction of esters contd.

c. By catalytic hydrogenation under high temperature and pressure

- **Production on industrial scale**

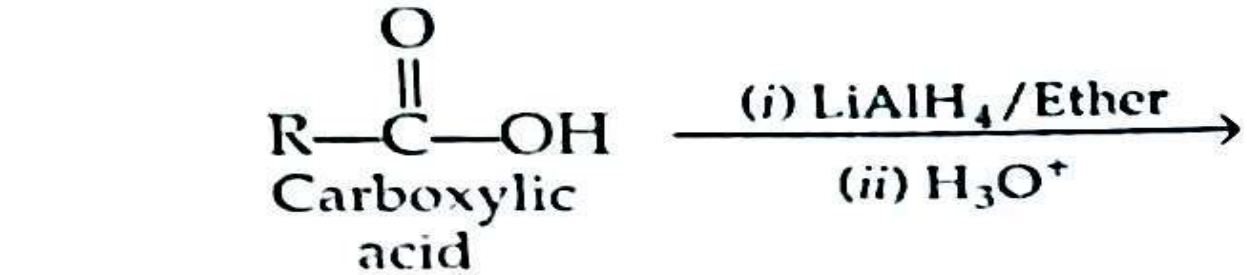


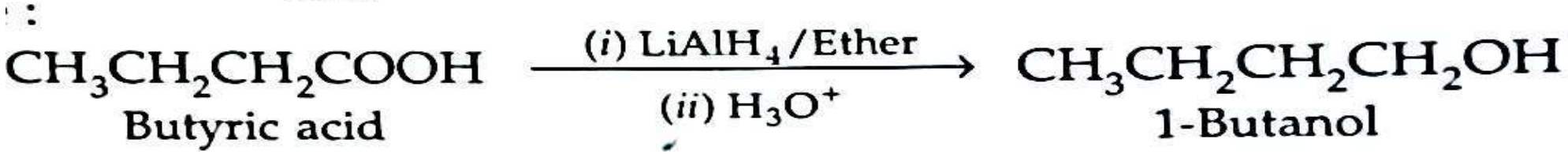


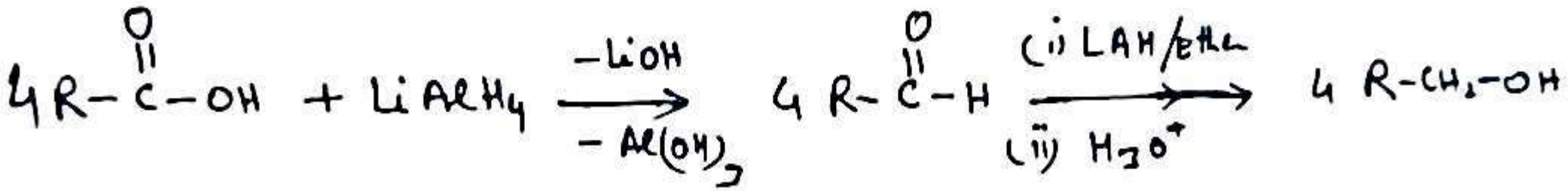
Methods of preparation of alcohols

3. By reduction of carboxylic acids

- **Reduction with LAH**



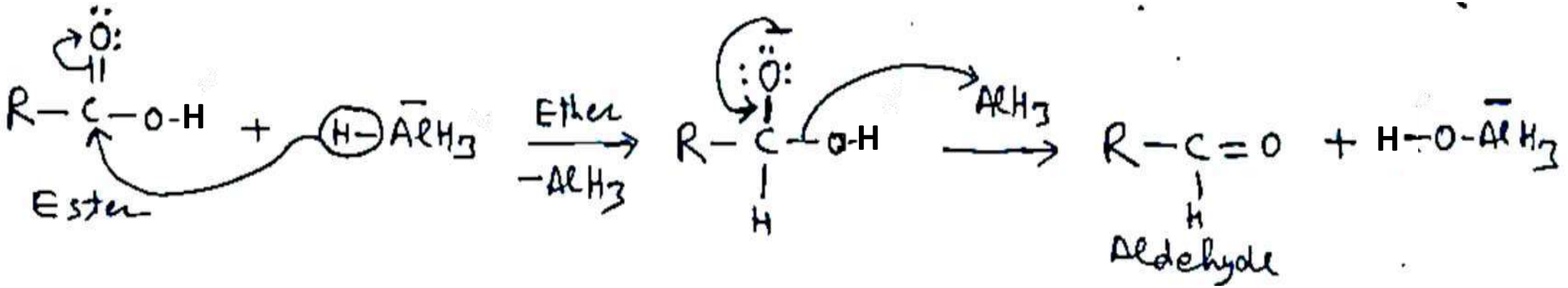


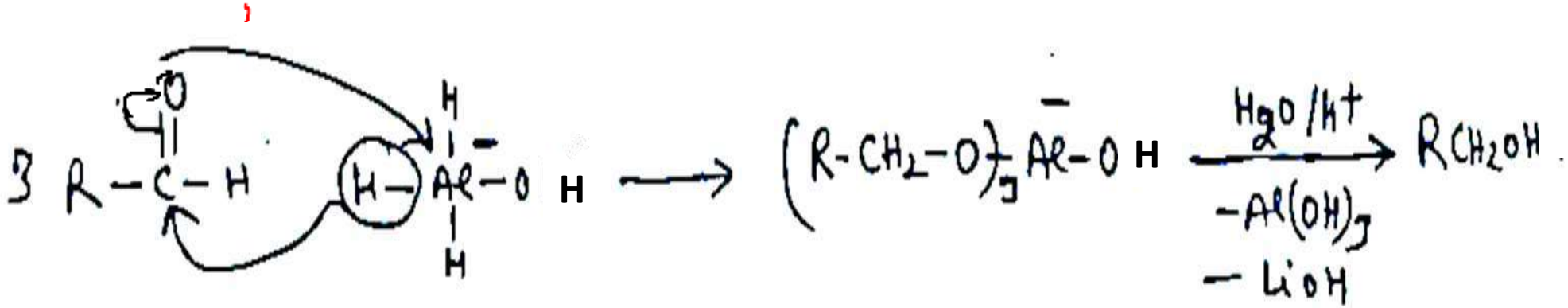


Methods of preparation of alcohols

3. By reduction of carboxylic acids contd.

➢ **Mechanism of Reduction with LAH**

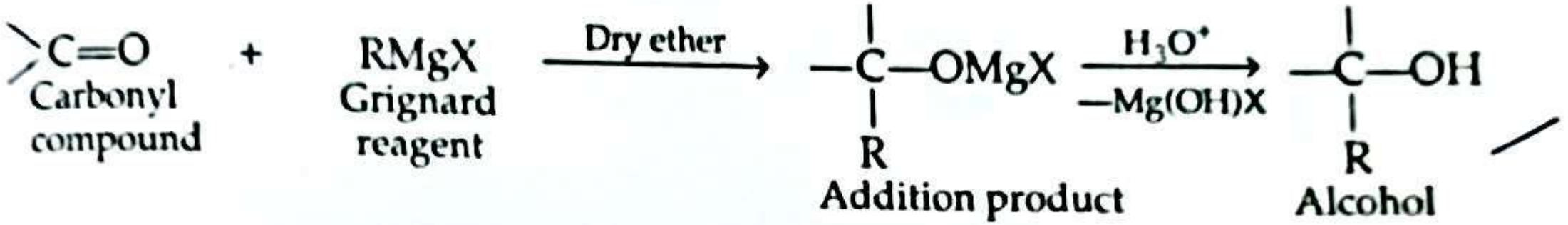


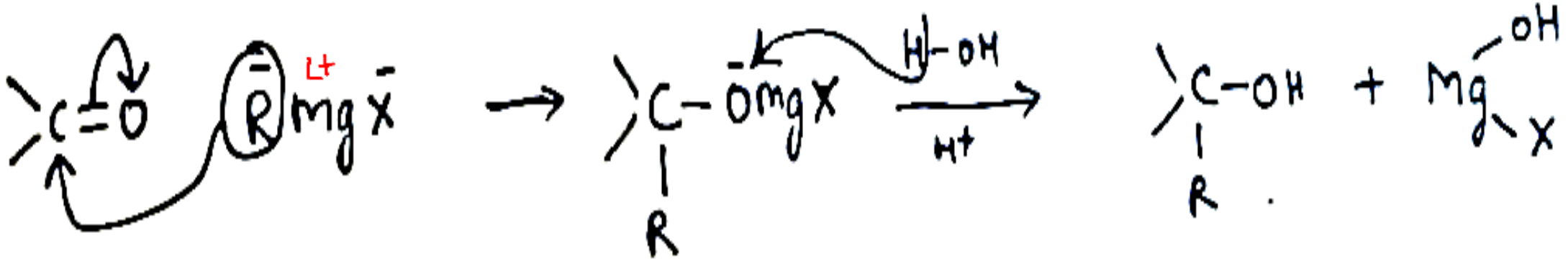


Methods of preparation of alcohols

4. Grignard Synthesis

- Carbonyl compounds can be converted in to 1°, 2° & 3° alcohols

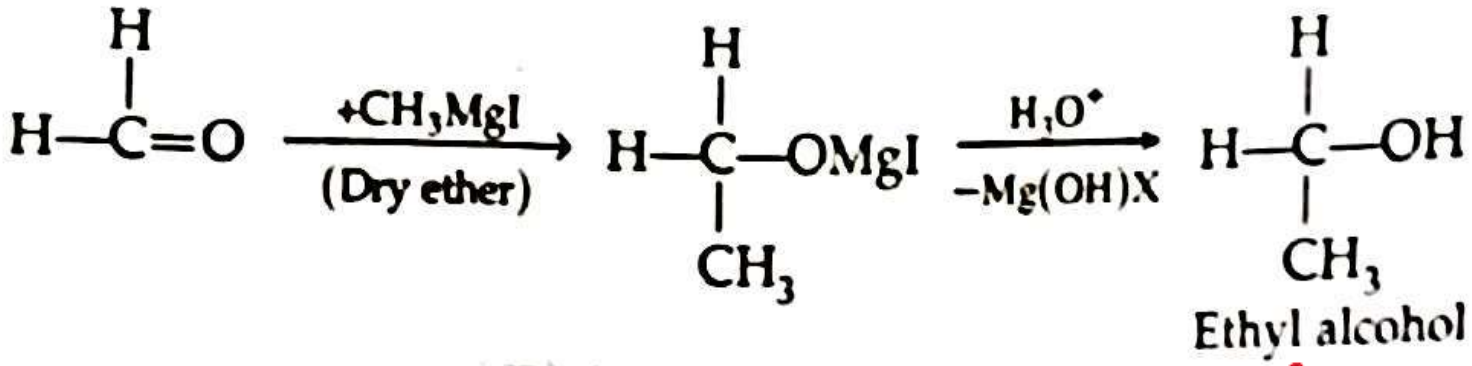




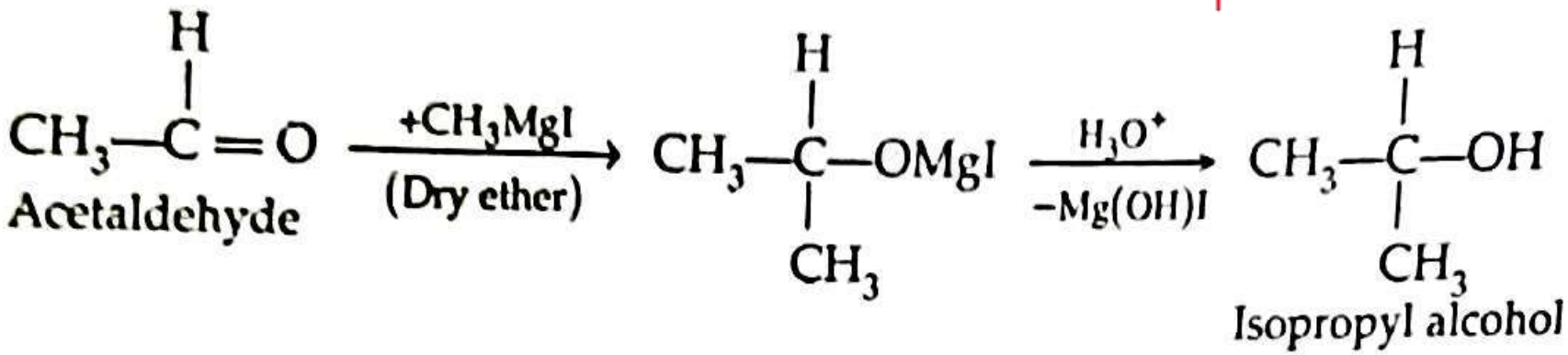
Methods of preparation of alcohols

4. Grignard Synthesis contd.

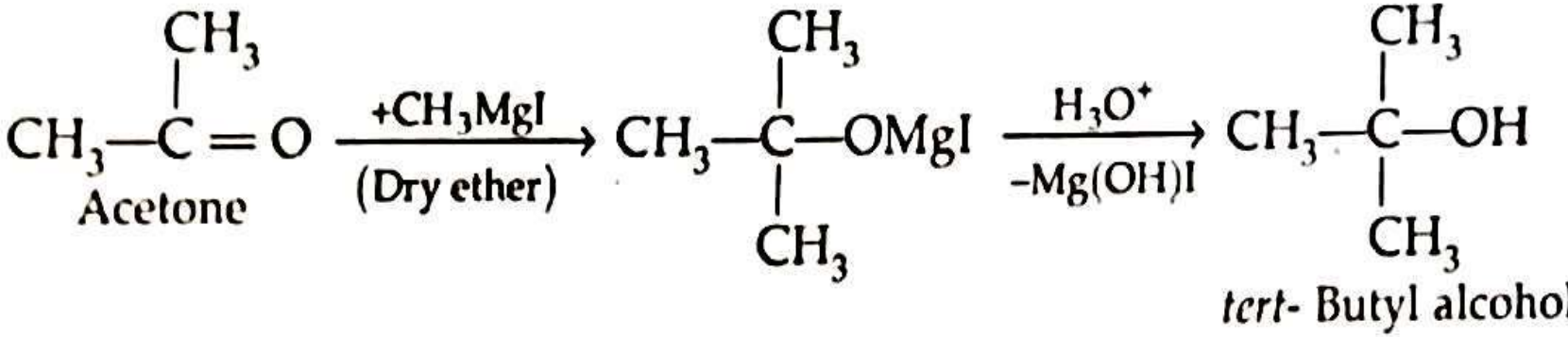
- Formaldehyde is converted in to primary alcohol



- Higher aldehydes are converted in to secondary alcohols



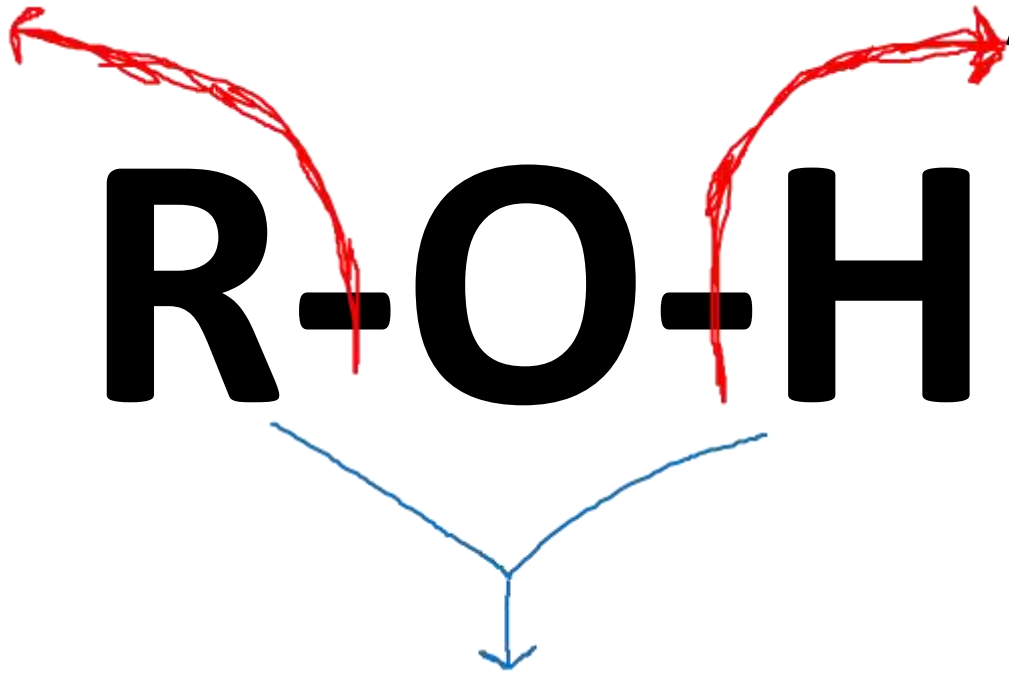
- Ketones are converted in to tertiary alcohols



Chemical properties of alcohols

- **Chemical reactions can be divided in to three categories**

B. Reactions in which R-OH bond breaks

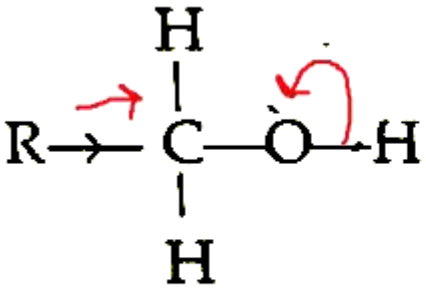


A. Reactions in which RO-H bond breaks

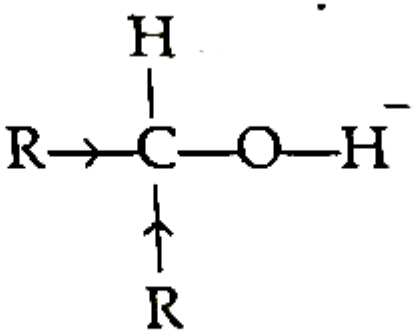
C. Reactions which involve both R & OH groups

Chemical properties of alcohols

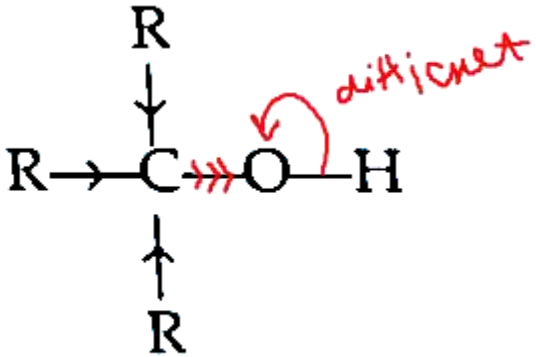
- **Type A reactions**
  - **Order of reactivity**
    - **Primary alcohol > Secondary alcohol > Tertiary alcohol**
    - **It is due to Positive inductive effect of alkyl groups. +I effect of alkyl groups increases electron density on oxygen atom so ease of shift of electron pair of O-H bond on to oxygen atom decreases**



Primary alcohol



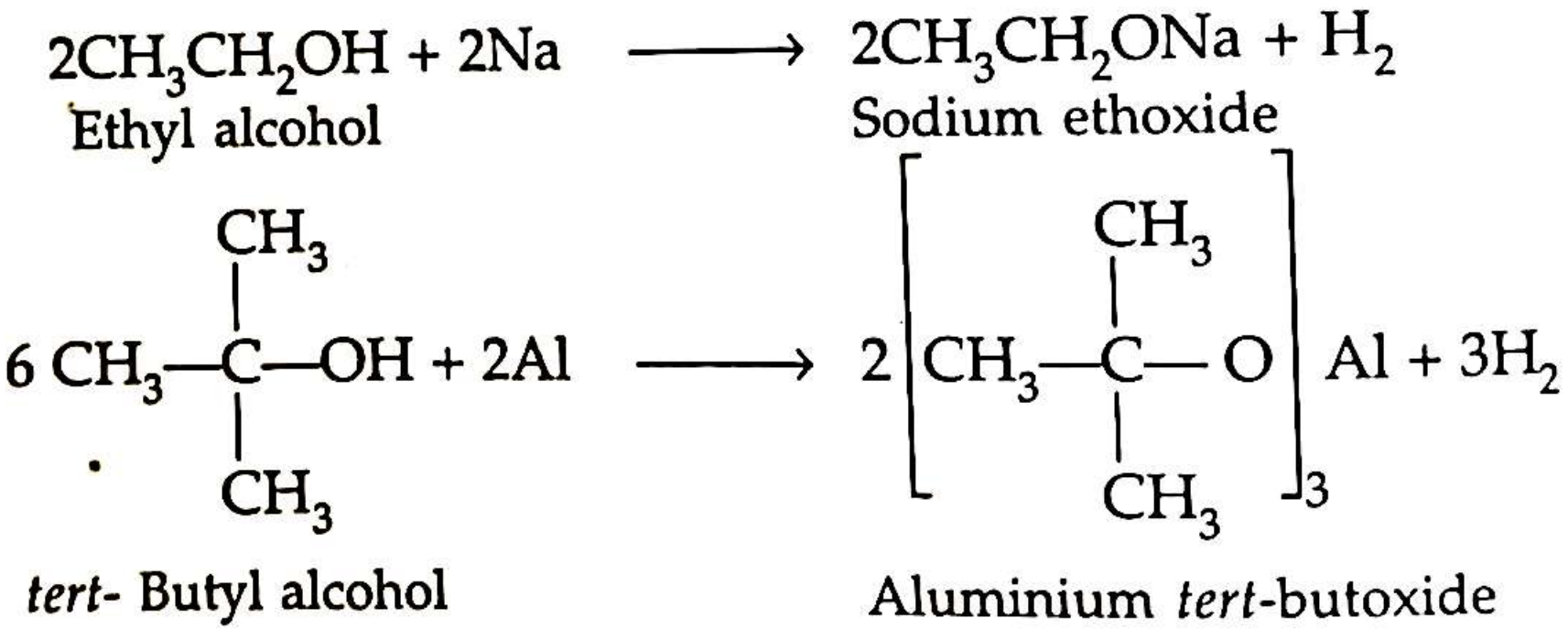
Secondary alcohol



Tertiary alcohol

Chemical properties of alcohols

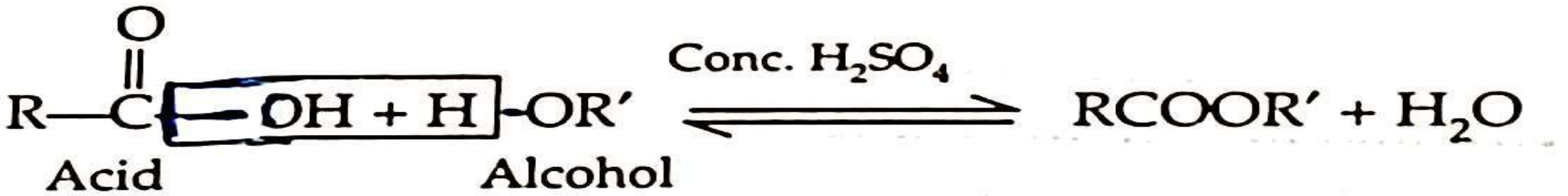
- **Type A reactions contd.**
  - **Acidic nature: Reaction with metals**
    - **2RO- H + 2M → 2ROM + H_2 (M can be Na, K, Mg, Al etc.)**

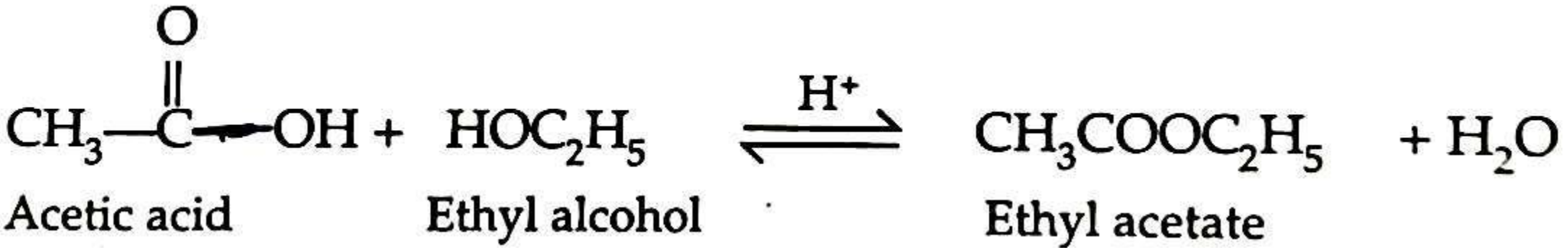


- **Very weak acids**
- **Order of acidic strength** $1^o > 2^o > 3^o$

Chemical properties of alcohols

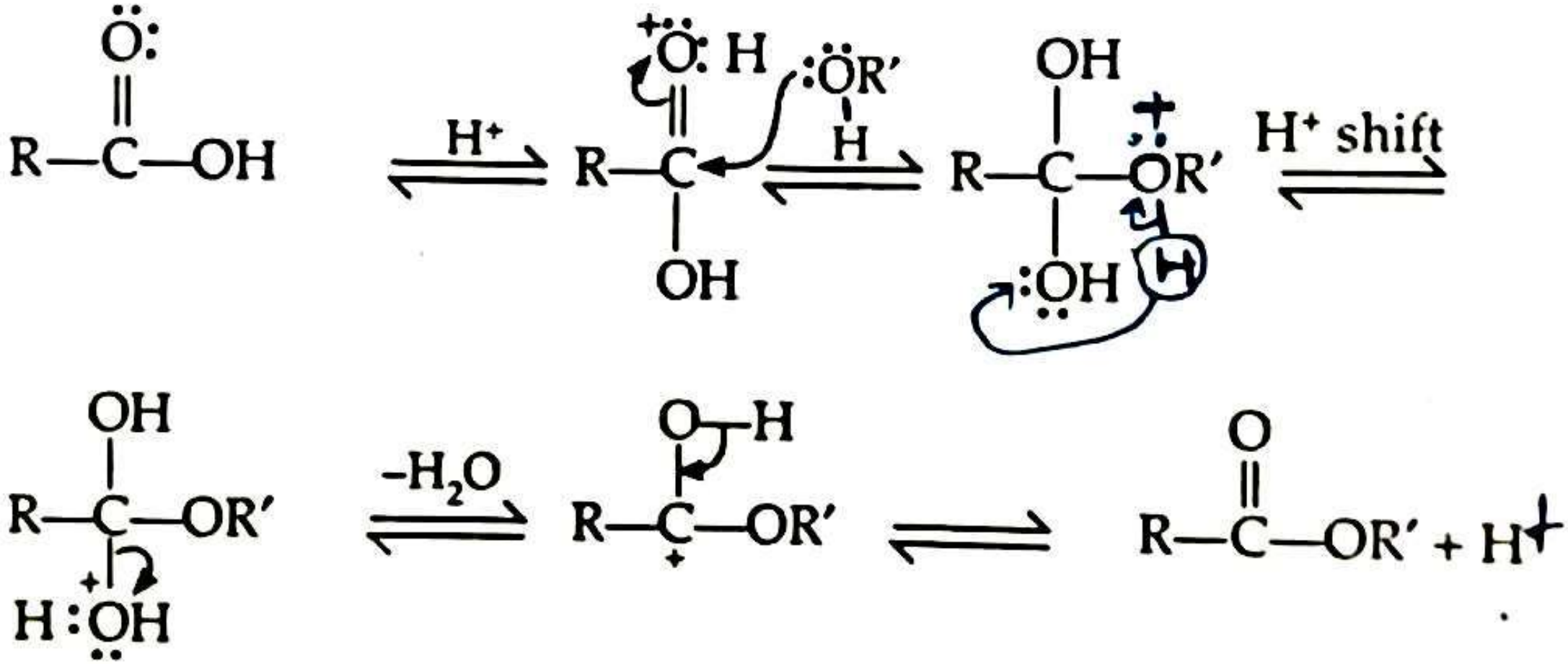
- **Type A reactions contd.**
  - **Reaction with organic acids (Esterification reaction)**





Chemical properties of alcohols

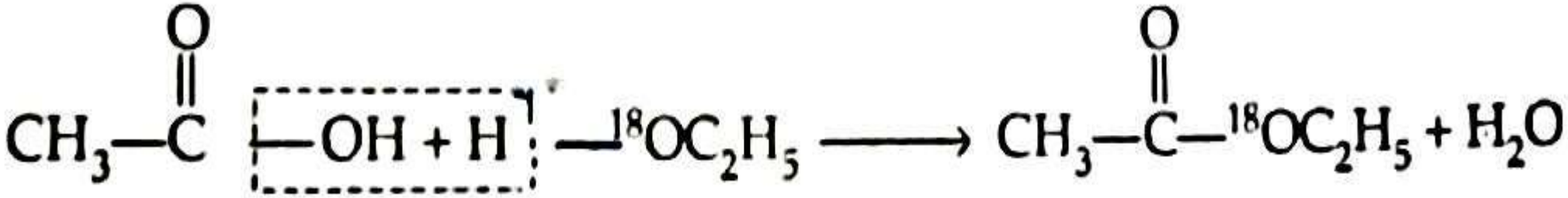
❑ Mechanism of esterification reaction



Chemical properties of alcohols

❑ Mechanism of esterification reaction contd.

- **Evidence for mechanism (Isotopic tracer studies)**



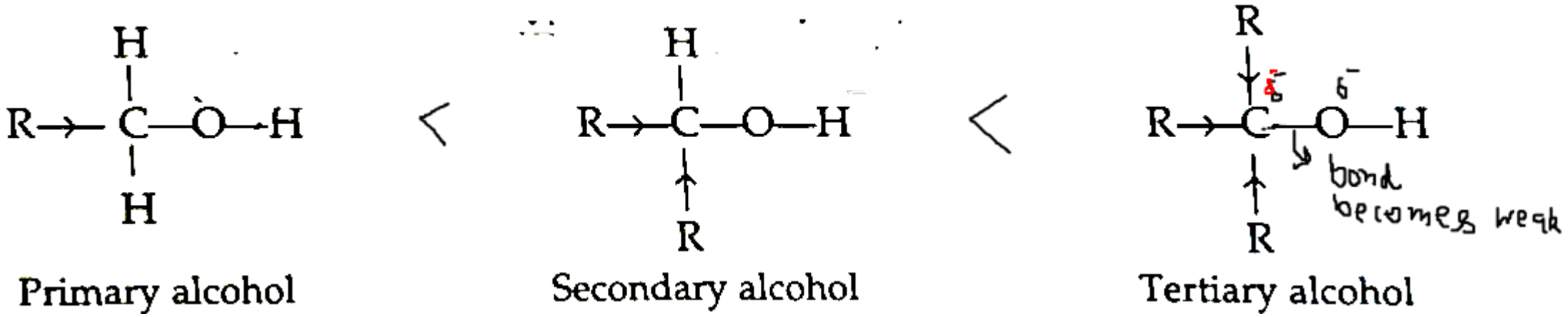
- **If we take isotopically labelled ethyl alcohol & react it with acetic acid, O^{18} isotope goes in to ester which proves that H comes from ethyl alcohol and OH comes from acetic acid in H_2O . So there is cleavage of RO-H bond during esterification reaction**

Chemical properties of alcohols

❑ Type B reactions (involving cleavage of C-OH bond)

❖ Order of reactivity

➢ **Tertiary alcohols > Secondary alcohols > Primary alcohols**



➢ **Electron releasing alkyl groups increase electron density on C and O atoms. So the C-O bond gets elongated and is weakened and its cleavage becomes easy. Hence greater is the number of alkyl groups greater is reactivity of alcohol.**

Chemical properties of alcohols

❑ Reaction with hydrogen halides

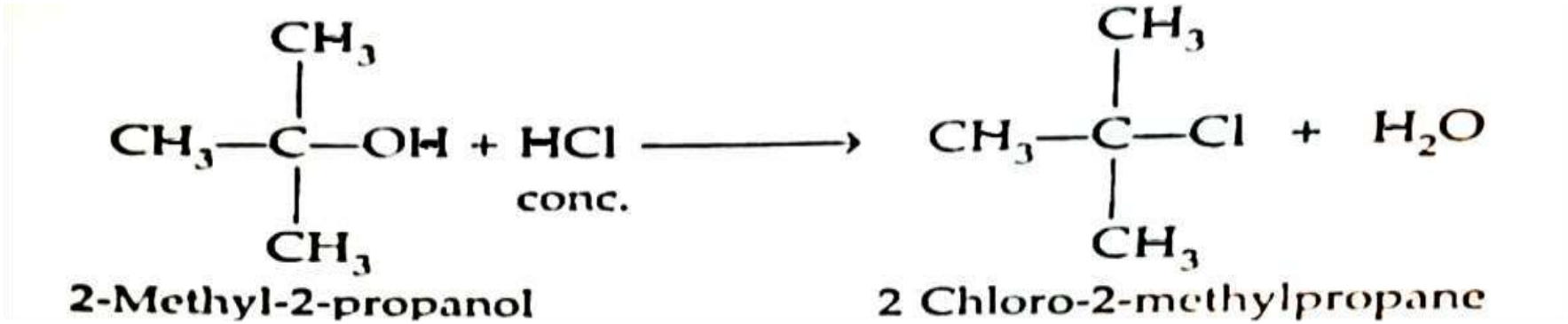
➢ **ROH + HX → RX + H_2O**

$$CH_3{-}CH_2OH + HCl\ (g) \xrightarrow{\text{Anhyd. } ZnCl_2} CH_3{-}CH_2Cl + H_2O$$

Ethanol — Chloroethane

$$CH_3{-}CHOH{-}CH_3 + HCl\ (g) \xrightarrow{\text{Anhyd. } ZnCl_2} CH_3{-}CHCl{-}CH_3 + H_2O$$

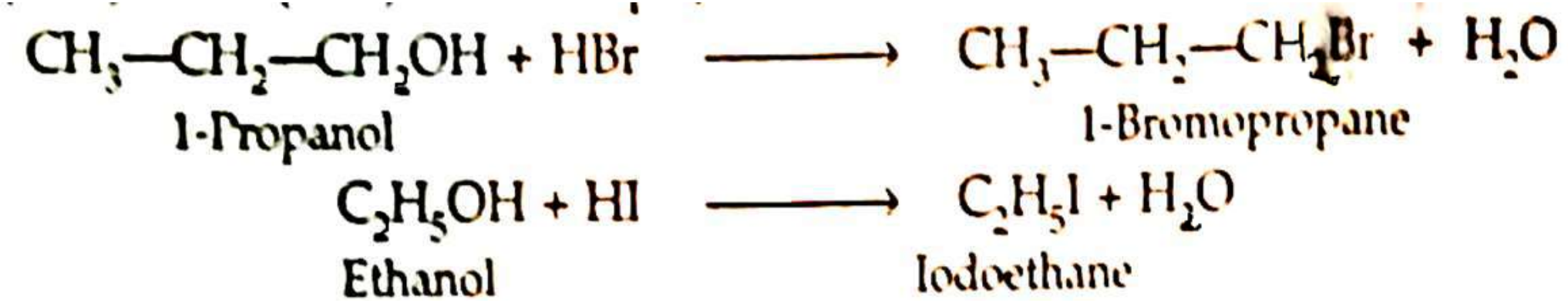
2 Propanol — 2-Chloropropane

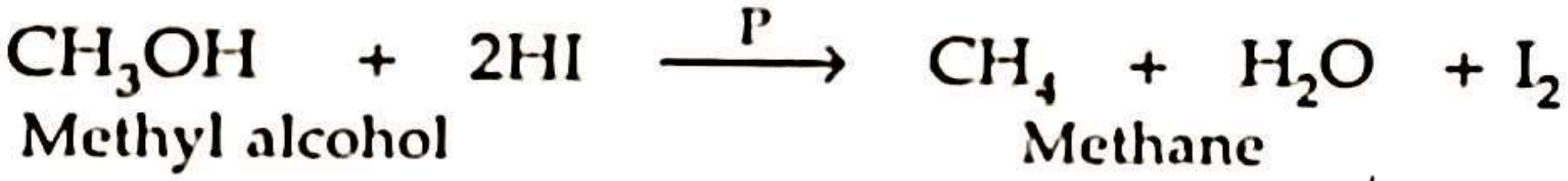


2-Methyl-2-propanol — 2 Chloro-2-methylpropane

Chemical properties of alcohols

- **Reaction with hydrogen halides contd.**





$2HI \rightarrow H_2 + I_2$

Chemical properties of alcohols

❑ Reaction with hydrogen halides contd.

❖ SN1 type mechanism

(*i*) $R-\ddot{O}H + HX \rightleftharpoons R-\overset{+}{\ddot{O}}H_2 + X^-$

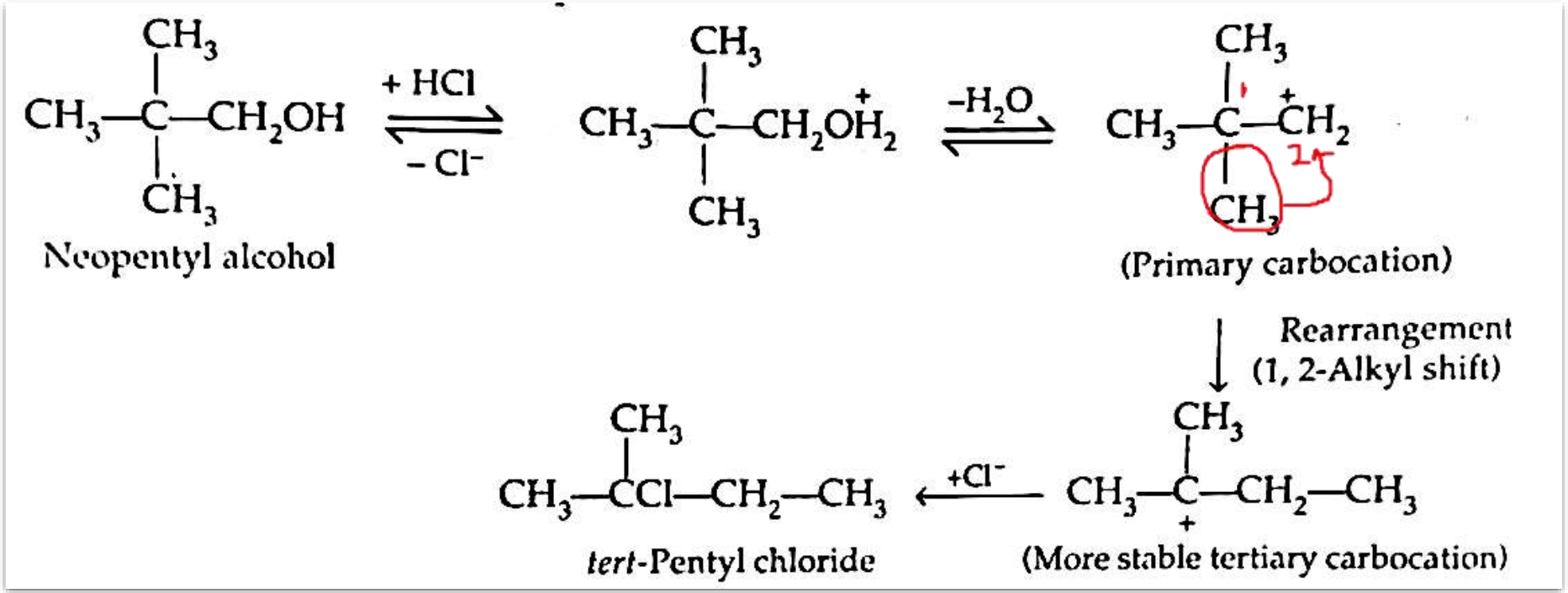
Protonated alcohol or Oxonium ion

(*ii*) $R-\overset{+}{\ddot{O}}H_2 \xrightleftharpoons{\text{Slow}} R^+ + H_2O$

Carbocation

(*iii*) $R^+ + X^- \longrightarrow RX$

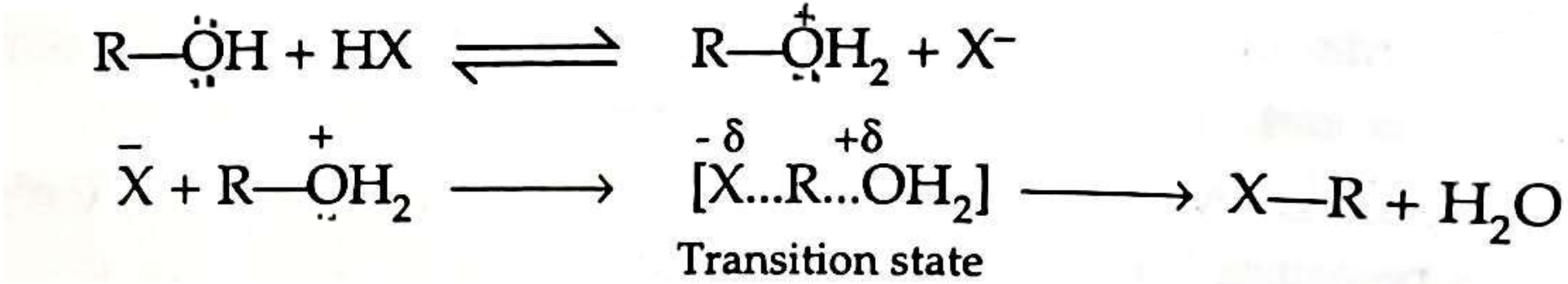
❖ Evidence



Chemical properties of alcohols

❑ Reaction with hydrogen halide contd.

❖ SN2 type mechanism



Chemical properties of alcohols

- **Distinction between 1°, 2° & 3° alcohols (Lucas Test)**
  - Based upon different reactivity of 1°, 2° & 3° alcohols
  - Given alcohol is reacted with equimolar mixture of conc. HCl and anhydrous $ZnCl_2$(Lucas reagent)
  - During reaction alkyl chloride is formed which causes cloudiness
  - ✓ If cloudiness appears immediately……indicates 3° alcohol
  - ✓ If cloudiness appears after 5 minutes……indicates 2° alcohol
  - ✓ If cloudiness does not appear at room temperature……indicates 1° alcohol

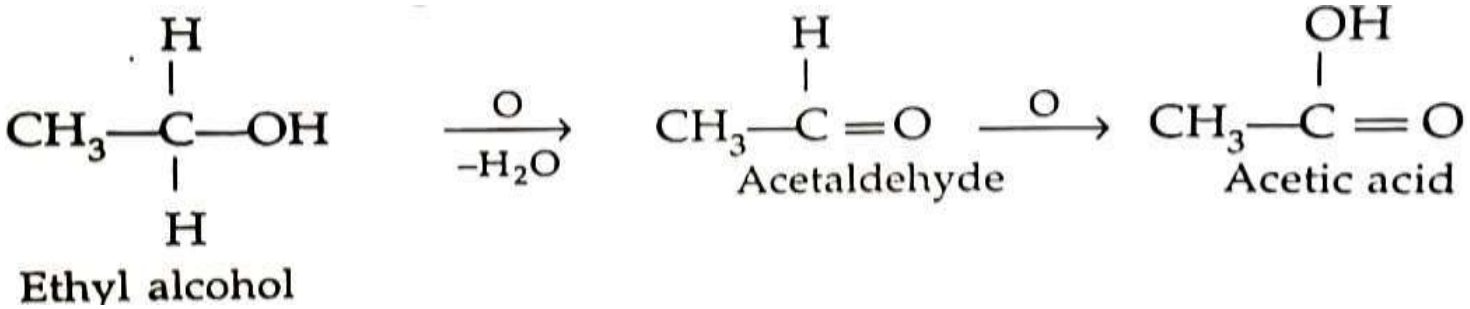
Primary alcohol	*Secondary alcohol*	*Tertiary alcohol*
RCH_2OH	R_2CHOH	$R_3C—OH$
$\xrightarrow{HCl/ZnCl_2}$	$\xrightarrow{HCl/ZnCl_2}$	$\xrightarrow{HCl/ZnCl_2}$
$RCH_2Cl + H_2O$	$R_2CHCl + H_2O$	$R_3C—Cl + H_2O$
No cloudiness at room temperature	*Cloudiness within five minutes*	*Cloudiness appears immediately*

Chemical properties of alcohols

❑ Type C reactions(Involving both R & OH groups)

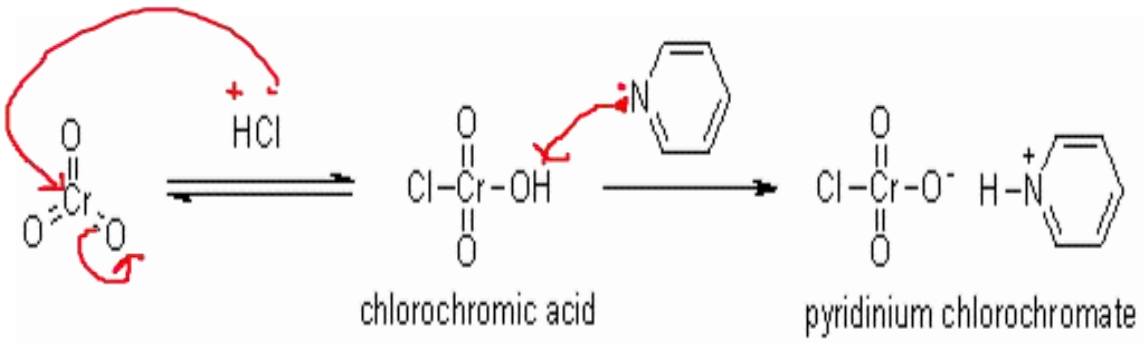
❖ Oxidation

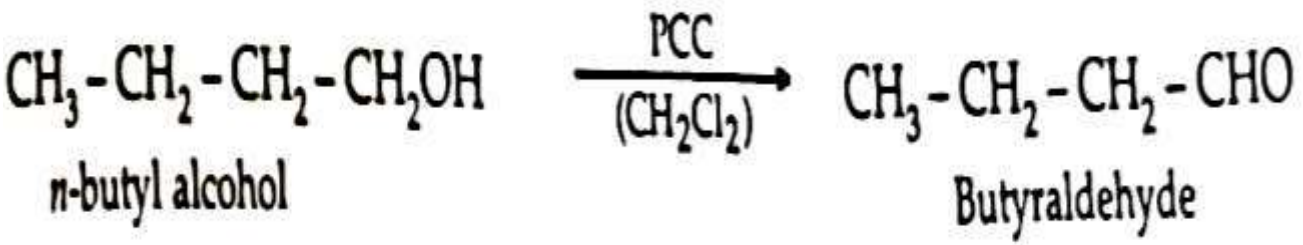
- Can be done with oxidising agents such as aqueous, alkaline or acidified $KMnO_4$, Acidified $K_2Cr_2O_7$, dil. HNO_3 or CrO_3 in pyridine
- 1, 2 & 3 alcohols give different products
- Oxidation of 1 alcohols



✓ How to stop the reaction at the aldehyde stage

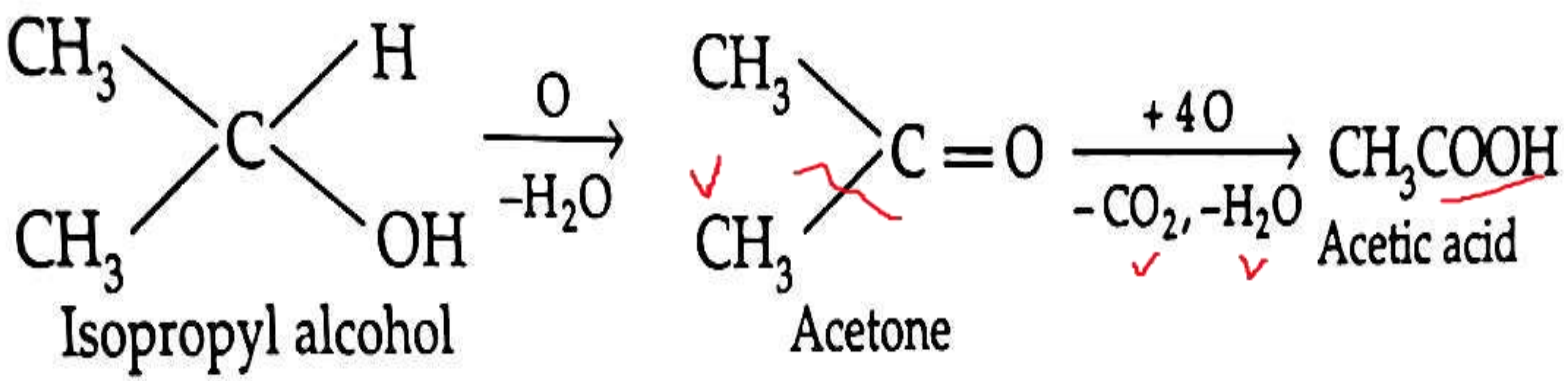
- By distilling off the aldehyde as soon as it is formed
- Or by using Pyridinium chlorochromate (PCC reagent)



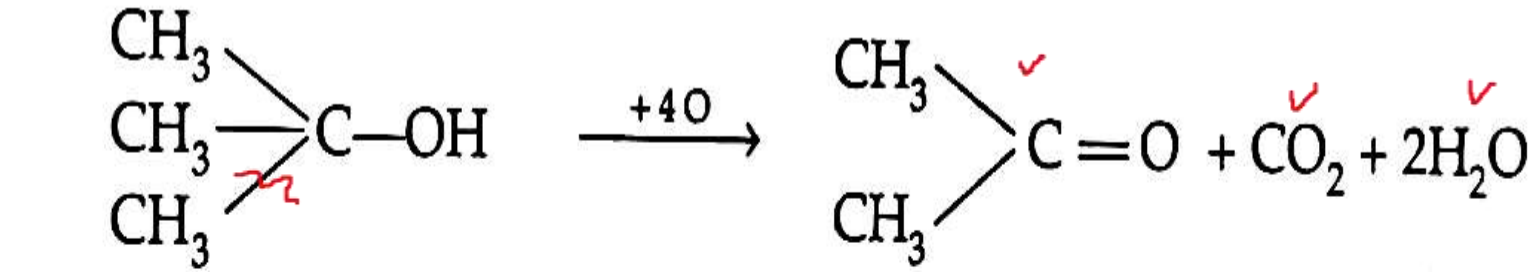


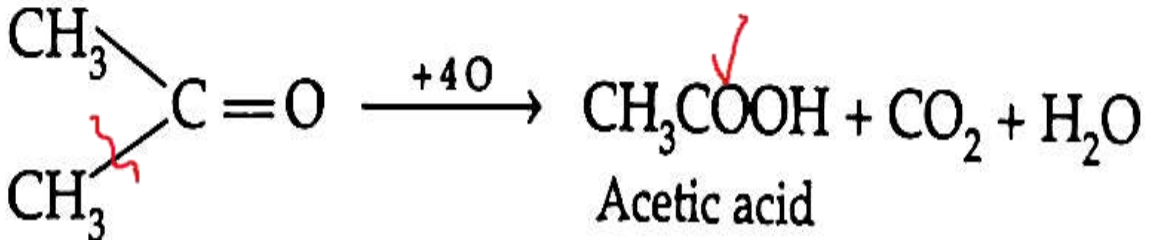
Chemical properties of alcohols

- **Oxidation of secondary alcohols** give ketones which under vigorous conditions give carboxylic acids with lesser number of carbon atoms than starting alcohol



- **Oxidation of tertiary alcohols** takes place with strong oxidising agents to give ketones which further give carboxylic acids with lesser number of carbon atoms than starting alcohol

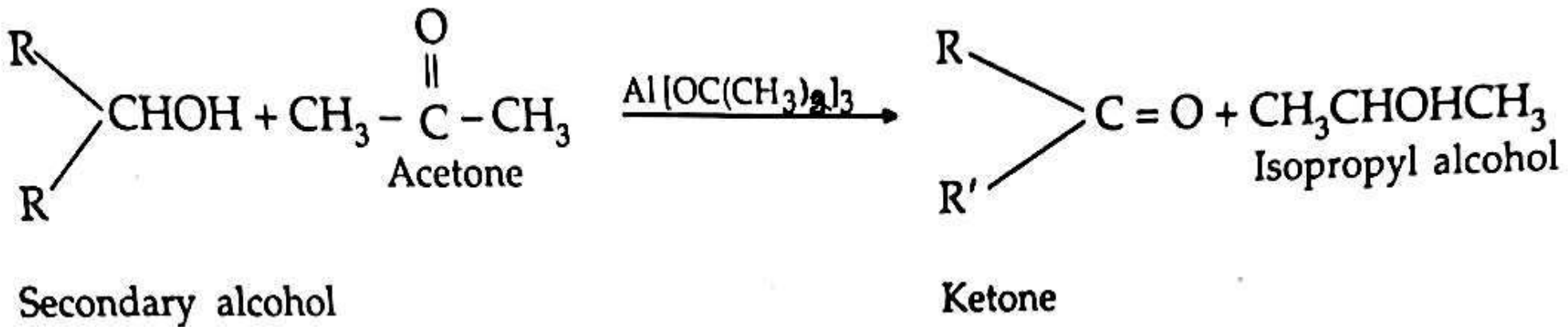




Chemical properties of alcohols

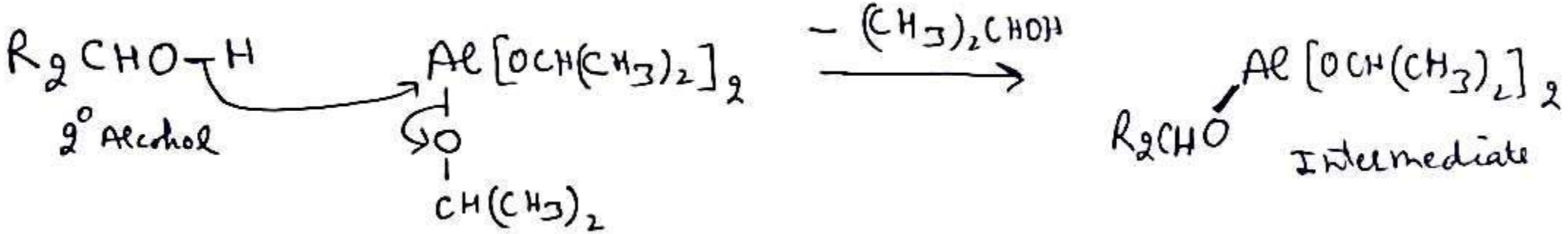
❖ **Oppenauer oxidation**

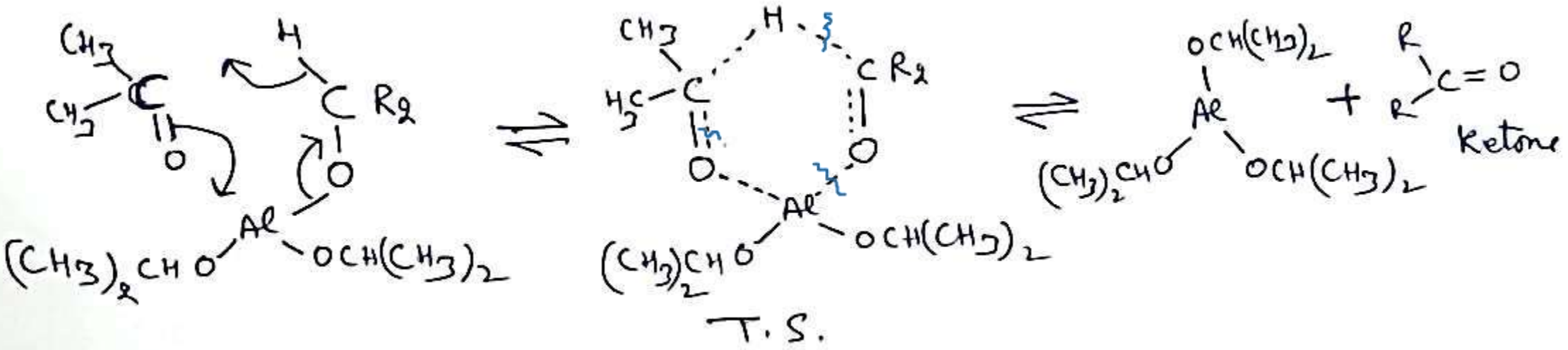
- **By this method secondary alcohols are oxidised to ketones by reaction with acetone in the presence of Aluminium isopropoxide**
- **It is reverse of Meerwein-Ponndorf-Verley Reduction**
- **Particularly useful in the oxidation of unsaturated alcohols (double bond is not affected at all)**



Chemical properties of alcohols

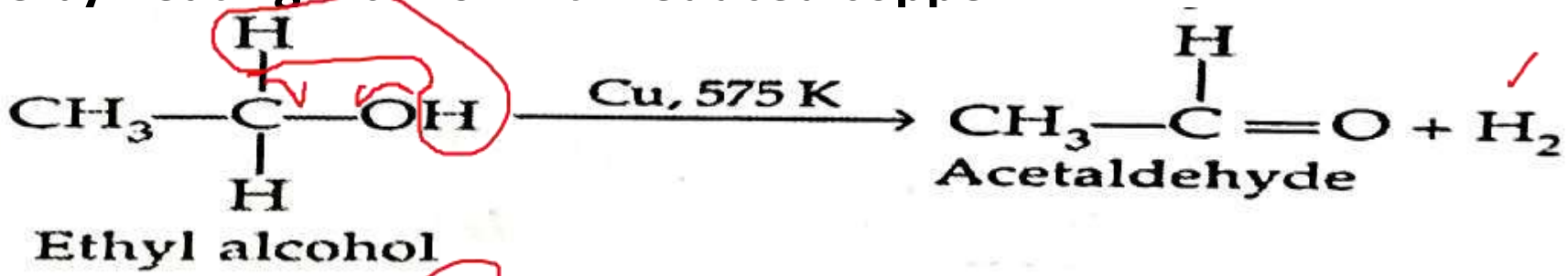
- **Mechanism of Oppenauer oxidation**
- **It is similar to Meerwein-Ponndorf-Verley Reduction**

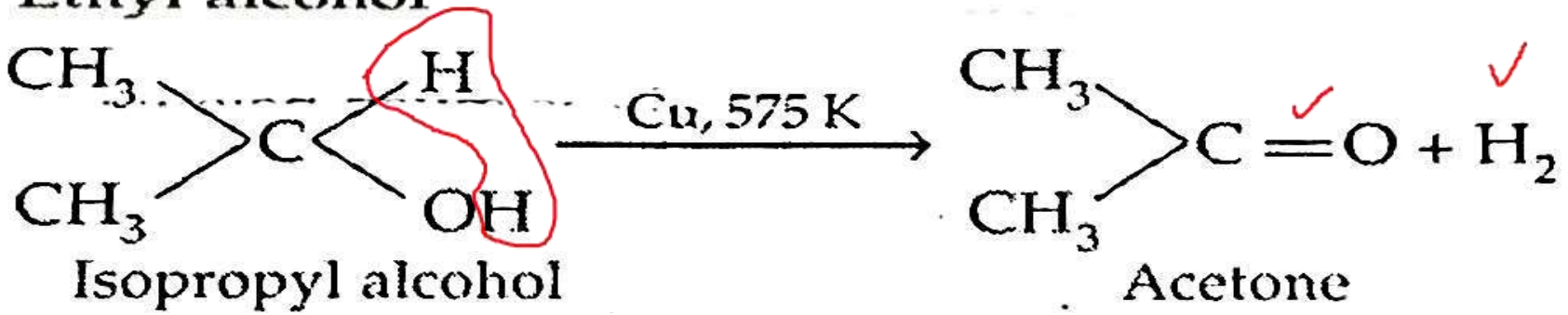


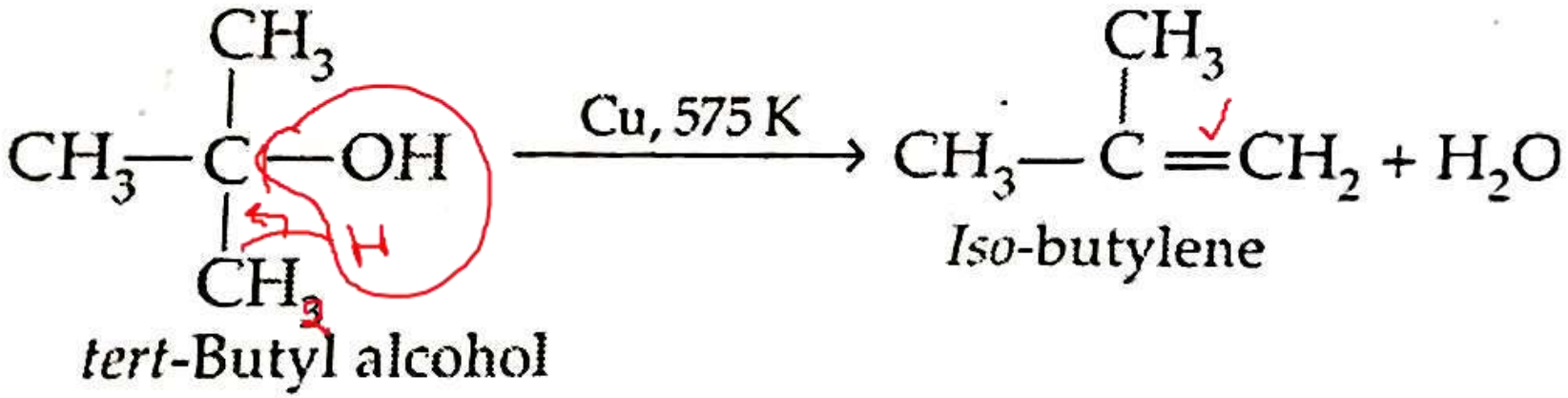


Chemical properties of alcohols

- **Type C reactions(Involving both R & OH groups) contd….**
  - **Dehydrogenation of alcohols**
    - **It is done by heating alcohol with reduced copper**

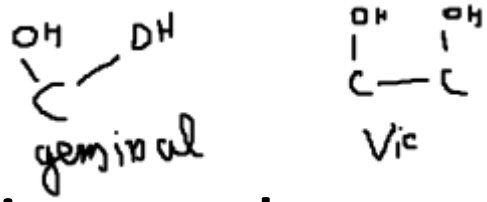


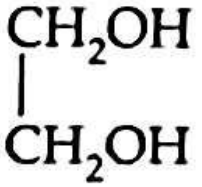




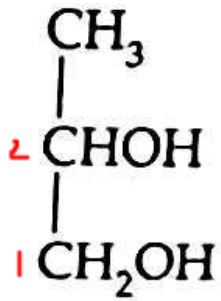
Dihydric alcohols

- **Nomenclature**
  - **Common system**
    - **Known as glycols in common system**
    - **Vicinal glycols if OH groups are present on adjacent carbons**
    - **Polymethylene glycols (If OH groups are not on adjacent carbons and are present on extreme carbons)**



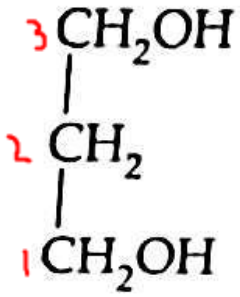


Ethylene glycol



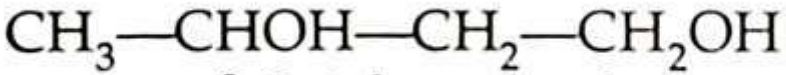
Propylene-1, 2-glycol

Or α-Propylene glycol



Trimethylene glycol

Or β-Propylene glycol

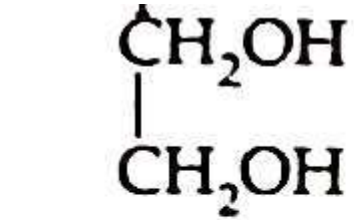


β-Butylene glycol

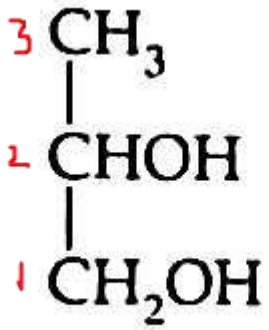
Or Butylene-1,3 - glycol

Dihydric alcohols

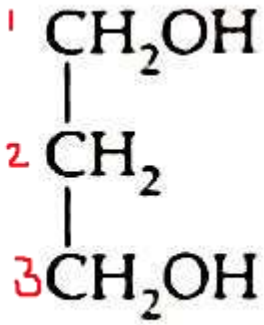
- **Nomenclature**
  - **IUPAC System**
    - **Known as diols in IUPAC system**



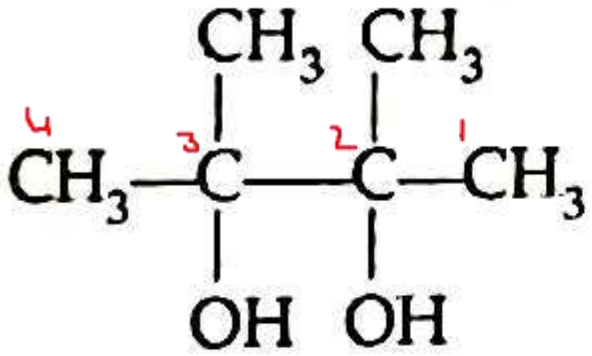
Ethane-1, 2-diol



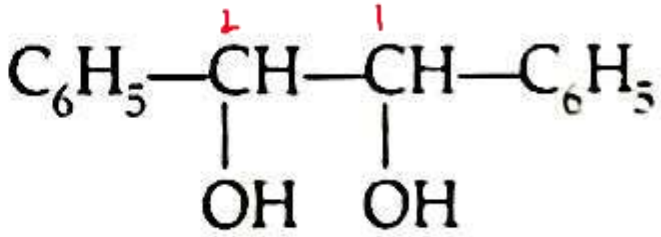
Propane-1, 2-diol



Propane-1, 3-diol



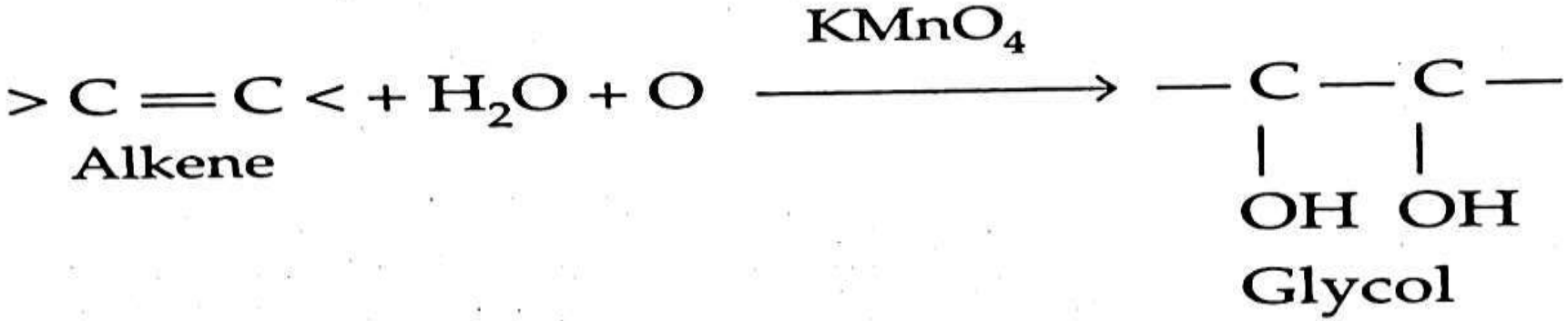
2, 3-Dimethylbutane-2, 3-diol

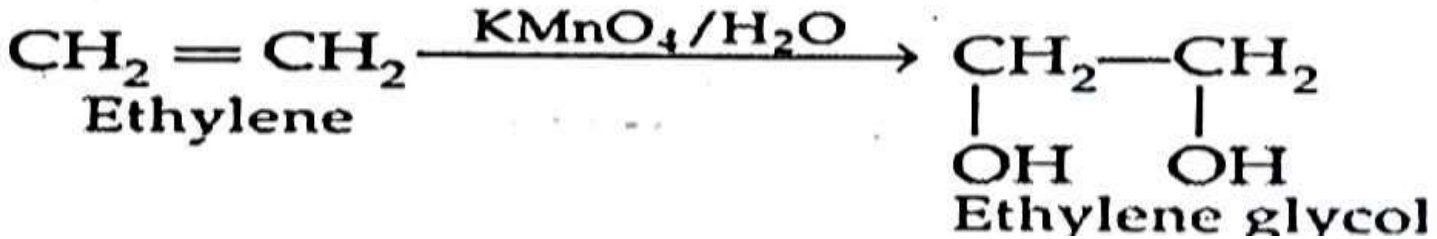


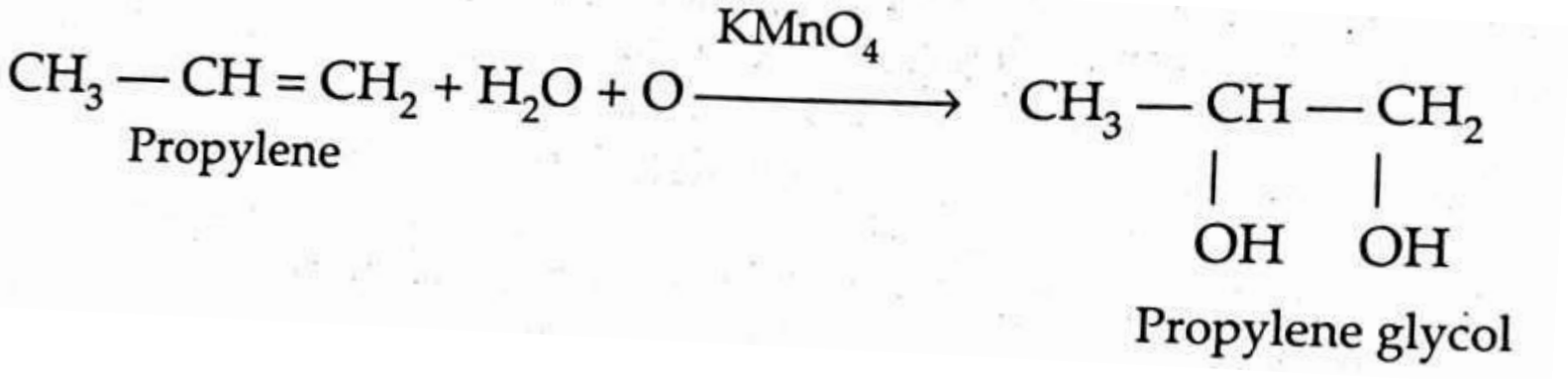
1, 2-Diphenylethane-1, 2-diol

Methods of preparation of Dihydric alcohols

- **By cis hydroxylation of alkenes**

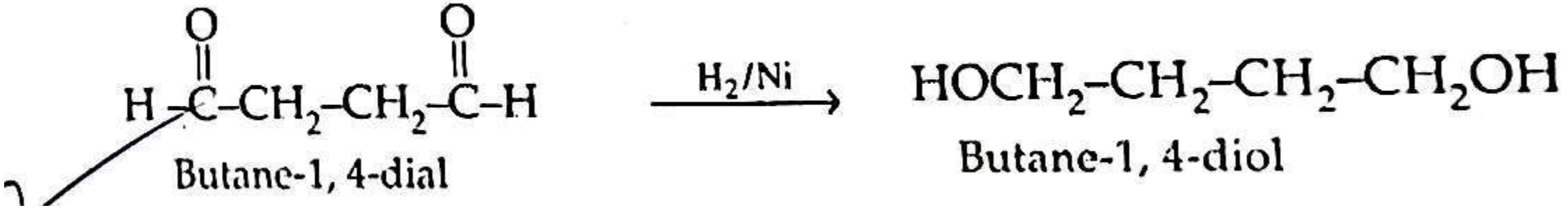




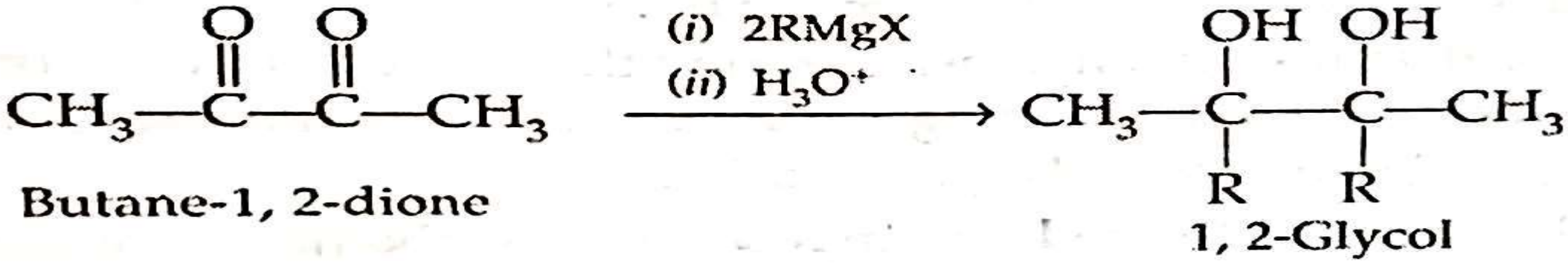


Methods of preparation of Dihydric alcohols

- **By reduction of dicarbonyl compounds**



- **By reaction of diketones with Grignard reagent**



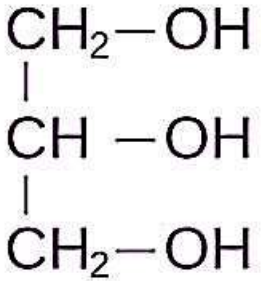
Physical properties of Dihydric alcohols

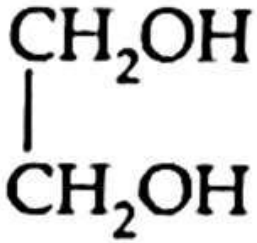
- **Colourless Viscous liquids**
  - Due to greater extent of hydrogen bonding

- **High Melting & Boiling points**
  - Again Due to greater extent of hydrogen bonding

- **Glycols have greater solubility in water as compared to monohydric alcohols**
  - Due to greater extent of hydrogen bond formation between water molecules and glycol molecules

- Glycerol > Ethylene glycol > Ethyl alcohol



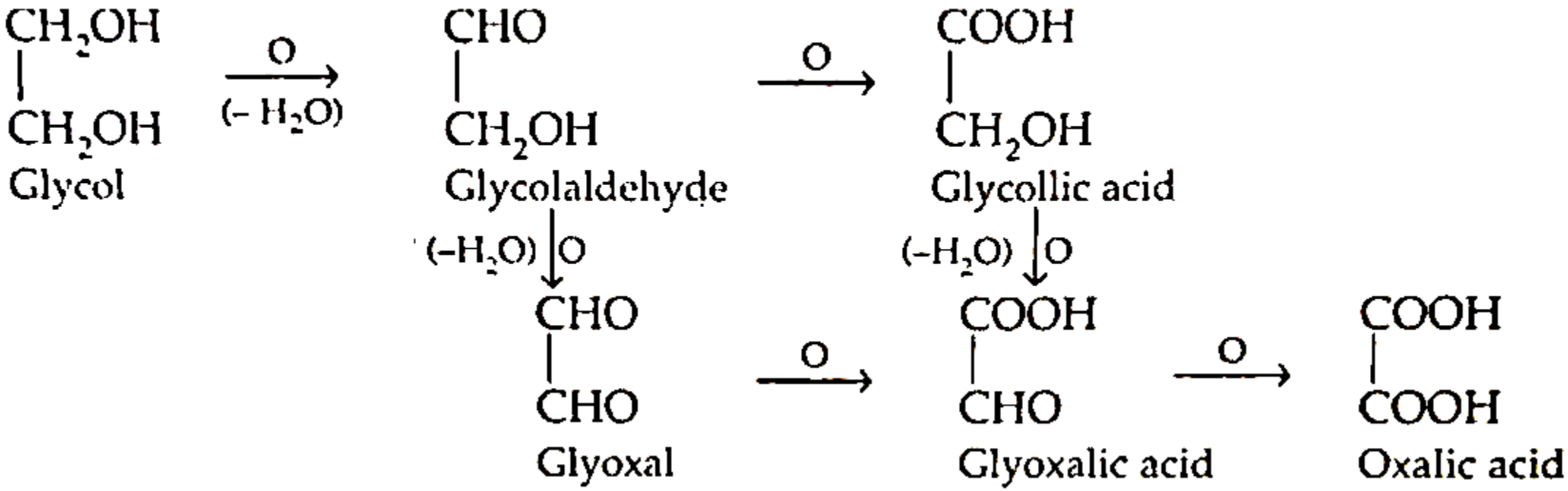


CH_3-CH_2-OH

Chemical reactions of Dihydric alcohols

❑ Oxidation

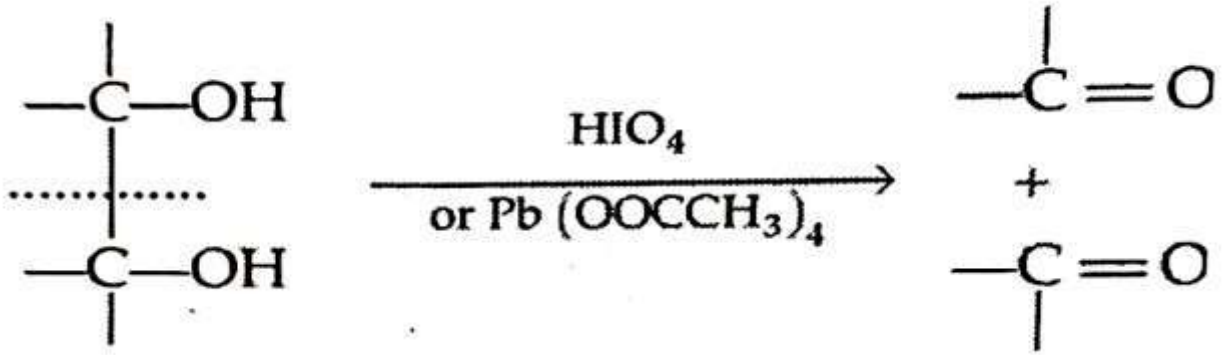
➢ **Different products under different conditions**

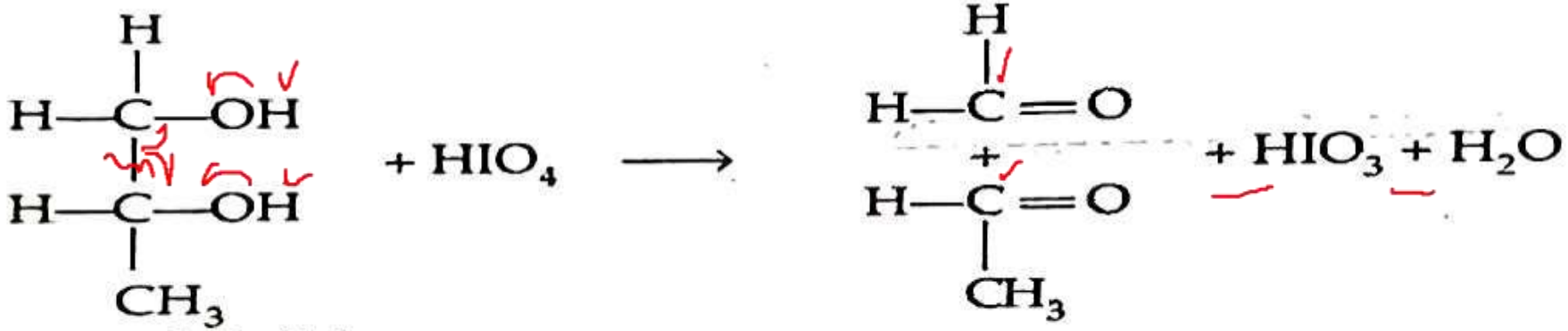


Chemical reactions of Dihydric alcohols

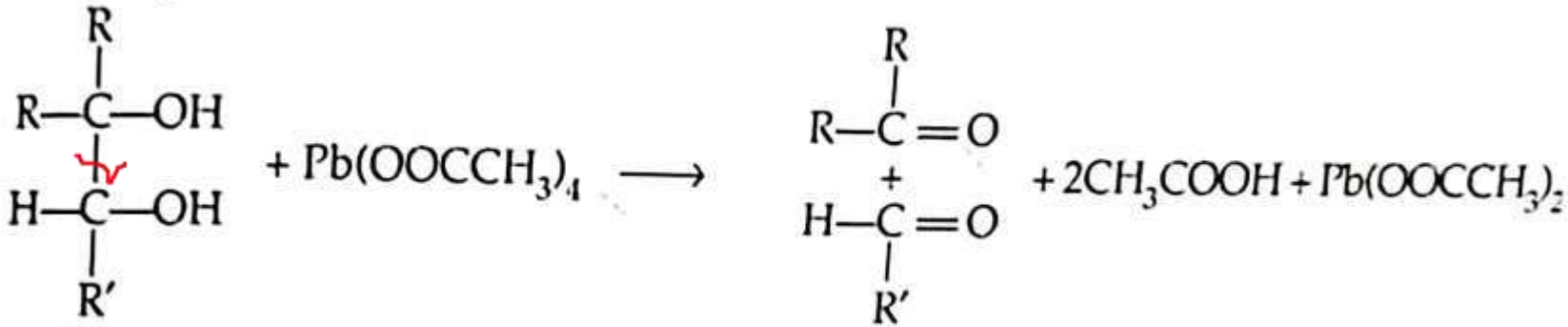
❑ Oxidative cleavage of 1,2- Glycols

- ➢ Can be done with Periodic acid or Lead tetra acetate
- ➢ Periodic acid is used in aq. Medium while Lead tetra acetate is used in organic solvents





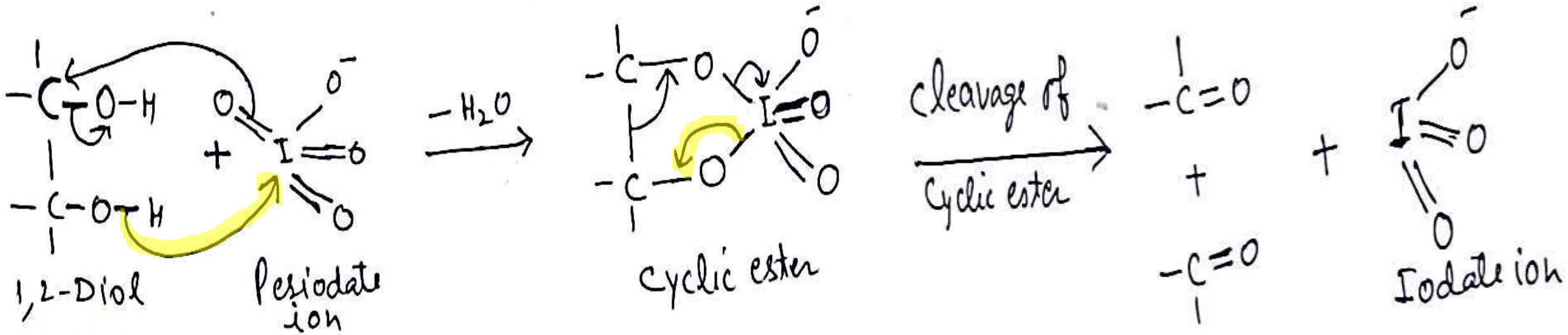
Propane-1, 2-diol



Chemical reactions of Dihydric alcohols

❑ Oxidative cleavage of 1,2- Glycols contd….

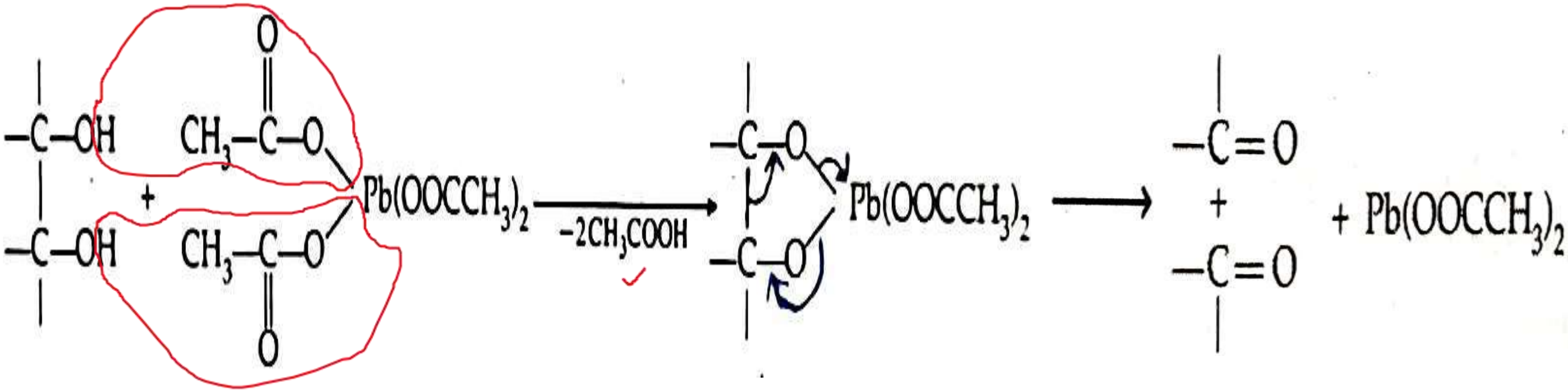
➢ **Mechanism with periodic acid**



Chemical reactions of Dihydric alcohols

❑ Oxidative cleavage of 1,2- Glycols …….

➢ Mechanism with Lead tetra acetate

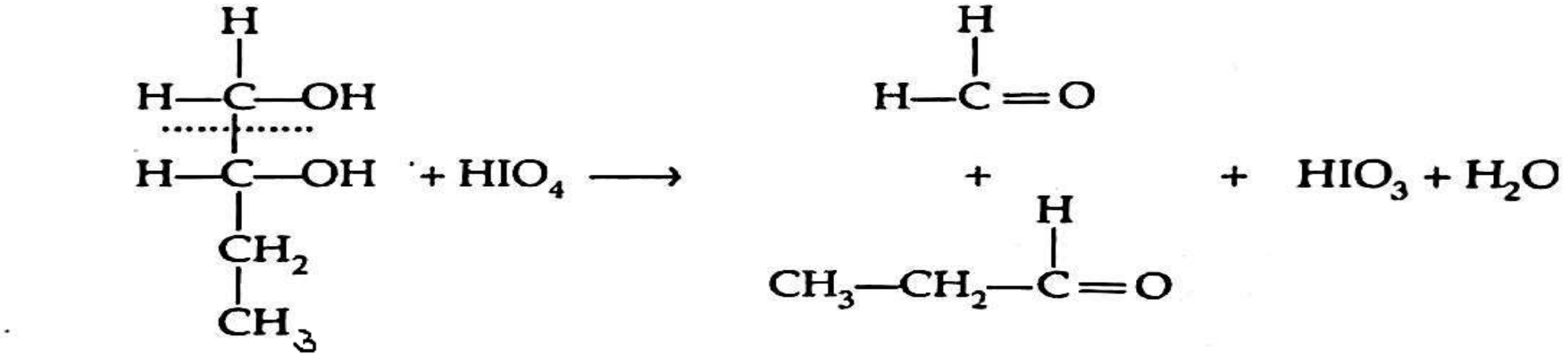


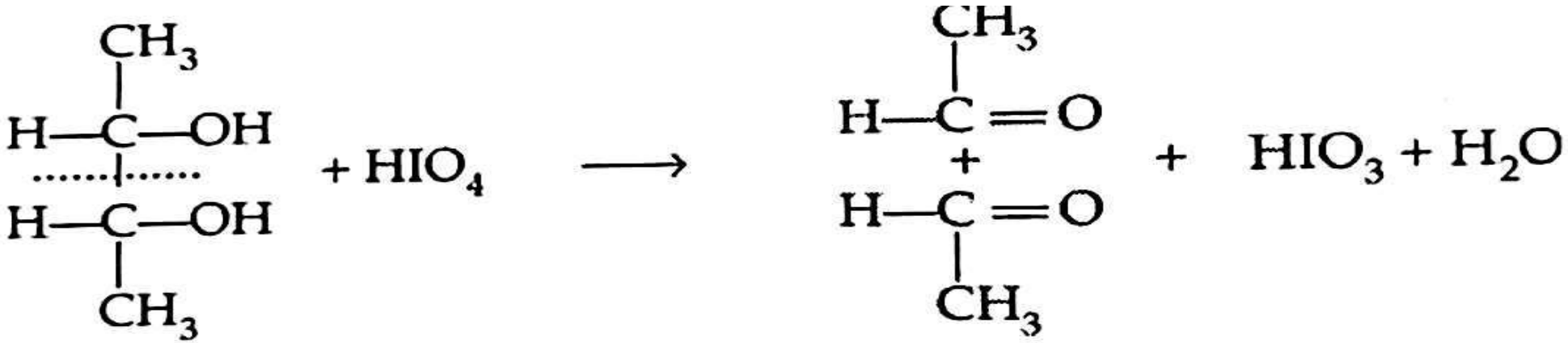
Chemical reactions of Dihydric alcohols

❑ Utility or importance of Oxidative cleavage of 1,2- Glycols

1. Structure determination of glycols

- If we have a sample of butylene glycol, it may be 1,2 –Butanediol or 1,3 –Butanediol or 2,3 –Butanediol or 1,4 –Butanediol
- By carrying out this reaction and by identification of products formed, we can ascertain the structure



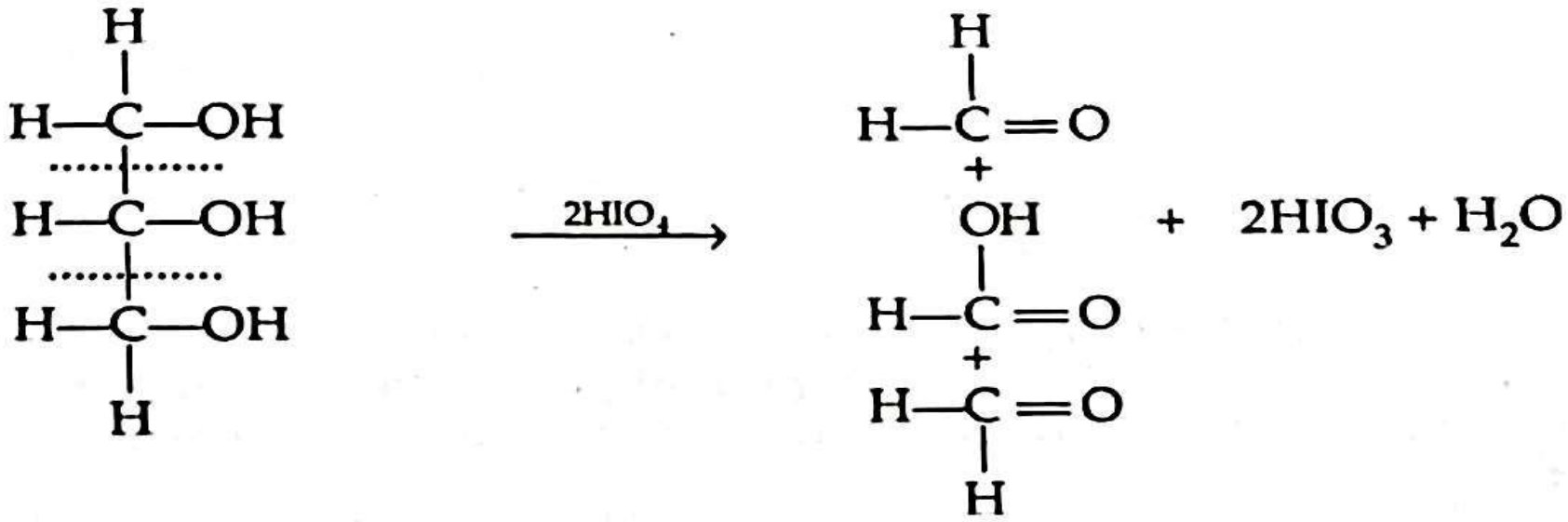


Chemical reactions of Dihydric alcohols

❑ Utility or importance of Oxidative cleavage of 1,2- Glycols

2. Determination of number of OH groups on adjacent carbons

- Particularly in polyhydric alcohols
- Number of moles of HIO_4 used for one mole of polyhydric alcohol tells us about the number of OH groups on adjacent carbons
- If one mole of HIO_4 is used then two OH groups are on adjacent carbons & if two moles are used then three OH groups are on adjacent carbons



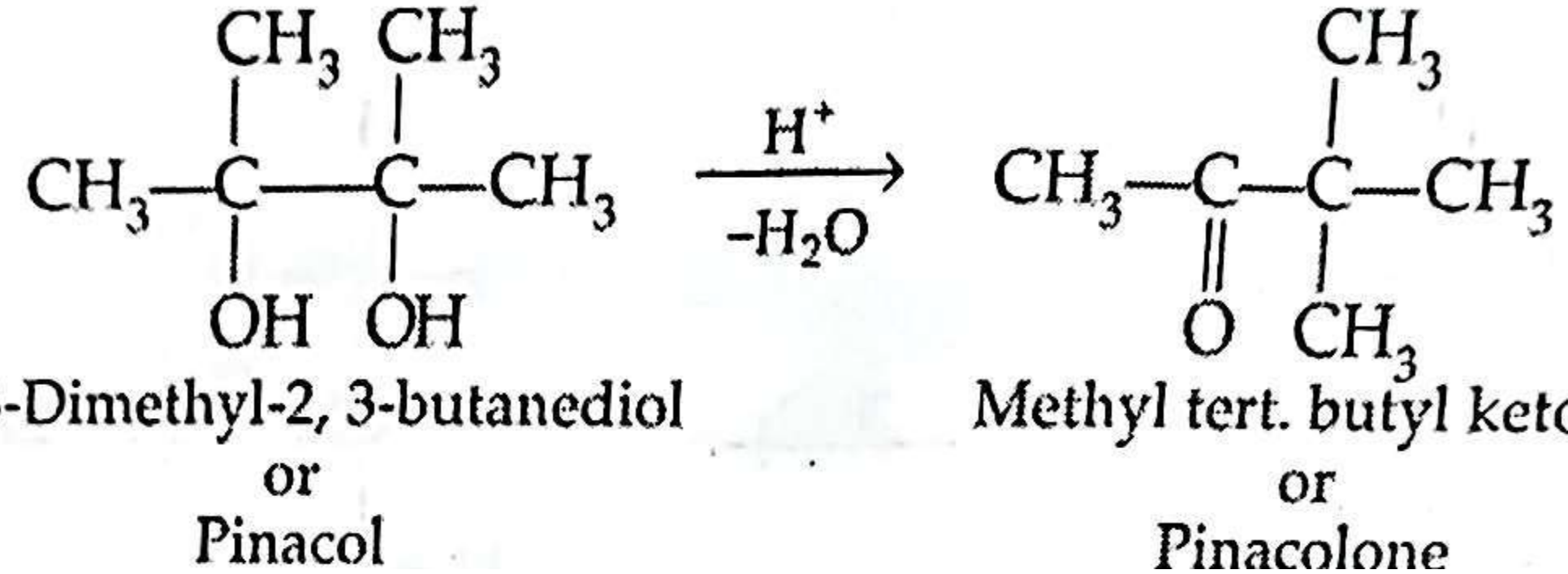
3. To determine whether OH groups are on adjacent carbons or not

- If OH groups are not on adjacent carbons then reaction will not take place

Chemical reactions of Dihydric alcohols

❑ Pinacol-Pinacolone Rearrangement

➢ **1,2-Glycols rearrange to ketones in the presence of acid catalyst**



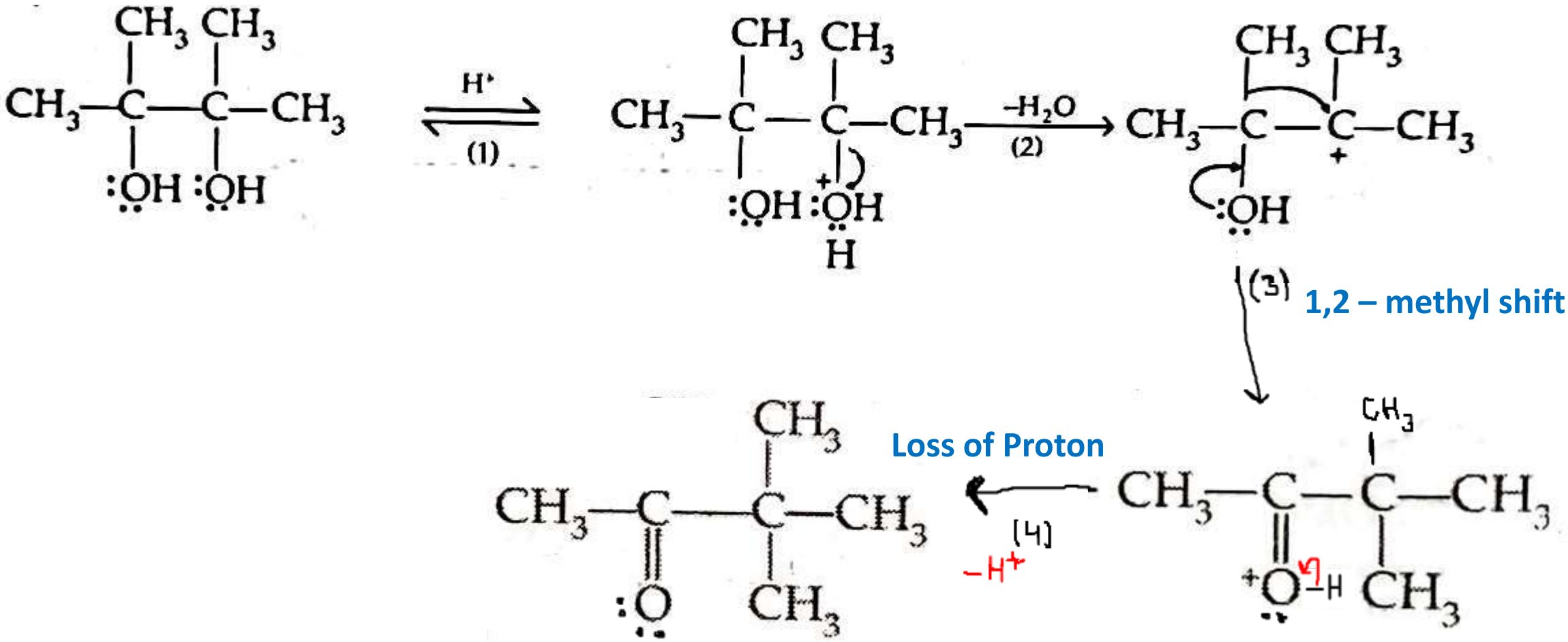
2, 3-Dimethyl-2, 3-butanediol
or
Pinacol

Methyl tert. butyl ketone
or
Pinacolone

Chemical reactions of Dihydric alcohols

❑ Mechanism of Pinacol-Pinacolone Rearrangement

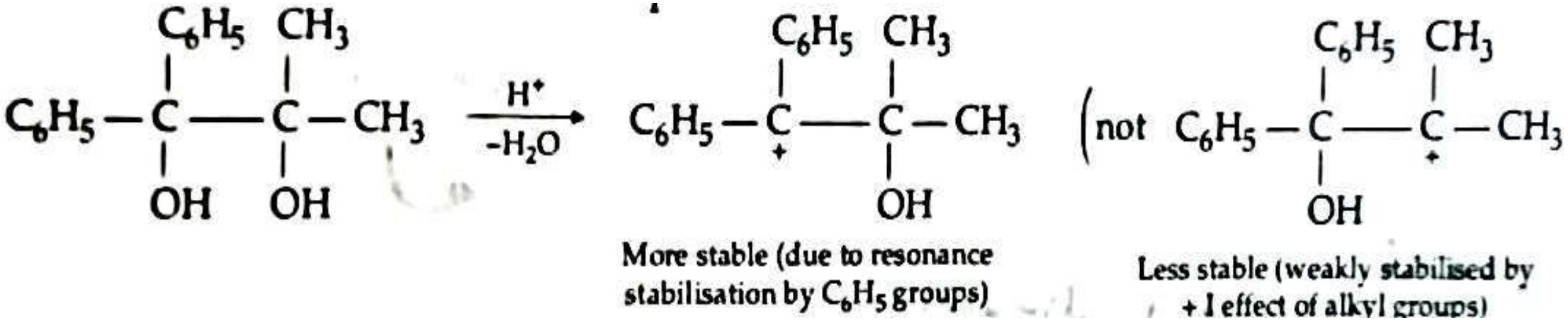
➢ It involves intermediate formation of carbocation followed by migration of alkyl group



Chemical reactions of Dihydric alcohols

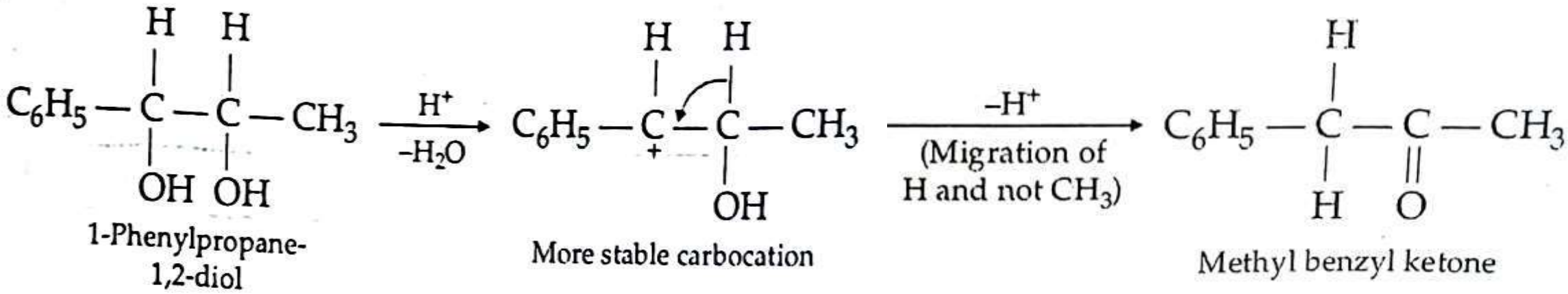
❑ Important features of Pinacol-Pinacolone Rearrangement

➢ **Of the two OH groups that OH group is eliminated which gives more stable carbocation**



❑ Migratory aptitude of groups

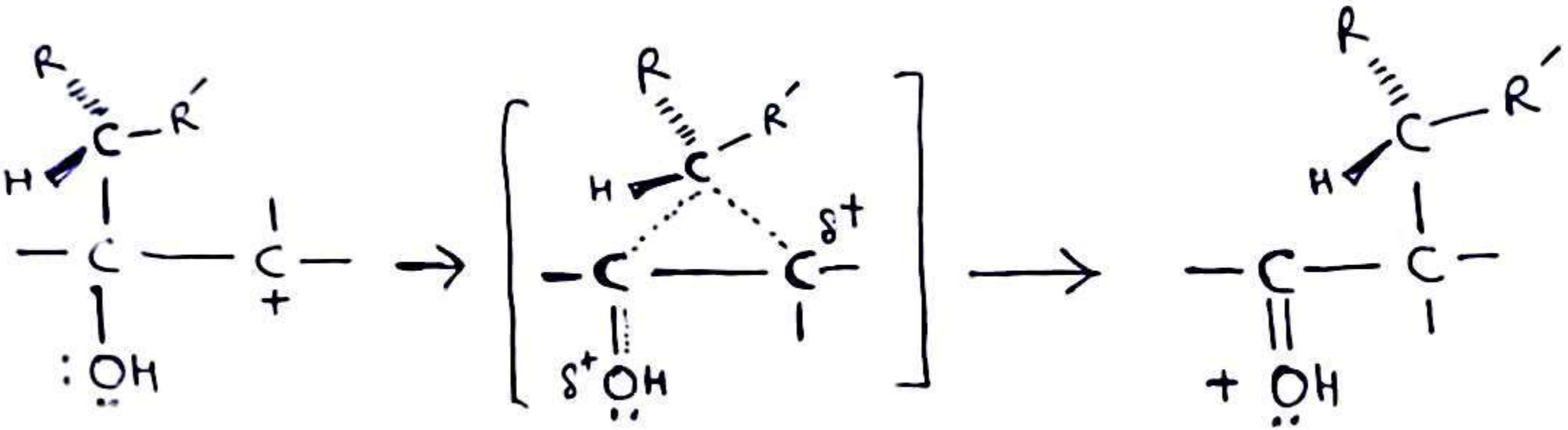
➢ **Hydrogen > Phenyl > Alkyl**



Chemical reactions of Dihydric alcohols

❑ Stereochemistry of Pinacol-Pinacolone Rearrangement

- ➢ **Migrating group does not become completely detached so the configuration around it does not change ie retention of configuration**
- ➢ **In other words, the stereochemistry of migrating group is retained**



Questions

1. Why do alcohols have higher boiling points than ethers of comparable molecular masses?
2. Lower alcohols have very high solubility in water whereas higher members do not. Explain
3. What is pinacol-pinacolone rearrangement? Give its mechanism.
4. Give a chemical test to distinguish primary, secondary and tertiary alcohols.
5. What happens when i. Propane-1,2-diol is treated with lead tetraacetate ii. Isopropyl alcohol is heated with acidified potassium permanganate solution.
6. What is Oppenauer oxidation. Give the mechanism of the reaction.
7. What happens when n-Butyl alcohol is heated with HI in the presence of red phosphorous?
8. Write balanced chemical equations for the following reactions
   i. Reaction of Magnesium metal with tert. Butyl alcohol
   ii. Reaction of isopropyl alcohol with potassium metal
9. Explain Bouveault-Blanc reduction with mechanism.