Organic Chemistry

B.Sc.II

by

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Unit II : Alcohols and Phenols

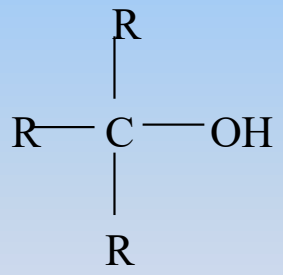
Types of Alcohols

On the basis of number of OH group

- Monohydric alcohol: ROH
- Dihydric alcohol: $HOCH_2CH_2OH$, $RCHOHCH_2OH$
- Trihydric alcohol: $OHCH_2CHOHCH_2OH$

On the basis of position of OH group

- Primary alcohol: RCH_2OH
- Secondary alcohol: RCHOHR
- Tertiary alcohol:



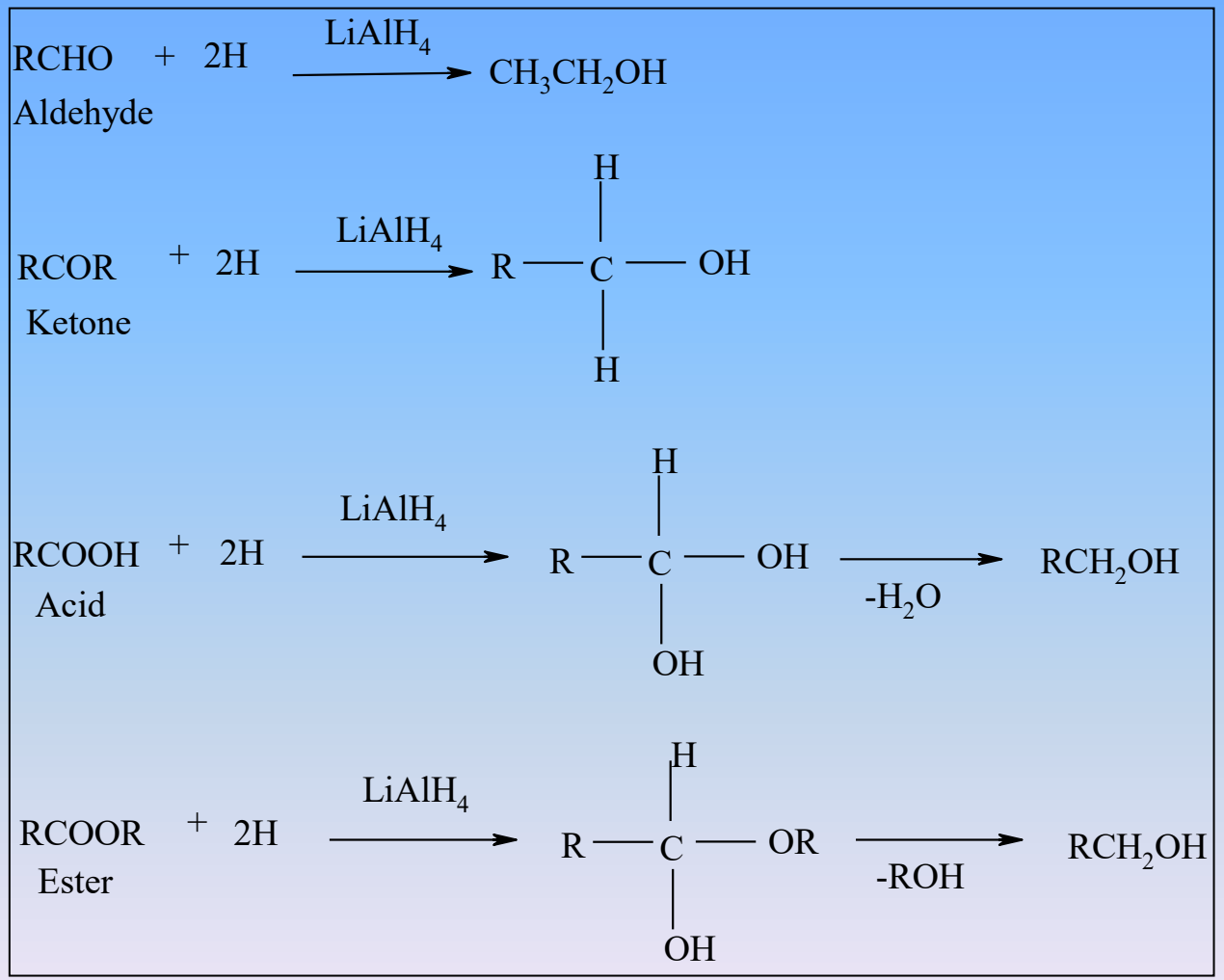
Synthesis of alcohols

- Various natural and synthetic methods of alcohol synthesis.
- **Natural method:** synthesis of Ethanol from molasses.
- **Synthetic methods include:**
- Reduction of aldehyde, ketone, alcohol and esters via metal hydride.
- Reaction of carbonyl compounds with Grignard reagent.
- Some other chemical synthesis.

Reduction of aldehydes, ketones, carboxylic acid and esters using $LiAlH_4$ or $NaBH_4$

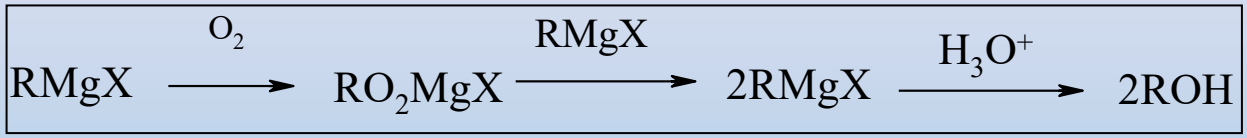
- Nucleophilic addition reaction occurs on carbonyl group.
- Reactions usually carried out in Et_2O or THF followed by H_3O^+ (The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid base reaction.
- Aldehydes and ketones are most readily reduced with hydride reagents.
- Carboxylic acids and esters are less reactive to Nu than aldehydes or ketones. They can only be reduced by $LiAlH_4$ but NOT by the less reactive$NaBH_4$.
- The reducing agents $LiAlH_4$ and $NaBH_4$ act as a source of H^- (hydride ion).
- Overall 2 H atoms are added across the C=O to give H-C-O-H.
- Hydride reacts with the carbonyl group, C=O, in aldehydes or ketones to give alcohols.
- Reduction of methanal (formaldehyde) gives methanol.Reduction of other aldehydes gives primary alcohols.Reduction of ketones gives secondary alcohols.

Reduction of aldehydes, ketones, carboxylic acid and esters using $LiAlH_4$ or $NaBH_4$

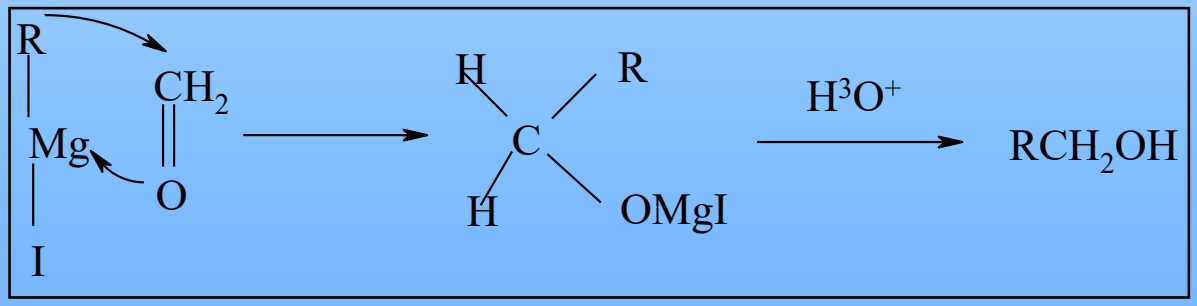


Synthesis of 1^0 Alcohols

When Grignard Reagent reacts with dry oxygen and then acidified to give 1^0 alcohol

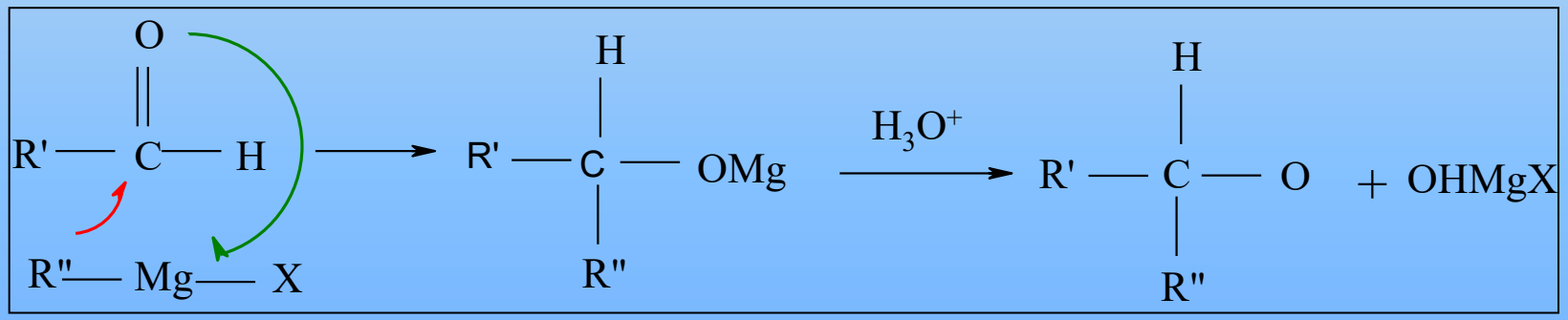


Reaction with formaldehyde:
Grignard Reagents reacts with formaldehyde formed a complex which on acidification gives primary alcohol.

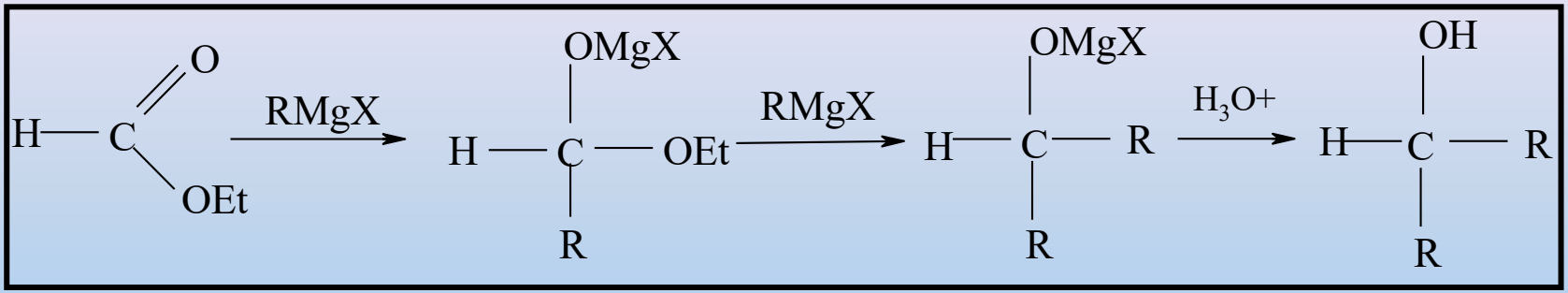


Synthesis of 2^0 alcohol

Reaction of GR with aldehyde other than formaldehyde gives secondary alcohols

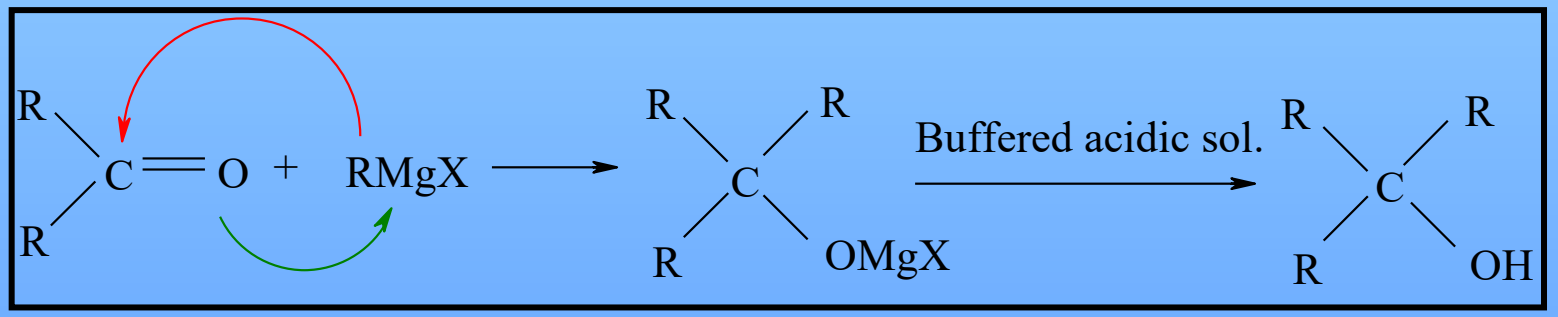


Reaction of GR (2 moles) with ethyl formate (1 mole) also gives secondary alcohol



Synthesis of 3^0 alcohol

Reaction of GR with ketone gives tertiary alcohol



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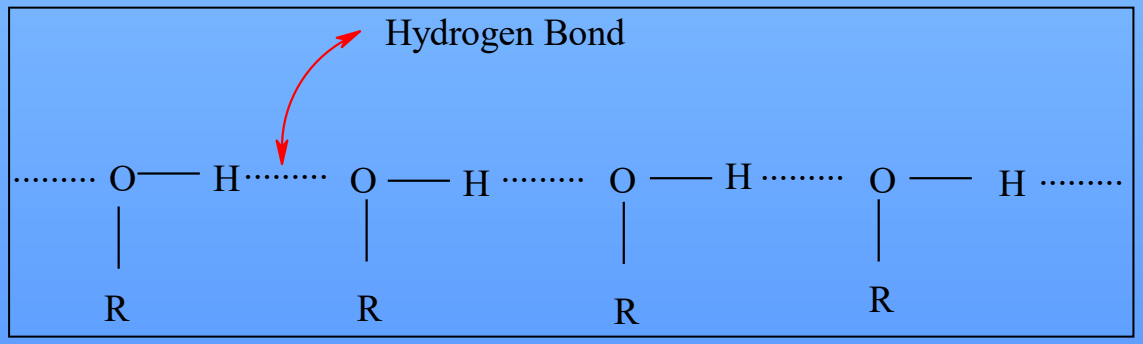
Properties of alcohols:

- Alcohols are neutral in nature.
- The lower members alcohols (up to five carbon) are liquid, from carbon number six to carbon number ten are viscous liquid and above that are solids.
- The lower alcohols are soluble in water and the solubility decreases as the molecular weight increases.
- Solubility of lower alcohols in water higher due to *hydrogen bonding*. However, solubility of higher alcohols in water decreases because in higher alcohols ,hydrocarbon (hydrophobic nature) character increases and hydroxyl group constitutes small portion of the molecule.
- In a group of isomeric alcohols order of boiling point is

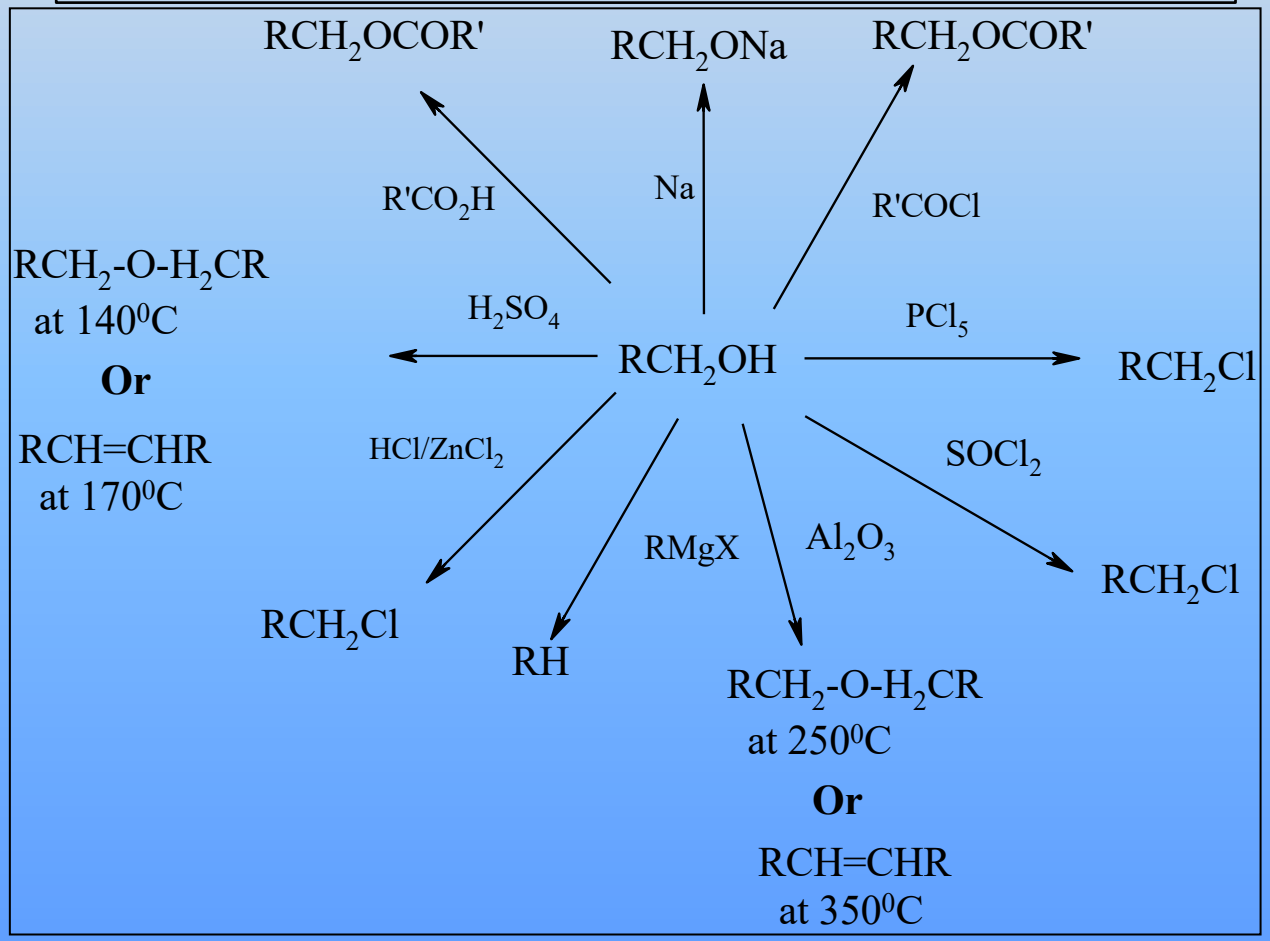
Primary alcohols> Secondary alcohols> Tertiary alcohols



Effect of H-Bonding

- Alcohols have higher boiling point than isomeric ethers.
- Hydrogen bonding occurs in the molecules of H_2O, CH_3OH and C_2H_5OH, then why H_2O having so less molecular weight have so high boiling point reason is number hydrogen bond per molecule, which is two in case of H_2O.
- Alcohols are soluble in water, whereas ethers are insoluble in water.

Reactions of Alcohols



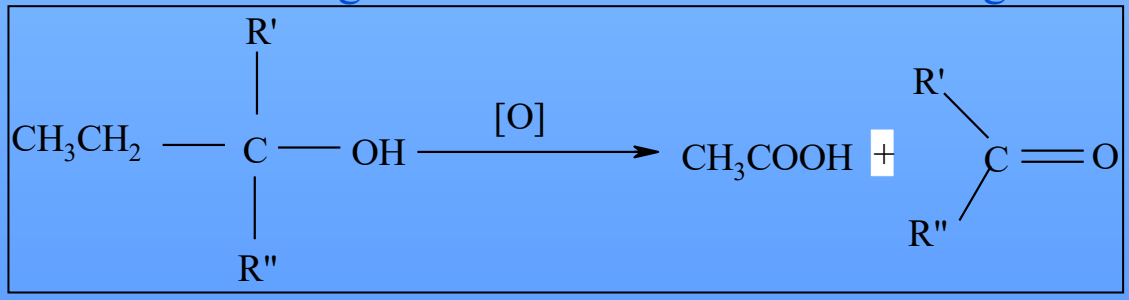
Distinguish between 1^0, 2^0 and 3^0 alcohols

By means of oxidation (oxidizing agents are acid dichromate, acid or alkaline $KMnO_4$ and dil. HNO_3)

- 1^0 alcohol on oxidation first gives an aldehyde and this on further oxidation gives an acid.
- Both aldehyde and acid contain the same number of carbon atom as the original alcohol.

- 2^0 alcohol on oxidation first gives a ketone with the same number of carbon atoms as the original alcohol.
- Ketones are difficult to oxidized but on prolonged action produces a mixture of acids, each congaing less carbon atoms than the original alcohols.

- 3^0 alcohols are resistant to oxidation in neutral and alkaline solution , however in acid oxidizing medium produces a mixture of ketone and acid.
- Both ketone and acid containing fewer carbon atoms than the original alcohols



When 1^0 ,2^0, and 3^0 alcohols vapour passed over copper at 300^0C

A primary alcohol is dehydrogenated to an aldehyde.

$$CH_3CH_2OH \xrightarrow[300^0C]{Cu} CH_3CHO + H_2$$

A secondary alcohol is dehydrogenated to ketone.

$$CH_3CH(OH)CH_3 \xrightarrow[300^0C]{Cu} CH_3COCH_3 + H_2$$

A tertiary alcohol is dehydrogenated to an alkene

$$(CH_3)_2C(OH)CH_2CH_3 \xrightarrow[300^0C]{Cu} (CH_3)_2{=}CHCH_3 + H_2O$$

Lucas reagent test: (*Anhydrous ZnCl2 and Conc. HCl is Lucas reagent*)
When an alcohol is mixed with Lucas reagent , an alkyl chloride formed. Since alkyl chloride insoluble in water, a turbidity is obtained at Room temperature.

3^0 alcohol gives turbidity immediately
2^0 alcohols gives turbidity after 5 minutes.
1^0 alcohols does not gives turbidity at RT

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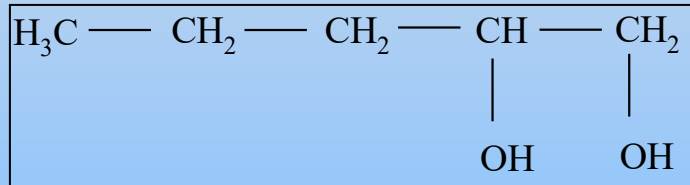
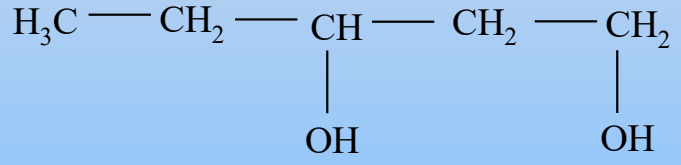
Dihydric alcohols or Glycols

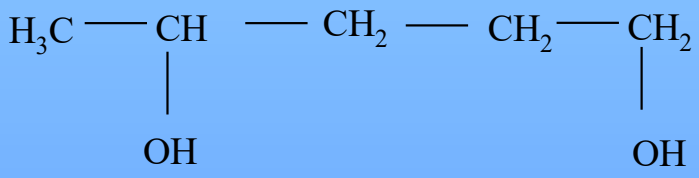
- Two hydroxyl group containing compounds are known as dihydric alcohols or Glycols.
- Glycols are classified as α - (1,2 glycols), β - (1,3 glycols) and γ - (1,4 glycols) depending on the relative position of two hydroxyl groups.



Pentane 1,2 diol



Pentane 1,3 diol

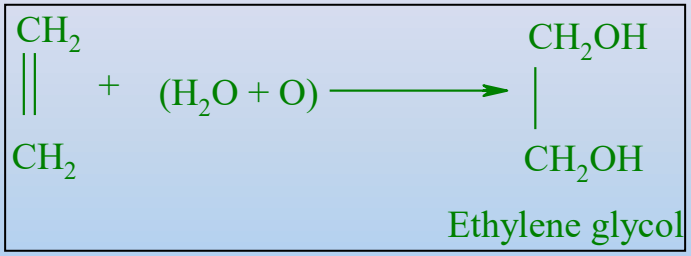


Pentane 1,4 diol

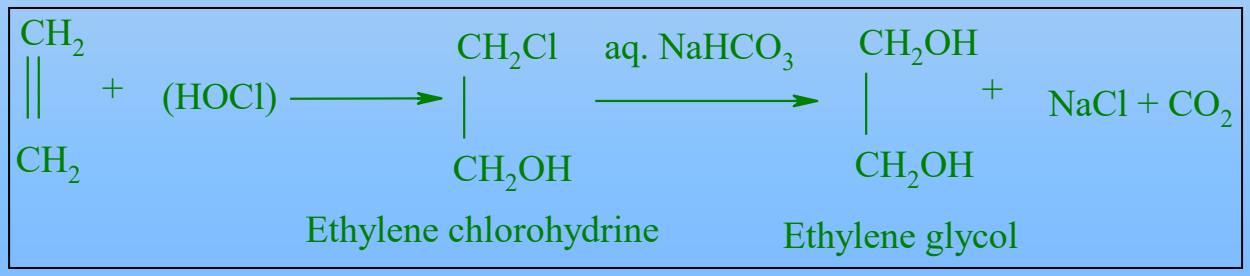
Ethylene glycol, vicinaldiol, glycol (ethane-1.2-diol) → CH_2OH | CH_2OH

Synthesis:

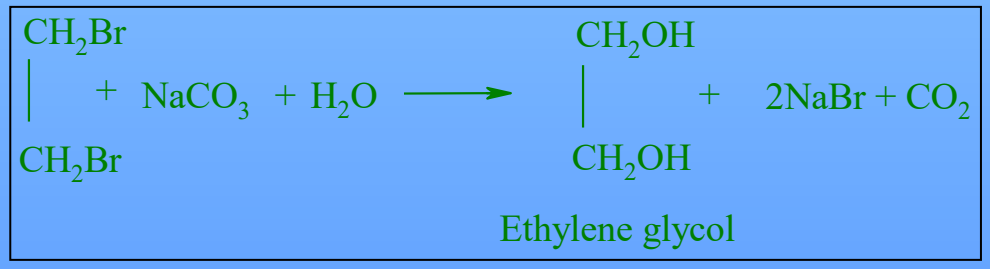
- By passing ethylene into cold dil. Alkaline permanganate solution.



- By passing ethylene into hypochlorous acid, and then hydrolysis the ethylene chlorohydrine by boiling with aq. $NaHCO_3$

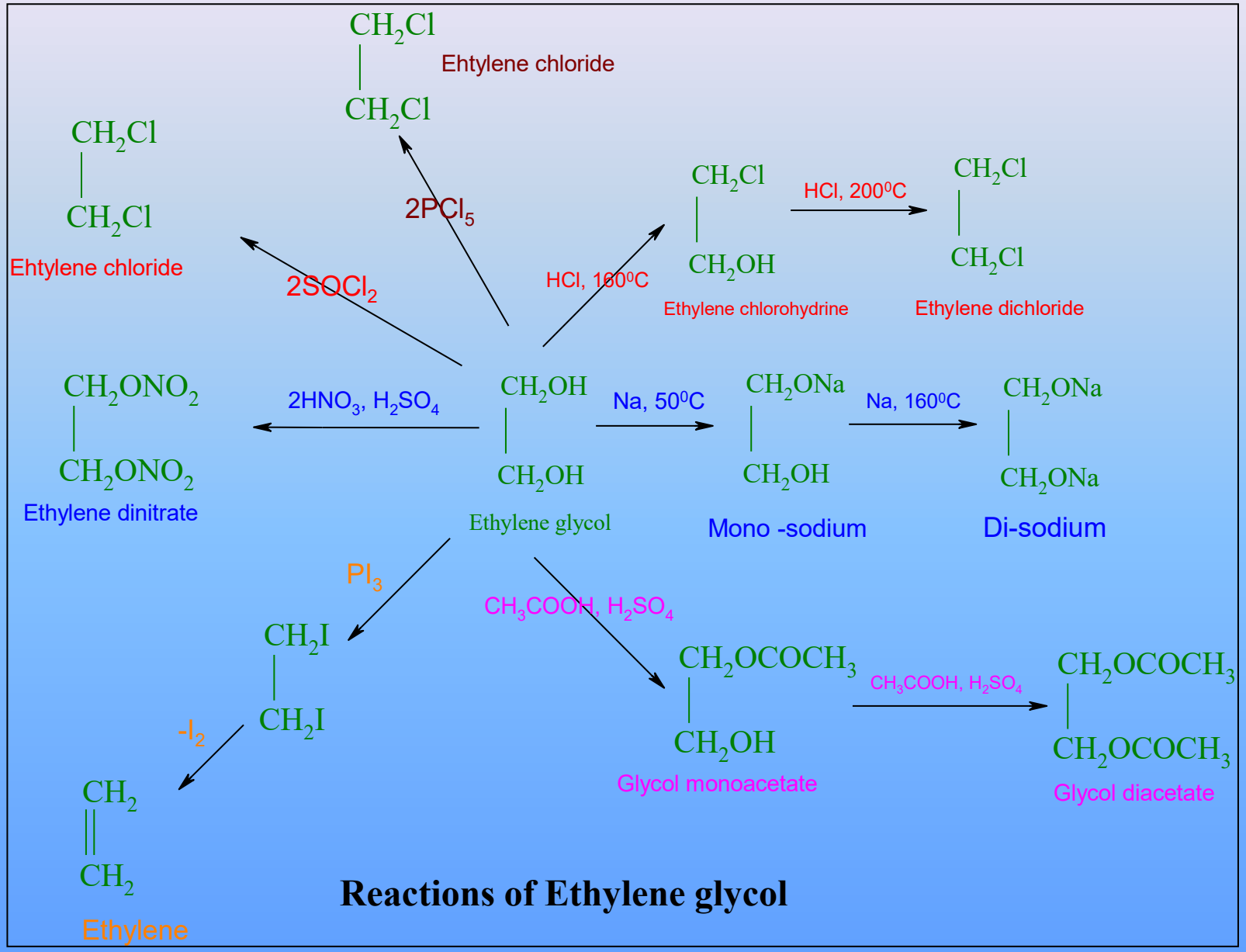


- By boiling ethylene dibromide with aq. sodium carbonate



- By oxidation of epoxide with dil. HCl. We will discuss it in ether chapter later

- Ethylene glycol is a colorless viscous liquid, sweet in taste having boiling point 197^0C.
- It is soluble with water and ethanol, however insoluble in ether.(Reason H- bonding).
- It is used as solvent and coolants in automobiles.



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Protection of carbonyl group:

- Glycol condenses with aldehyde or ketones in the presence of p-toluenesulphonic acid to form respectively cyclic acetals or ketals(1,3-dioxolans).
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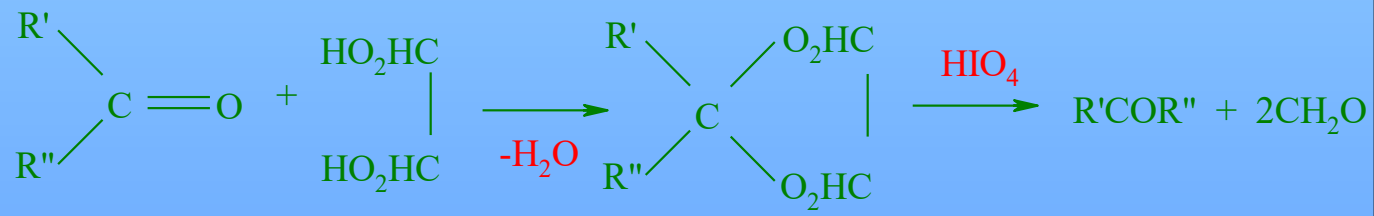
- These cyclic compounds are non- reactive in alkaline medium.
- However, in mild acidic condition these cyclic compounds converted to starting carbonyl compound.

Protection and deprotection of carbonyl group via glycol

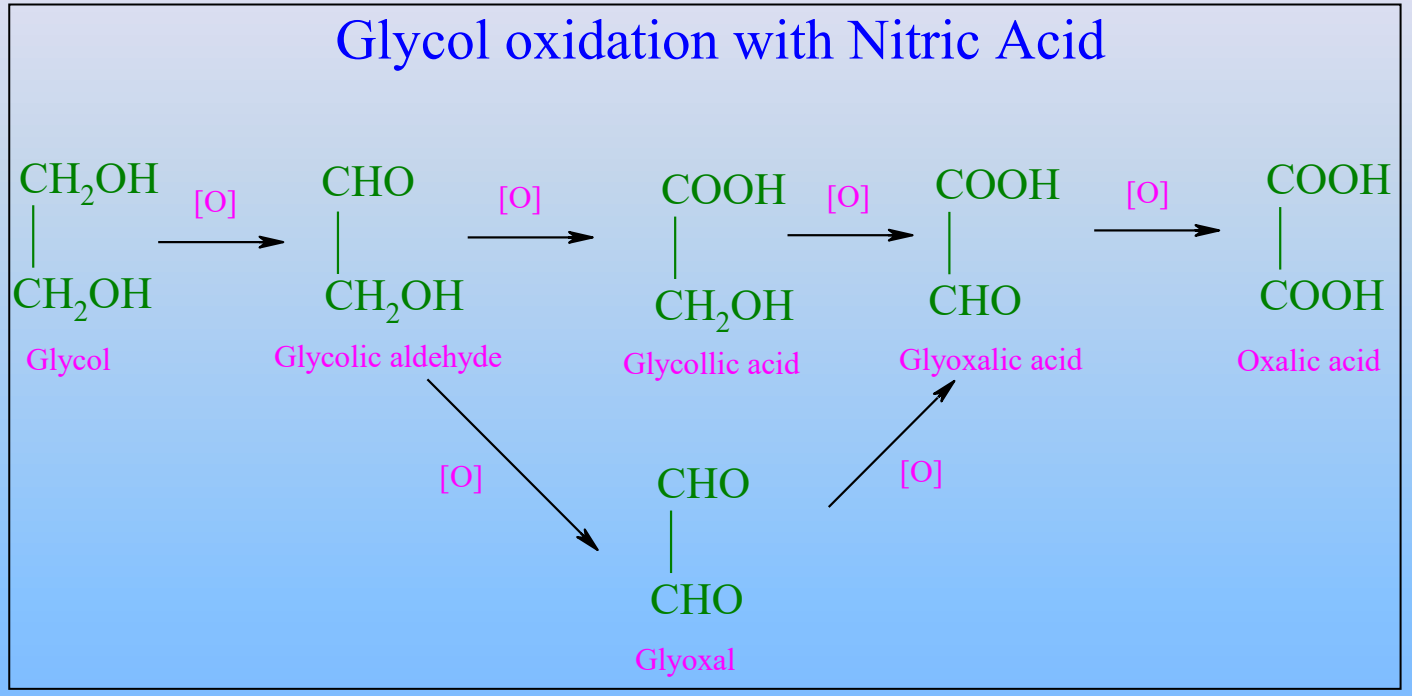


R' and R"= R (Ketone)
R'=R and R"=H (Aldehyde)

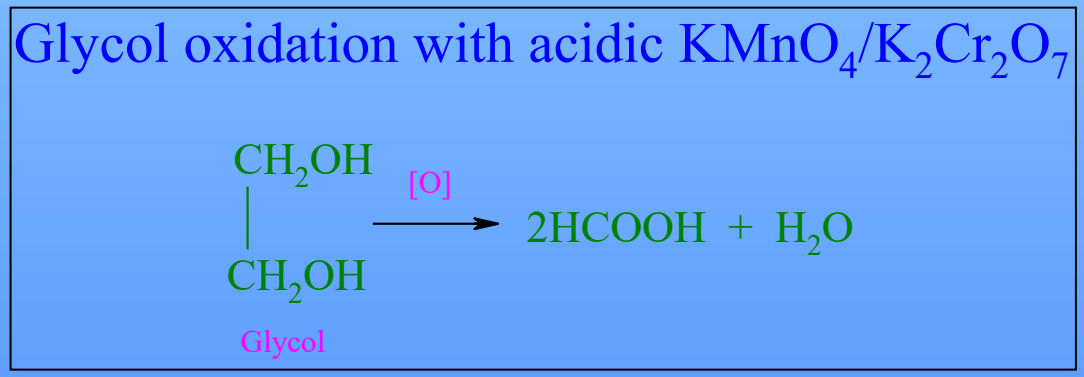
1,3- dioxolans

- In glycol both OH groups are primary in nature, so oxidation product depends on the nature of oxidising agent.

Oxidation of glycol with HNO_3:

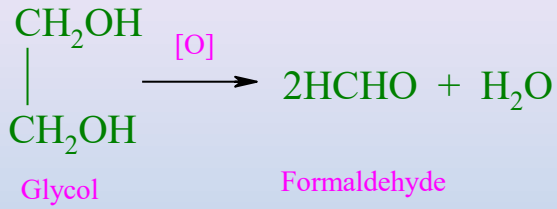


- Oxidation of glycol with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ leads to formic acid.

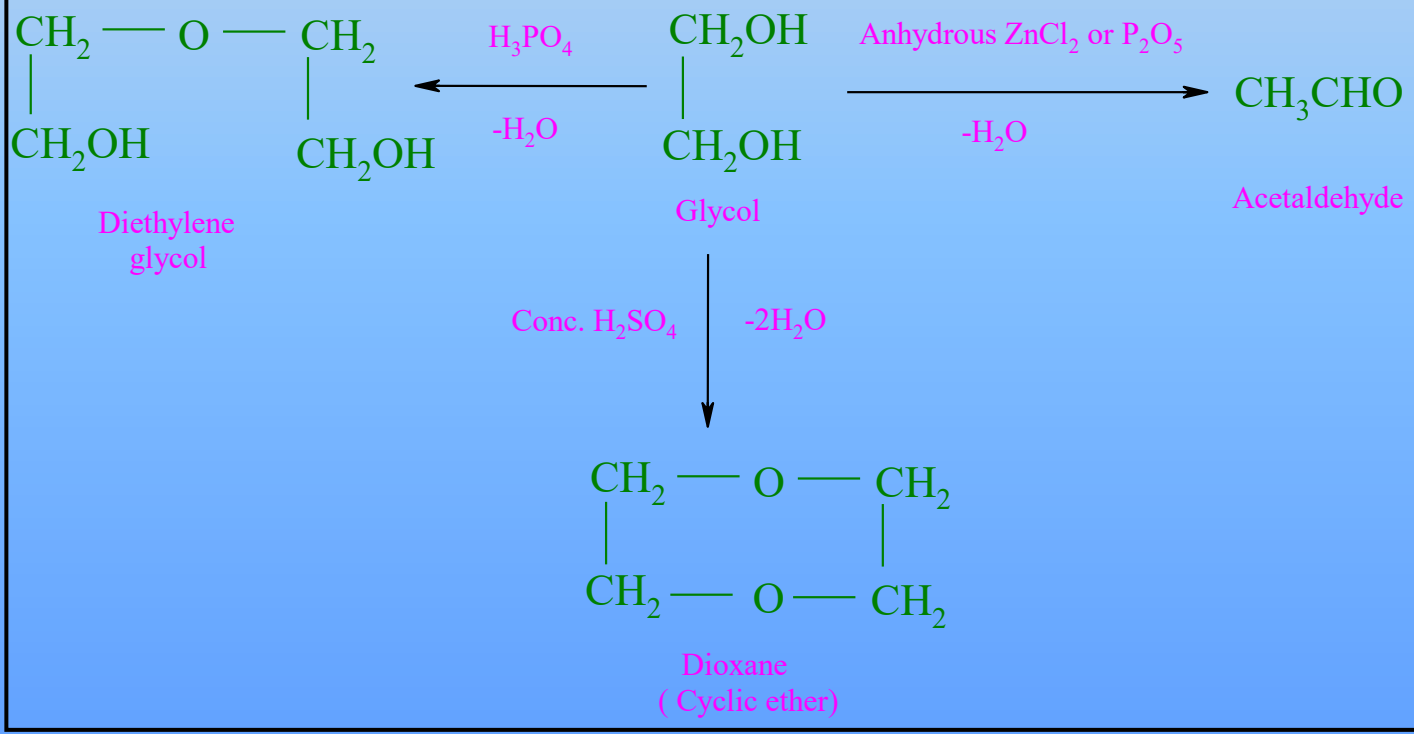


- Oxidation of glycol with *Lead tetra-acetate* [$(AcO)_4Pb$] or *Periodic acid* [HIO_4] results in fission of the carbon-carbon bond to give formaldehyde.

Glycol oxidation with $(AcO)_4Pb$ or HIO_4

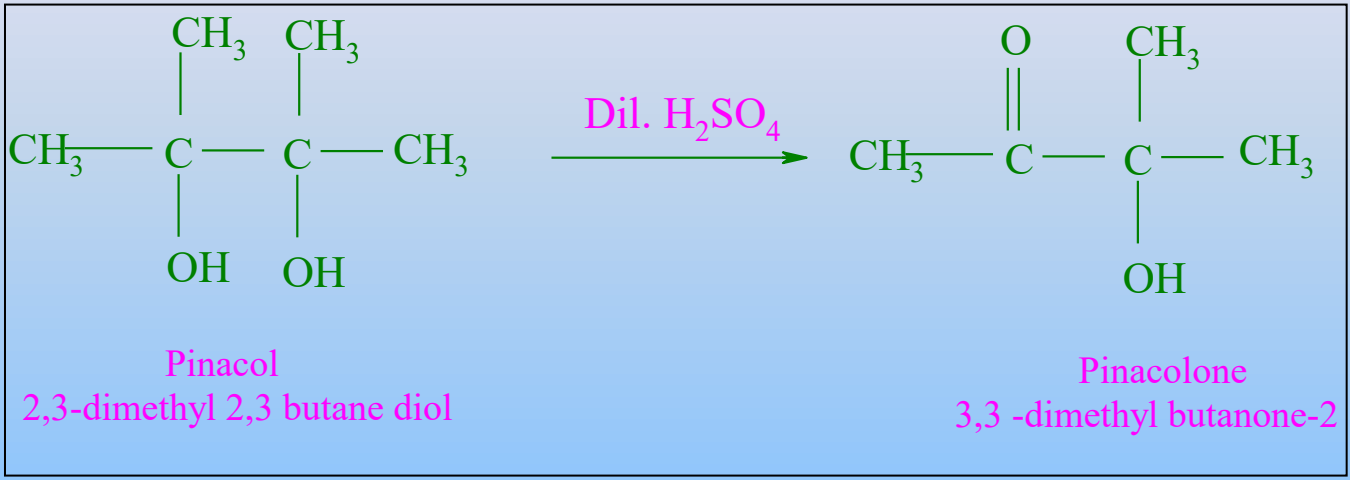


Dehydration of Glycol in different dehydrating agent



Pinacol-pinacolone rearrangement

- The conversion of pinacols (1,2 diol) into pinacolone under acidic condition.
- It is an example of 1,2 shift.



Pinacol
2,3-dimethyl 2,3 butane diol

Pinacolone
3,3 -dimethyl butanone-2

Mechanism of Pinacol-pinacolone rearrangement involves following steps:

Step1: Protonation of one hydroxyl group of pinacol by H^+.

Step 2: Protonated pinacol then loses a water molecule to form a carbocation.

Step 3: Actual rearrangement step (migration of a group) i.e. cabocation formed in the above step is unstable so it get rearranged in a more stable form of carbocation.(*Carbon having +ve charge attach to more electronegative atom is more stable*).

Step4: Rearranged carbocation loses a proton to give pinacolone.

Pinacol- pinacolone rearrangement