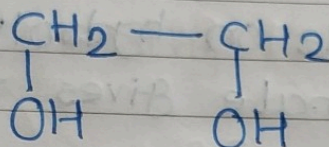


C. ALCOHOLS :-

* Dihydric Alcohols $\Rightarrow$

Alcohols containing two hydroxyl groups are commonly called as dihydric alcohols or glycols.

In IUPAC system they are named as diols.

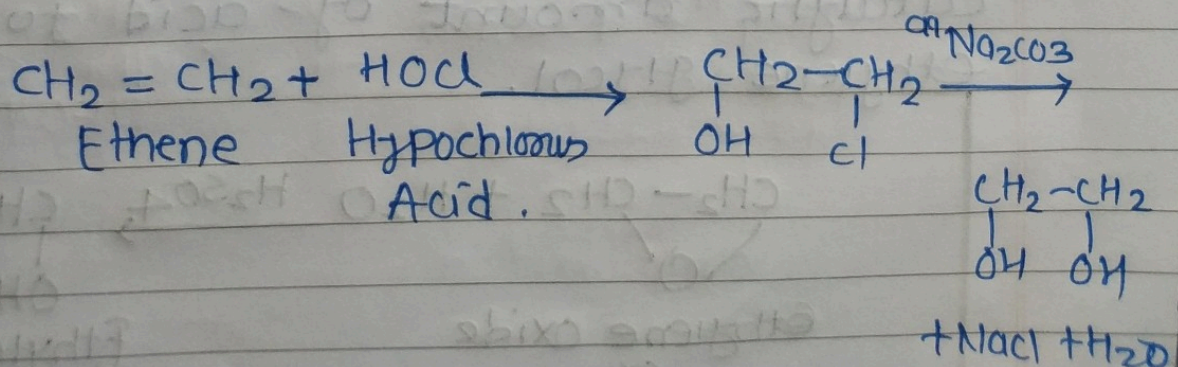


Ethane-1,2-diol.

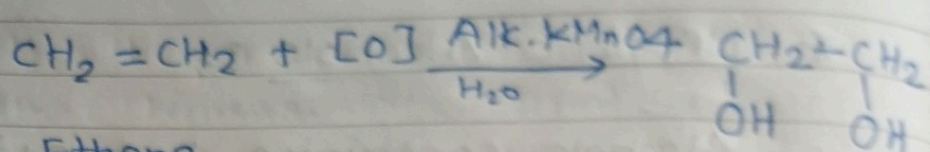
* Methods of Preparation:

1. From ethylene:-

a] Ethylene when treated with hypochlorous acid (HOCl) gives ethylene chlorohydrin which on hydrolysis with aq. Na_2CO_3 gives ethylene glycol.



b) Ethylene on treatment with cold, dilute, alkaline KMnO_4 , gives ethylene glycol.

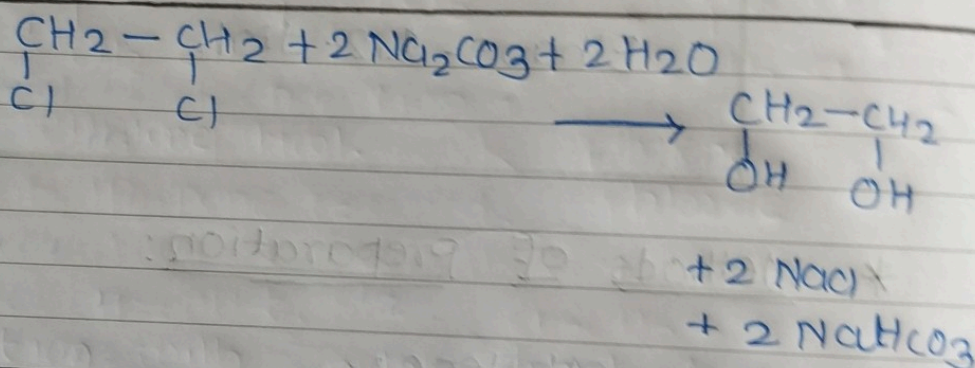


Ethene.

Ethylene Glycol

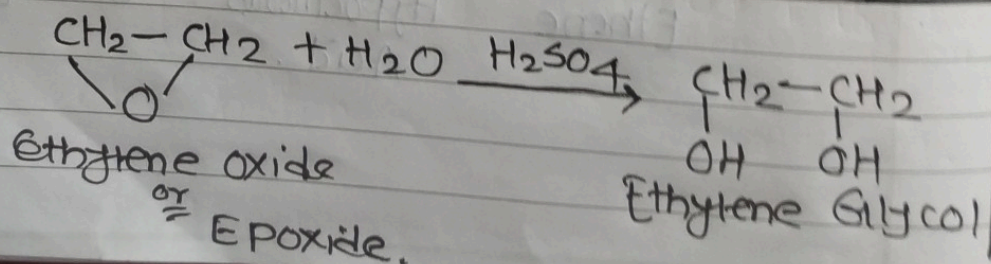
2. From ethylene chloride $\Rightarrow$

Ethylene chloride on hydrolysis with aq. Sodium carbonate gives ethylene glycol.



3. From ethylene oxide $\Rightarrow$

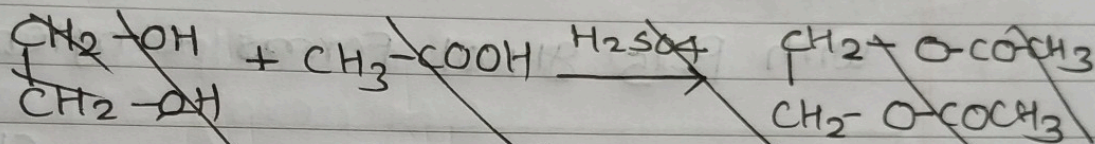
Ethylene oxide undergoes ring opening reaction with water in presence of catalytic amount of acid to give ethylene glycol.



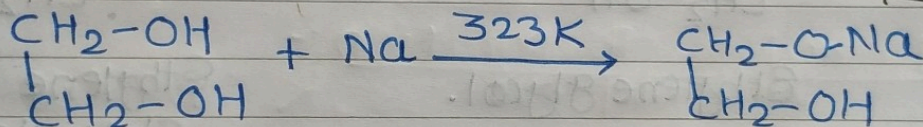
* Reactions of ethylene glycol :-

1) Reaction with sodium metal:

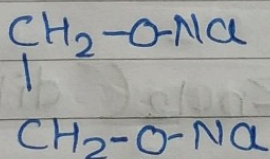
At 323 K glycol reacts with sodium metal to form monosodium glycolate whereas, at 433 K it gives disodium glycolate.



~~Glycoldiacetate~~



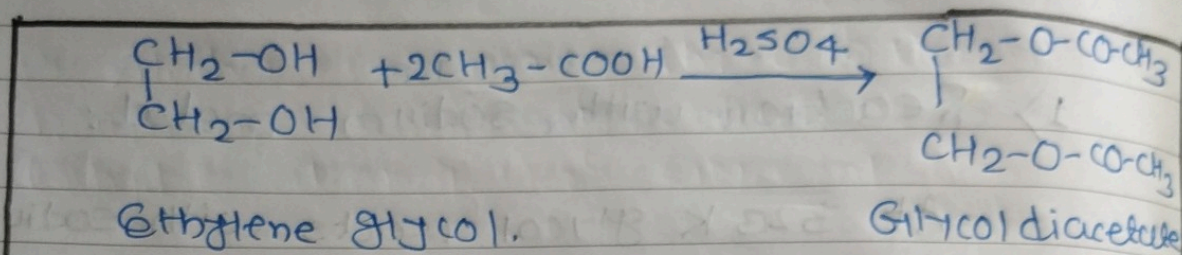
Monosodium glycolate



Na
433K

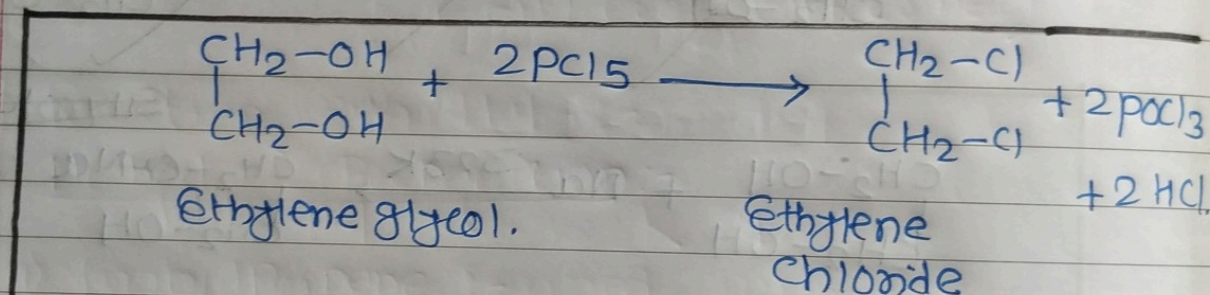
Disodium glycolate.

2. Reaction with acetic acid:-



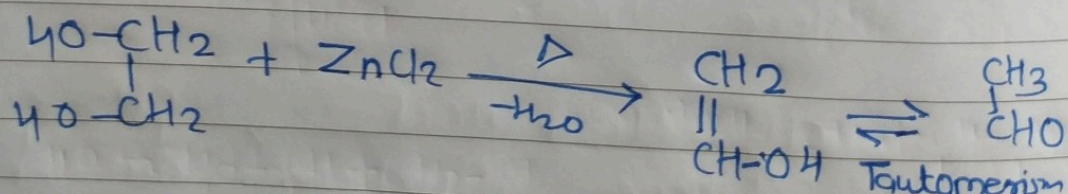
3. Reaction with PCl₅

With PCl₅ glycol forms ethylene chloride.



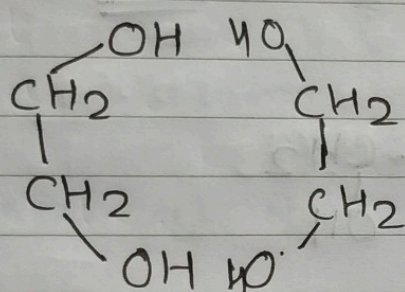
4) Reaction with ZnCl₂ (dihydration reaction)

When heated with ZnCl₂, glycol gives vinyl alcohol which tautomerizes to acetaldehyde.

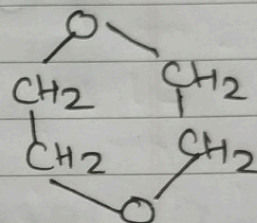


5] Reaction with conc H_2SO_4 (dehydration reaction)

Glycol when distilled with conc. H_2SO_4 gives 1,4-dioxane.



conc. H_2SO_4
Distillation

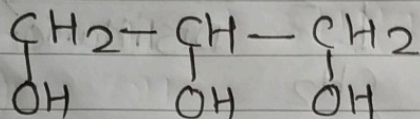


1,4-dioxane.

+ 2H₂O

* Trihydric Alcohols :-

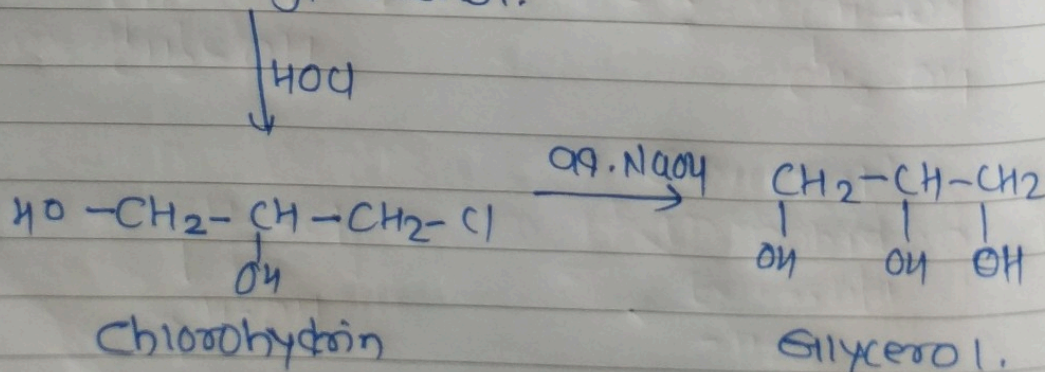
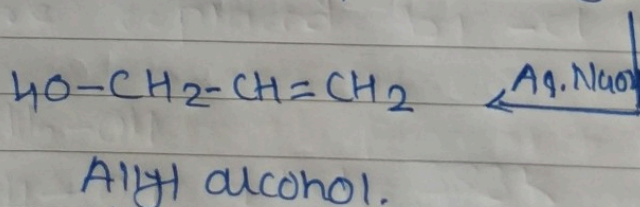
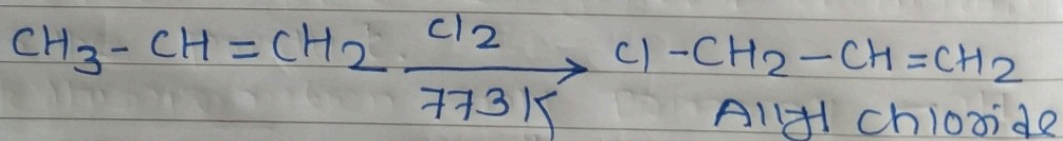
Alcohols containing three hydroxyl groups are commonly called as trihydric alcohol. or Glycerol



1,2,3-Trihydroxypropane
(Glycerol / Glyc erine)

* Method of Preparation :-

a) from Propene :-

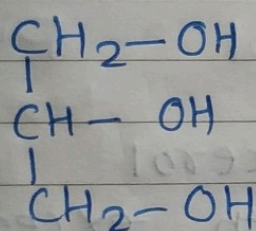


Propene on chlorination with Cl_2 at 773 K gives allyl chloride which on hydrolysis with dil. NaOH gives allyl alcohol.

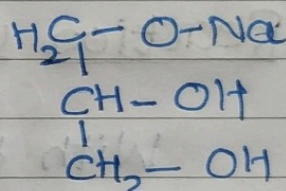
Allyl alcohol when treated with hypochlorous acid (HOCl) gives chlorohydrin which on hydrolysis with aq. NaOH gives glycerol.

* Chemical Reactions of Glycerol $\Rightarrow$

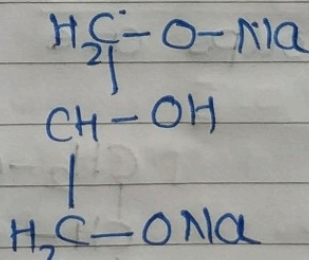
1] Reaction with Sodium metal :-



+ Na Room temp.



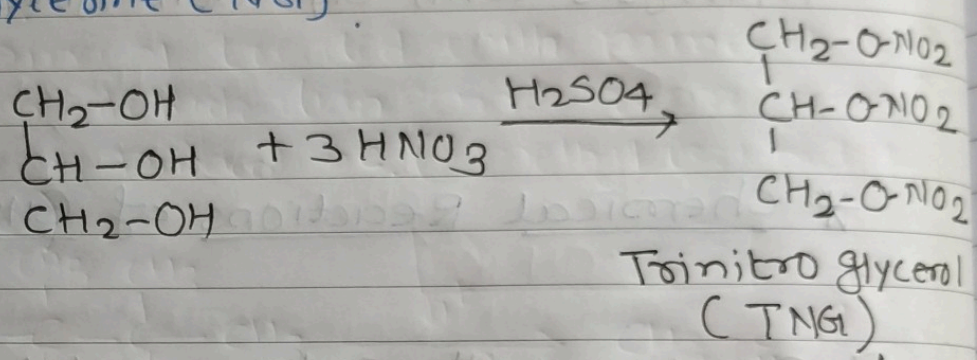
$\downarrow$ Na
High temp.



Disodium Glycerolate.

2] Reaction with Nitric acid :-

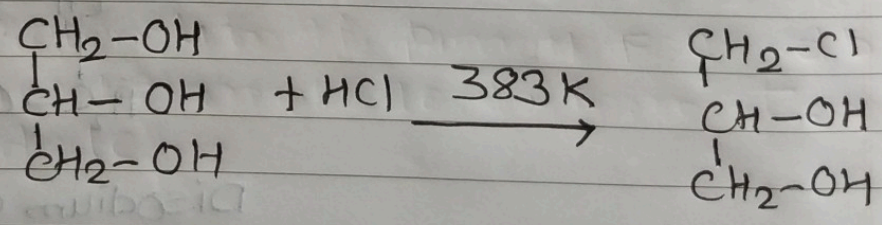
Glycerol reacts with Nitric acid in presence of sulphuric acid as catalyst to give trinitroglycerol (TNG) or nitroglycerine (NG).



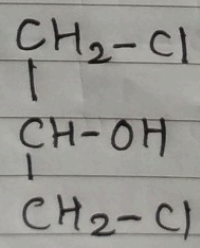
3] Reaction with HCl :-

With HCl at 383K glycerol monohydrin is formed. With excess of HCl for longer time, glycerol dichlorohydrin is the product.

In this reaction only primary -OH groups are replaced by -Cl group.



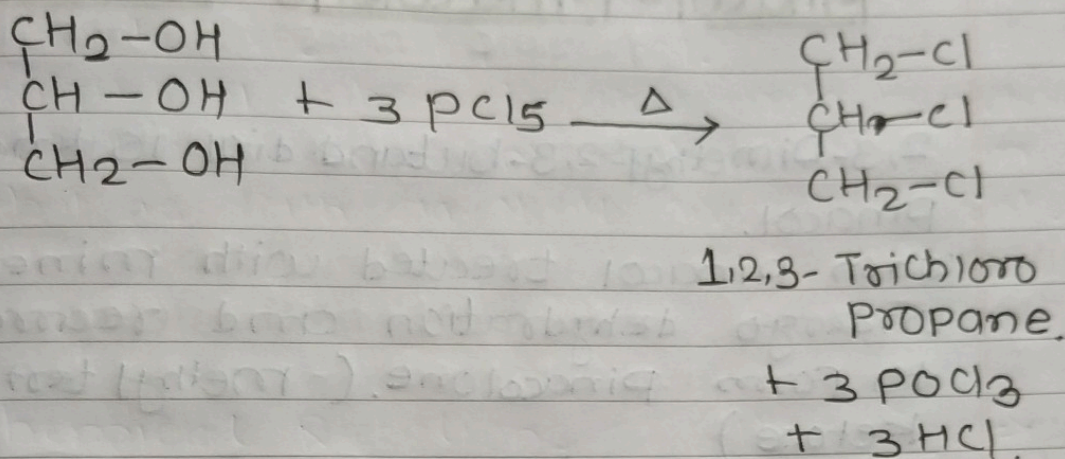
Glycerol monohydrin.



← Excess HCl
- H₂O

Glycerol dichlorohydrin.

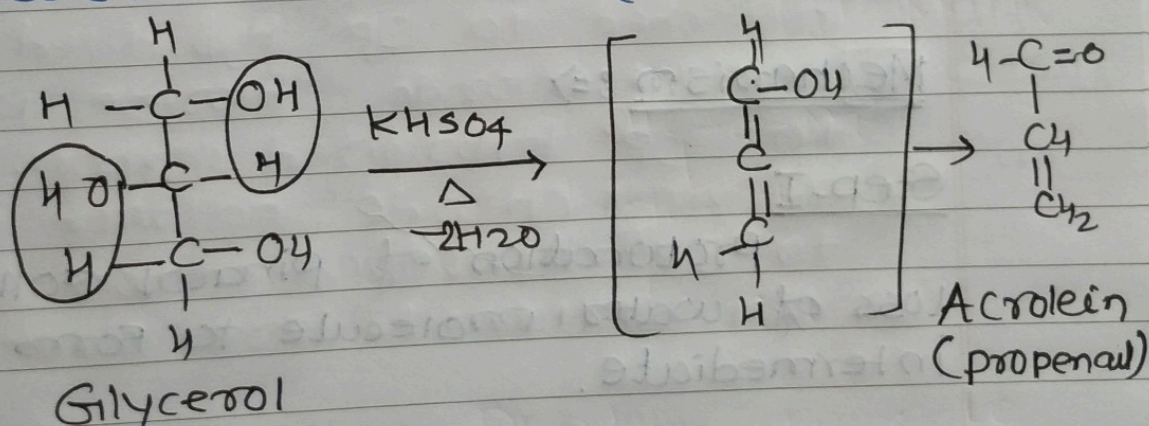
4) Reaction with PCl_5 :-



With PCl_5 Glycerol forms 1,2,3-trichloro, propane.

In this reaction all OH groups are replaced by $-\text{Cl}$ group.

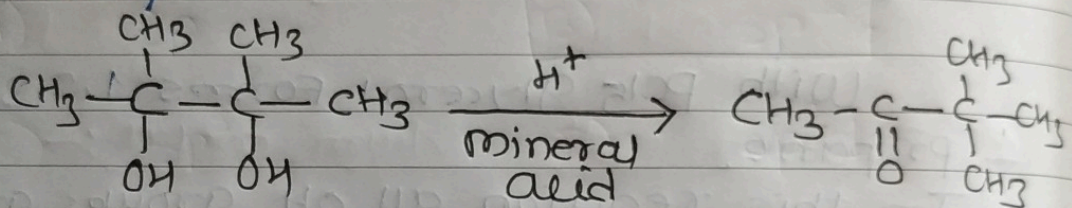
5] Reaction with KHSO_4 (Dehydration reaction)



Pinacol - Pinacolone Rearrangement

2,3-Dimethyl-2,3-butane diol is known as Pinacol.

When pinacol treated with mineral acid undergo dehydration and rearrangement to form pinacolone. (methyl tert-butyl ketone)



2,3-Dimethylbutane-2,3-diol
(Pinacol)

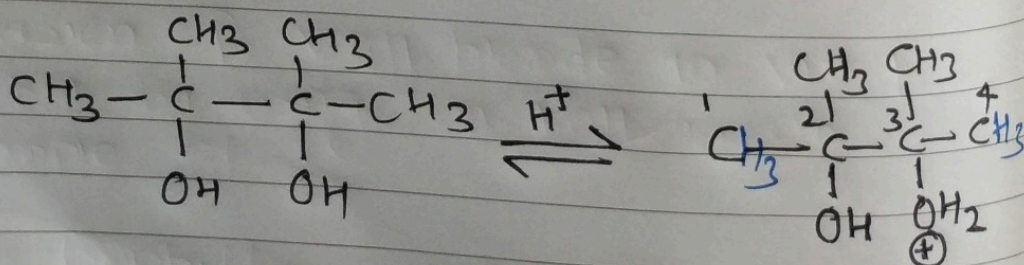
Pinacolone
tert-butyl
ketone.

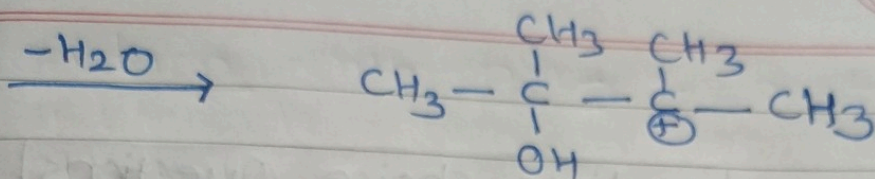
+ H₂O.

Mechanism $\Rightarrow$

Step-I

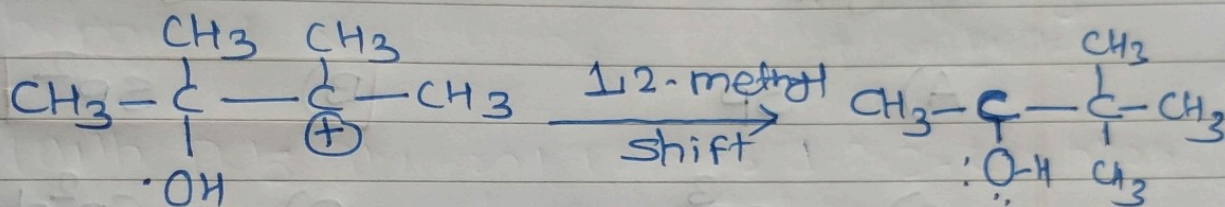
Protonation of Pinacol Followed by the loss of water molecule to form carbocation intermediate.





Carbocation

Step-II :- Rearrangement of the carbocation by a 1,2-shift to yield the protonated ketone.



Carbocation.

Protonated Ketone.

Step-III :- Loss of proton to form pinacolone.

