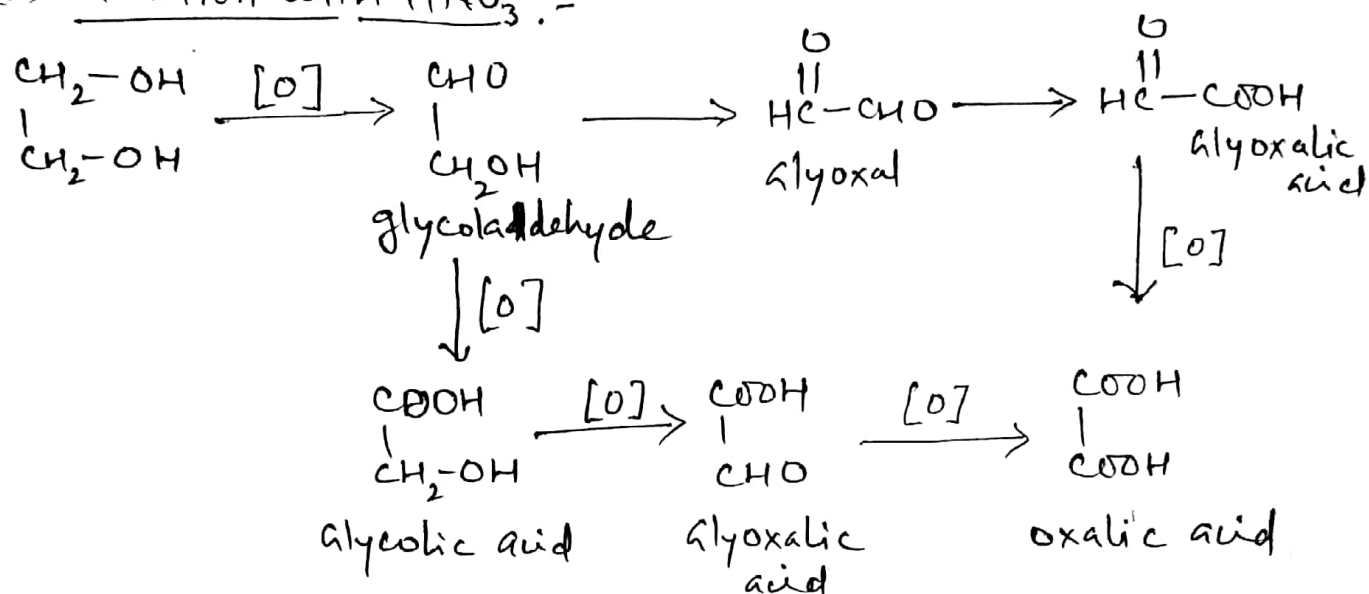


# Unit 6 (B) Diols BSc PS I<sup>st</sup> year II sem. Sec A

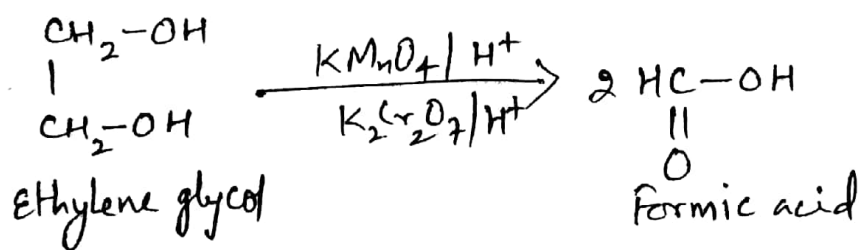
Dihydroxy alcohols containing the two -OH groups on adjacent carbons. They are also known as glycols.

Oxidation Reactions :- 1,2-diols contains two primary hydroxyl groups. Therefore it gives different products depending on the nature of oxidizing agents.

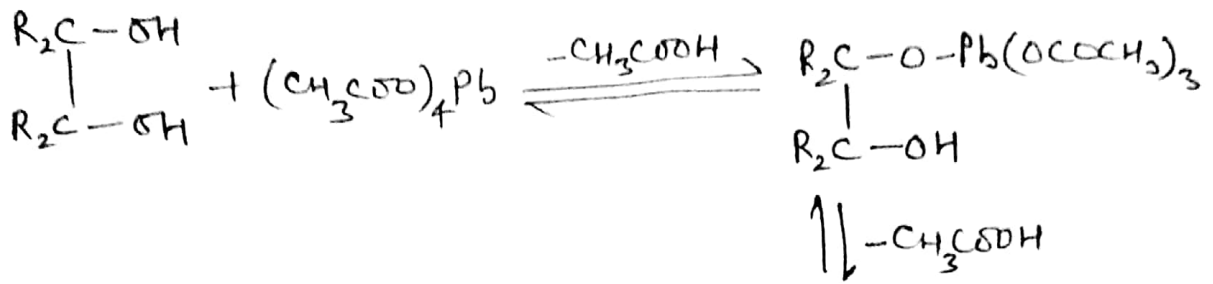
(1) Reaction with HNO<sub>3</sub> :-



(2) Oxidation by KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> :- Acidic, basic or neutral permanganate solution or acidic potassium dichromate undergoes carbon-carbon bond cleavage resulting in formation of formic acid.



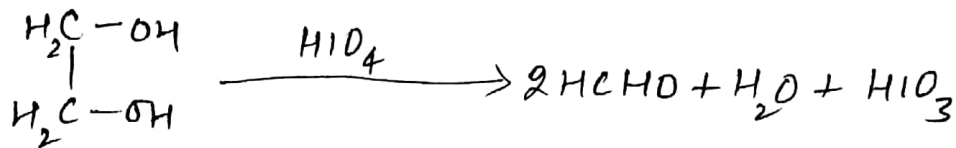
(3) Oxidation by Lead tetraacetate :- This is also undergoes c-c bond cleavage resulting in formation of carbonyl compounds. The reagent does not react with 1,3- or 1,4-diols.



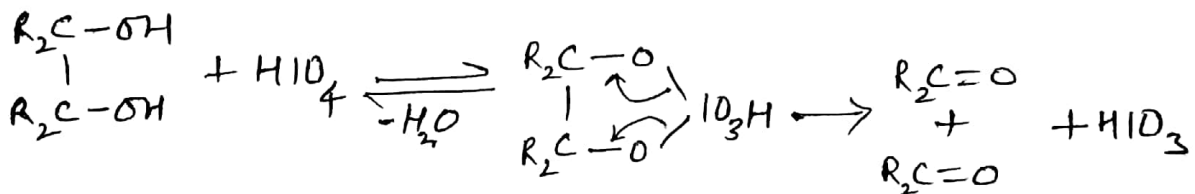
Carbonyls

Mechanism shows a tetrameric intermediate which resulted into carbonyls.

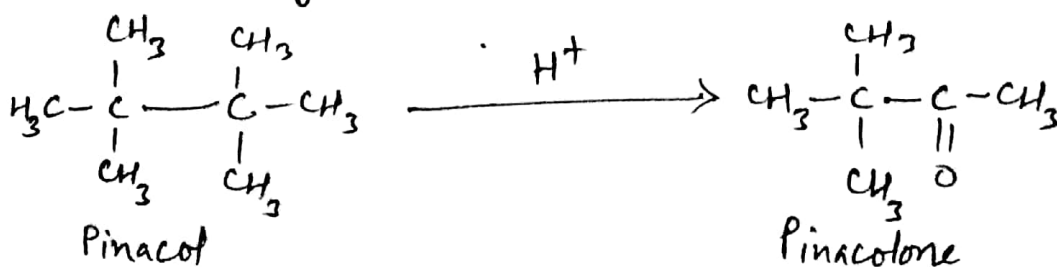
(4) Oxidation by Periodic acid :- Periodic acid brings about oxidative cleavage of C-C bonds with adjacent -OH groups to yield carbonyl compounds. The reagent also does not react with 1,3- or 1-4 diols.



mechanism :- Reaction proceed via a cyclic intermediate.



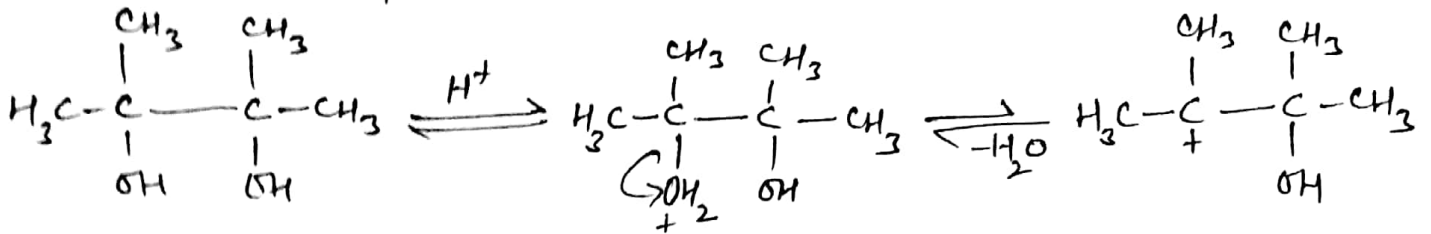
Pinacol-Pinacolone Rearrangement :- 1,2-diols in which two adjacent tertiary carbon atoms bearing two -OH groups called Pinacol. The 1,2-rearrangement takes place under acidic conditions. The name of the rearrangement of Pinacol into Pinacolone  $Me_3C-C(=O)-Me$ .



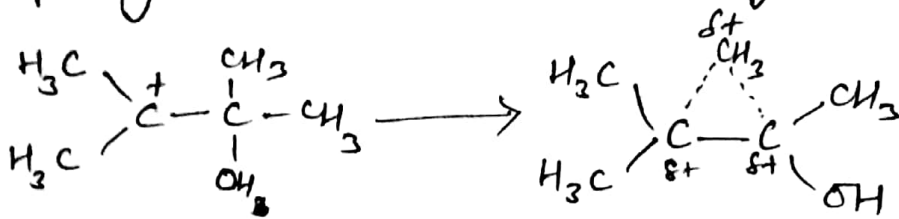
(2)

Mechanism:- Reaction mechanism is given by following steps:

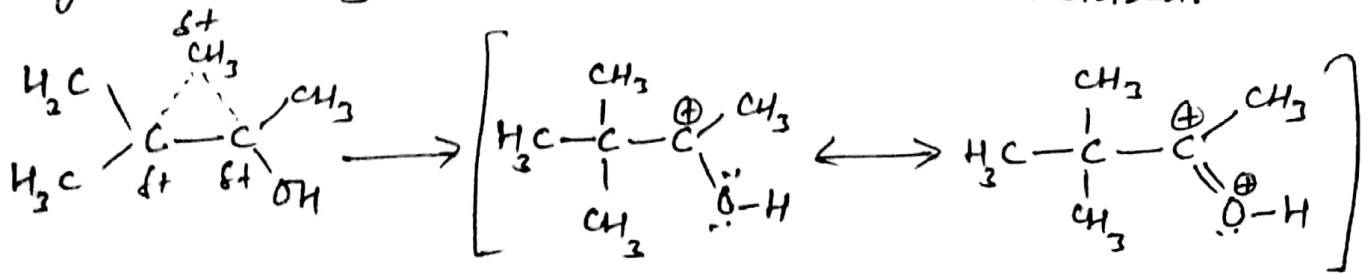
Step-I:- In the course of reaction protonation of one of the -OH group occurs and by losing one water molecule convert into electron deficient tertiary carbocation.



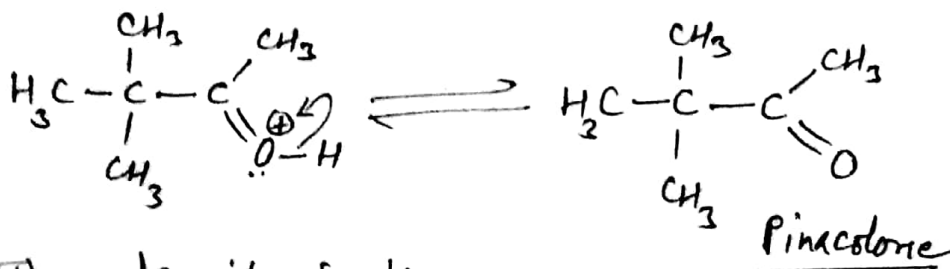
Step-II:- The above carbocation forms a cyclic intermediate in which methyl group is migrate to onto carbocation centre by 1,2-rearrangement. Actually in the intermediate this migrant  $\text{CH}_3$  group is not completely detached even it partially bonded with both the centres.



Step-III:- Complete 1,2 rearrangement happened and  $\text{CH}_3$  group is completely migrated forming carbocation which resonance stabilized.



Step-IV:- above carbocation on deprotonation yielded into pinacolone.



The order of migrating groups in pinacol is followwise  
 $\text{Ph} > (\text{Me})_3\text{C} > \text{CH}_2\text{CH}_3 > \text{CH}_3$

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