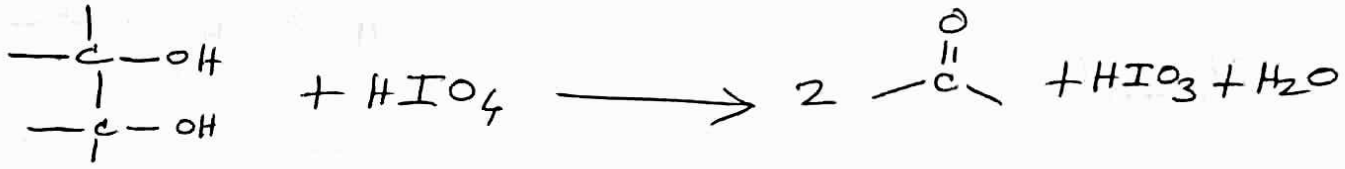
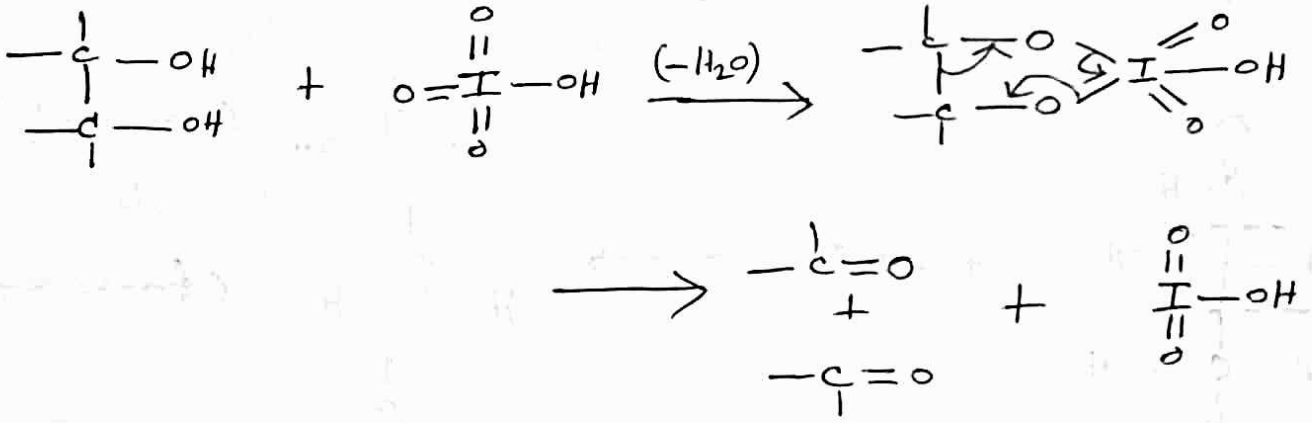
Reactions of Diols

Cleavage of Glycols and Related Compounds by HIO_4

Compounds that have hydroxyl groups on adjacent atoms undergo oxidative cleavage when they are treated with aqueous periodic acid (HIO_4). The reaction breaks carbon–carbon bonds and produces carbonyl compounds.



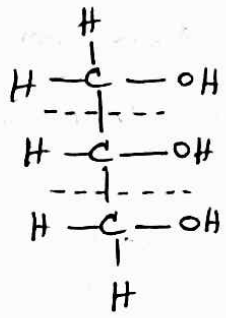
Mechanism



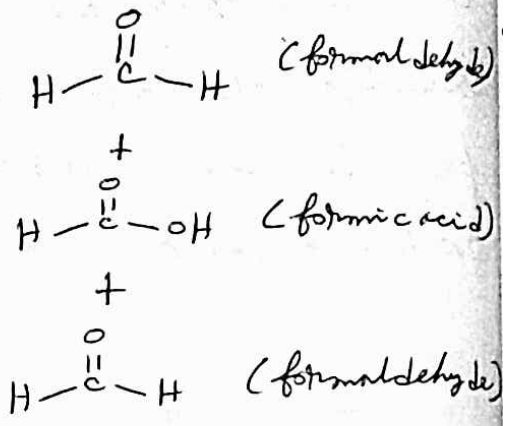
Periodate oxidations are thought to take place through a cyclic intermediate. Two hydroxyl groups of a diol should be positioned appropriately to form this cyclic intermediate.

Examples

1. When three or more —CHOH groups are contigrous, the internal ones are obtained as formic acid.

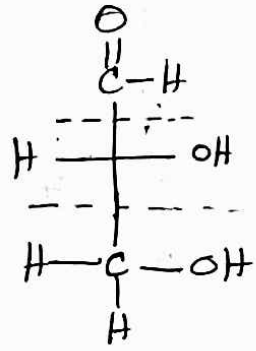


+ 2 HIO_4 ⟶

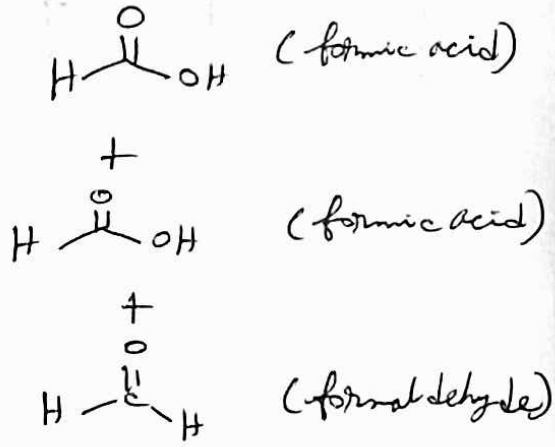


Glycerol

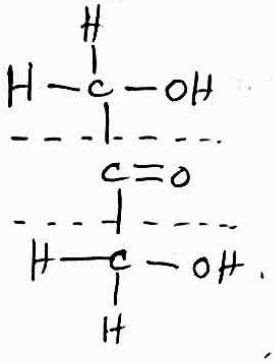
2. Oxidative cleavage also takes place when an —OH group is adjacent to the an aldehyde or ketone group.



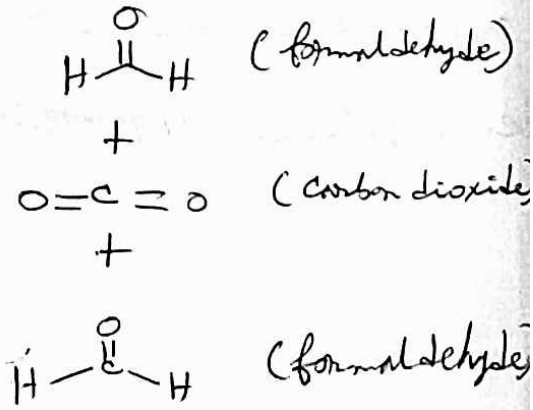
+ 2 HIO_4 ⟶



Glyceraldehyde



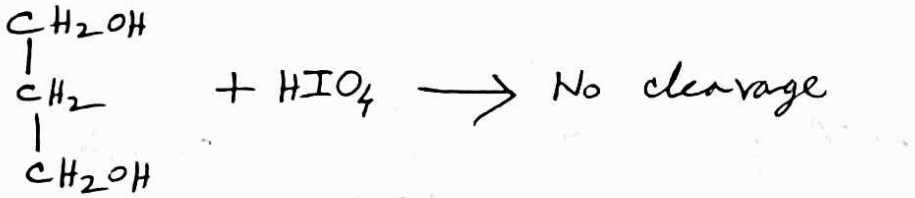
+ 2 HIO_4 ⟶

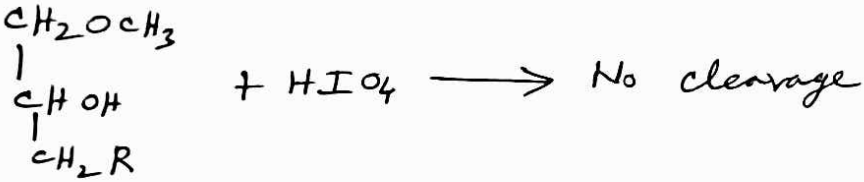


Dihydroxy acetone

NOTE

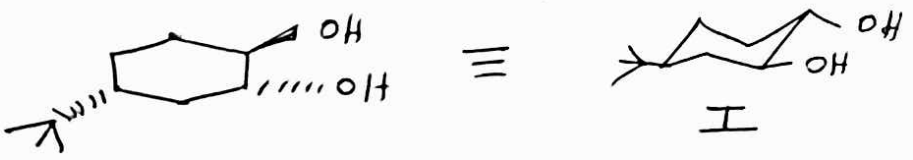
Periodic acid does not cleave compounds in which the hydroxyl groups are separated by an intervening $-CH_2-$ group, nor those in which a hydroxyl group is adjacent to an ether or acetal function.



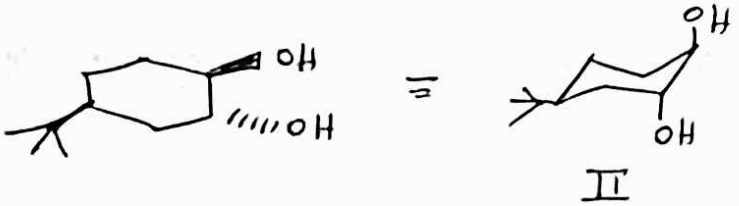


NOTE

In the case of 1,2-cyclohexane diol, when the two $-OH$ groups occupy axial positions, they are too far away from each other to form the cyclic intermediate and such conformer will not react with HIO_4.



I



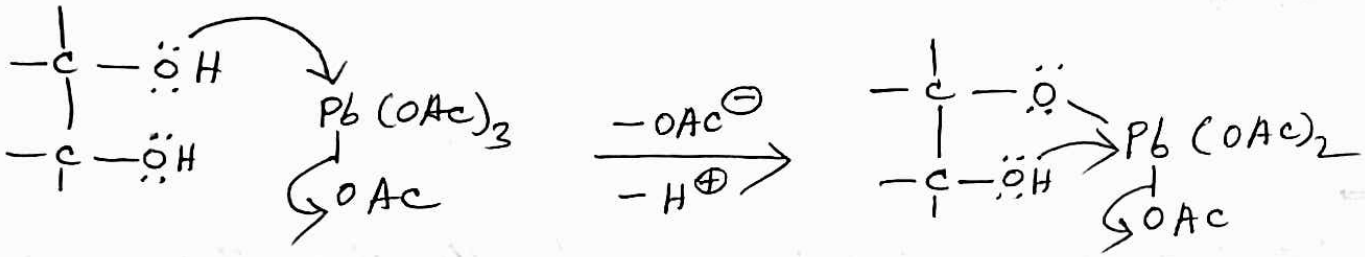
II

Between (I) and (II), (II) does not react with HIO_4.

Cleavage of Glycols via Lead tetraacetate

Glycols (1,2-diols) are cleaved by the reaction with lead tetraacetate.

Mechanism



NOTE

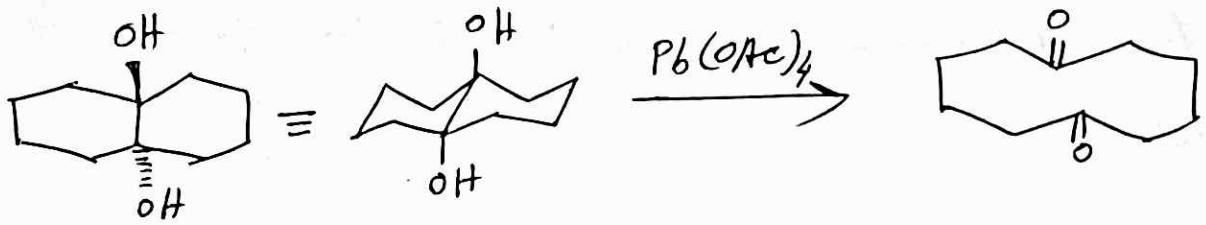
The reagent lead tetraacetate brings about cleavage similar to those of periodic acid.

Periodic acid works well in aqueous solution and lead tetraacetate gives good result in organic solvents.

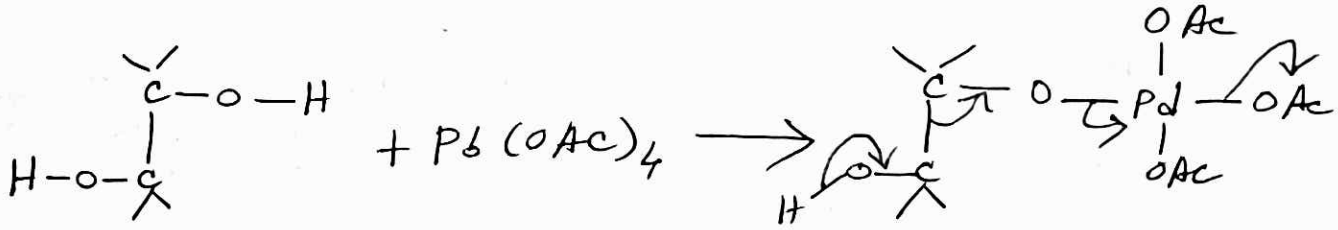
Examples

Glycols that can not form cyclic intermediates are eventually oxidized.

1. For example, trans 9,10-dihydroxydecalin is oxidized, but the rate is 100 times less than the cis-isomer.



Mechanism



$$\longrightarrow \; >C=O + >C=O + Pb(OAc)_2$$

2.