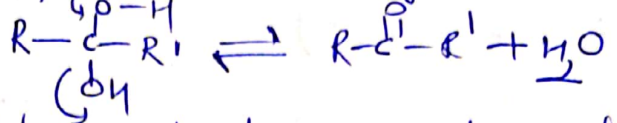
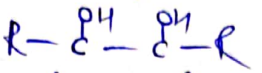
(Diols)

Dihydric alcohols

Gem diols → Gem diols are unstable compounds which converts into carbonyl compound on dehydration

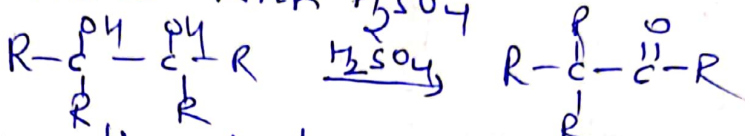


Vicinal diols (also known as pinacol)



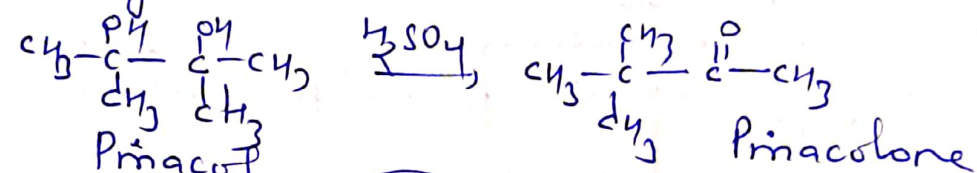
Pinacol-Pinacolone Rearrangement

Dibertiary-1,2-diols converts into ketones on treatment with H_2SO_4



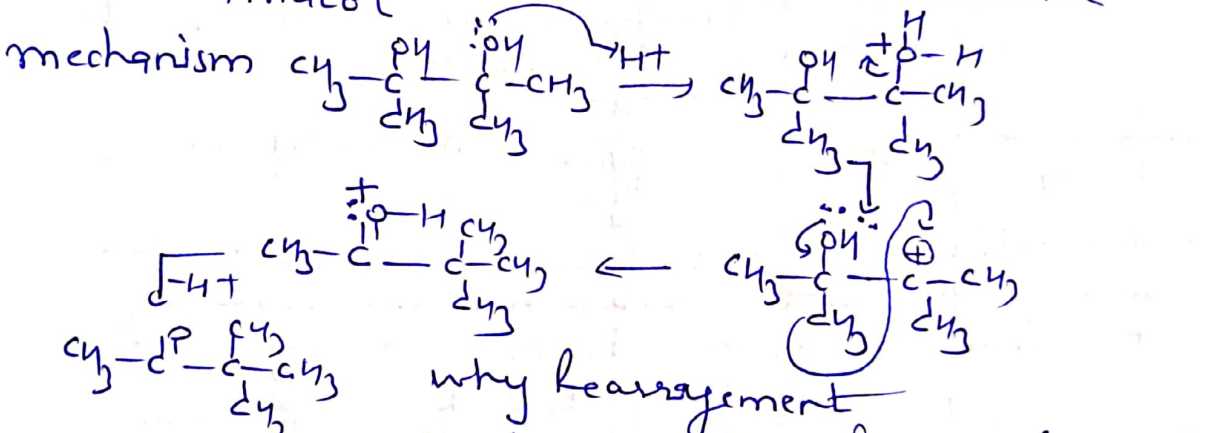
This reaction is known as Pinacol-Pinacolone rearrangement

Eg



Pinacol — Pinacolone

mechanism



Why Rearrangement

Due to migration of methyl group, positive charge move on oxygen thus giving Oxonium cation. In carbocation, carbon has an incomplete octect but in Oxonium cation, every atom has complete octect, hence more stable

Pinacol-Pinacolone rearrangements in pinacols where two different groups are attached to carbons

→ Rearrangement depends upon two factors, namely, stability of carbocation & migratory aptitude of groups.

Eg 1 $Ph-\underset{OH}{\overset{Ph}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{H^+} Ph-\overset{Ph}{\underset{CH_3}{C}}-\overset{O}{C}-CH_3$

(Removal of this (-OH) group as carbocation is formed is more stable)

Eg 2 $CH_3-\underset{OH}{\overset{Ph}{C}}-\underset{OH}{\overset{Ph}{C}}-CH_3 \xrightarrow{H^+} CH_3-\overset{O}{C}-\underset{Ph}{C}-CH_3$

(Migrating aptitude of groups governs the formation of product

Order $-Ph > C_6H_5 > -CH_3 > -H$

Oxidation of diols

→ Oxidation with dil HNO_3 or $KMnO_4/OH^-$

$CH_2OH \xrightarrow{[O]} CHO \xrightarrow{[O]} COOH$
$CH_2OH \qquad CH_2OH \qquad CH_2OH$

$CHO \xrightarrow{[O]} COOH$
$CHO \qquad COOH$

Periodate Oxidation

Periodic acid (HIO_4), Sodium periodate ($NaIO_4$) or potassium periodate (KIO_4) oxidises compound having Vic-diol groups

→ Each Vicinal diol group consumes one mole of the reagent for breaking of C-C bond

1 mole of HIO_4 ← CH_2OH / CH_2OH

CH_2OH / $CHOH$ / $CHOH$ / CH_2OH → 3 moles of HIO_4

→ During the course of oxidation, if there is breaking of only one bond of carbon, then carbon having hydroxyl group converts into carbonyl group

$R-\underset{R-C-OH}{\overset{R}{\underset{|}{C}}}-OH \xrightarrow{HIO_4} R-\overset{O}{C}-R + R-\overset{O}{C}-H$
$\qquad\qquad H$

→ If there is breaking of two bonds of the same carbon having hydroxyl groups, then that carbon is oxidized to carboxylic acid.

$R-\underset{R-C-OH}{\overset{R}{\underset{|}{C}}}-OH \xrightarrow{2HIO_4} R-\overset{O}{C}-R + R-\overset{O}{C}-OH + R-\overset{O}{C}-H$
$\qquad\qquad H$

→ In a case of oxidation of α-hydroxy carbonyl compounds

CHO / $CHOH$ / $CHOH$ / CH_3 $\xrightarrow{2HIO_4}$ $HCOOH + HCOOH + CH_3CHO$

→ CH_2OH / $CHOH$ $\xrightarrow{HIO_4}$ $H-\overset{O}{C}-H + H-\overset{O}{C}-H$