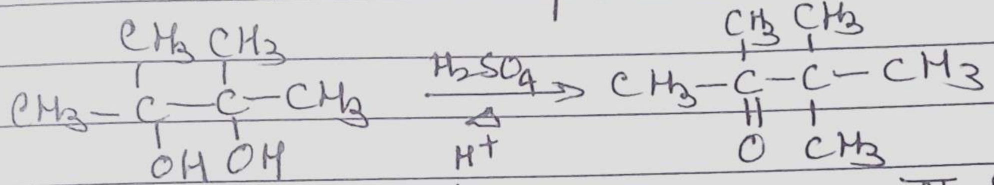
DATE:

Pinacol Pinacolone Rearrangement

Pinacol (1-2 diol) forms pinacolone (Mono-ketone) in presence of hot dil H_2SO_4 acid.

It is known as pinacole - Pinacolone rearrangement



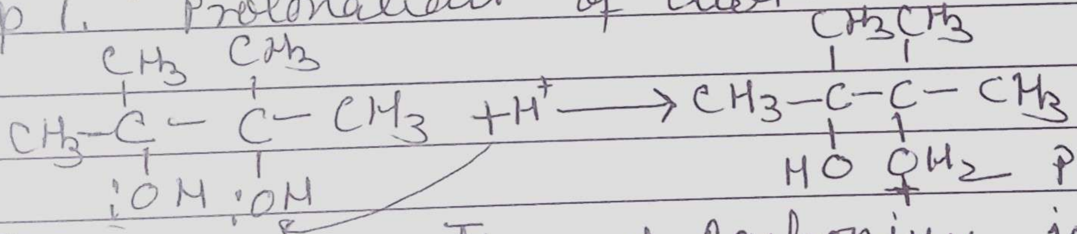
$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\Delta \; H^+]{H_2SO_4} CH_3-\underset{\overset{\|}{O}}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

2,3-Dimethyl 2,3-butanediol
(Pinacol)

3,3-Dimethyl-2-butanone
(Pinacolone)

The mechanism of the above reaction involves the following four steps.

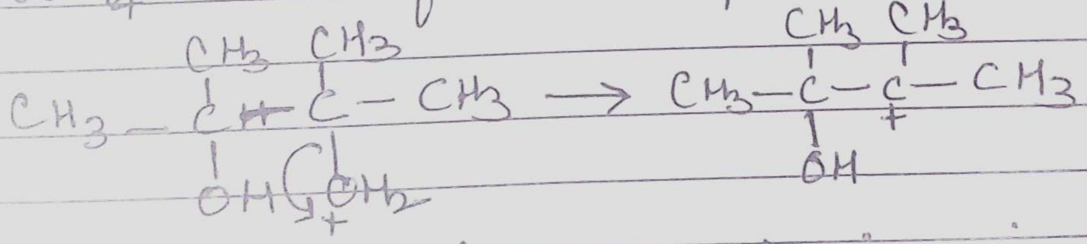
Step I. Protonation of diol.



$$CH_3-\underset{\ddot{O}H}{\overset{CH_3}{C}}-\underset{\ddot{O}H}{\overset{CH_3}{C}}-CH_3 + H^+ \longrightarrow CH_3-\underset{HO}{\overset{CH_3}{C}}-\underset{\overset{+}{O}H_2}{\overset{CH_3}{C}}-CH_3$$

Protonated diol

Step II - Formation of carbonium ion by loss of water from the protonated diol.

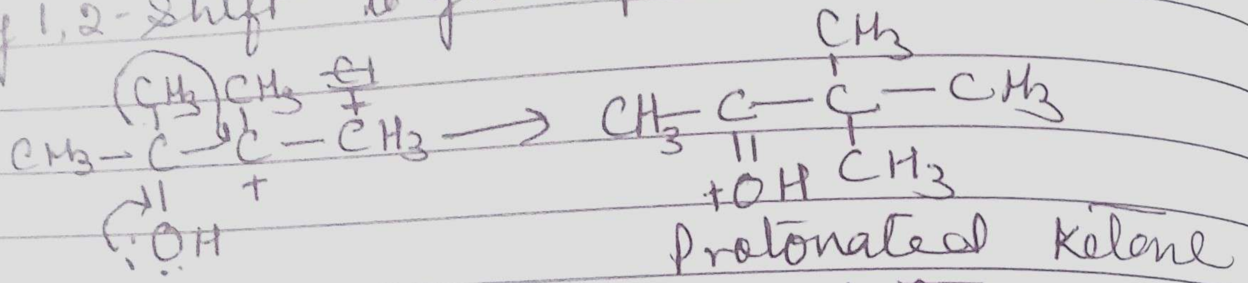


$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{\overset{+}{O}H_2}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{+}{\overset{CH_3}{C}}-CH_3$$

Protonated diol

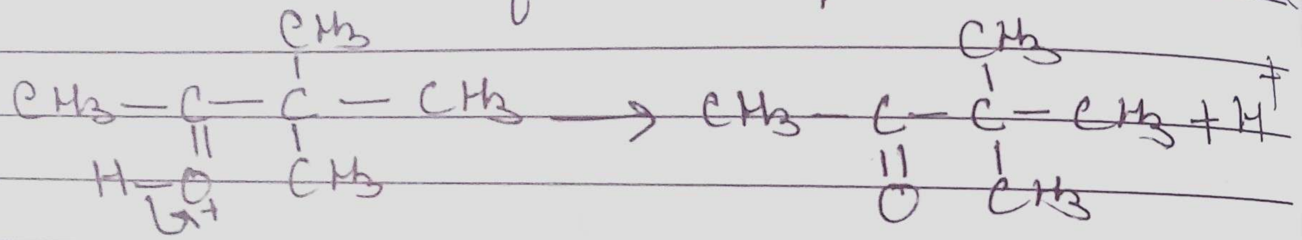
Carbonium ion

Step III – Rearrangment of carbonium ion by 1,2-shift to give protonated ketone.



Protonated Ketone

Step IV – The formation of ketone by ~~loss~~ loss of Proton from the protonated ketone

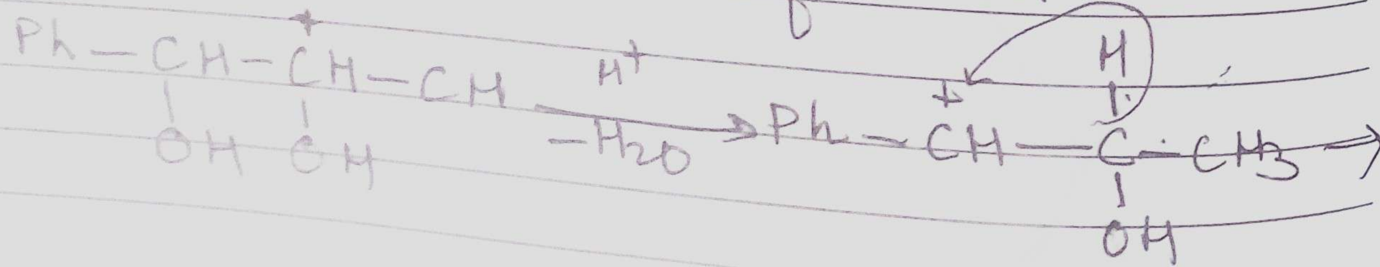


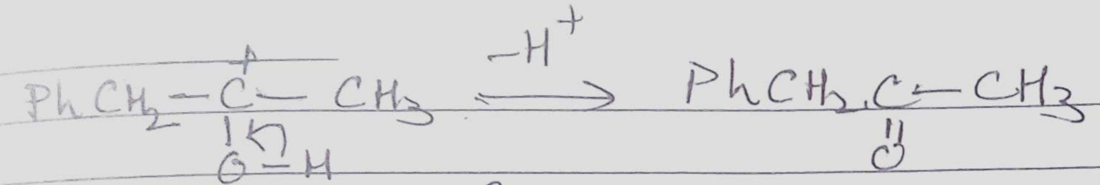
Protonated ketone

Pinacolone

The Order of migratory attitude is Ar >> H > R

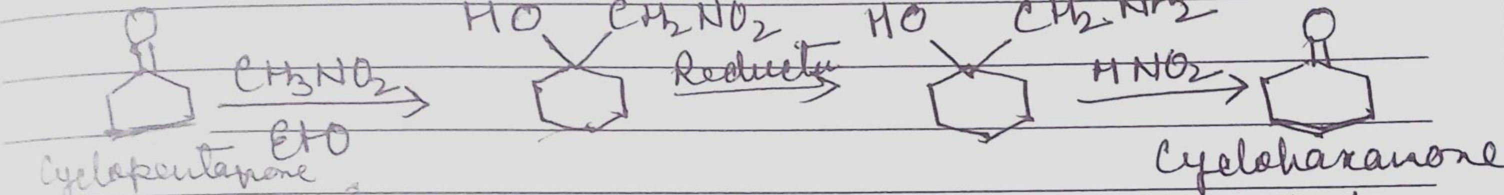
In the following example of unsymmetrical migration of hydride (H^+) ion is more stable benzylic carbocation is formed.



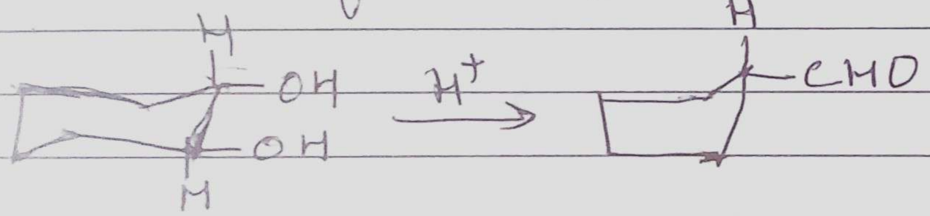


$$PhCH_2-\overset{+}{\underset{O-H}{C}}-CH_3 \xrightarrow{-H^+} PhCH_2-\underset{O}{\overset{\|}{C}}-CH_3$$

Application — (2) Ring expension → Formata from cyclopentanone to cyclohexanone.

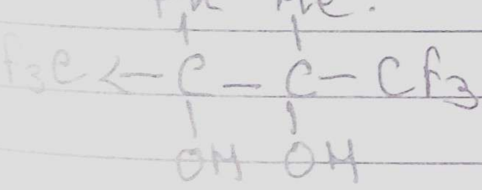


(2) Ring contraction → Synthesis of cycloheptanone from cyclohexanone.



Trans-1,2-Cyclohexanediol cyclopentane Carboxaldehyde

Limitations — 1,2-Diols having strong -I groups as substituents do not show this rearrangement.



$$F_3C-\underset{OH}{\overset{Ph}{C}}-\underset{OH}{\overset{Me}{C}}-CF_3 \xrightarrow{H^+} \text{No reaction.}$$