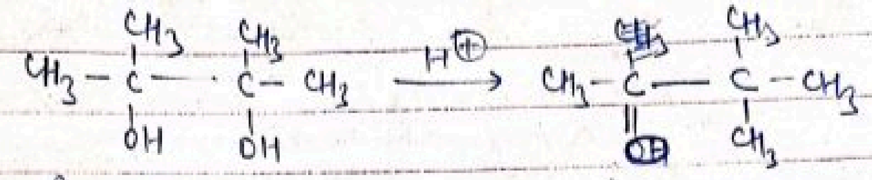
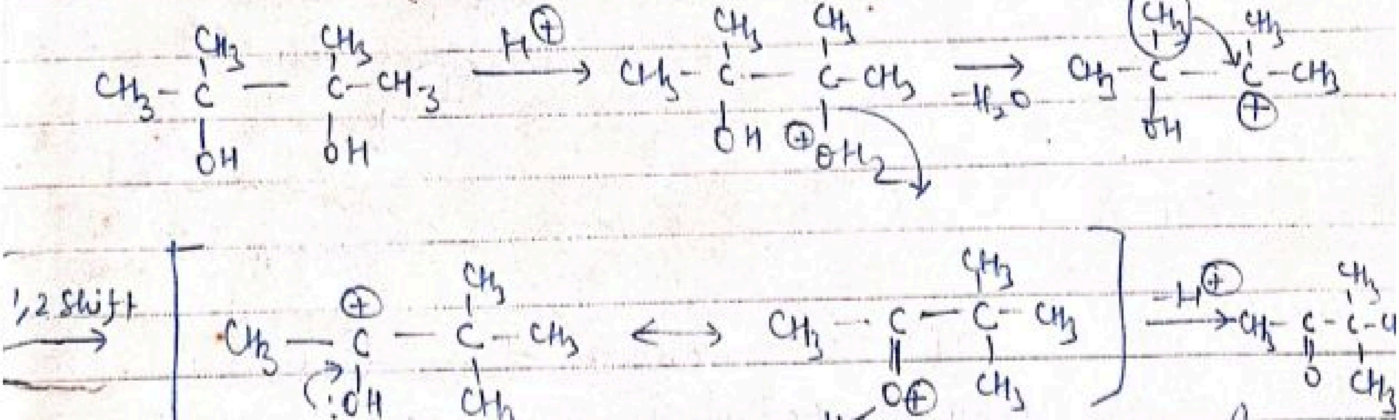
Pinacol- Pinacolone Rearrangement:

Substituted vic-diols usually lead to rearrangements, with formation of ketones, when dehydration was attempted with acids. (Though elimination without rearrangement can also be accomplished.) This reaction is called: Pinacol-Pinacolone rearrangement. The reaction getting its name from the typical compound Pinacol $[Me_2-\underset{OH}{C}-\underset{OH}{C}-Me_2]$ which is rearranged to Pinacolone $[Me_3-\underset{\|\atop O}{C}-Me]$



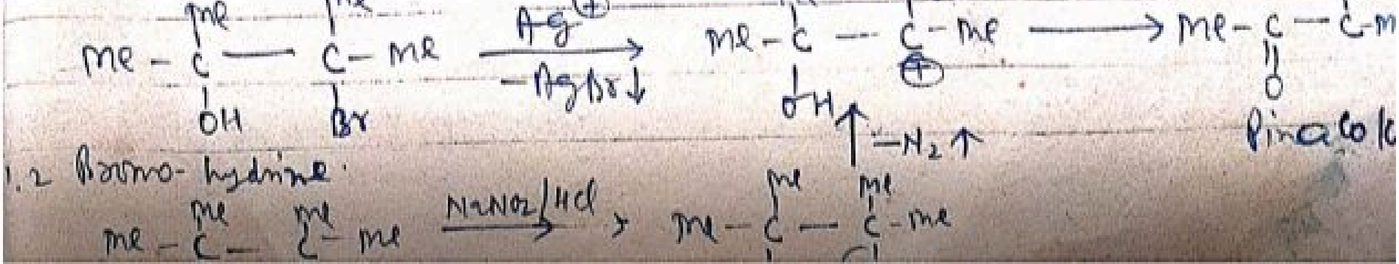
Pinacol. Pinacolone.

Mechanism: The mechanism involves a simple whitemore (1,2 shift) shift, in which the driving force is stabilisation of the rearranged carbonium ion by elimination of a proton from OH.



(Branched ketones)

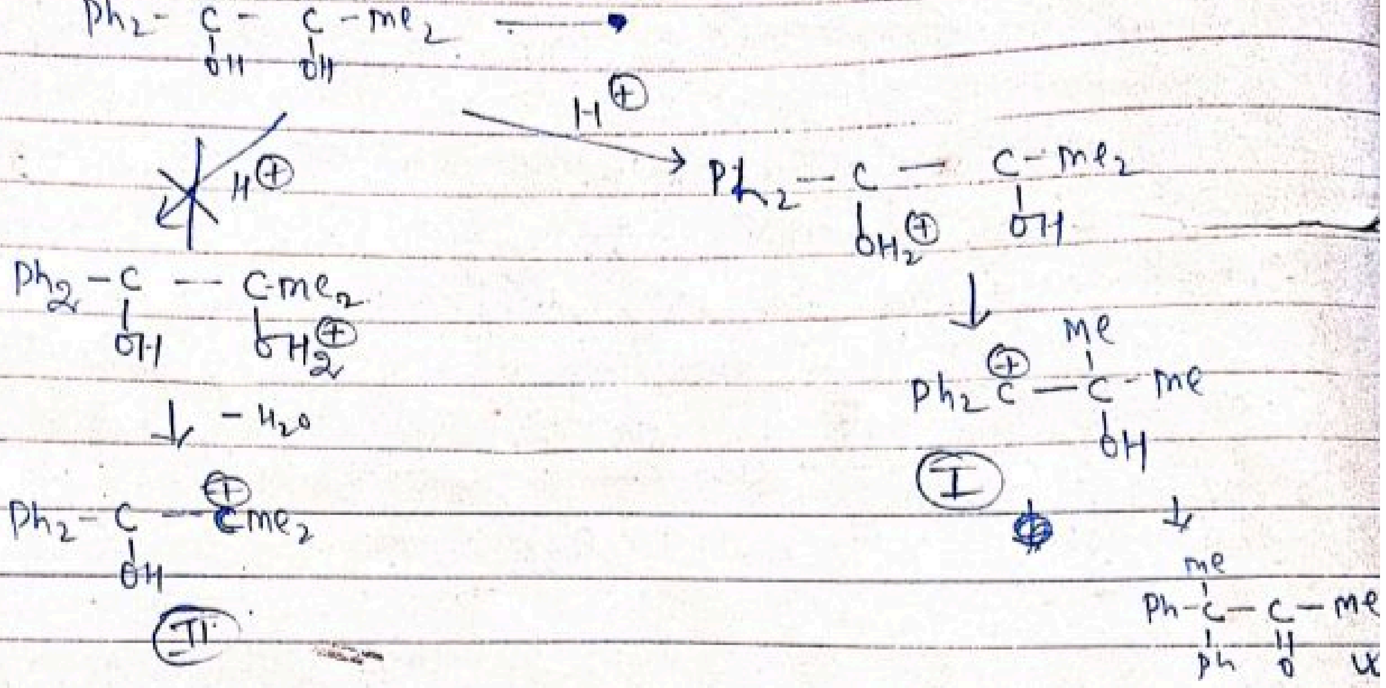
It is obvious that other compounds in which a positive charge can be placed on a carbon α- to the one bearing an -OH group can also give the rearrangement. Thus, 1,2-bromohydrine & 1,2 amino alcohol (β-amino alc are found to yield pinacolone, when treated with $Ag^{\oplus}$ $(AgNO_3)$ and $NaNO_2/HCl$, respectively.



Applications:- A number of experiments has been carried out to determine the relative migratory aptitude of groups in Pinacol/Pinacolone type rearrangements & in general relative ease of migration is found to be

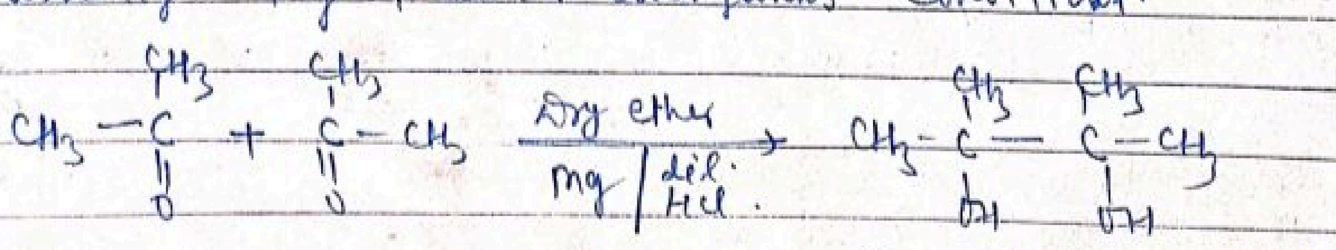
$$Ph > Me_3C > MeCH_2 > Me$$

But it should be recognised that there are considerable difficulties involved in choosing suitable models for such experiments & in interpreting the results when we have got them. Thus in the rearrangement of the 1,2-diol $Ph_2C(OH)C(OH)Me_2$, it is Me that is found to be migrate & not Ph, as might have been expected from the sequence above (from the migratory aptitude sequence) *



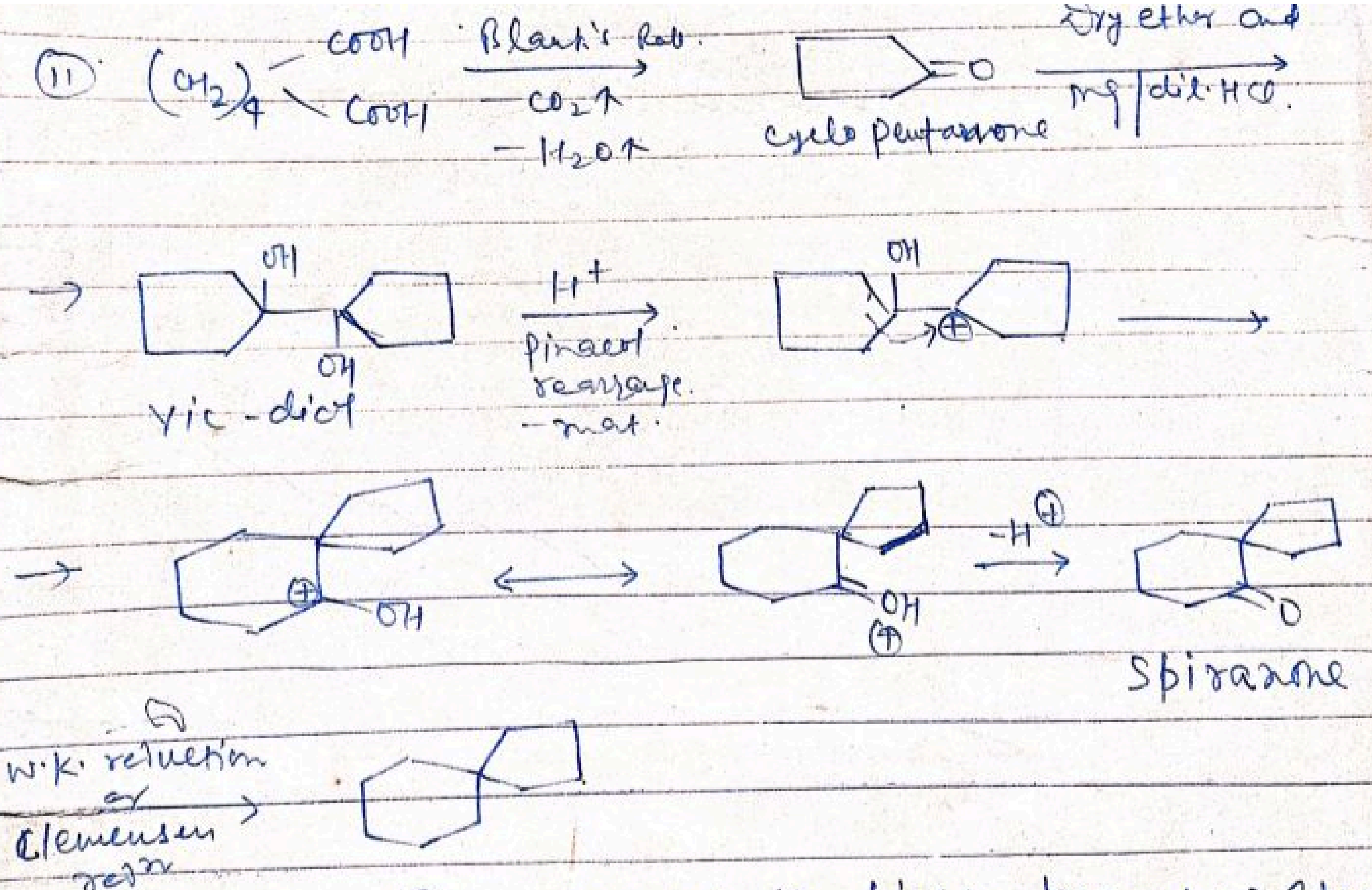
* This is because of the fact that Ⓘ is more stable carbonium ion Ⓘ rather than (II) & hence migration of Me rather than Ph takes pla

Applications:- Pinacols themselves are prepared by reductive dimerisation of Ketones with bivalent me usually Mg, under anhydrous conditions.

(1) 

$$CH_3-\underset{\overset{\|}{O}}{\overset{CH_3}{C}} + \underset{\overset{\|}{O}}{\overset{CH_3}{C}}-CH_3 \xrightarrow[Mg/\text{dil. } HCl]{\text{Dry ether}} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

Pinacol (vic diol)



Because of the highly branched Struc of the products they are not formed easily by oth methods. So this rearrangement is important in synthesis: (of these compounds).