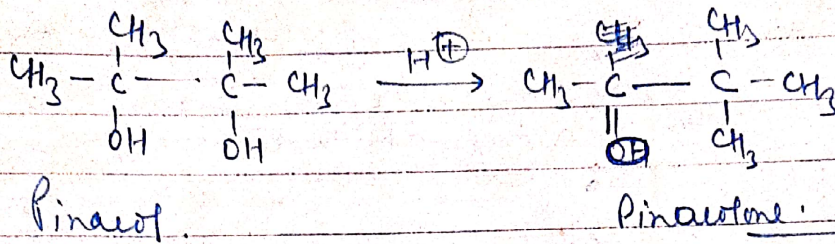
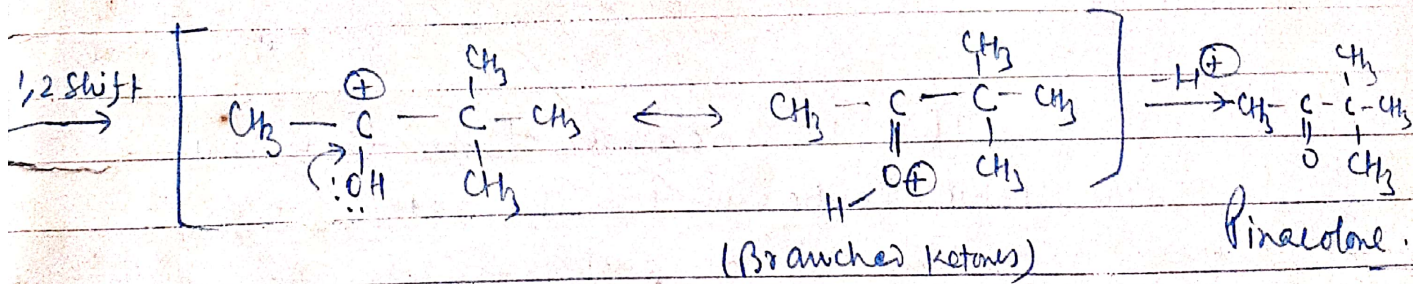
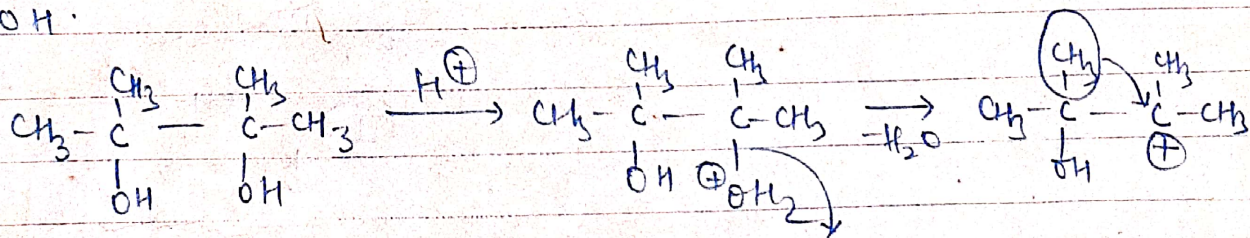


Pinacol-Pinacolone Rearrangement

Substituted vic-diols usually lead to rearrangement 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 $\left[\begin{array}{c} \text{Me}_2\text{C}-\text{C}-\text{C}-\text{Me}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array} \right]$ which is rearranged to Pinacolone $\left[\begin{array}{c} \text{Me}_2\text{C}-\text{C}-\text{Me}_2 \\ || \\ \text{O} \end{array} \right]$

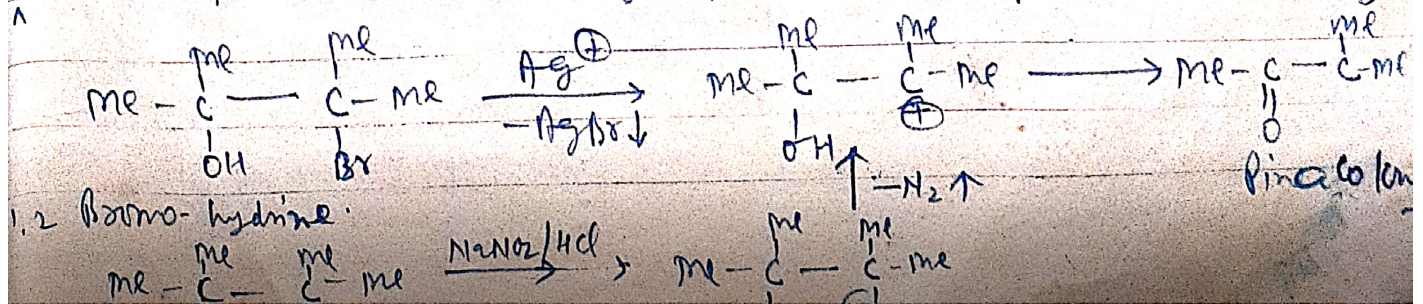


Mechanism: The mechanism involves a simple Whitmore (1,2 shift) in which the driving force is stabilisation of the rearranged carbonium ion by elimination of a proton from OH.

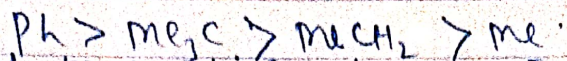


It is obvious that other compounds in which a positive charge can be placed on a carbon α -to one bearing an -OH group can also give ^{this} rearrangement.

Thus, 1,2-bromohydrine & 1,2-amino alcohol (β -amino alcohols) are found to yield pinacolone, when treated with Ag^+ (as AgNO_3) and NaNO_2/HCl , respectively.

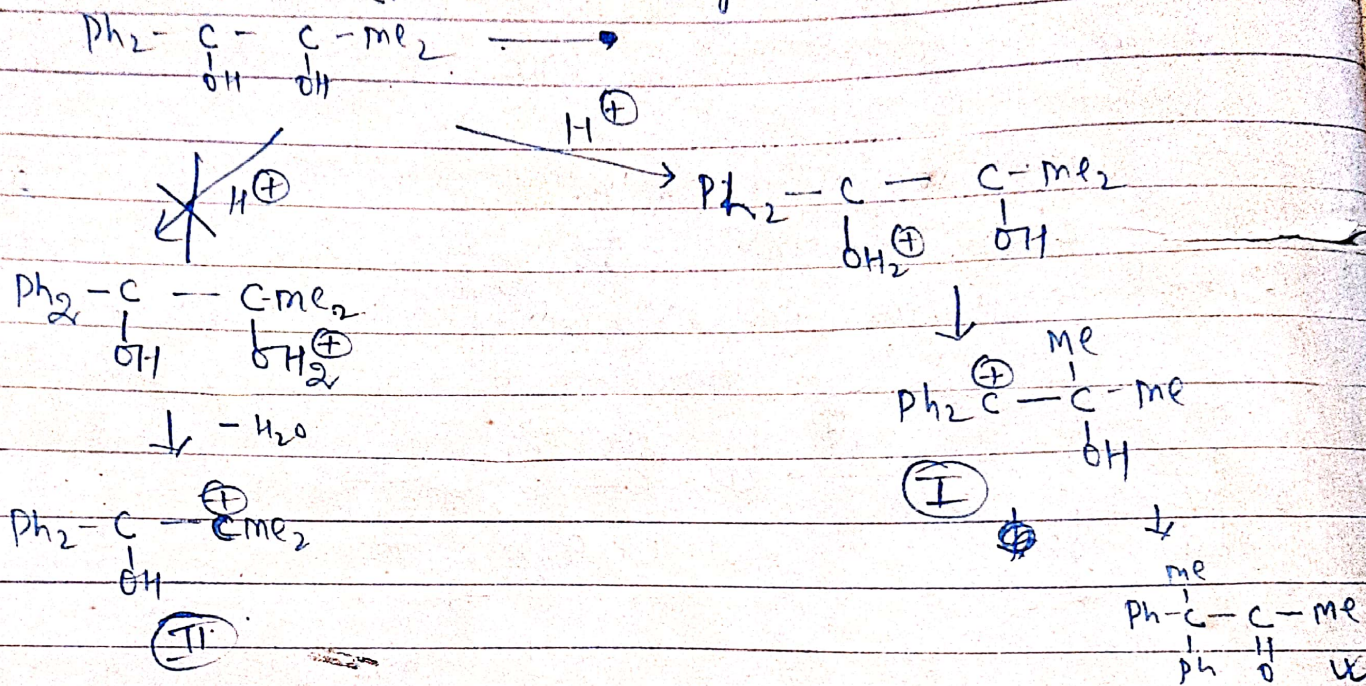


Applications: A number of experiments has been carried out to determine the relative migratory aptitude of groups in Pinacol/Pinacolone type rearrangements & in general relative ~~case~~ ease of migration is found to be



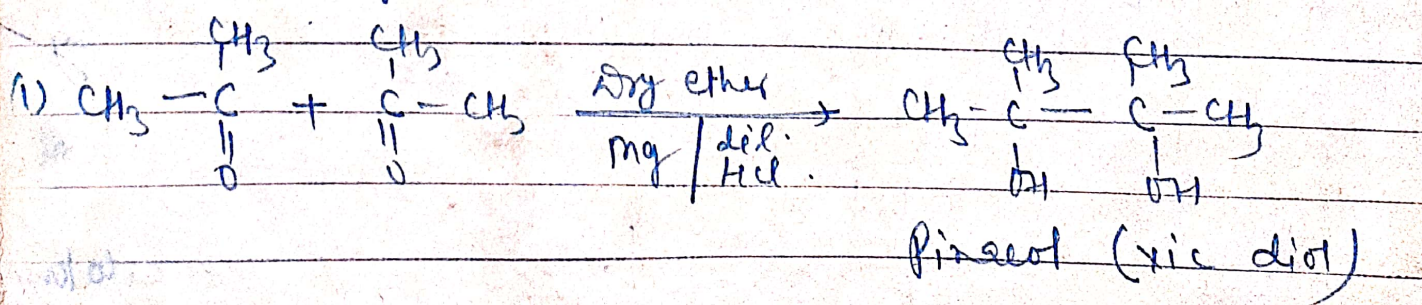
But it should be realised that there are considerable difficulties involved in choosing suitable models for these experiments, in interpreting the results which we have got them. Thus in the rearrangement of the

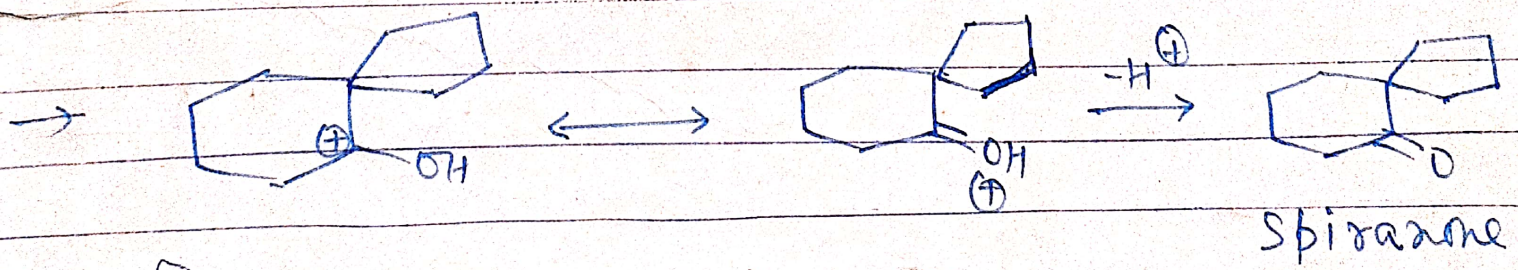
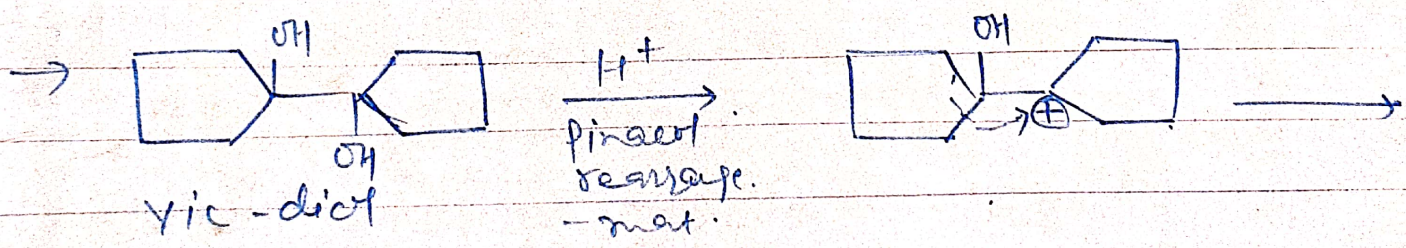
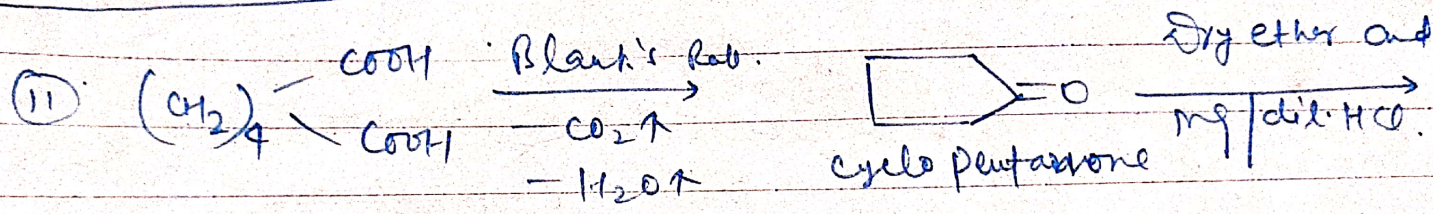
1,2-diol $Ph_2C(OH)C(OH)Me_2$, it is Me that is found to migrate & not Ph, as might have been expected from the sequence above (from the migratory aptitude sequence) *



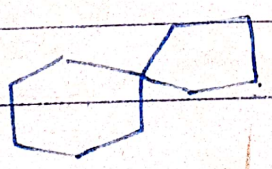
* This is because of the fact that (I) is more stable Carboxium ion (I) rather than (II) & hence migration of Me rather than Ph takes place

Applications: Pinacols themselves are prepared by reductive dimerisation of ketones with bivalent metal usually Mg, under anhydrous conditions.





\rightarrow w.k. reduction
 or
 Clemmensen
 reagent



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