

In some cases, there is a pair of unshared electrons on the migrating group which facilitates the formation of the intermediate. In other cases, carbon or hydrogen ($I; X = \text{—C—}$ or H), one pair of electrons remains sufficient to bind three atoms momentarily together. The formation of the bridged carbonium ions in 1, 2-shifts is an example of *neighbouring group participation*, and when the rate is increased because of this effect, the rearrangement is said to be *anchimerically assisted* (Winstein *et al.* 1953).

The rearrangements of this group may further be divided into three types on the basis of the nature of the atom where the migrating group moves. These three types are (i) rearrangements to electron deficient carbon, (ii) rearrangements to electron deficient nitrogen, and (iii) rearrangements to electron deficient oxygen.

16.2a Rearrangements to Electron Deficient Carbon (Carbonium ion Rearrangements) *(Nu⁻ Rearrangement)*

Since in this case the electron deficient atom is carbon, the intermediate is known as carbonium ion and hence, the rearrangements of this class are known as carbonium ion rearrangements.

Carbonium ion rearrangements take place far more readily than those involving either a free radical or a carbanion. In the carbonium ion transition state there is a new molecular orbital which is formed as a result of combination of an atomic orbital of the migrating group with the atomic orbitals of the other two carbon atoms. This M.O. can accommodate only two electrons. On the other hand, free radical and carbanion rearrangements have to pass through cyclic transition states in which three or four electrons, respectively, are to be accommodated in M.O. embracing three carbon atoms and therefore these should be less stable than the carbonium ion transition states.

Carbonium ion rearrangements are most likely to occur when normal reaction produces an unstable carbonium ion which can be converted to a more stable one ($3^\circ > 2^\circ > 1^\circ$) by 1, 2-shift.

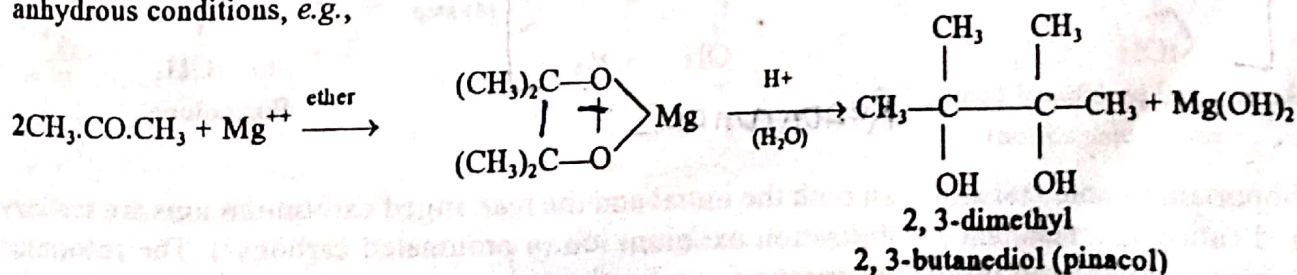
These rearrangements can further be divided into two classes *viz.* (i) those in which a change of actual carbon skeleton takes place and (ii) those which proceed without change in carbon skeleton. The former are more important.

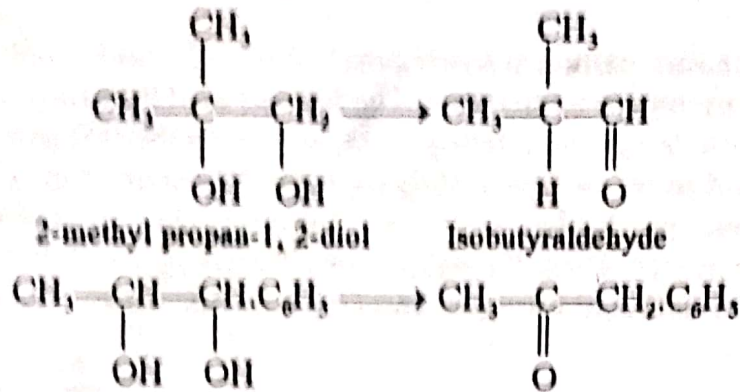
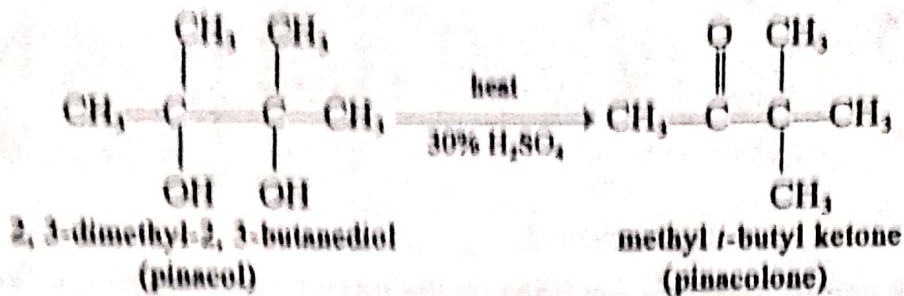
(A) Carbonium ion rearrangements with change in carbon skeleton :

The important examples of this group are described below.

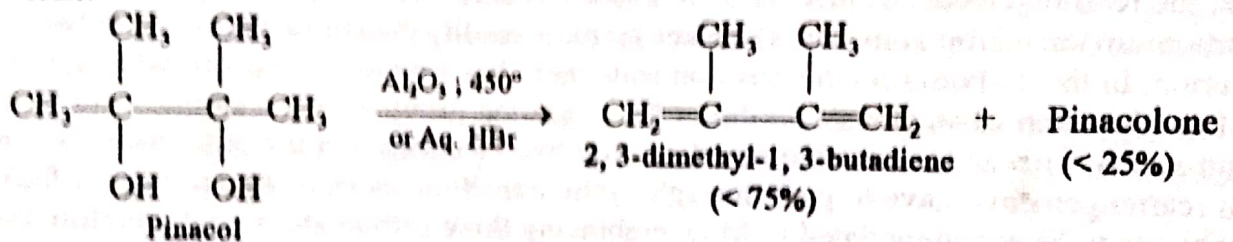
1. Pinacol-pinacolone rearrangements (pinacol rearrangements). The conversion of pinacols* (1, 2-glycols) to ketones or aldehydes by means of acids is known as pinacol rearrangements (R. Fittig, 1860).

* Pinacols are obtained by reducing the corresponding ketone or aldehyde with bivalent metals generally Mg^{++} under anhydrous conditions, e.g.,



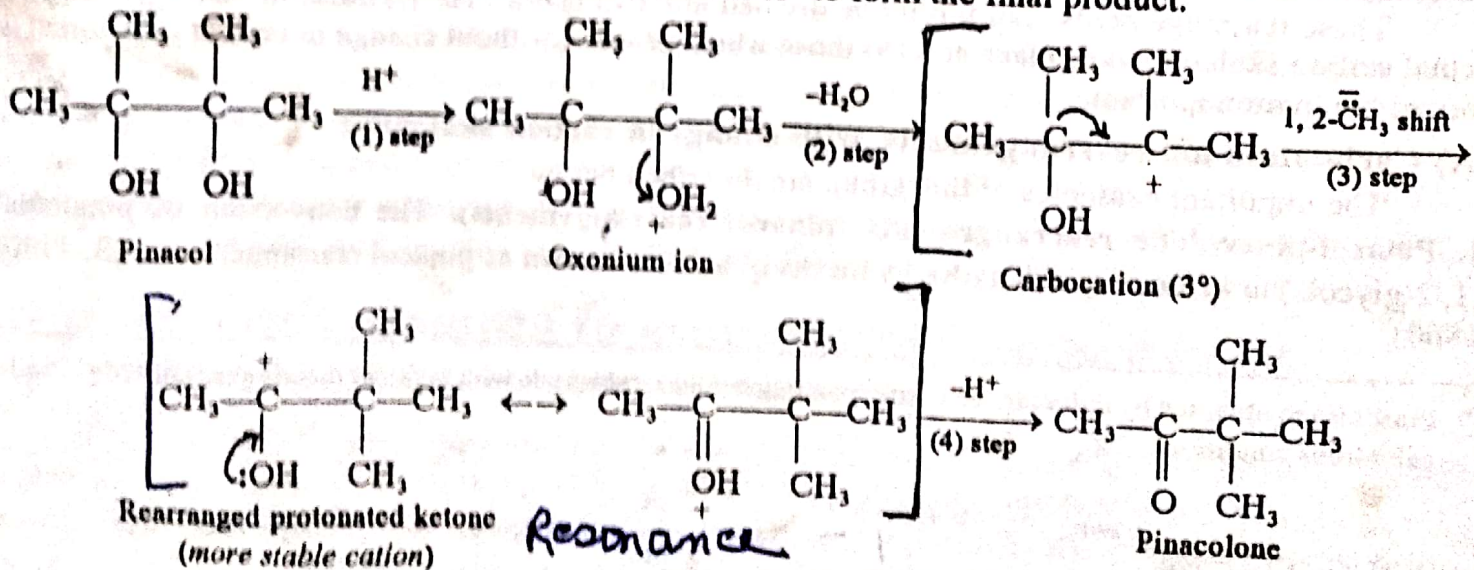


It is interesting to note that diols other than 1, 2-diols dehydrate normally, *i.e.*, without any rearrangement and even the pinacols can be dehydrated to normal product *i.e.*, olefins either by passing their vapours over alumina (alkaline conditions) at high temperature or by distilling the mixture of pinacol and aqueous HBr.



Mechanism. The reaction involves four steps.

1. Protonation of the hydroxyl group; 2. Loss of H₂O to form a carbocation; 3. 1, 2-shift of H, R or Ar to form a more stable cation; and 4. loss of H⁺ to form the final product.



It is important to note that although both the initial and the rearranged carbonium ions are tertiary, the rearranged cation is a resonance stabilization oxonium ion (a protonated carbonyl). The resonance stabilization is undoubtedly an important driving force for the rearrangement. Loss of proton from the