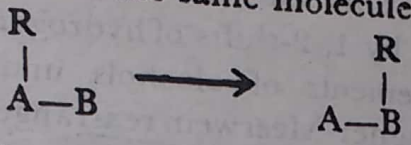
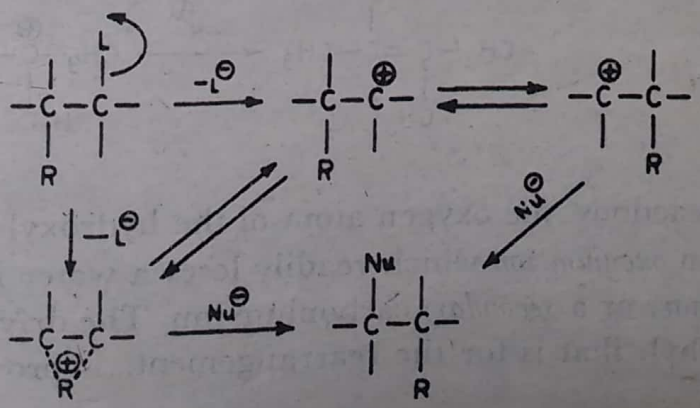
10 Molecular Rearrangements Involving Electron-deficient Species

The term 'molecular rearrangement' refers to the migration of a group from one atom to another within the same molecule.



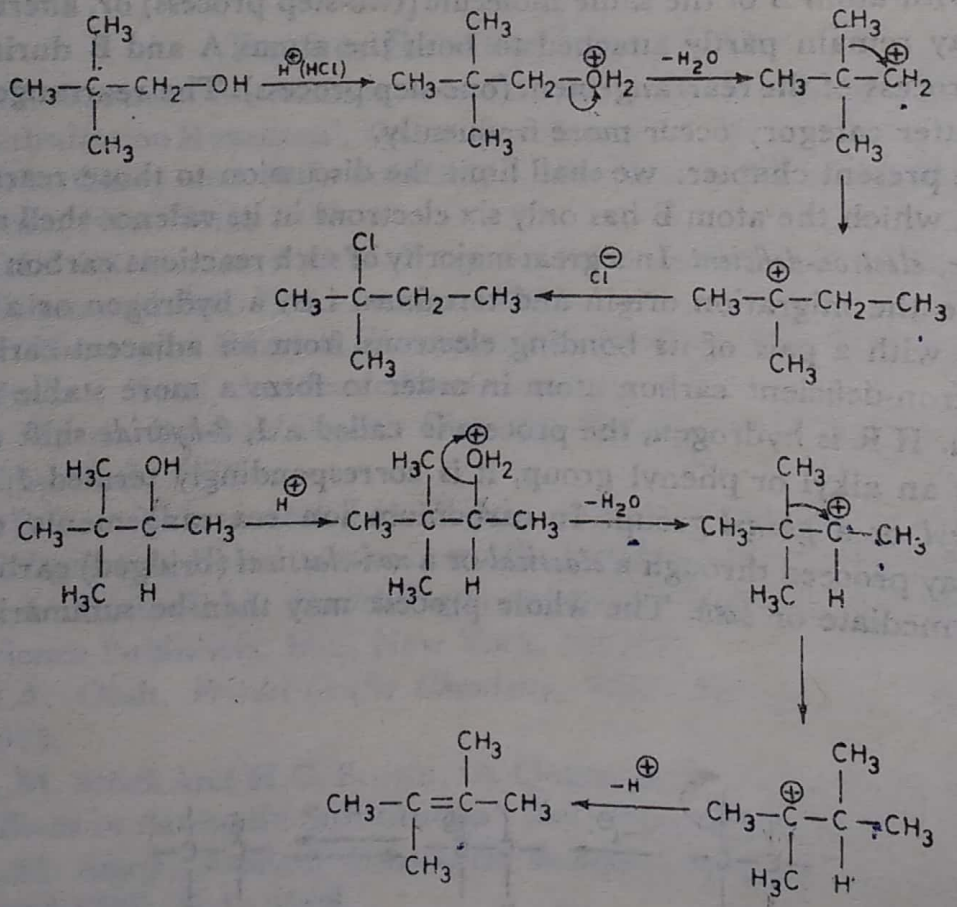
The group R may either completely detach itself from atom A before combining with atom B of the same molecule (two-step process) or, alternatively, it may remain partly attached to both the atoms A and B during the whole process of the rearrangement (one-step process). The rearrangements of the latter category occur more frequently.

In the present chapter, we shall limit the discussion to those rearrangements in which the atom B has only six electrons in its valence shell and is, therefore, *electron-deficient*. In a great majority of such reactions carbon atoms constitute the migration origin and terminus, i.e., a hydrogen or a group migrates with a pair of its bonding electrons from an adjacent carbon to the electron-deficient carbon atom in order to form a more stable carbonium ion. If R is hydrogen, the process is called a *1, 2-hydride* shift and in case it is an alkyl or phenyl group, it is correspondingly termed *1, 2-shift* of an *alkyl* or a *phenyl* group. In carbonium ion rearrangements the reaction may proceed through a *classical* or a *non-classical* (bridged) carbonium ion intermediate or *both*. The whole process may then be summarized as below:



Carbonium ion rearrangements take place far more readily than those involving either a free radical or a carbanion. A reasonable explanation for this observation depends upon the number of electrons in the transition states. 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 molecular orbital can accommodate only two electrons. In contrast, free radical and carbanion rearrangements have to pass through cyclic transition states in which three and four electrons, respectively, are to be accommodated in molecular orbital embracing the three carbon atoms and should therefore be less stable than carbonium ion transition states.

We have already seen that the two important reactions of carbonium ions are: (i) reaction with a nucleophile (S_N1 reaction) and (ii) elimination of proton (E_1 reaction). The third alternative is its rearrangement to a more stable carbonium ion by 1, 2-shifts of hydrogen atoms or of alkyl or aryl groups. The rearrangements of alcohols under acidic conditions (commonly known as the Wagner-Meerwein rearrangement) provide typical examples.



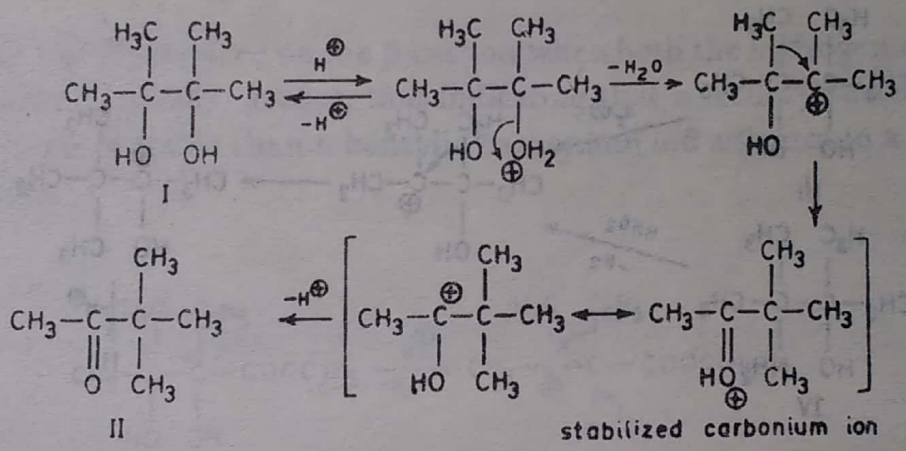
In the above reactions the oxygen atom of the hydroxyl group accepts a proton yielding an *oxonium ion* which readily loses a water molecule to produce either a *primary* or a *secondary* carbonium ion. The driving force for the migration of methyl, that is for the rearrangement, is provided by the in-

creased stability of the rearranged ion which happens to be a *tertiary* carbonium ion in both the cases. Nucleophilic addition of chloride ion or elimination of a proton then completes the reaction sequence. With this background we are now in a position to appreciate some common carbonium ion rearrangements described in the following pages.

10.1 Carbonium Ion Rearrangements

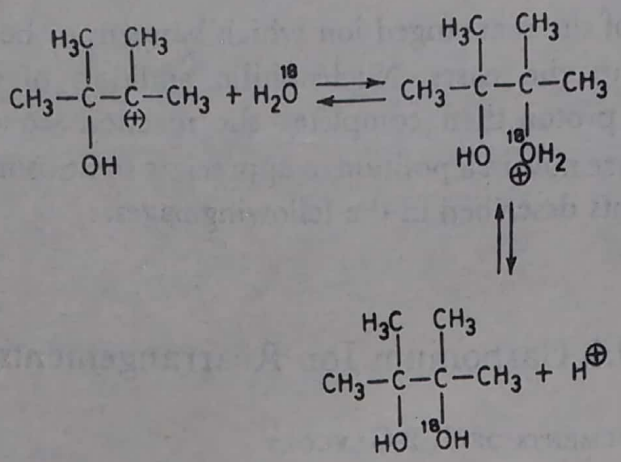
10.1.1 Rearrangements of 1, 2-Glycols

Acid catalyzed rearrangement of 1, 2-glycols yields carbonyl compounds, the classical example being the acid-catalyzed rearrangement of pinacol (I) to pinacolone (II).

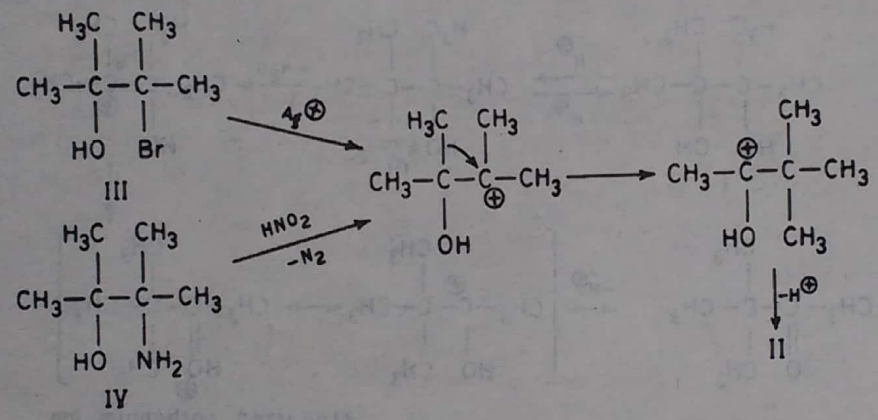


The driving force for the migration of the methyl group is provided by the resonance stabilization of the rearranged ion by the attached oxygen. The rearrangement is an intramolecular process in which the methyl group begins to attach itself to the positive carbon before separating from its original position. This is verified experimentally by rearranging two different pinacols together, which results in the formation of only two rearranged products. The absence of mixed products indicates that the migrating group of one compound never becomes sufficiently free of the initial carbonium ion so as to get itself attached to the carbonium ion produced from the other pinacol.

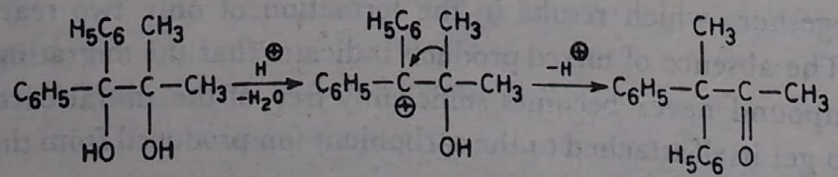
The intermediacy of carbonium ions in this rearrangement can be demonstrated in a variety of ways. First, when the pinacol is rearranged in $H_2{}^{18}O$ and the reaction is stopped before completion, the recovered pinacol is found to contain the ^{18}O isotope suggesting the reversible formation of a carbonium ion.



Second, any other reaction capable of producing the same carbonium ion results in the formation of pinacolone. For example, the reaction of the bromohydrin (III) with silver oxide, and the deamination of the aminohydrin (IV) with nitrous acid yields pinacolone.

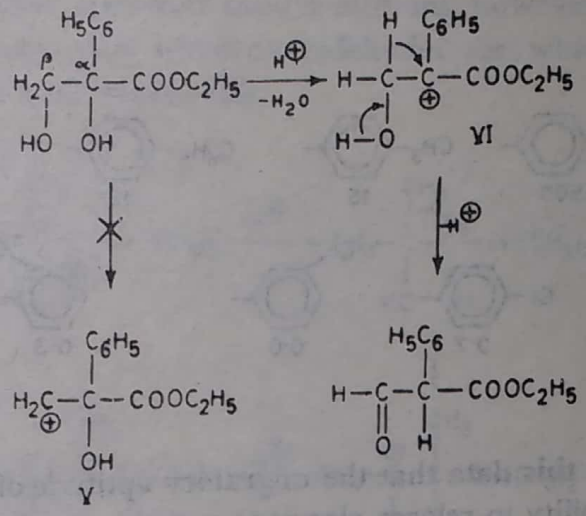


In the case of unsymmetrically substituted glycols the positive charge is generated on that carbon which is best able to support it. Thus it can easily be predicted that in the following example the carbonium is produced on the phenylated carbon rather than on the methylated carbon because of resonance stabilization.

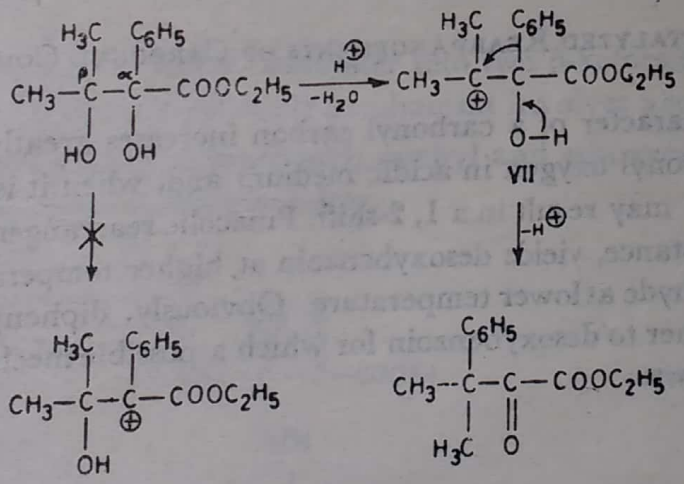


Particularly instructive examples of the relative stabilities of carbonium ions are provided by the rearrangements of αβ-diol esters. The carbonyl carbon of the ester group is partially positive and it, therefore, prevents generation of a carbonium ion at the α-carbon because of mutual repulsion between two similar charges. However, the positive charge can be forced to develop

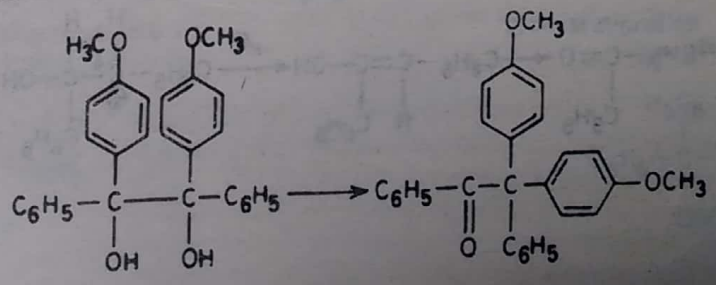
at the α-carbon by stabilizing it over a phenyl substituent (VI) together with increasing the energy of the alternate β-carbonium by making it a primary one (V).



Carbonium ion is produced on the β-carbon when both the hydrogen atoms are substituted by methyl groups, thus indicating that a tertiary carbonium ion (VII) is more stable than a benzylic carbonium ion adjacent to a carbethoxy group.

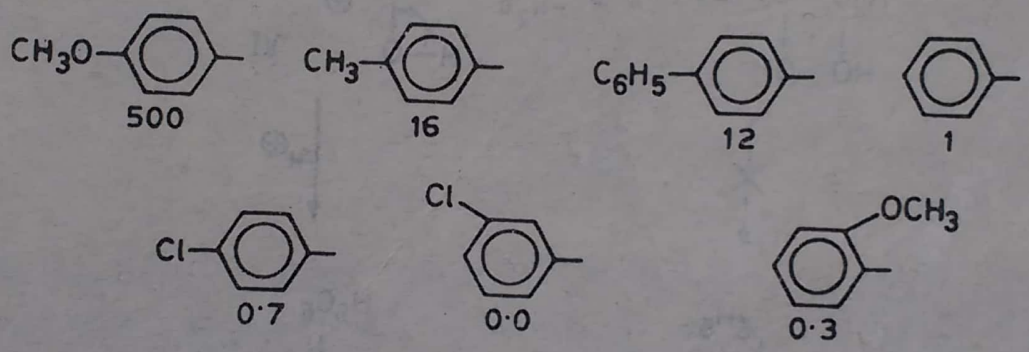


When the two groups on the non-ionic carbon are different, then the one which is a better nucleophile (more powerful electron donor towards carbon) migrates preferentially. Thus in the example below *p*-$MeOC_6H_4$ migrates in preference to phenyl because it is a better nucleophile due to the electron donating effects of the —OCH_3 group.



Usually the phenyl group migrates in preference to alkyl groups.

The following values were established for the migratory aptitude of substituted phenyl groups with reference to phenyl which has been assigned the value 1.



It is evident from this data that the migratory aptitude of a group is closely linked with its ability to release electrons and this can be taken as an indication that the migrating group starts forming a bond with the adjacent electron-deficient centre even though the departing group (H_2O) is not completely broken from the molecule. The anomalous behaviour of *o*-$MeOC_6H_4$—may be due to its steric interference in the transition state with the non-migrating groups.