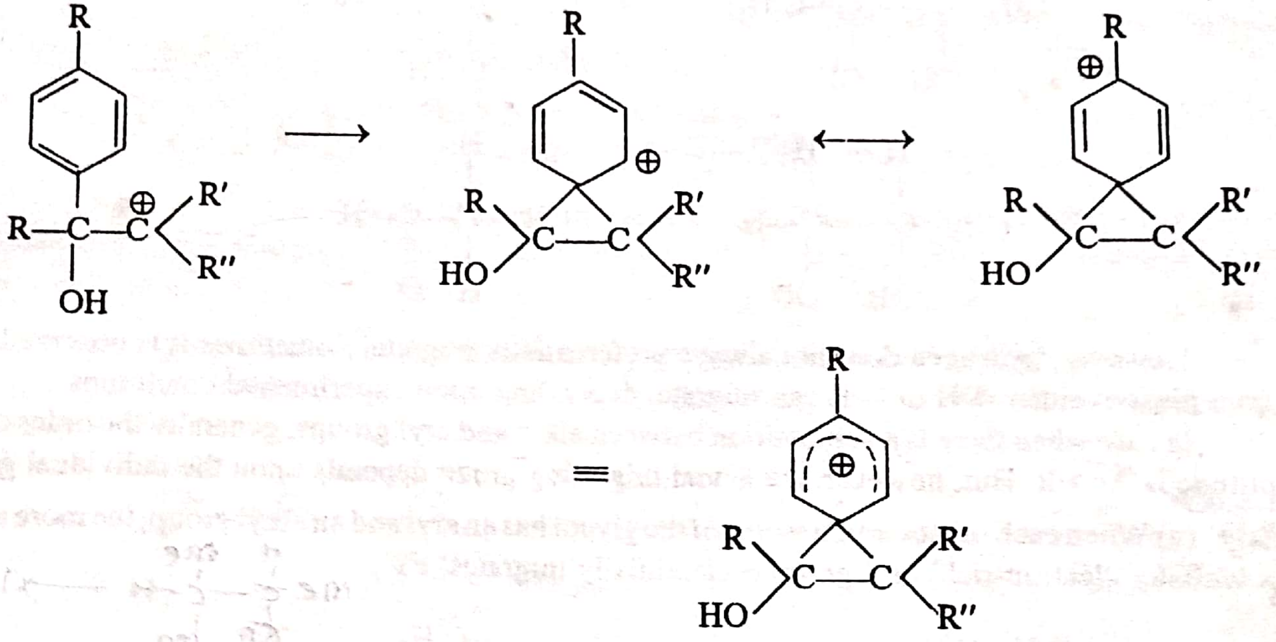
rearranged ion produces pinacolone. The special feature of the pinacol rearrangement is the presence of second oxygen atom which provides its unshared pair of electrons needed during the rearrangement of the cation.

When an aryl group migrates, an intermediate of structure I is obtained. The resonance hybrid of I is called phenonium ion.

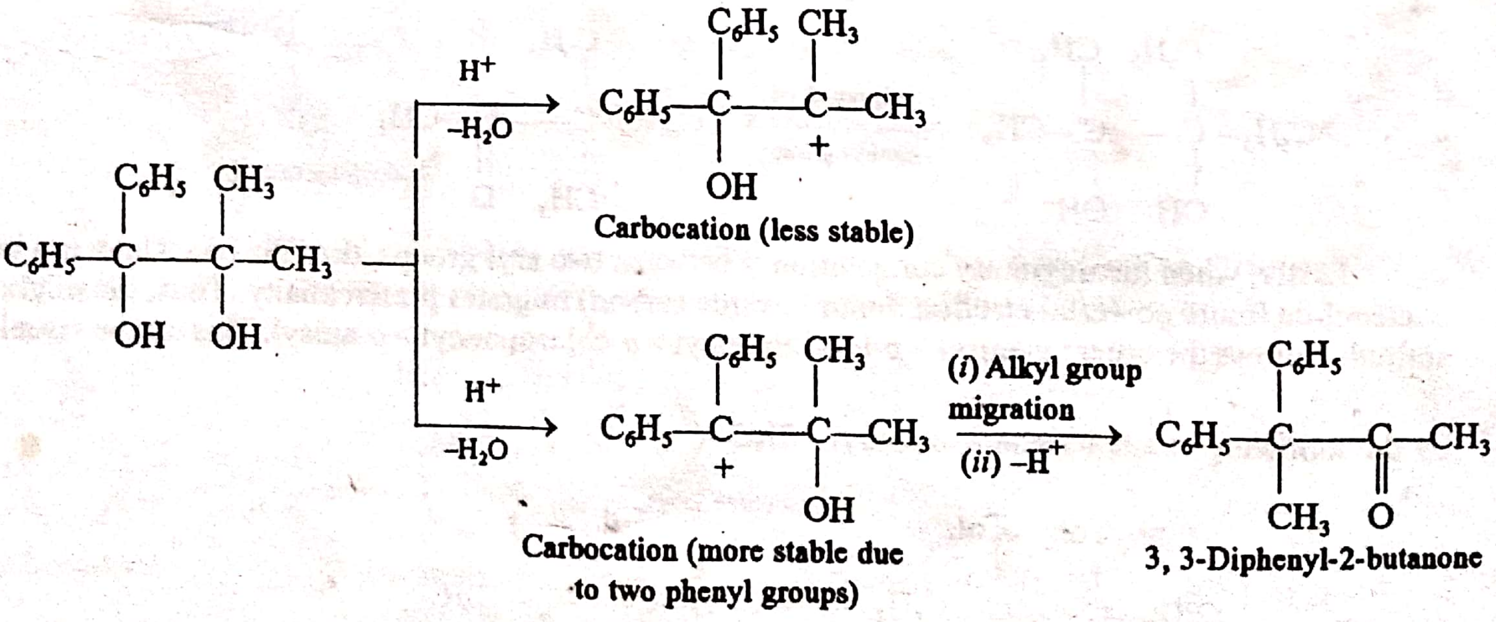


Phenonium ion

In case the group R is electron-donating (*viz.* R, OR, etc.), the migration of the aryl group is facilitated.

Features of pinacol rearrangements :

(*i*) *Stability of the carbonium ion.* When there is a choice as which hydroxyl group will be preferentially removed, *i.e.*, when two OH groups are different then that OH group will be removed which produces the more stable carbocation (difference from Wagner-Meerwein rearrangement), *e.g.*,

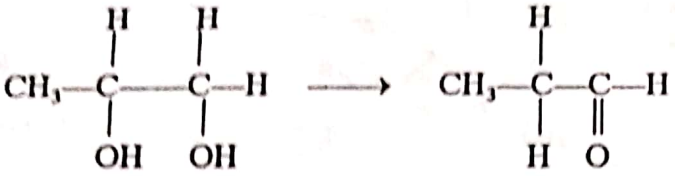


Carbocation (less stable)

Carbocation (more stable due to two phenyl groups)

3, 3-Diphenyl-2-butanone

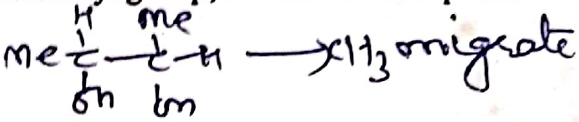
(*ii*) *Migratory aptitude of the group*. The migrating group in the pinacols may be alkyl, aryl or even hydrogen atom. Hydrogen may migrate in preference to —R or —Ar, as in the following examples.

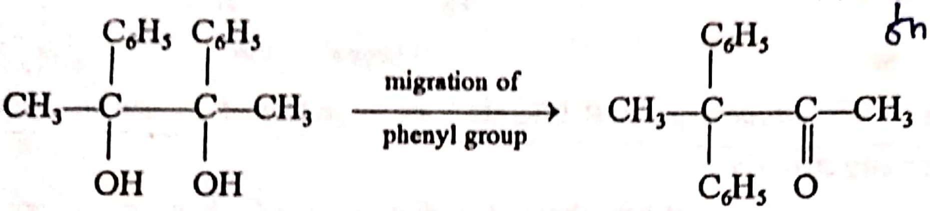


However, hydrogen does not always preferentially migrate. Sometimes it is observed that with a given pinacol either —H or —R can migrate, depending upon experimental conditions.

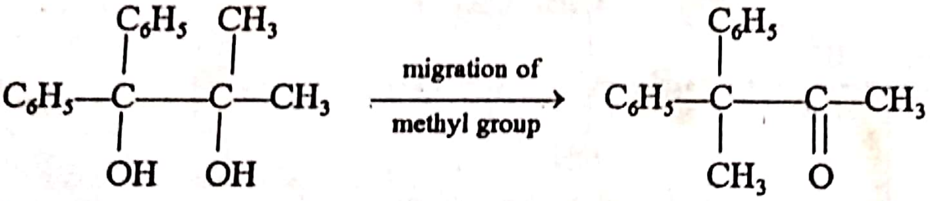
In case when there is a competition between alkyl and aryl groups, generally the order of migratory aptitude is Ar > R. But, however, the actual migrating group depends upon the individual glycol.

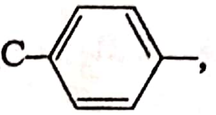
(a) When each of the carbon atoms of the glycol has an aryl and an alkyl group, the more nucleophilic (potentially electron-rich) aryl group preferentially migrates, *e.g.*,

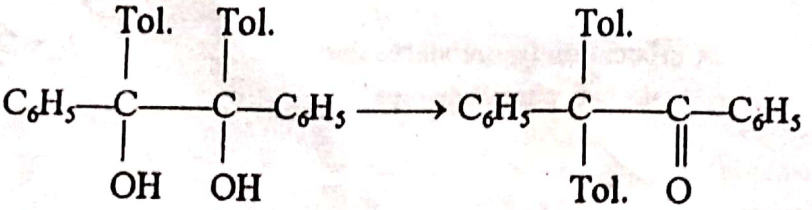




(b) When one carbon atom of the glycol possesses two aryl groups while the other two alkyl groups, the alkyl group migrates owing to the greater stability of its carbonium ion [see feature (*i*)], *viz.*



Lastly, when the migratory competition is between two aryl groups, then the one which is a better nucleophile (more powerful electron donor towards carbon) migrates preferentially. Thus, the migratory aptitude follows the order : *p*-anisyl > *p*-tolyl > phenyl > *p*-chlorophenyl > *o*-anisyl. This can be visualised by the following example(where, *p*-toluyl = H_3C–  ,

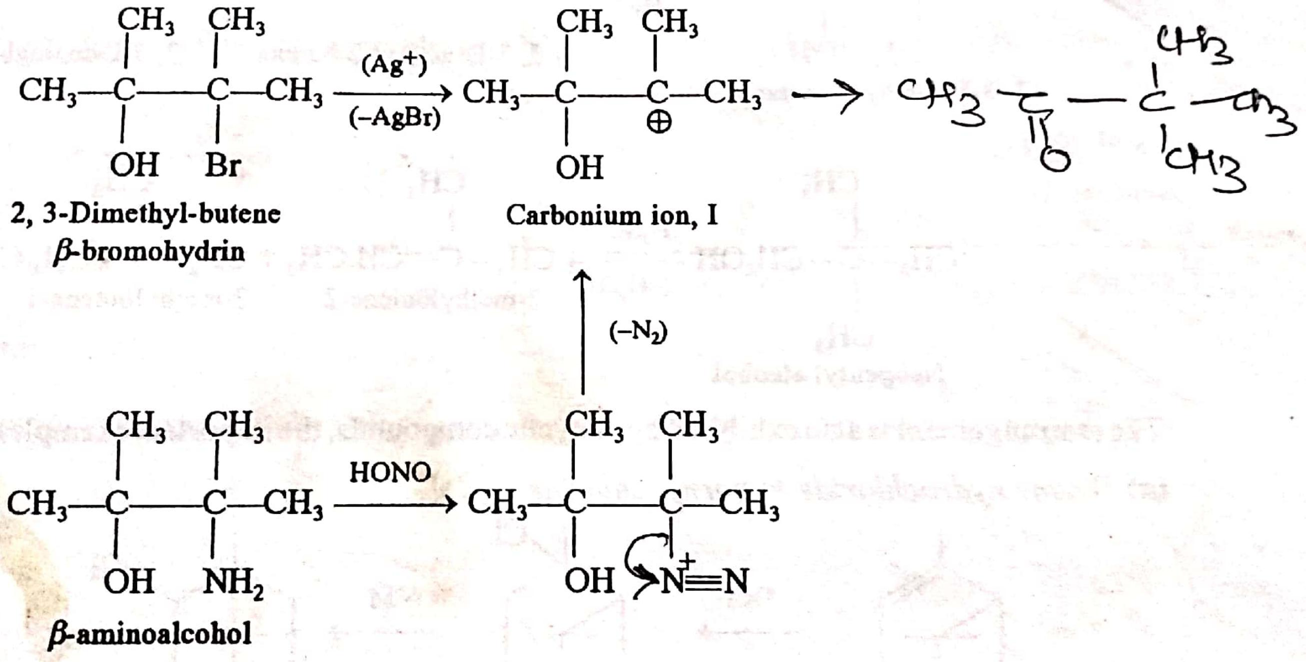


(iii) *Intramolecular migration.* As mentioned in the mechanism, the migrating group migrates within molecule *i.e.*, it never becomes free from the rest of the molecule as it retains its configuration in the product. Moreover, the intramolecular migration is further evidenced by the fact that when a mixture of two different pinacols is heated with H_2SO_4, no cross product is obtained. The intramolecular nature of the rearrangement is further indicated by the use of tracer technique. If rearrangement, in which there is a hydride shift, is carried out in deuteriated solvent (*e.g.*, D_2O. MeOD, etc.) no deuterium is incorporated into the new C—H(D) bond in the final rearranged product.

(iv) *Steric effect.* The migration of the group is also effected by steric factor viz. *o*-MeO.C_6H_4— group migrates thousand times less than the *p*-MeO.C_6H_4— group.

(v) *Transmigration.* The migrating group migrates to the opposite (*trans*) side of the leaving group (see mechanism) which has important consequences in alicyclic system (for details please see chapter on conformational analysis)

Extension and Applications : In addition to 1, 2-diols, *β*-halohydrins undergo rearrangement in the presence of Lewis acid, and *β*-amino alcohols *via* the diazonium ion, on treatment with nitrous acid to pinacolone.

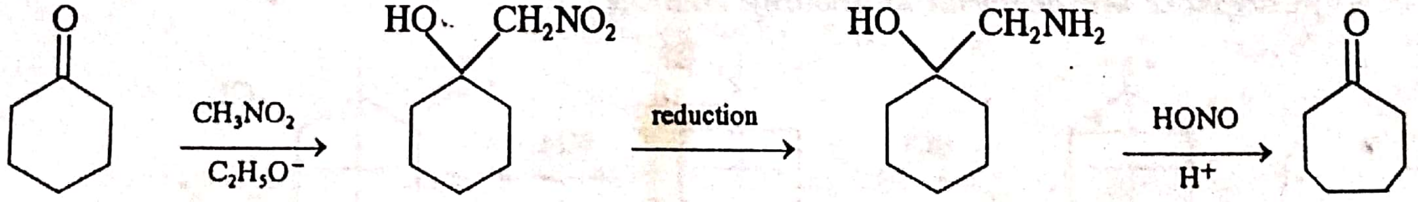


2, 3-Dimethyl-butene *β*-bromohydrin

Carbonium ion, I

***β*-aminoalcohol**

The latter extension of pinacol rearrangement has a synthetic application *e.g.*, synthesis of cycloheptanone from aminomethylcyclohexanol which in turn is obtained from cyclohexanone.



Cyclohexanone **1-Nitromethyl-cyclohexanol** **1-Aminomethyl-cyclohexanol** **Cycloheptanone (40%)**