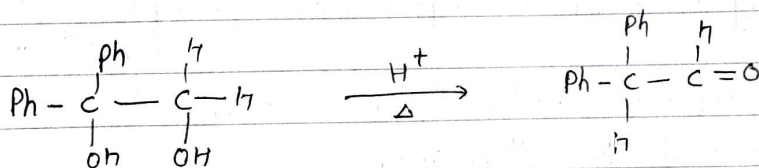
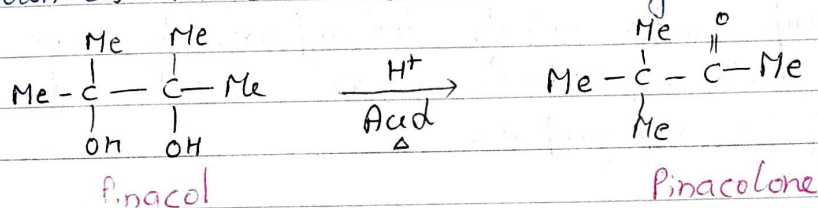
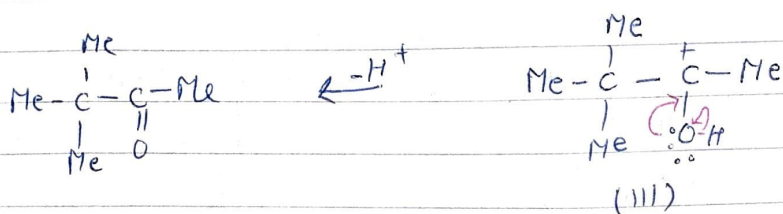
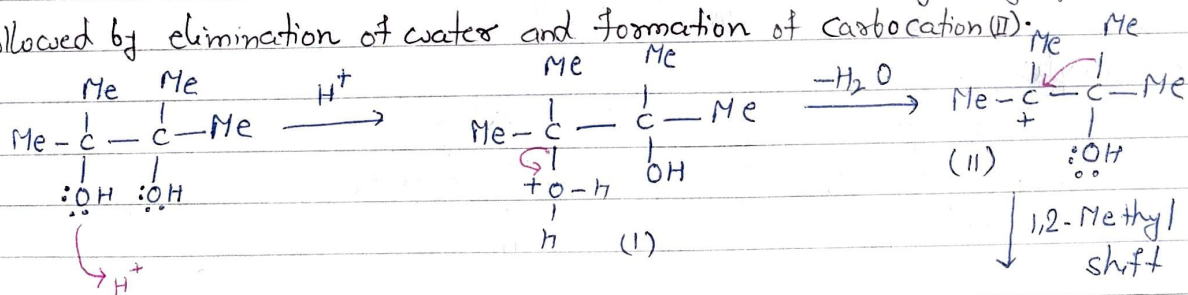


## Pinacol - Pinacolone Rearrangement

The acid catalyzed rearrangement of vicinal-diols (1,2-diols) to ketone or aldehyde with the elimination of water is known as Pinacol - Pinacolone rearrangement.

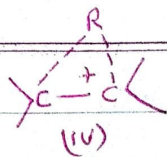


**Mechanism:** The reaction starts with the protonation of hydroxyl group followed by elimination of water and formation of carbocation (II).

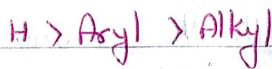


The carbocation (II) is tertiary but it re-forms to form (III) due to its resonance stability. Finally elimination of proton from the stable carbocation (III) gives the carbonyl compound.

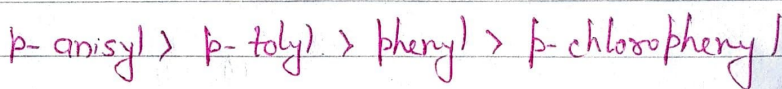
**Note 1:** This is a type of intramolecular rearrangement. It is a concerted reaction and migrating group retains its configuration. Furthermore no cross over products are obtained when a mixture of two nearly similar 1,2-diols is treated with acid.



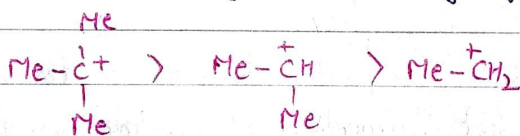
Note 2: Migrating order is -



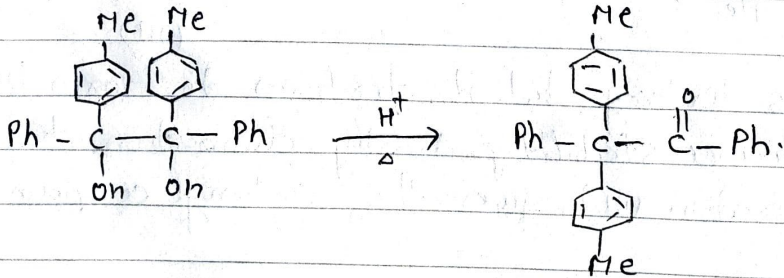
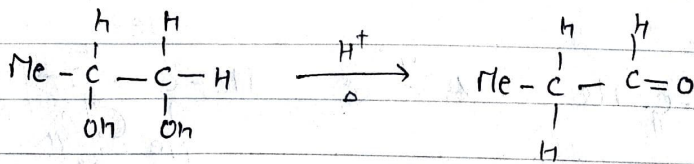
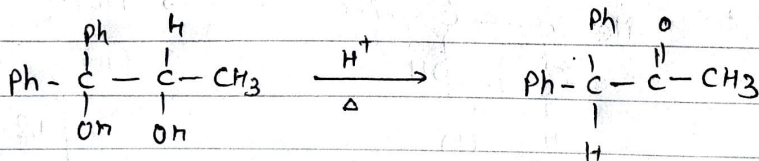
As the migrating group migrates with its electron pair, the more nucleophilic group might be expected to migrate. Thus the order of migration amongst the aryl group is -



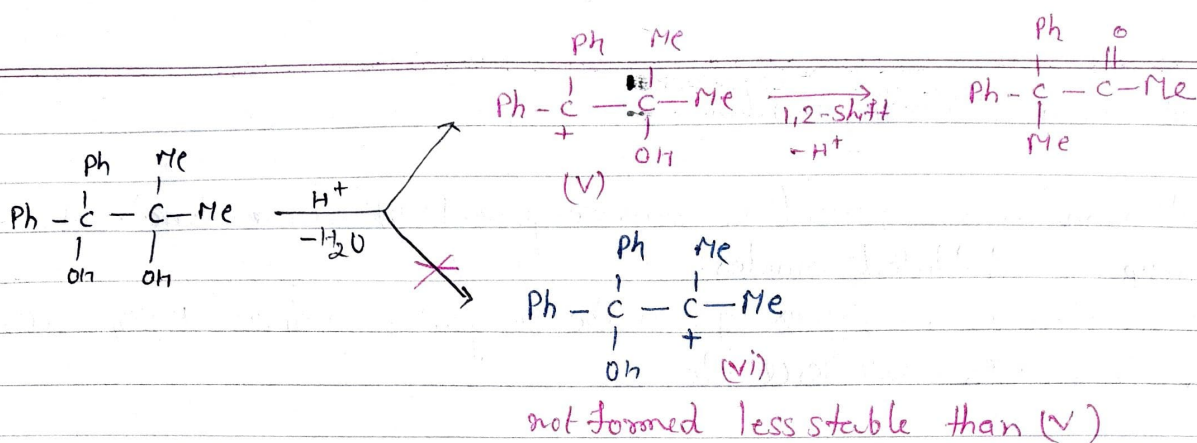
Electron withdrawing group will retard the reaction. The migratory aptitude amongst the alkyl group is -



For example:



Note 3: The stability of initially formed carbocation may offset the migratory aptitude order. e.g



**Note 4:** Steric hinderance may affect the rate of migration - p-anisyl group migrates 1000 times faster than o-anisyl group.

**Note 5:** The migrating group attack from the trans-position (back side) of the leaving group. This has important effect in cyclic system.

