

STUDY MATERIAL



Dumkal College
Basantapur Dumkal

Topic: Rearrangement reaction : Pinacol-Pinacolone rearrangement

Course Code: CHEMHT-10

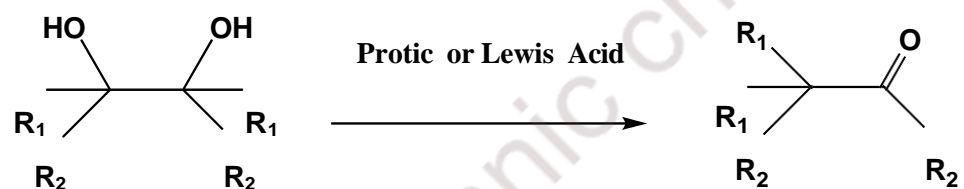
Semester: IV (Hons)

Name of the Teacher: Md Muttakin Sarkar

Name of the Department: Chemistry

Pinacol-Pinacolone Rearrangement

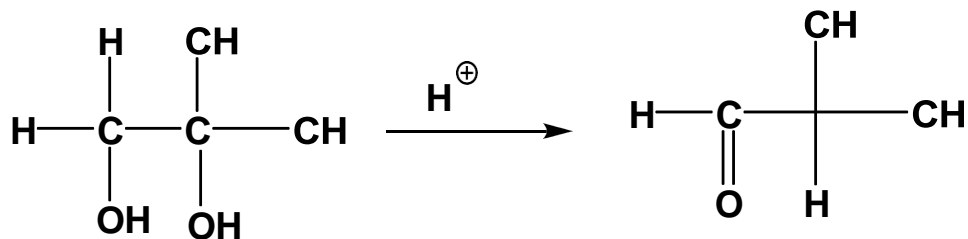
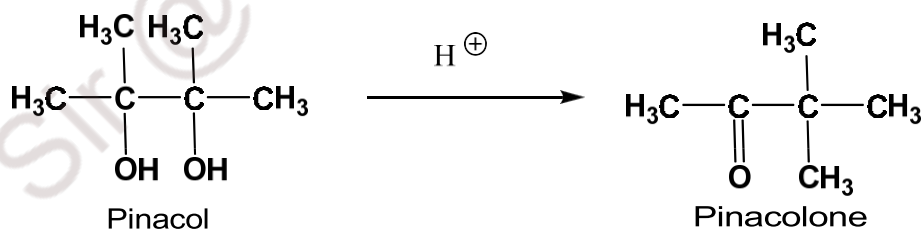
Acid catalyzed rearrangement of 1,2-diol into oxo-compounds (aldehyde / ketone).



R1-2 = H, Alkyl, Aryl, Acyl

Acids : 20% H₂SO₄, AcOH, BF₃.Et₂O

The name originated from classical example of conversion of Pinacol to Pinacolone.

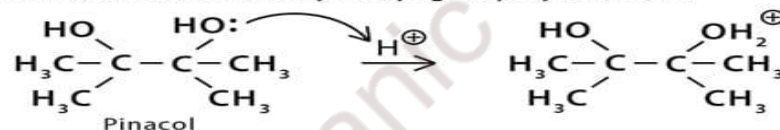


MECHANISM :

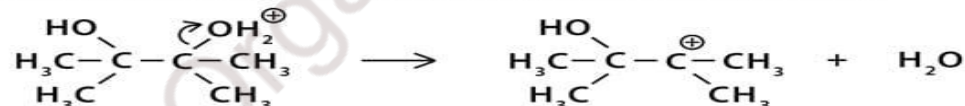
- Protonation of hydroxyl group to form a carbocation
- 1,2-shift of : H, : R or : Ar to form a more stable cation (Rearrangement)
- Deprotonation to form the final product

Mechanism of Pinacol Rearrangement

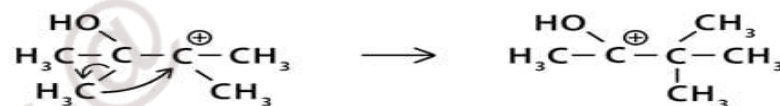
Step 1: Protonation of the hydroxyl group by the acid.



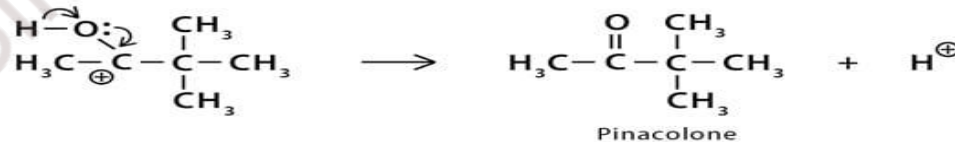
Step 2: Removal of water from the compound to form a carbocation.



Step 3: Shifting of the methyl group to the positively charged carbon.

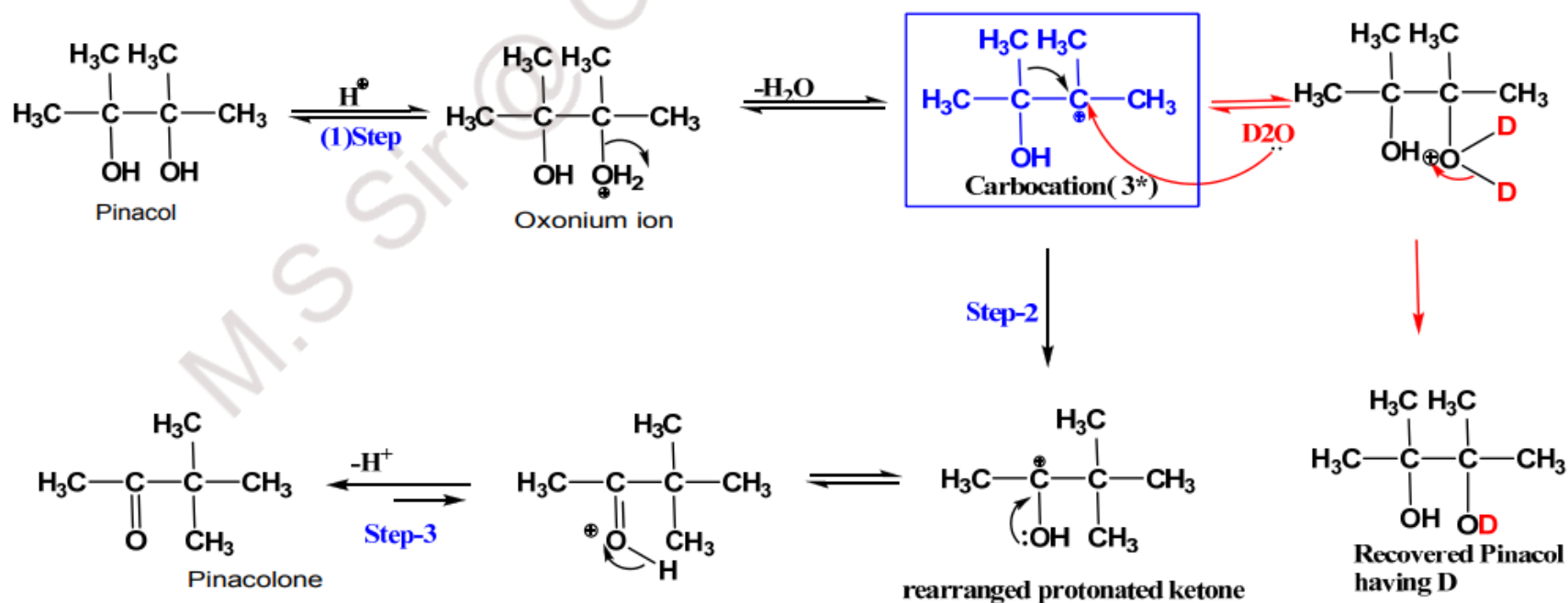
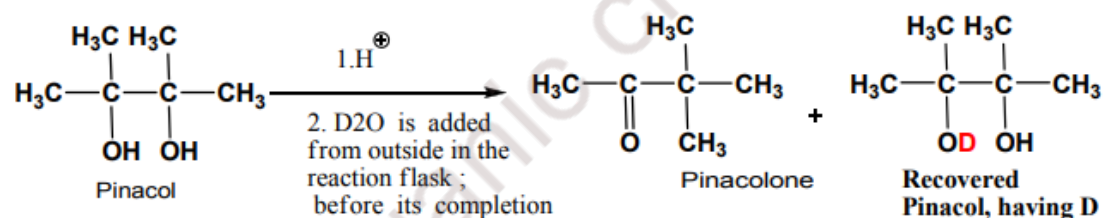


Step 4: Deprotonation of the oxygen which is bonded to carbon.

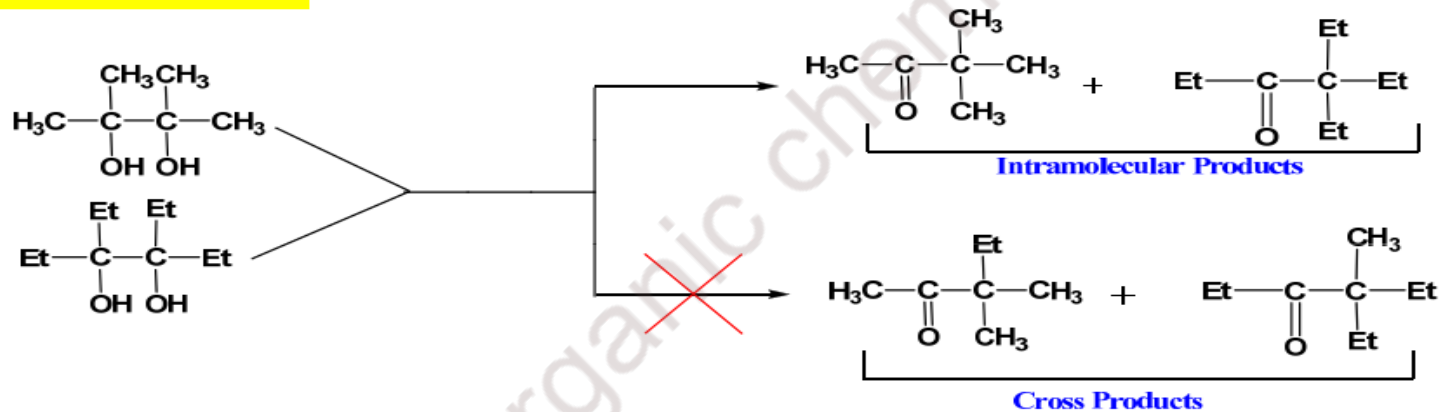


Evidences For Carbocation Intermediate :

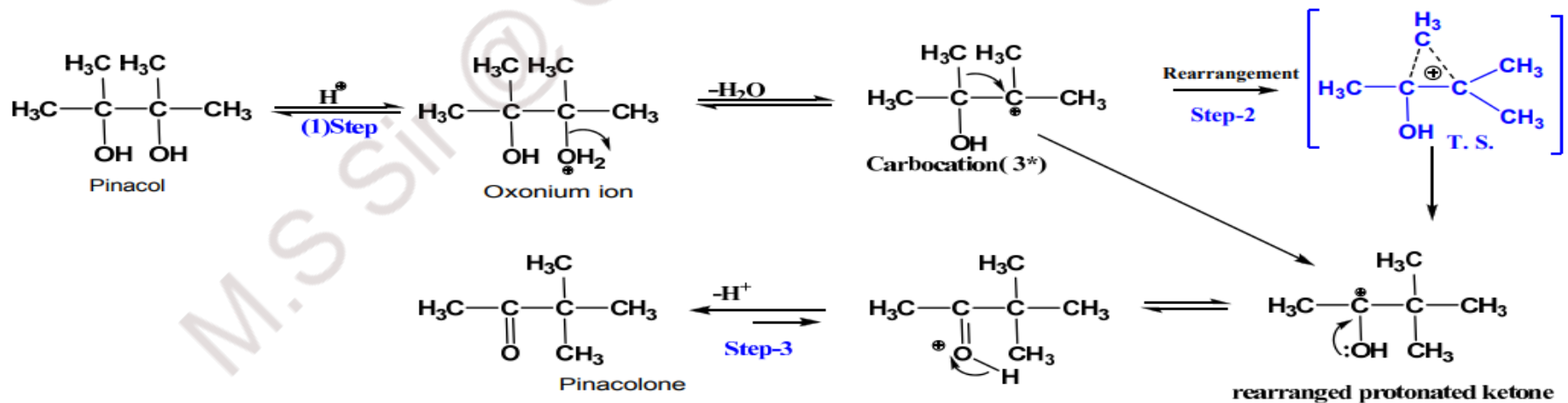
1. Isotopic Labelling Experiment :



Intramolecularity :



Modified Mechanism : T. S. Is formed

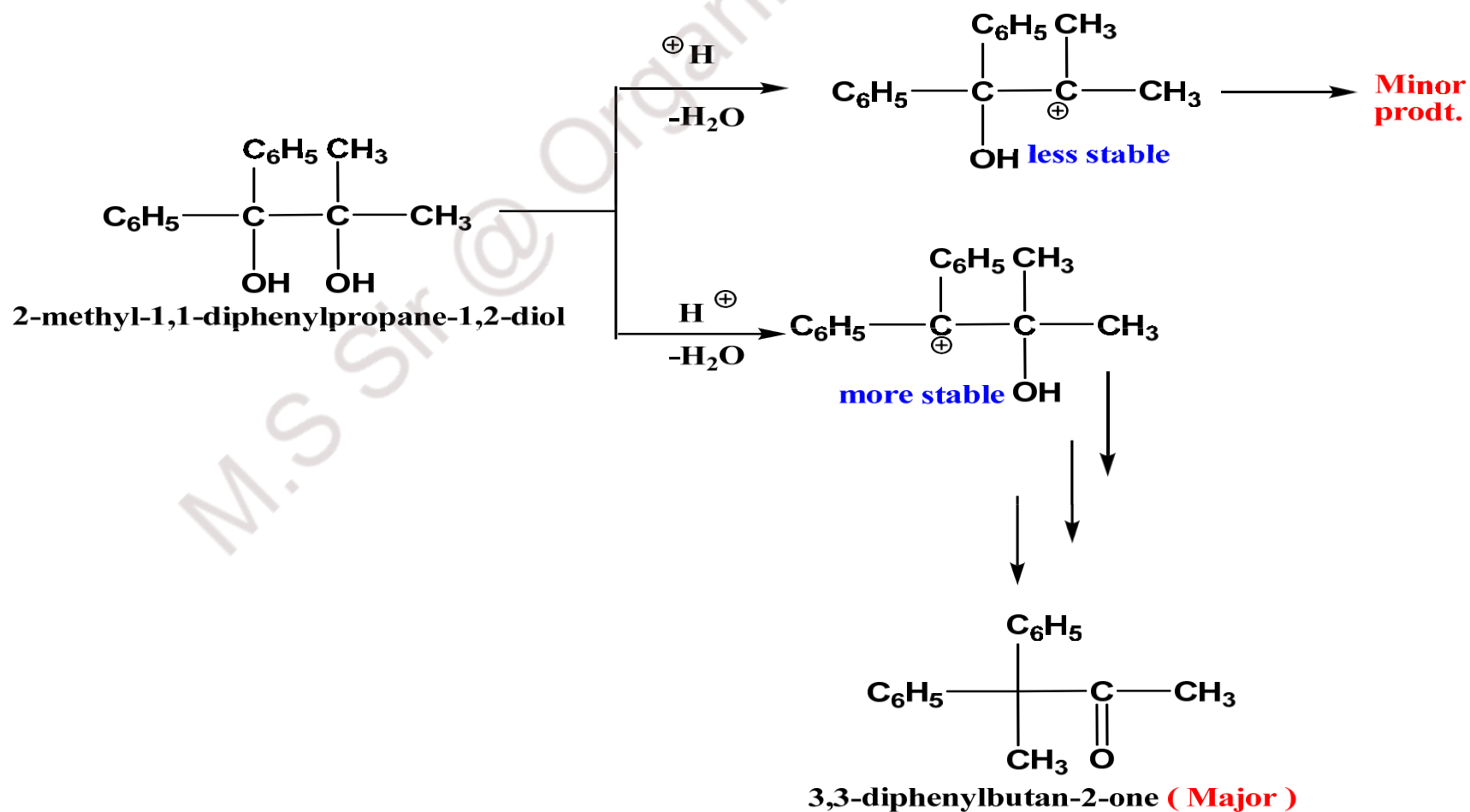


1. If migrating group is chiral then retention of configuration occurs
2. No cross product is formed when the reaction is carried out in presence of two different pinacol.

Pinacol - Pinacolone Rearrangement with Asymmetrical 1,2- Diols

1. Stability of carbocation
2. Migratory aptitude of groups

1. Stability of carbocation:



2. Migratory Aptitude of Groups :

Different groups have different migratory aptitude.

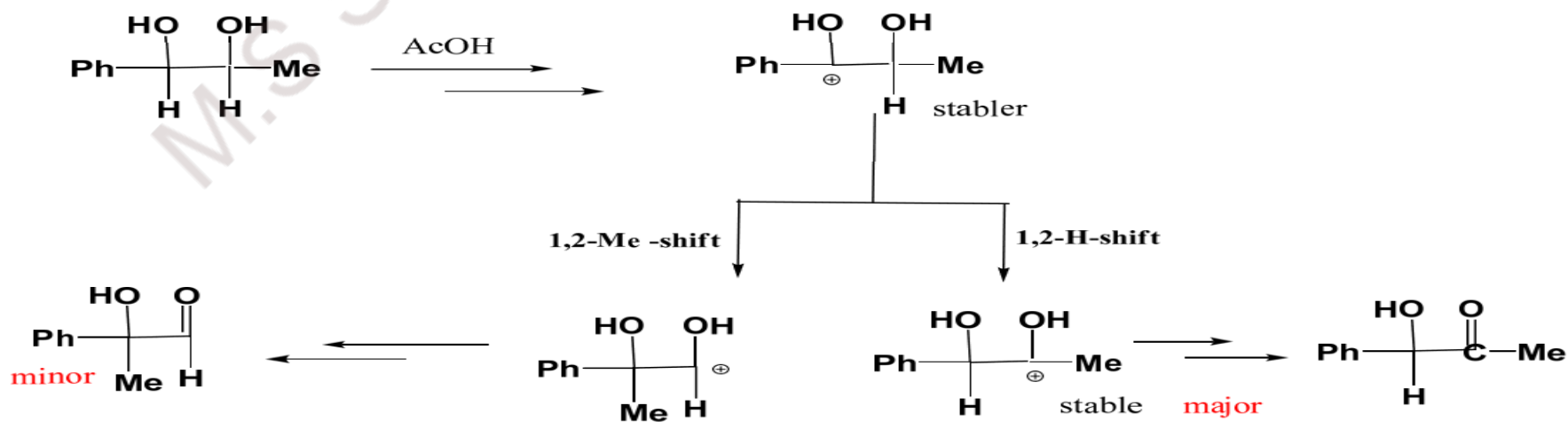
1. $H > \text{Ar} > \text{Alkyl}$

2. $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$

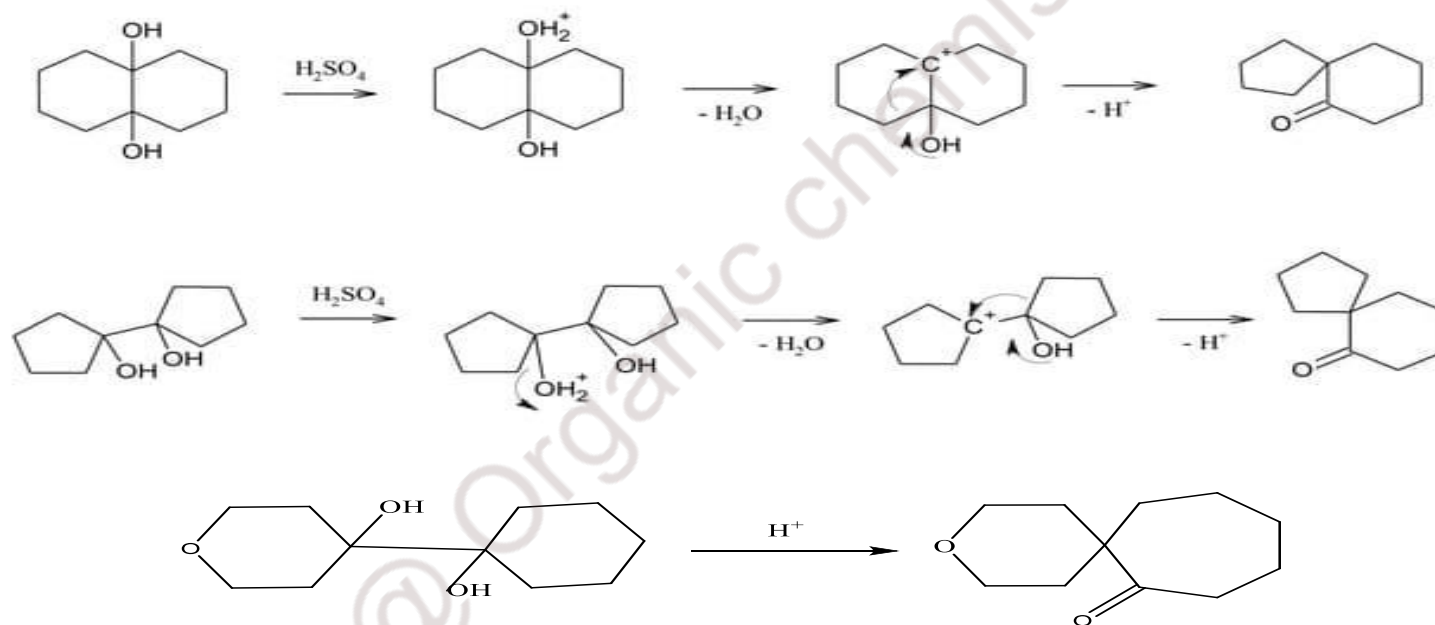
3. $\text{Aryl} > H > \text{vinyl (alkenyl)} > \text{Alkyl}$

4. $4\text{-OMe-Ph} > 4\text{-Me-Ph} > 2\text{-OMe-Ph} > \text{Ph} > 4\text{-Cl-Ph}$ etc.

If there is possibility of migration of H and alkyl group ; it is H which migrates preferably ,as it gives the formation of stabler carbocation.

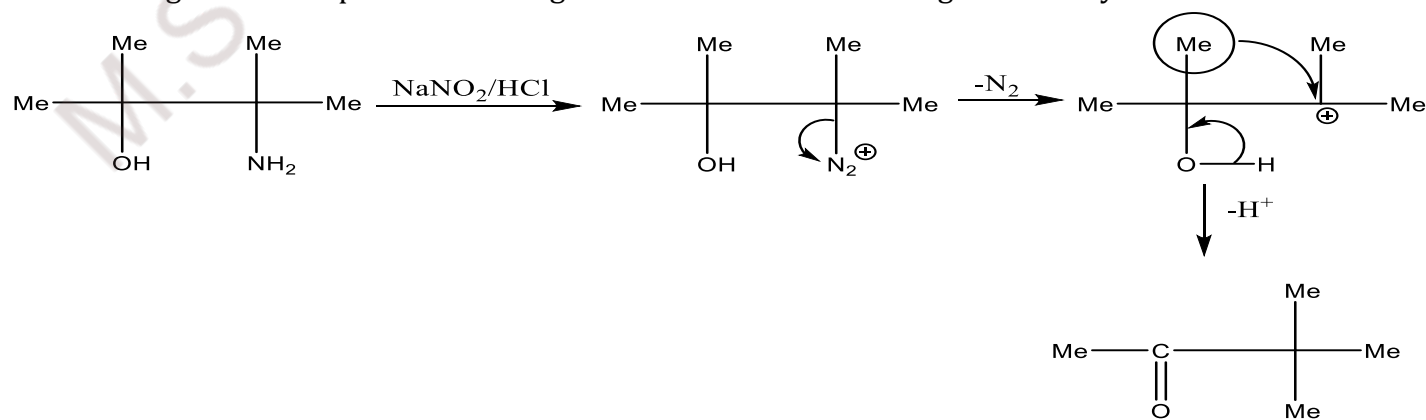


Some Examples

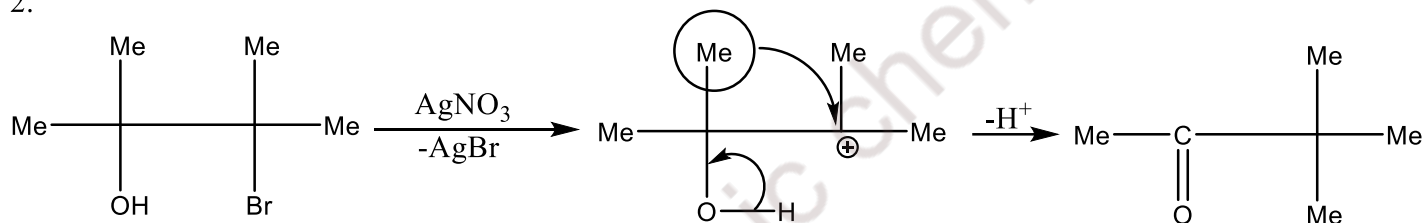


Semipinacol rearrangement

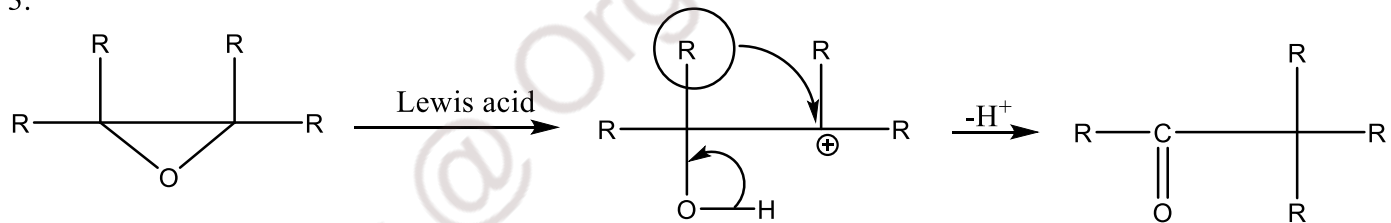
1. β - amino alcohol undergoes semi - pinacol rearrangement. Here carbocation is generated by diazotization followed by loss of N_2 .



2.



3.



Reference Books

1. Organic name reaction by Jie Jack Li.
2. Clayden, J., Greeves, N., Warren, S., Organic Chemistry, Second edition, Oxford University Press 2012.
3. Harwood, L. M., Polar Rearrangements, Oxford Chemistry Primer, Oxford University Press..