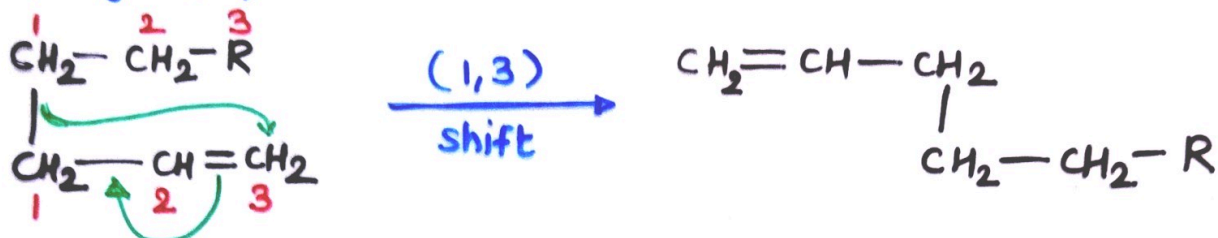


# \* Sigmatropic Rearrangement \*

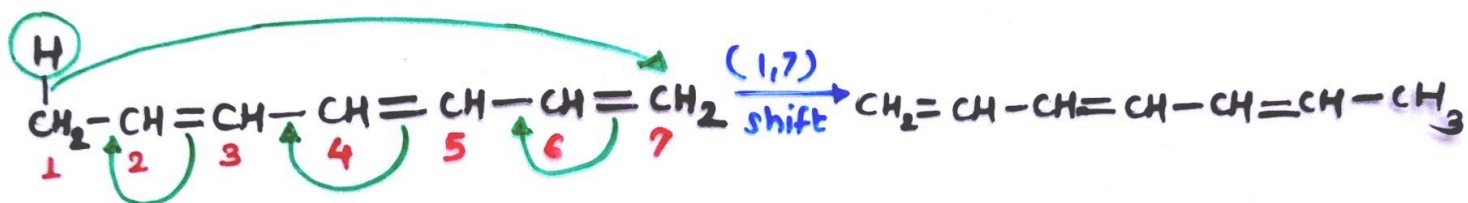
\* A sigmatropic rearrangement is a concerted intramolecular shift of an atom or group of atoms. During this rearrangement a  $\sigma$  bond is broken in the reactant and a new  $\sigma$  bond is formed in the product and  $\pi$  bonds rearrange.

\* There are following types of sigmatropic rearrangement.

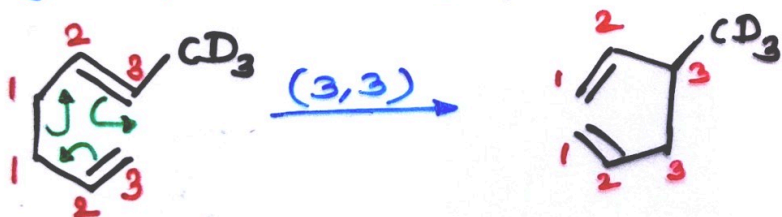
(1,3) sigmatropic shift :-



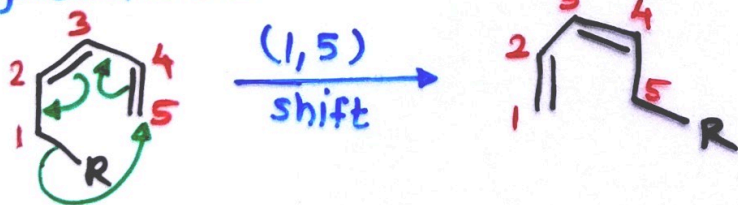
(1,7) sigmatropic shift :-



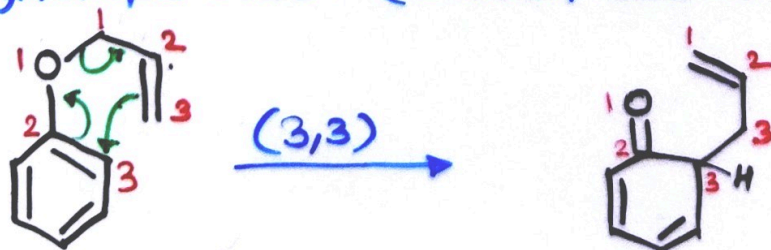
(3,3) sigmatropic shift :- (Cope Rearrangement)



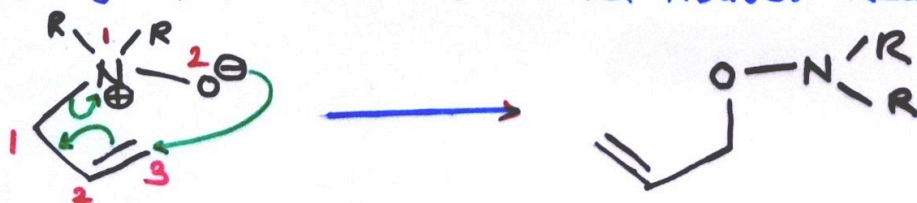
(1,5) sigmatropic shift :-



(3,3) sigmatropic shift :- (Claisen Rearrangement)

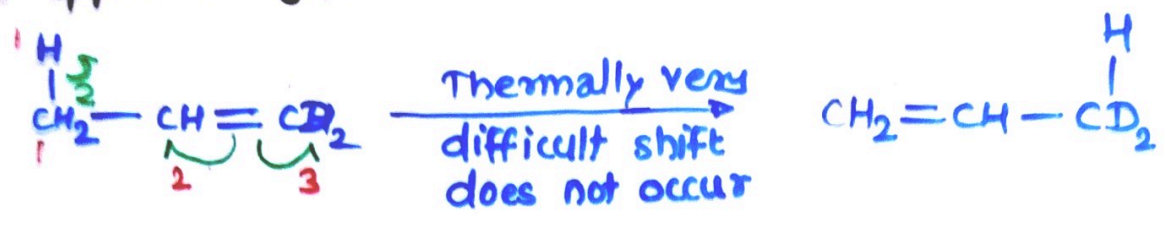


(2,3) sigmatropic shift :- (Sommet Houser Rearrangement)

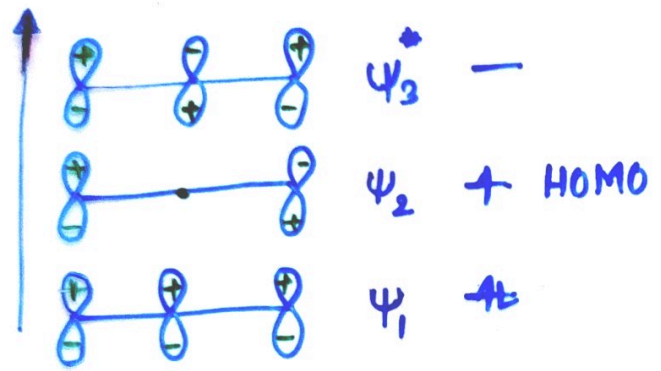


**[1,3] sigmatropic Rearrangement (Hydrogen shift)**

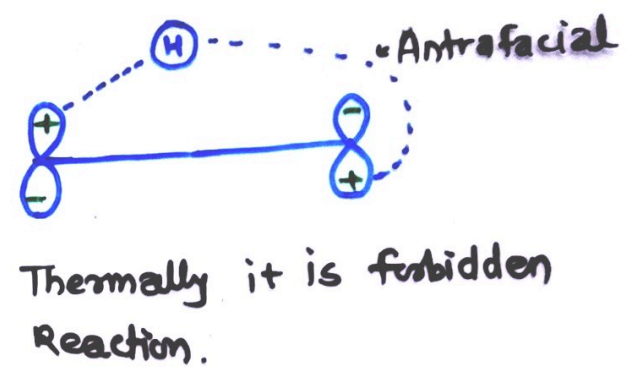
In the migration of Hydrogen the H must move from a plus to plus or from minus to minus lobe of HOMO, it cannot move to a lobe of opposite sign.



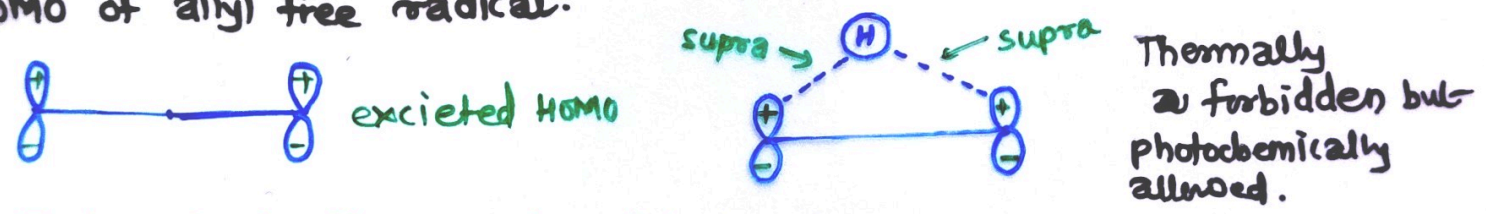
**Thermal Reaction:-**



Molecular orbitals of allyl free radical

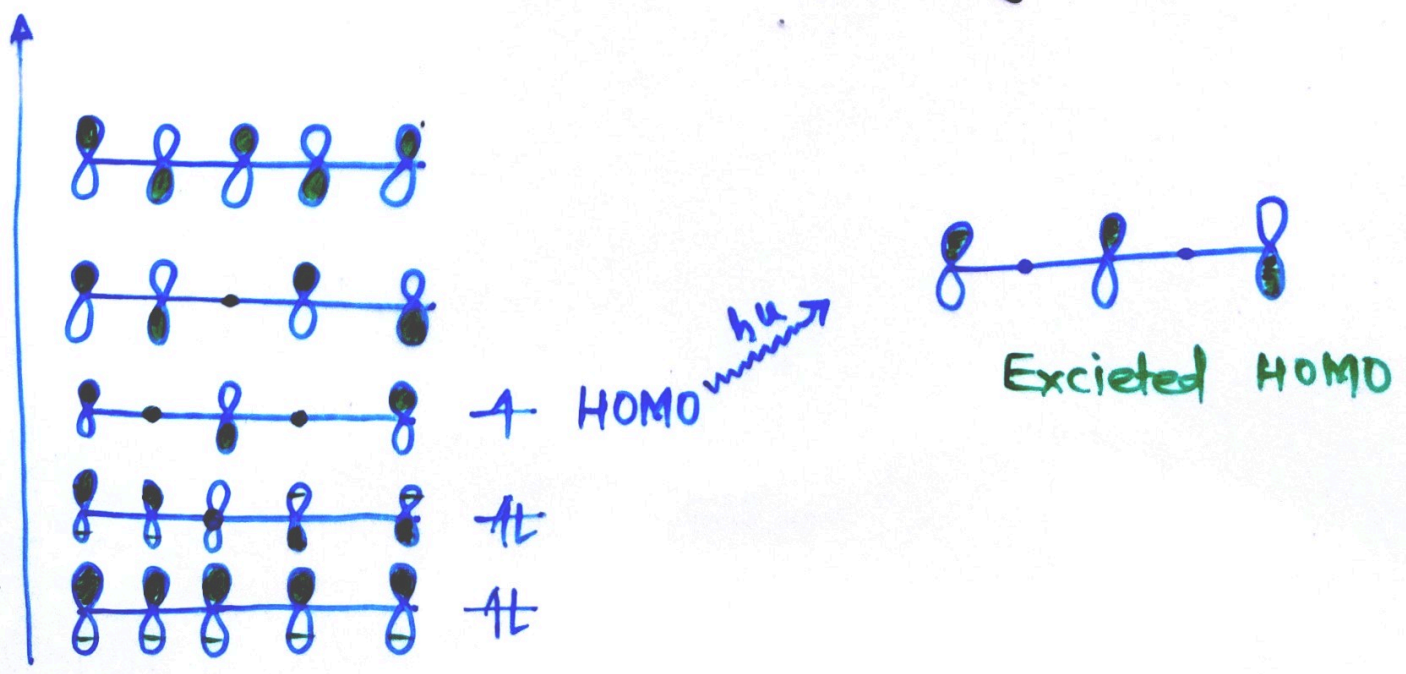


**Photochemical Reaction:-** In photochemical reaction consider excited HOMO of allyl free radical.

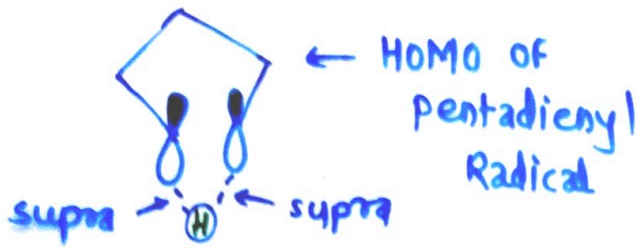


**[1,5] Sigmatropic Rearrangement:- (Hydrogen shift)**

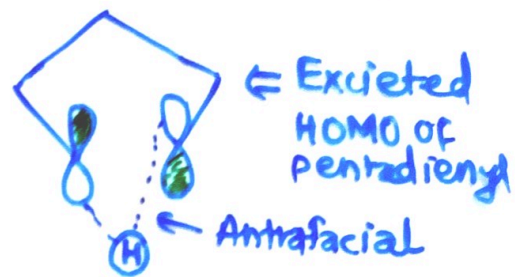
consider the molecular orbitals of pentadienyl radical



\* (1,5) shift in presence of heat it is possible supra-supra. (18)



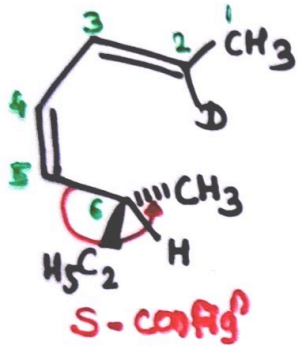
Allowed.



Forbidden

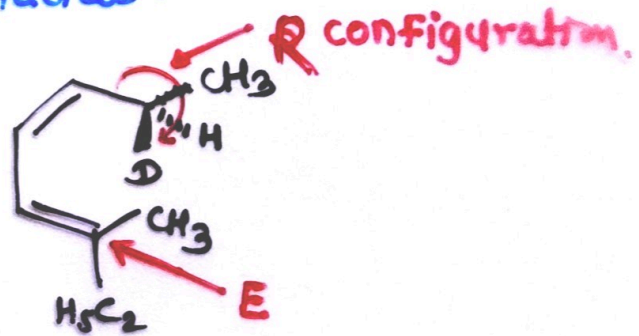
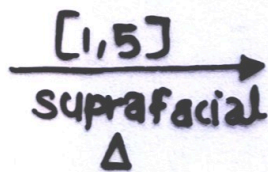
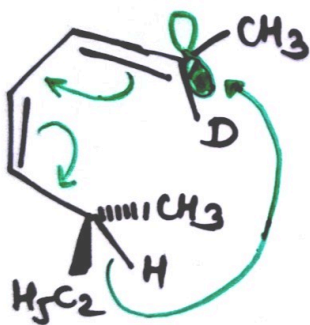
**Stereochemistry of [5,5] sigmatropic Rearrangement:-**

\* consider following compound.

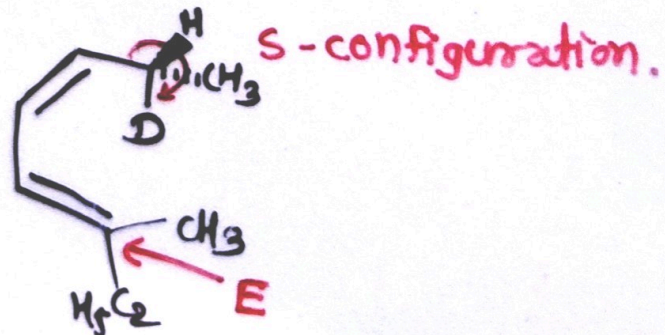
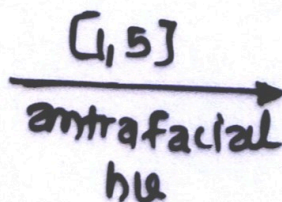
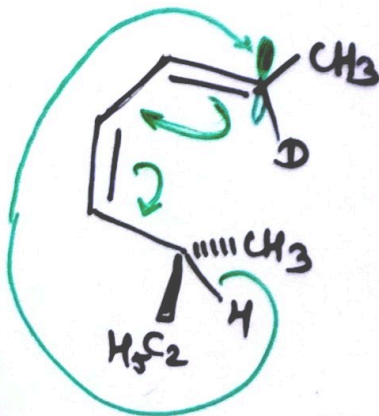


S configuration at C6  
E configuration at C-2

Case I: suppose migration is suprafacial.

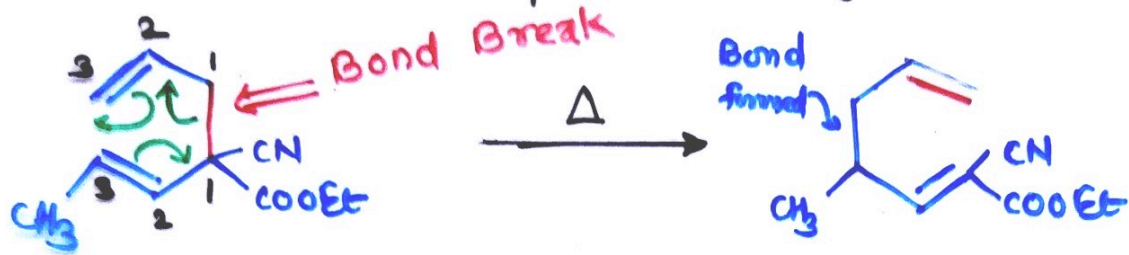


Case II: migration is antarafacial :-

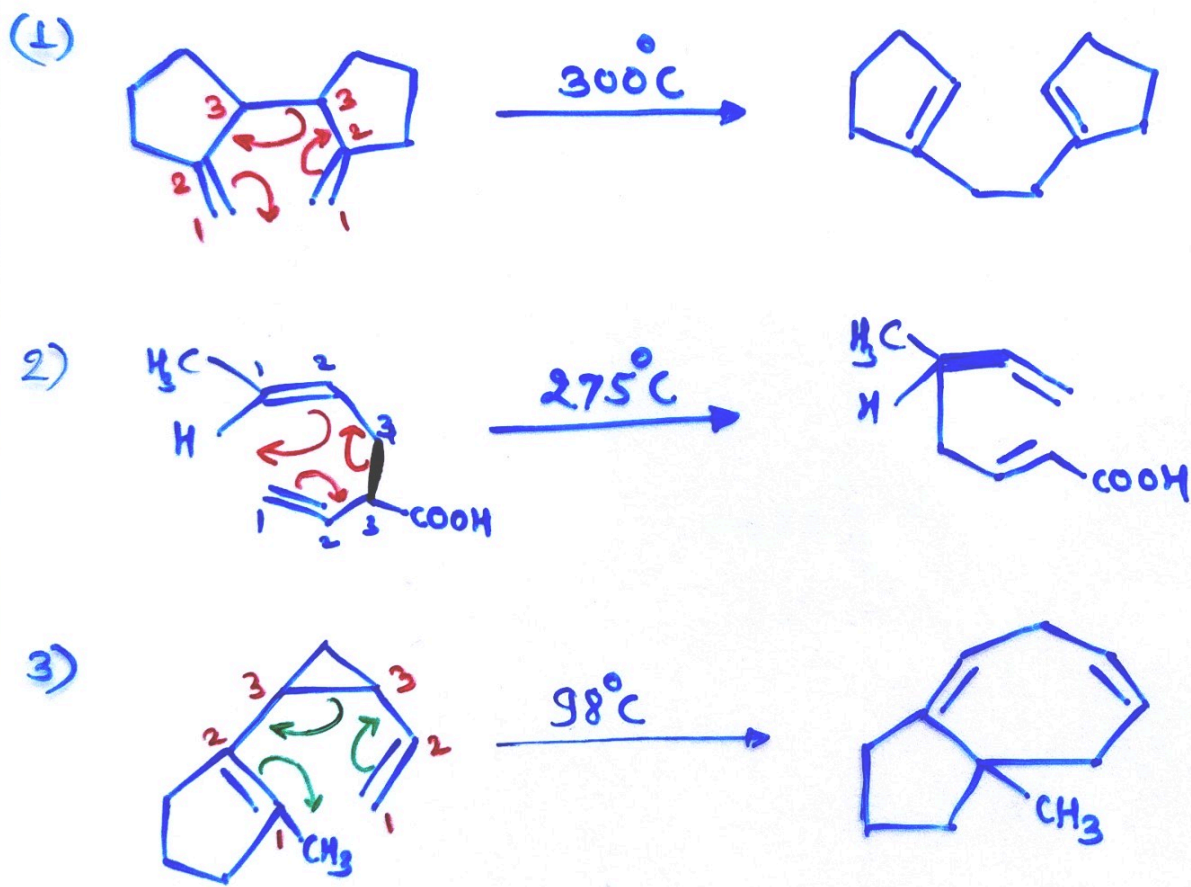


### (3,3) sigmatropic Rearrangement:-

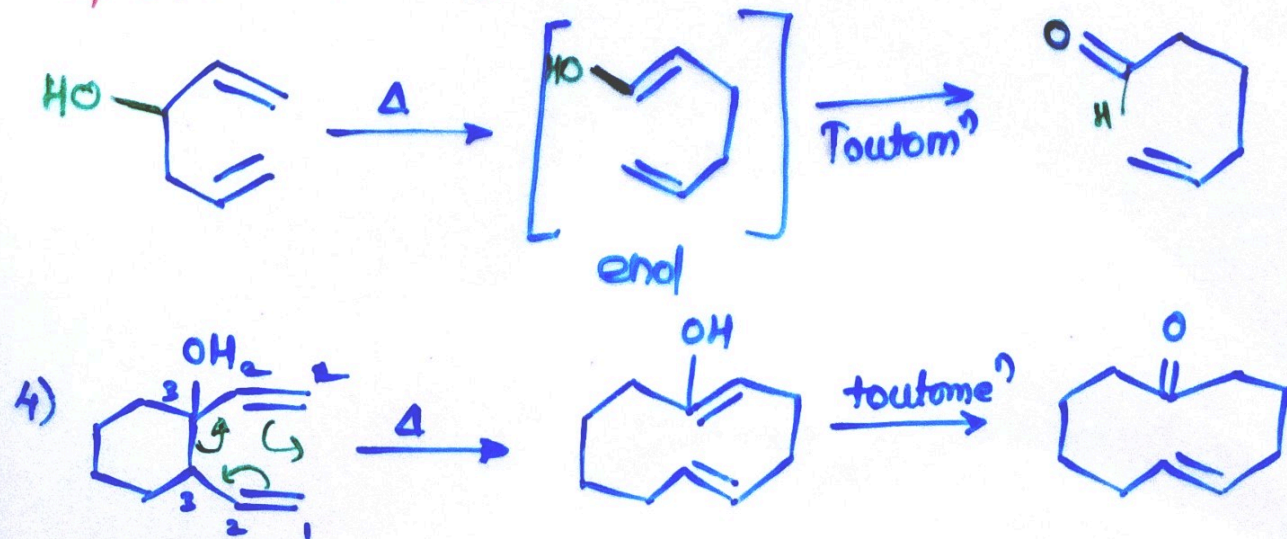
The thermal rearrangement of 1,5 dienes by [3,3] sigmatropic shift is known as cope Rearrangement.



### Examples:-



### oxy cope Rearrangement:-

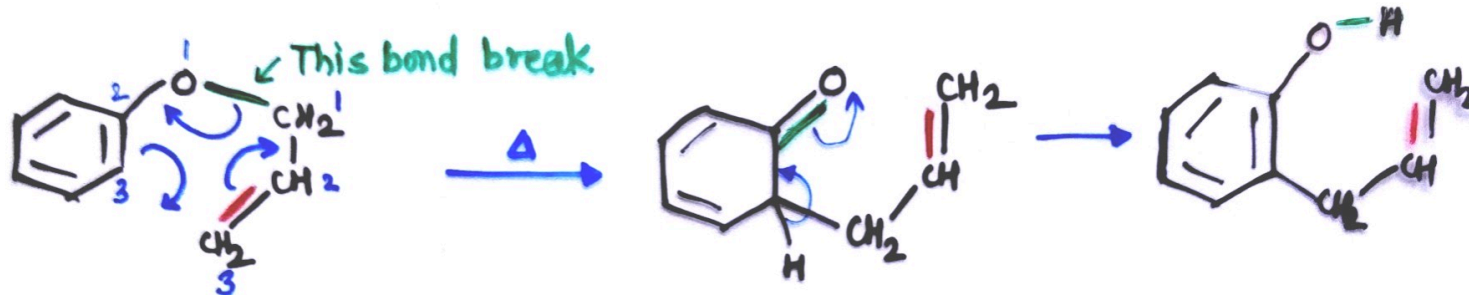
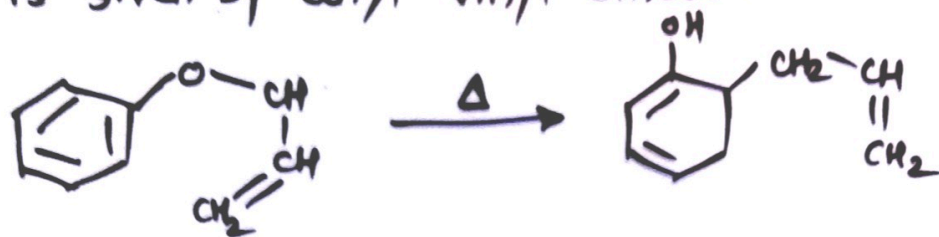


# CLAISEN Rearrangement

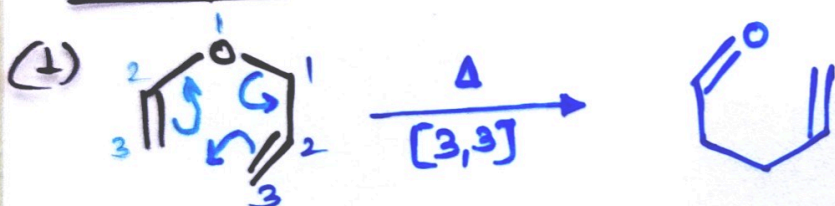
2.0

\* It is the first sigmatropic rearrangement which was discovered by Claisen.

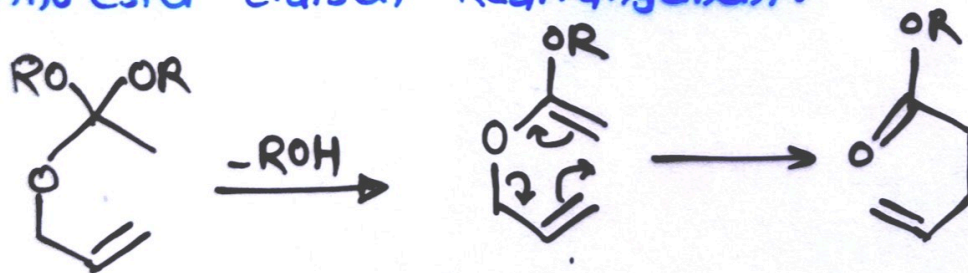
\* It is given by allyl vinyl ethers.



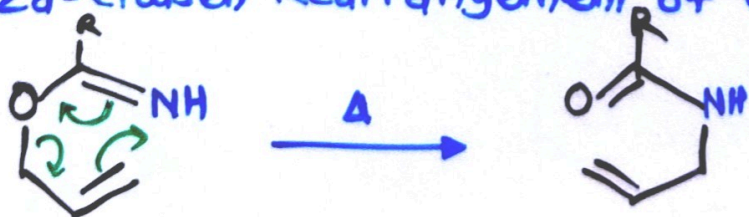
## Example:-



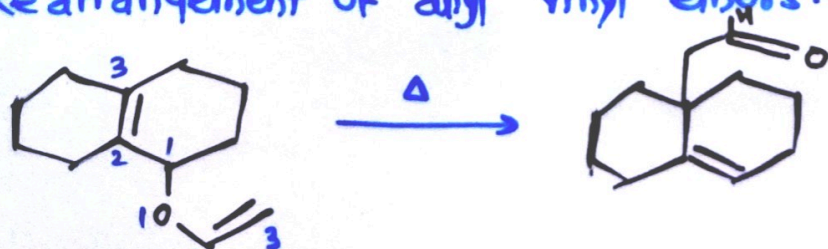
## (2) ortho ester claisen Rearrangement:-



## (3) Aza-claisen Rearrangement of o-allyl imidates.



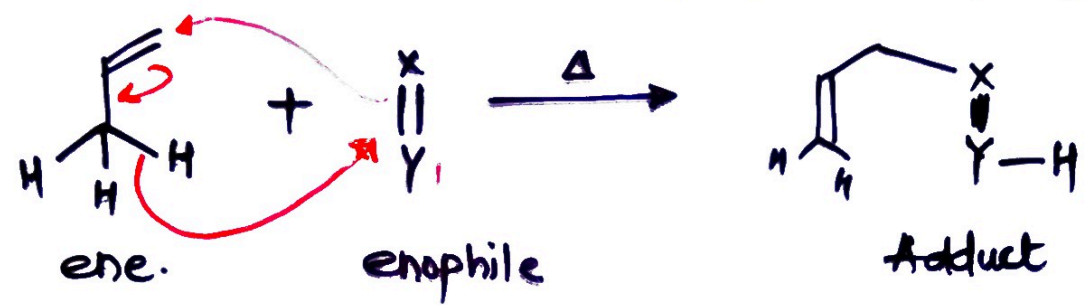
## (4) Rearrangement of allyl vinyl ethers:-



# Ene Reaction:-

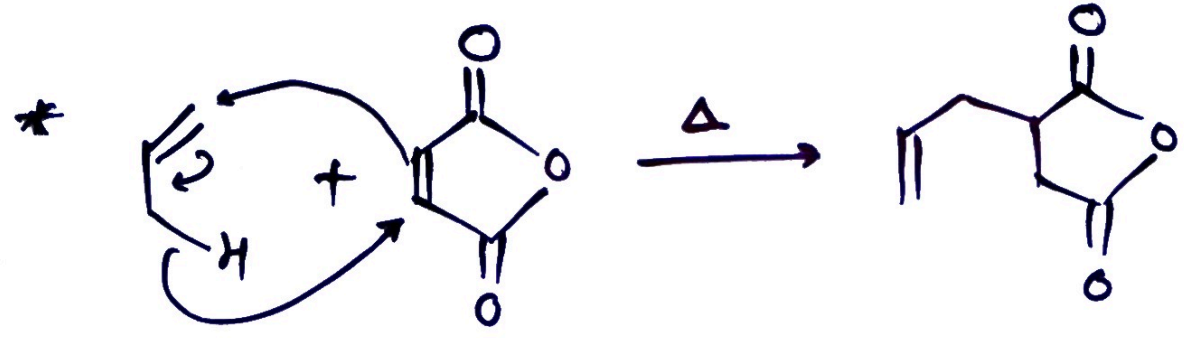
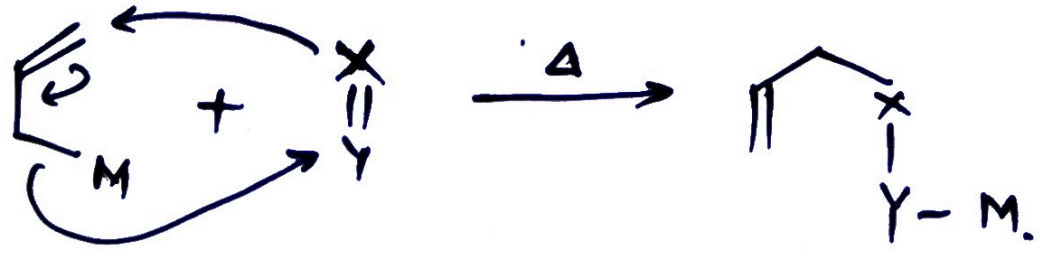
Ene reaction involves the thermal reaction of an alkene (called ene) having an allylic hydrogen with a compound having multiple bond ( $X=Y, X\equiv Y$ ) called enophile.

\* During the reaction, transfer of allylic hydrogen and allylic double bond and bonding between two unsaturated termini (one terminus of ene and other terminus of enophile)



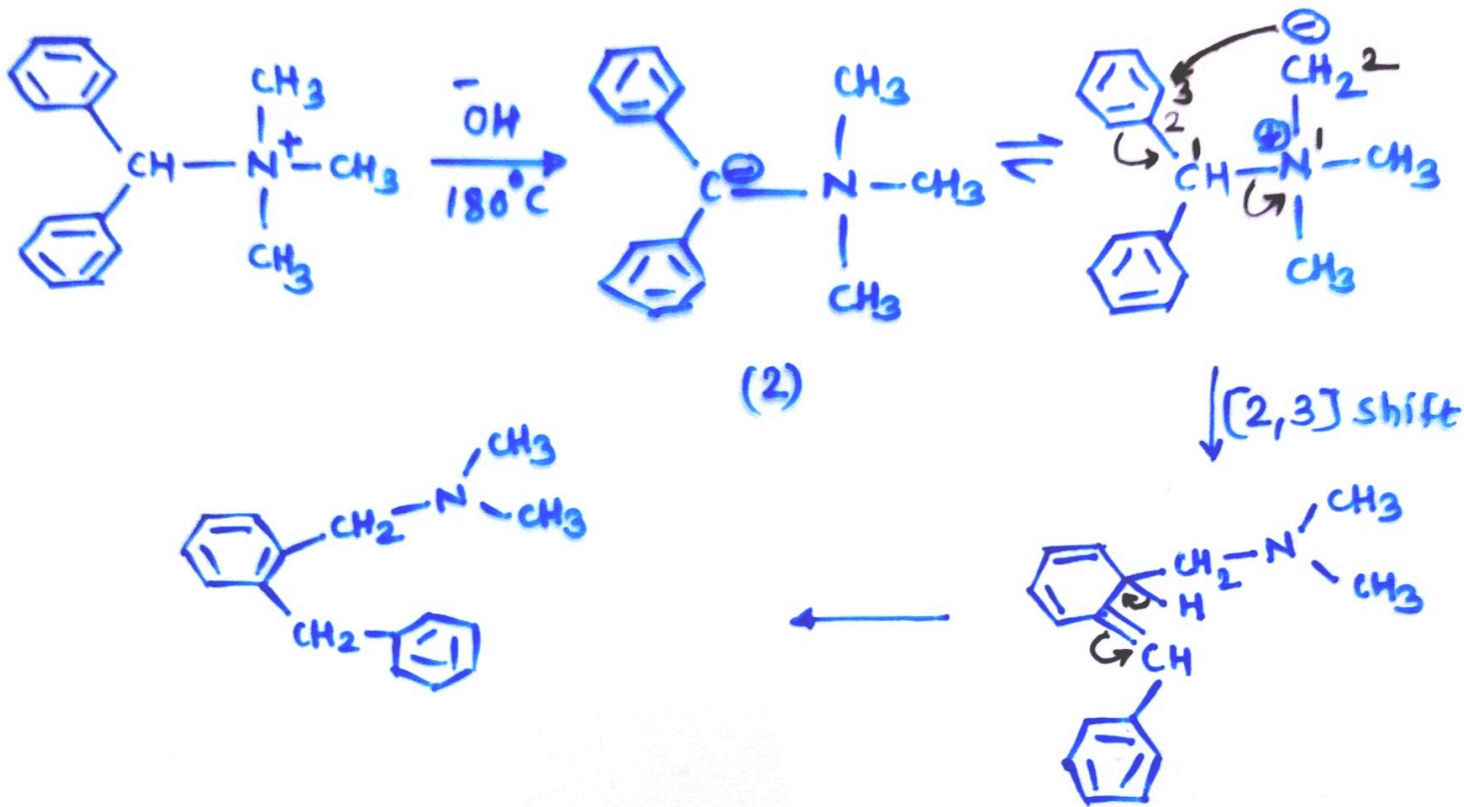
- |          |                |
|----------|----------------|
| $X=Y$ is | $X\equiv Y$ is |
| $C=C$    | $C\equiv C$    |
| $C=O$    | $C\equiv N$    |
| $C=S$    |                |
| $C=N$    |                |
| $N=O$    |                |
| $-N=N-$  |                |
| $O=O$    |                |

\* When metals or element migrated then called as metalla-ene reaction.  $M = Li, Mg, Al$ .

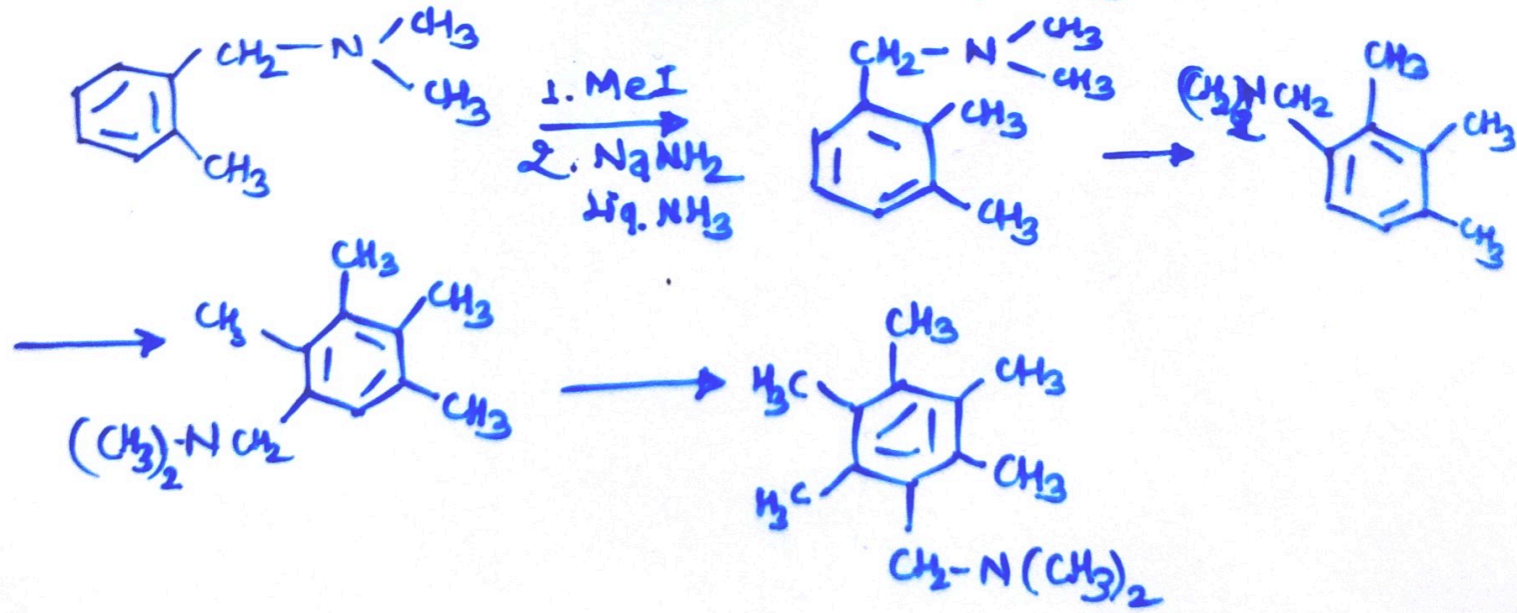


# Sommet-Hauser Rearrangement: (2,3) sigmatropic Rearrangement.

The initial deprotonation of the benzylic position to produce (2) which is in equilibrium with ylide (3) which is in small amount it undergoes 2,3-sigmatropic rearrangement & aromatization to form final product.



The abstraction of H can be made by using PhLi or NaNH<sub>2</sub>



E - N - D