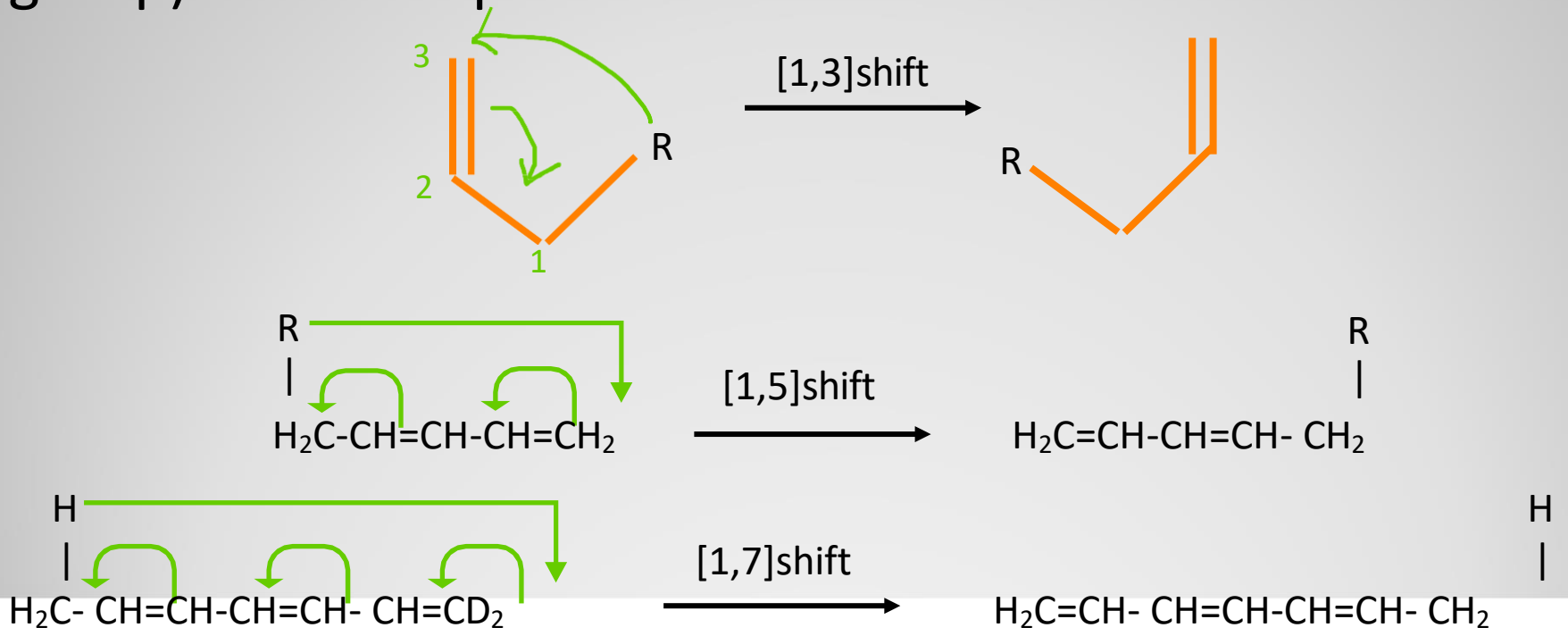
Sigmatropic Rearrangements

M.B.R.K.V.P. Singh College, Ara

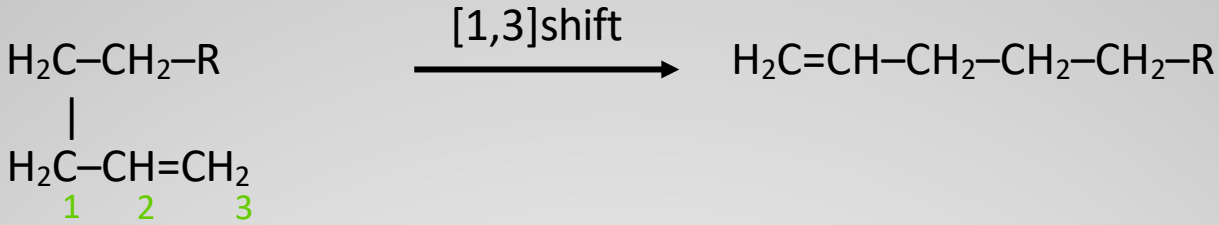
An Overview

- ThewordSigmatropicismadeupoftwowordsSigma(forSigma bond) and Tropos (Greek work meaning turn).
- SigmatropicrearrangementsareaclassofPericyclicreactions.
- Likeanypericyclicreaction,itmaybethermalorphotochemical reaction and it involves concerted cyclic shift of electrons.
- Itisanintramolecularreaction.
- In this rearrangement, a sigma bond shifts from one part of a pi-bondedsystemtoanotherpartwithsimultaneousrearrangementof the pi-system. The total number of sigma and pi bonds remain unchanged.

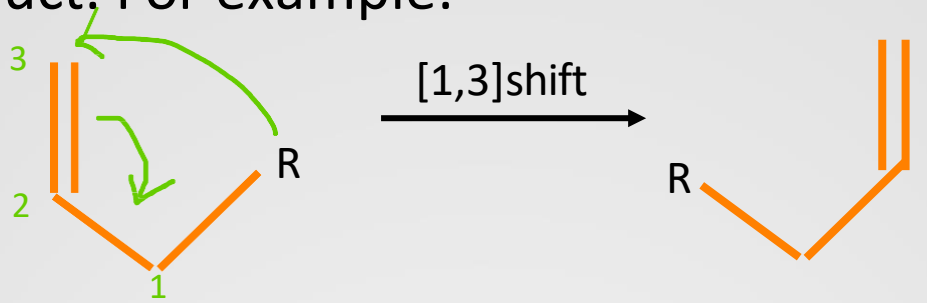
- The order of the Sigmatropic rearrangements is indicated by two numberswithinabracket[i,j].Thefirstnumbershowstheoriginal position of the migrating sigma bond (of atom or group) and the secondnumberisfornewpositionofthemigratingsigmabond(of atom or group). For example:

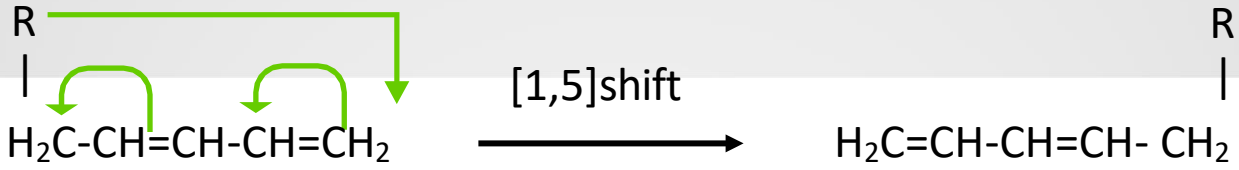


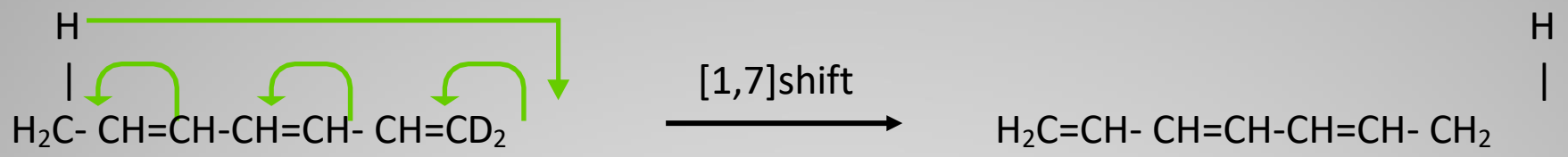
- Thesubstratesshouldhaveatleastoneallylicsystemandmigrating atom of group bonded with allylic carbon by sigma bond is given numberone.



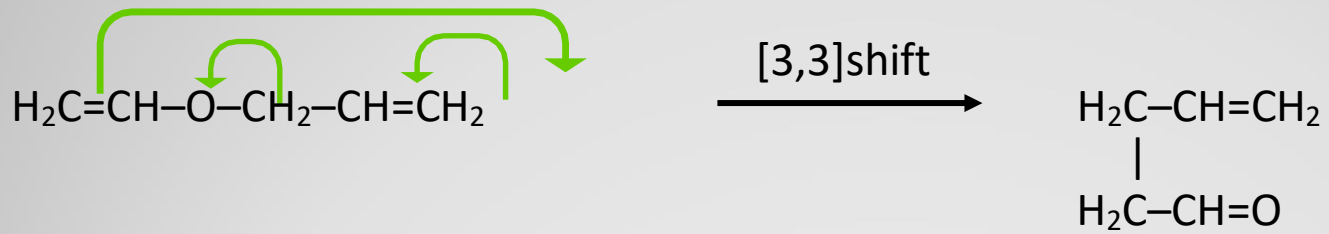
- Sigmatropicrearrangementscanbedividedintotwocategories.
  - One,inwhichmigratingatomorgroupisbondedthroughthesameatomin both reactant and product. For example:





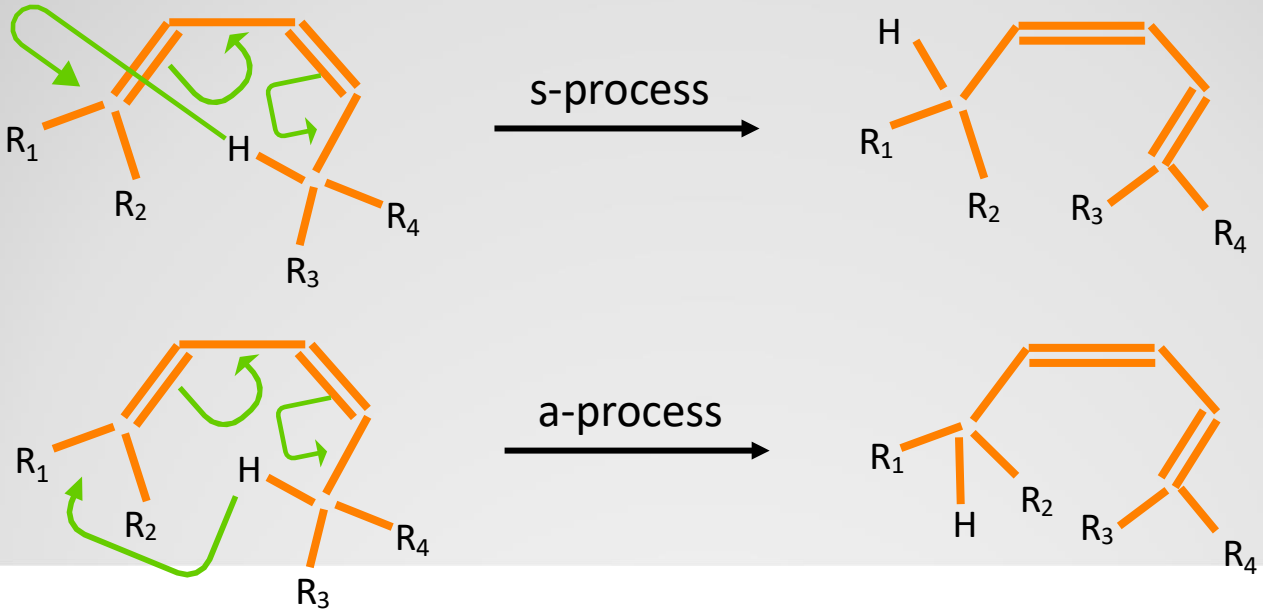


- Second,inwhichthemigratingatomorgroupisbondedthroughdifferent atoms in reactant and in product. For example:



Claisen– Cope Rearrangement

- The process of sigmatropic shifts may be ‘s’ (suprafacial) or ‘a’ (antarafacial). In s-process the migrating sigma bond moves across the same face of conjugated system whereas in a-process the migratingsigmabondisreformedontheoppositepi-electronfaceof the conjugated system. Due to steric reasons, s-processes are more common than a-processes.



- Sigmatropic rearrangements are common for hydrogen atom shifts with examples of [1,2], [1,3],[1,4], [1,5],[1,6], [1,7] etc. In these reactions, if the total number of pi-electrons ([i+j] in a [i,j]shift) is (4n+2),thens-processisallowedandiftotalnumberofpi-electrons is 4n then a-process is allowed.
- Stereochemistryoftheproductsunderthermalorphotochemical condition can be explained using Woodward-Hoffmann rule:
  - Forsupra/supraorantara/antara[i,j]sigmatropicshifts if i+j = 4n+2 they are thermally allowed ifi+j=4ntheyarehv(photochemically)allowed
  - Forsupra/antara[i,j]sigmatropicshifts if i+j = 4n they are thermally allowed ifi+j=4n+2theyarehv(photochemically)allowed

ExamplesofsomereactionsinvolvingSigmatropicshifts:

[1,2]shifts

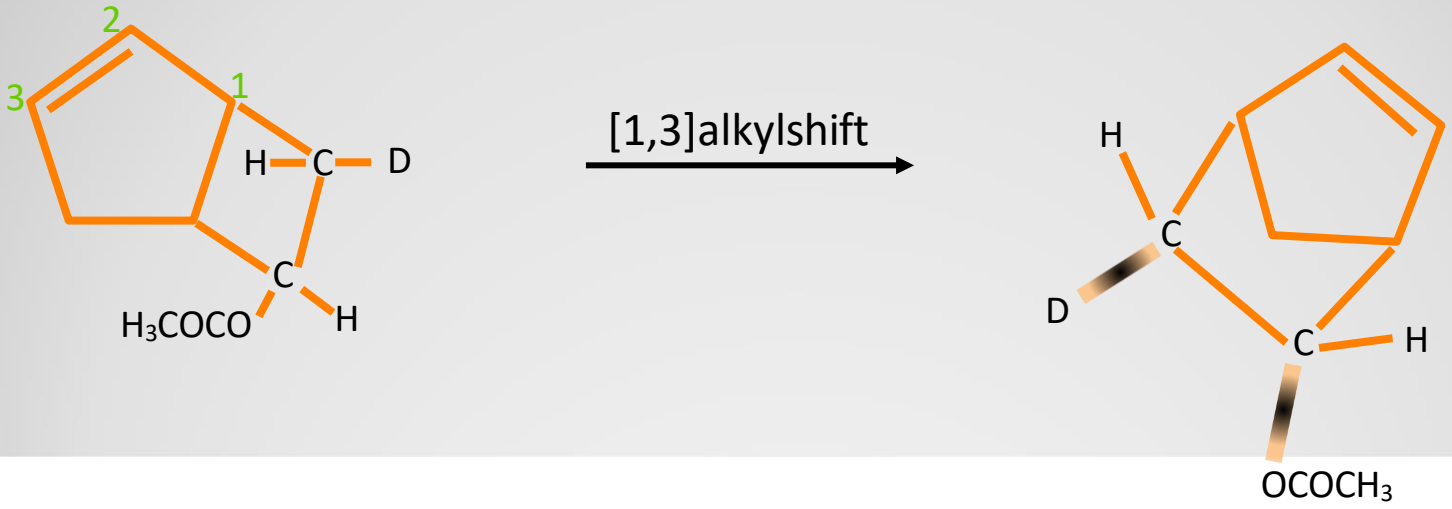
Wagner-Meerwein Rearrangement: Migration of a Carbon atom (ofagroup)fromanoriginhavingCarbontoaterminuscontaining Carbon atom.

Curtius,Beckmann&LossenRearrangement: Migrationterminus has a Nitrogen atom but the migratinggroup and origin have groups containing carbon atom.

[1,3]shifts

In symmetry allowed 1,3 shifts, the migrating group must shift by antara-facialprocess.ThisisnotfeasiblewithHydrogenatomwith1s orbital (smallest orbital in size).

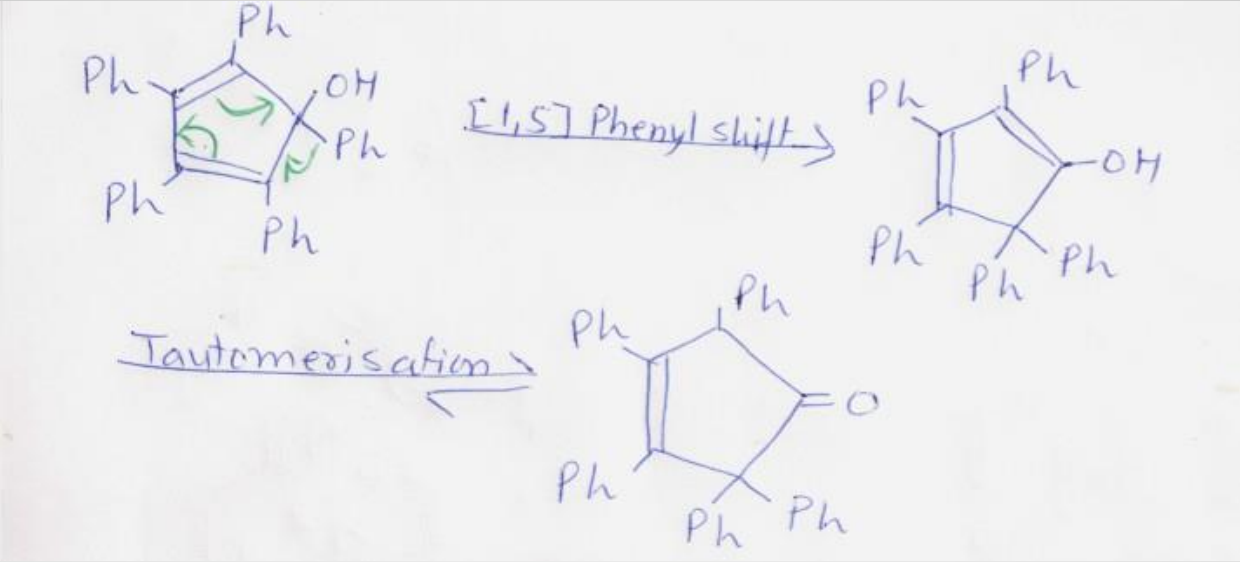
Suprafacial1,3shiftofCarbonatom(ofalkylgroups)occurswith inversionofconfigurationwhereSigmabondtakesuptheroleof antarafacial component.



Inversionofconfiguration

[1,5]shifts

This is thermally allowed shift with retention of configuration by suprafacial mode of overlap. It is more common than [1,3] shifts. Reactionsshowmigrationofmethylandphenylgroups.Forexample:



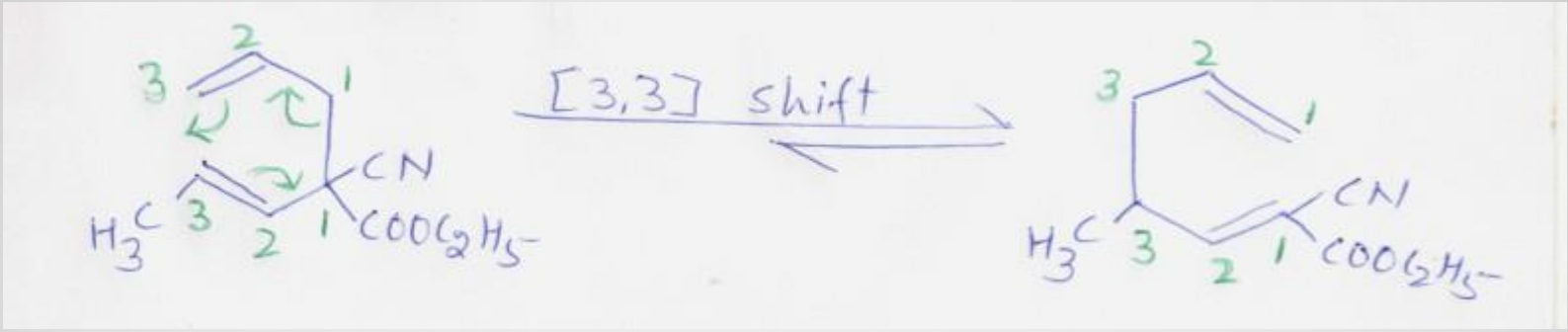
Walk Rearrangement is an example of [1,5] shift. In a bicyclic molecule,migrationofdivalentgroupssuchasO,S,-NR,-CR_2which are a part of three membered ring occurs in this rearrangement.

[1,7]shifts

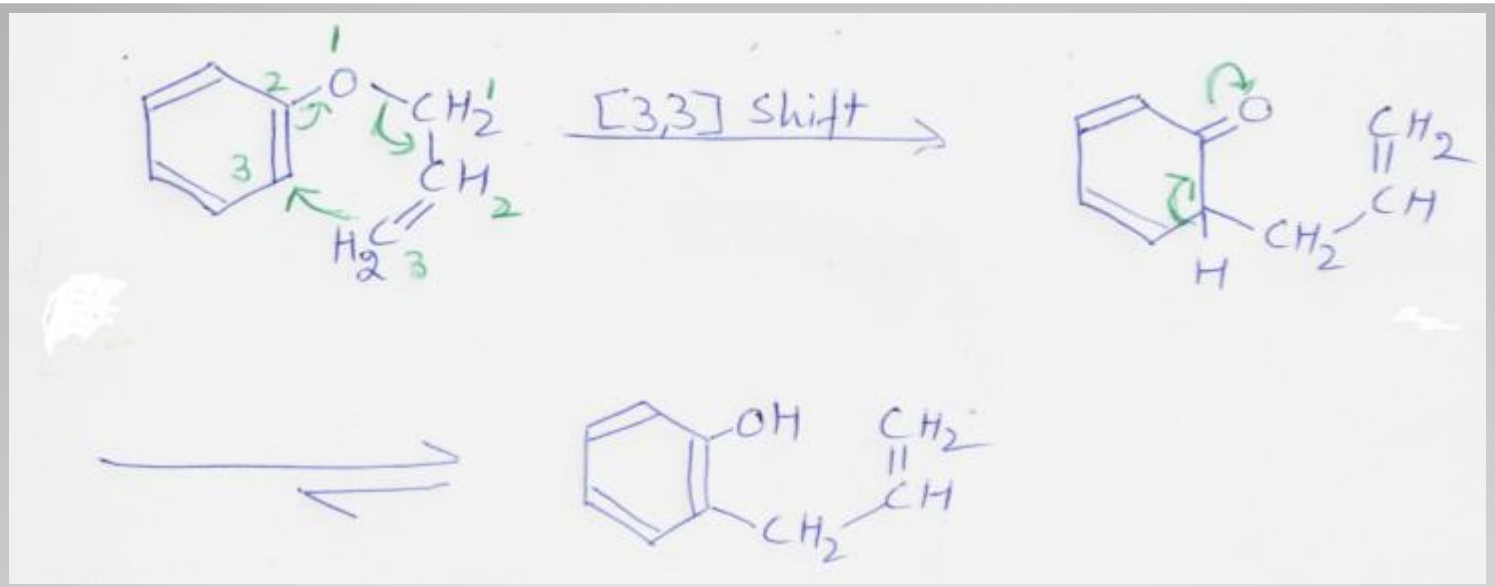
Like[1,3]shiftsthesearephotochemicalshiftsbysuprafacialmode of overlap. It occurs mainly in bicyclic compounds.

[3,3]shifts

CopeandClaisenrearrangementsareimportantnamereactionsin this category:



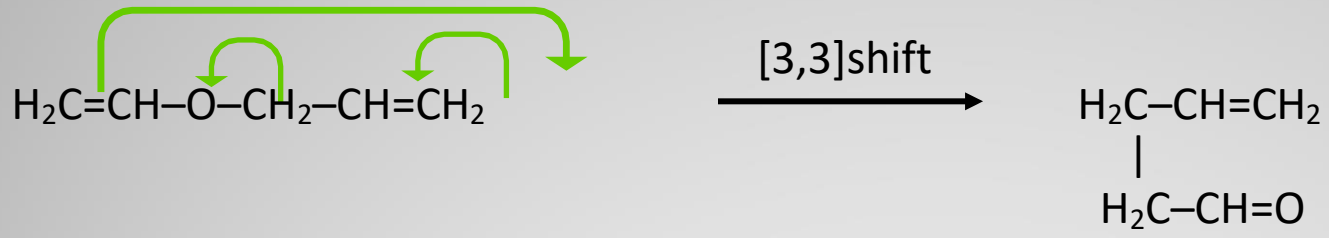
CopeRearrangement



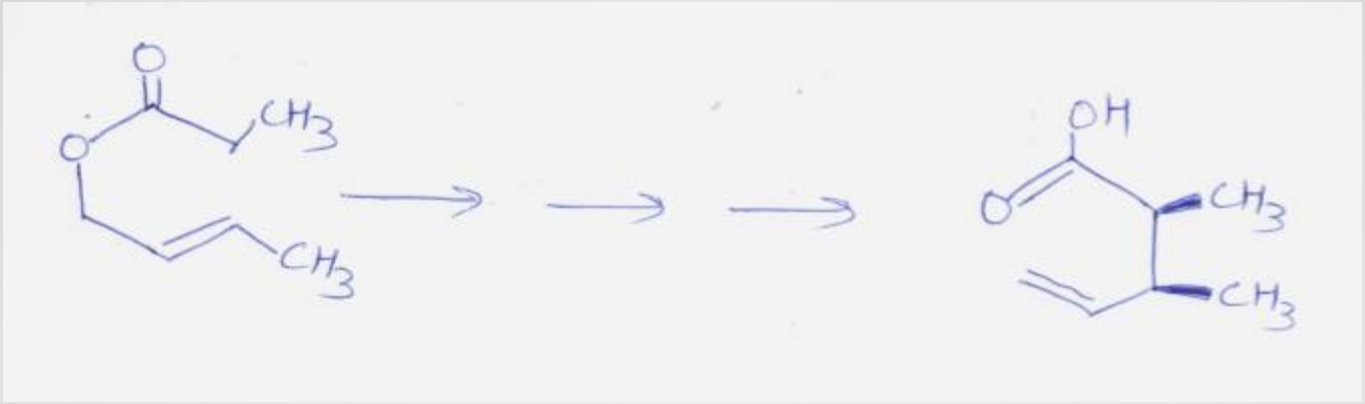
ClaisenRearrangement

This is called a [3,3] shift because the new sigma bond has a 3,3 relationshiptotheoldsigmabond.Thisisthereactionof1,5dienes.A chair like six membered transition state is formed which has six partially delocalized electrons. [3,3] sigmatropic shifts are stereospecific reactions.

Otherexamplesof[3,3]shiftsareAliphaticClaisenorClaisen-Cope rearrangement, Fischer – Indole synthesis, Carroll rearrangement, Ireland – Claisen rearrangement etc.



Claisen– CopeRearrangement



Ireland–ClaisenRearrangement

[5,5]shifts

It occurs in ten electron systems. The [5,5] – Sigmatropic rearrangementof2,4-pentadienylphenylethersishomologousto Claisen rearrangement :