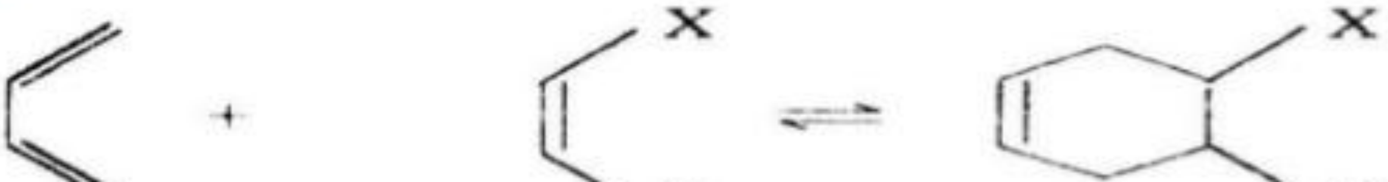
Peri cyclic Reactions

- The majority of organic reactions proceed either by a polar or by a radical pathway.
- there is a group (although small) of reactions that ***do not involve polar or radical reagents***, i. e. they are substantially ***uninfluenced by change of polarity of solvent or by the presence of radical initiators.***
- ***E.g:*** Diel's - Alder reaction



Definition of Peri cyclic Reactions

- Reactions are apparently ***concerted***, i.e. ***the electronic rearrangements involved in bond breaking/bond-making proceed simultaneously, i.e. it is a one step process***.
- *The transition states are cyclic and the reactions are attended by a high degree of stereo selectivity*. Many of such reactions are reversible.
- ***All such concerted reactions which proceed via cyclic transition states are known as pericyclic reactions*.**
- Unaffected by polar reagents, solvent change, radical initiators, etc.
- Influenced by **Heat** or **Light.**

Stereochemistry of Pericyclic Reactions

- While simple dimerisation of olefins to cyclobutane gives very poor results, except when photo chemically induced.
- Woodward, Hofmann and others have shown that these contrasting results can be explained by the principle of ***conservation of orbital symmetry*** which predicts that certain reactions are ***symmetry allowed and others are symmetry forbidden.***
- **The orbital symmetry rules (also called the Woodward-Hofmann rules) apply only to concerted reactions.**
- There are several ways of applying the orbital symmetry principle of which the ***FRONTIER ORBITAL METHOD*** is the most common.

Frontier orbital's and orbital symmetry

- Just as the outer shell of electrons of an atom is regarded as especially significant in determining the chemistry of that atom.
- So it is reasonable that, for a molecule, it is the **highest occupied molecular orbital (HOMO)** which is the ***key in determining reactivity***.
- *This is termed the frontier orbital, The theory*

I.principle

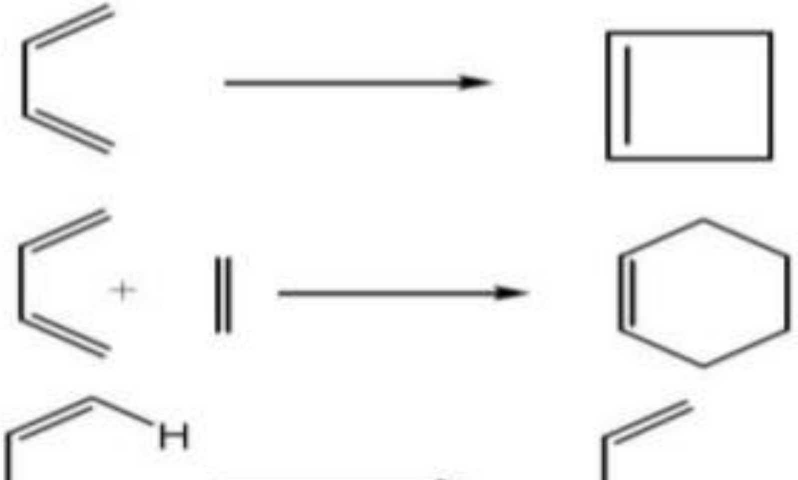
- Since the ground state of almost all molecules has a pair of electrons in the HOMO,
- *bonding interaction between two molecules* or *between two atoms in the same molecule cannot involve* only the HOMO of each because this would lead to an orbital occupancy greater than two which is contrary to Pauli's principle.
- **The HOMO of one reactant needs to interact with an unoccupied molecular orbital of the second.**
- Now since the bonding interaction between two orbital's increases as the energies of the two become more nearly equal, ***it is expected that the HOMO of one reactant would interact efficiently with the lowest unoccupied molecular orbital (LUMO) of the second.***

2.principle

- The shaded (positive) lobe overlaps only with the shaded (positive) lobe of another orbital,
- An unshaded (negative) lobe only with the un shaded (negative) lobe of another orbital. Overlap of orbital's of unlike phase results repulsion.

Classification of Peri cyclic Reactions

1. Cycloadditions
2. Electrocyclic reactions
3. Sigmatropic rearrangements



Elctrocylic reaction

Cycloaddition reaction

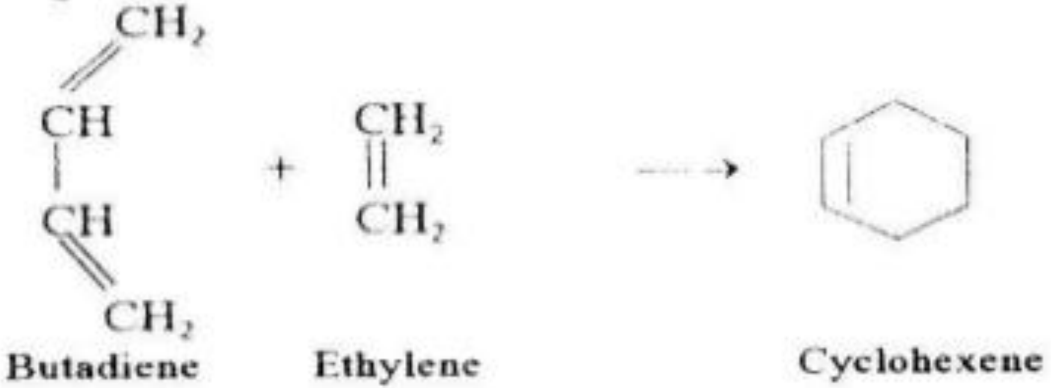
Sigmatropic reaction

Cycloadditions

- A reaction in which two unsaturated molecules combine to form a cyclic compound, with π-*electrons being used to form two new* σ bonds is known as *Cycloadditions reaction.*
- **Cycloadditions reaction may again be of two types depending upon the number of π *electrons in the two components.***
- (i) (2 + 2) Cycloadditions
- (ii) (4 +2) Cycloadditions

(4 +2) Cycloadditions

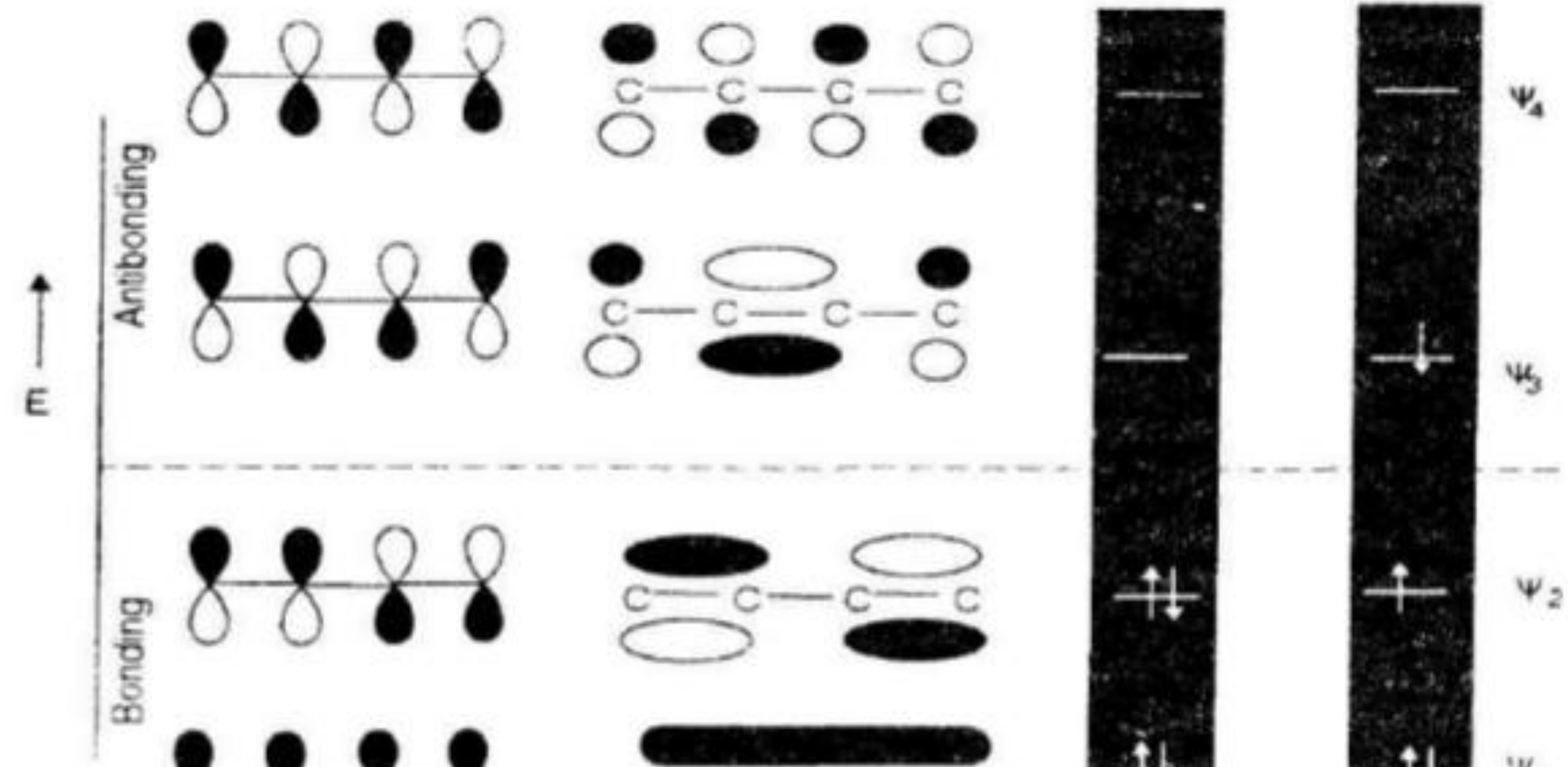
- When one of the systems has 4 π *electrons and the other has 2 π electrons*. *Diels-Alder reactions are the most common example of* this type,



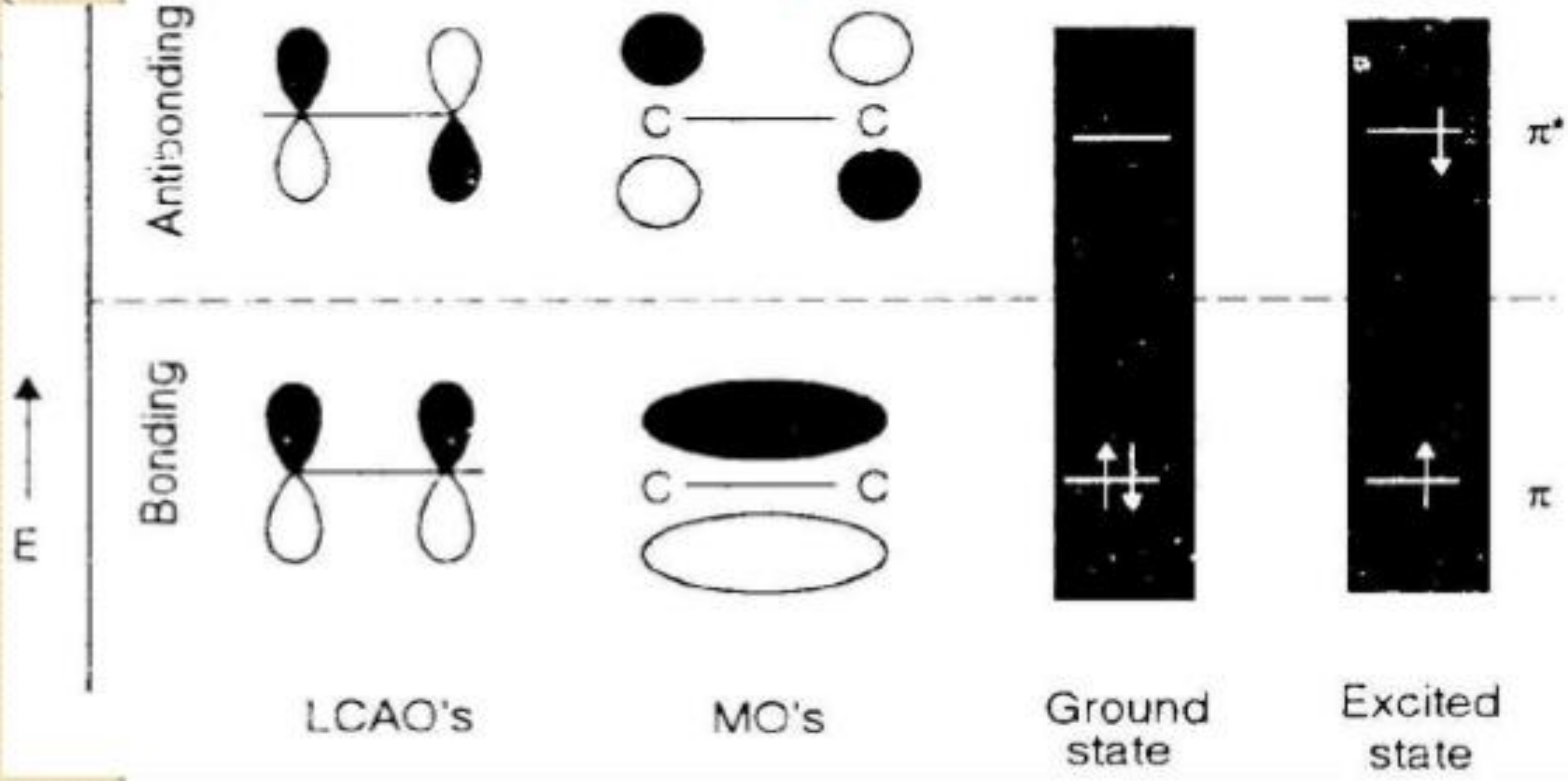
(4 +2) Cycloadditions

- The best known (4 π + 2 π *) Cycloadditions is the Diel's -Alder reaction of* which the simplest possible example is the reaction between butadiene and ethylene to form six-membered ring. Diels-Alder reactions take place very easily, often spontaneously, and at most requires moderate application of heat.
- Before considering the reaction between butadiene and ethylene, let us first study the electronic configuration of 1, 3-butadiene and ethylene.

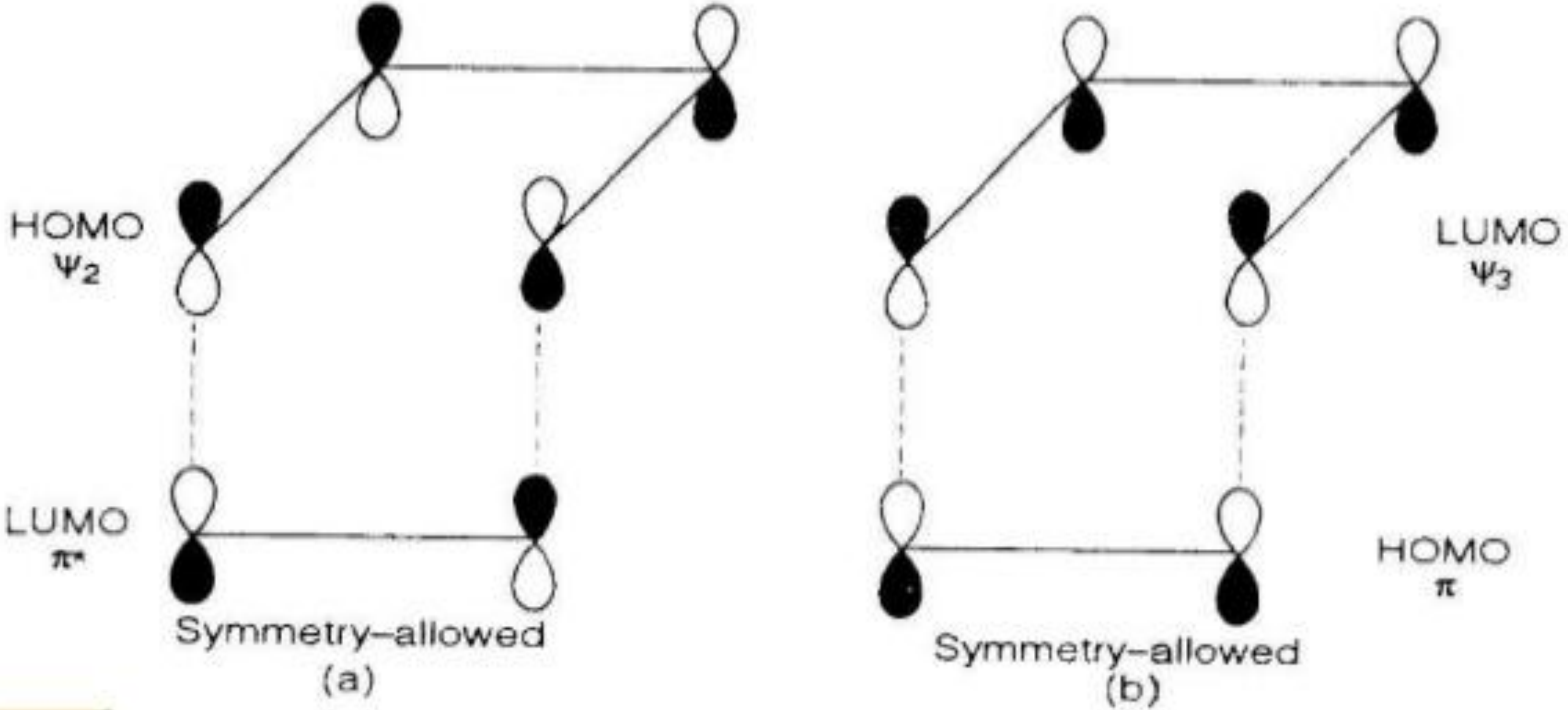
Configuration of π *electrons of 1.3-butadiene in the ground state and* first excited state.



Electronic configuration of ethylene



molecular planes parallel, two new C-C bonds can be formed at the same time.



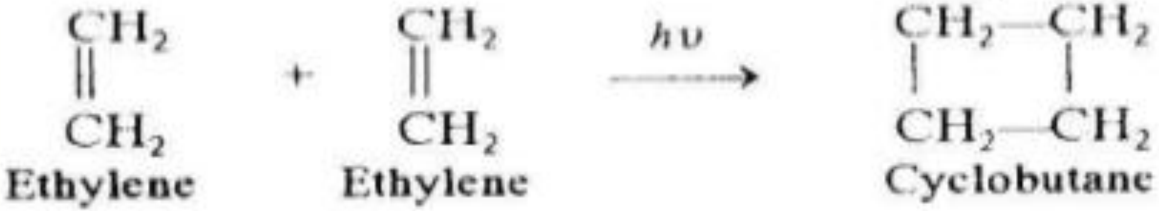
Symmetry–allowed
(a)

Symmetry–allowed
(b)

Symmetry-allowed thermal [4 + 2] cycloaddition of I, 3-butadiene and

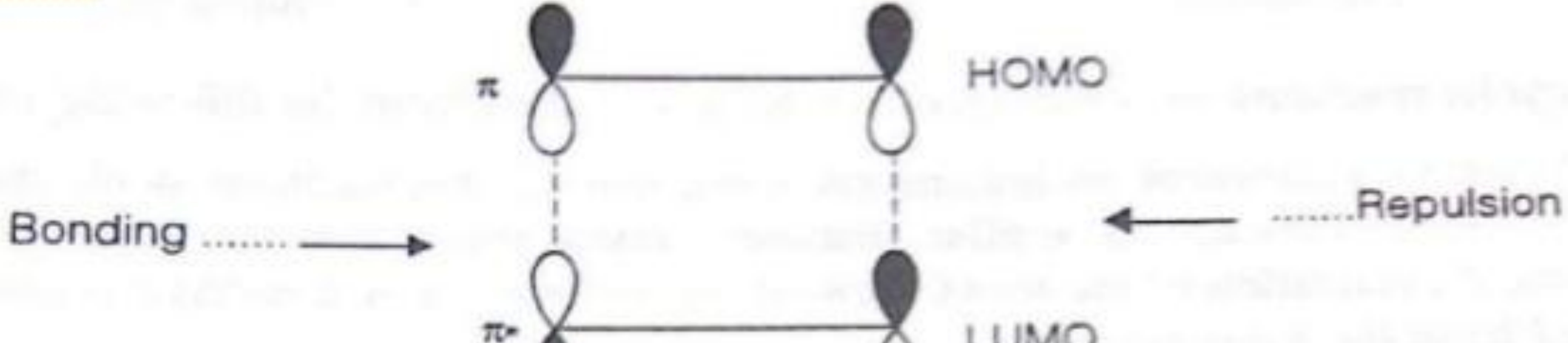
(2+2) Cycloadditions

- (2 + 2) Cycloadditions. When both the unsaturated molecules have 2 π electrons each, e.g.

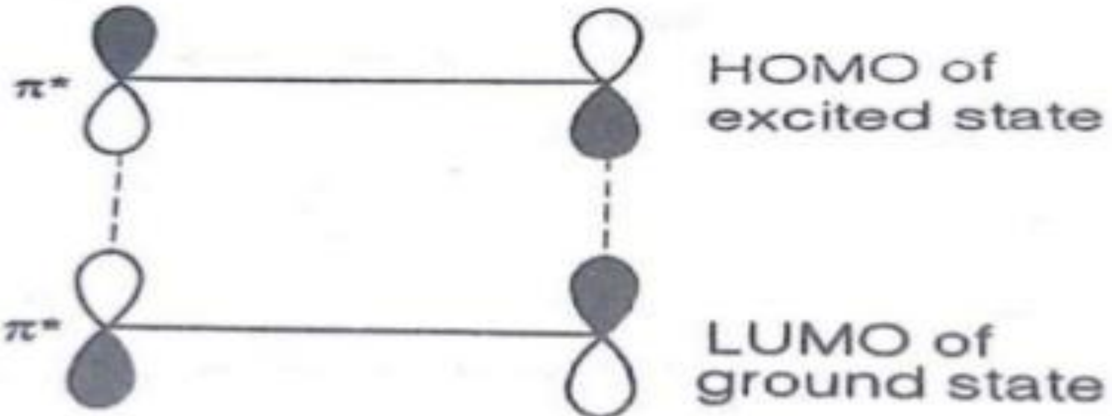


- The [4+2] cycloadditions are common and take place very easily and spontaneously. On the other hand, cyclodimerisation of alkenes,
- e.g.conversion, of ethylene to cyclobutane, is very difficult and not very common. Further, it is interesting to

- The reason being in presence of heat, dimerization of ethylene would involve overlap of the HOMO, π_2 *of one molecule with the LUMO,* π^**, of the other.* Now since nand π^* *are of opposite symmetry, lobes of opposite phase would* approach each other. Hence interaction is antibonding and repulsive, and concerted reaction does not occur due to symmetry-forbidden overlapping.

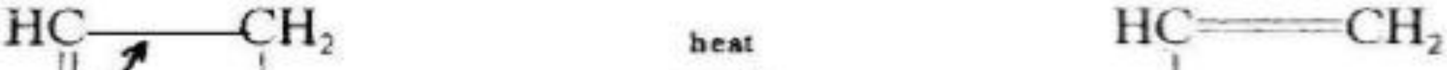


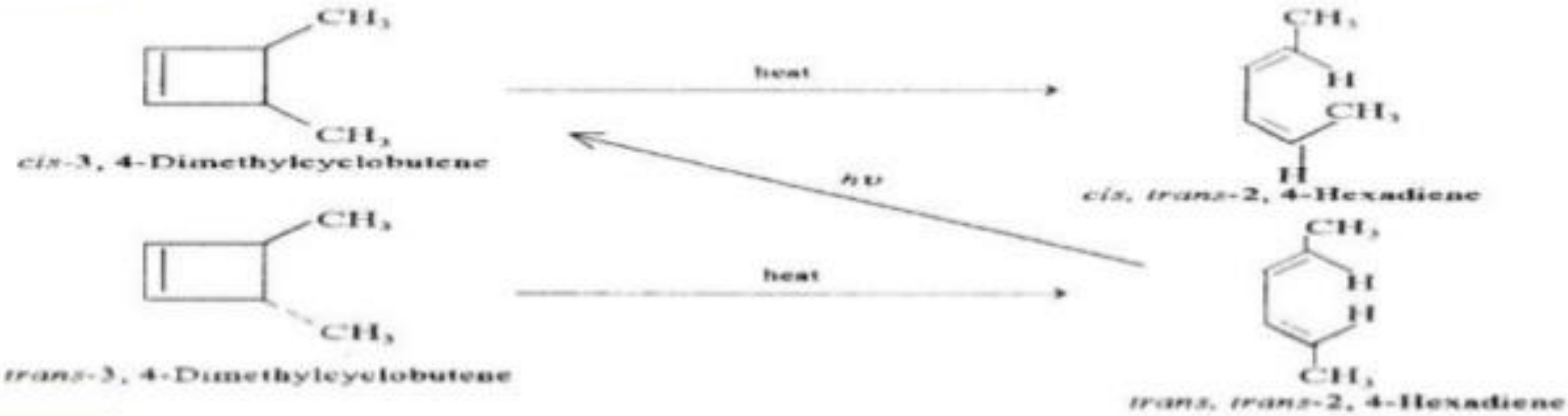
- photochemical [2 + 2] cycloadditions are symmetry allowed. The simplest interpretation of this is as follows. When an olefin molecule absorbs a quantum of light, an electron is promoted from the HOMO to the LUMO, so that there are now two singly occupied molecular orbitals (SOMO). The excited HOMO therefore has the symmetry of the ground state LUMO, i.e. π * *and* consequently the two can now interact.



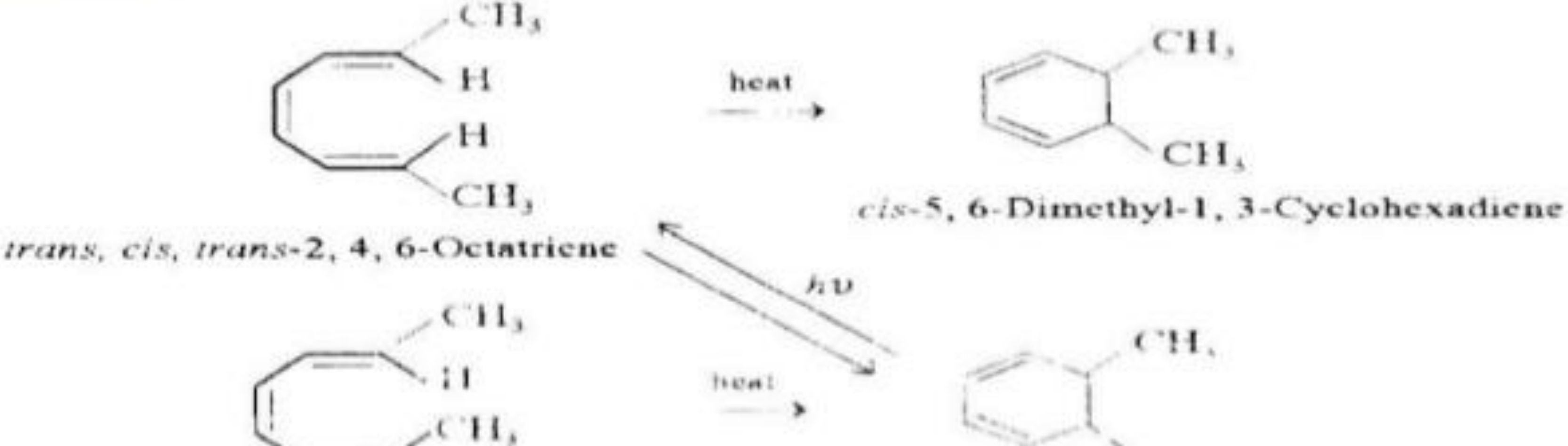
Electrocyclic Reactions

- Electrocyclic reactions are those in which either a ring is formed with the generation of a new (σ *bond and the loss of a* - π *bond or a ring is broken with* the opposite consequence, e.g.,





Interconversions of 3, 4-dimethylcyclobutenes and 2, 4-hexadienes



Methods of analysing pericylic reaction

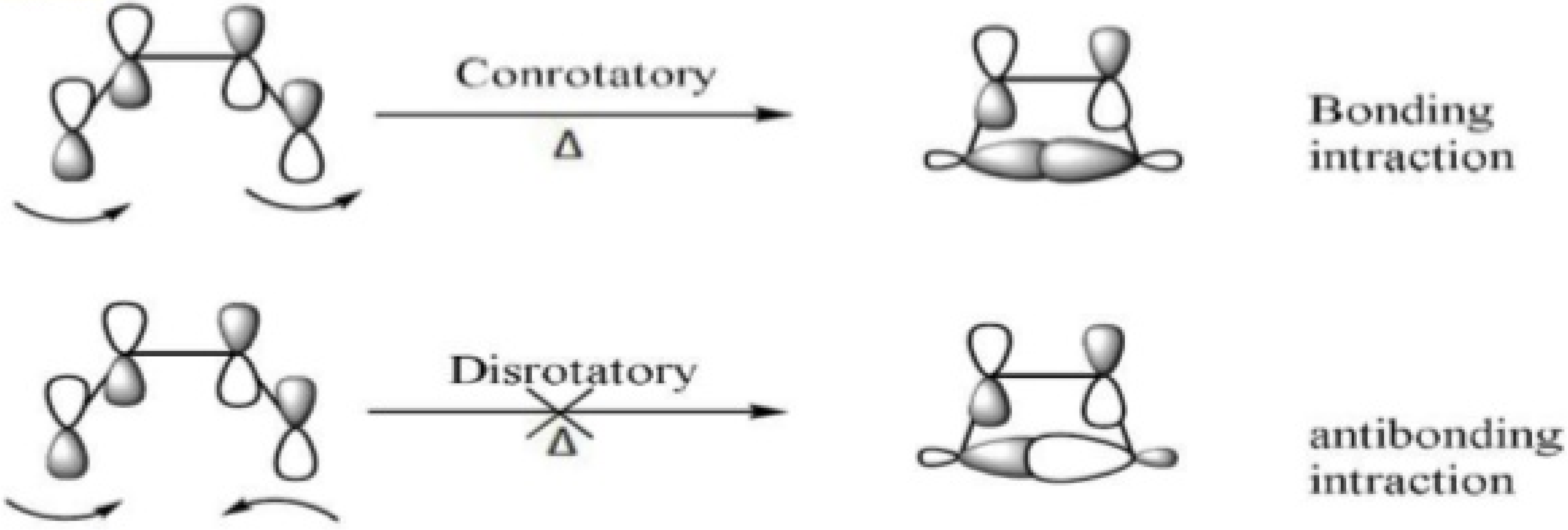
1. The frontier molecular orbital (FMO)
2. Orbital symmetry correlation diagrams
3. Huckel-Mobius theory or Perturbation Molecular Orbital (PMO)

1. Frontier Molecular Orbital (FMO) approach

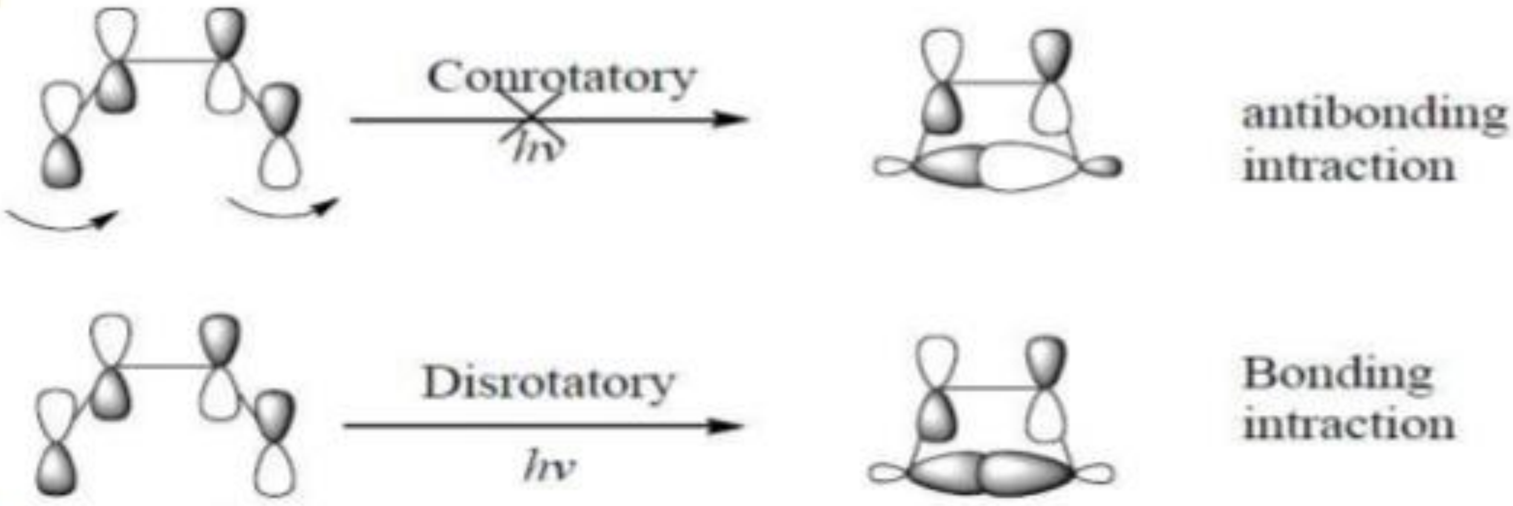
- The mechanism of electrocyclic reactions can be understood in terms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffman rules. The pathway of such reactions is determined by the symmetry properties of the orbitals that are directly involved. ***The orbital symmetry must be same during overall mechanism.***
- In electrocyclic reactions, *only one reactant is involved and thus only the highest occupied molecular orbital (HOMO) needs to be considered*. Thus, the ***stereochemistry of the reactions is controlled by the symmetry*** properties of the HOMO of the reacting system. These reactions take place thermally or photochemically.
- In thermal condition, the **ground state HOMO is involved in the**

- The orbitals of terminal atoms of HOMO rotate through 90^0 to allow of their potential overlap.
- *The rotation occurs in the same direction, i.e., clockwise or counterclockwise is called conrotatory process.*
- *But rotation occurs in the opposite direction is called disrotatory process.* The rotation of terminal orbital depends on the type of polyene, i.e., number of double bond and condition of reaction. It is illustrated by following system.

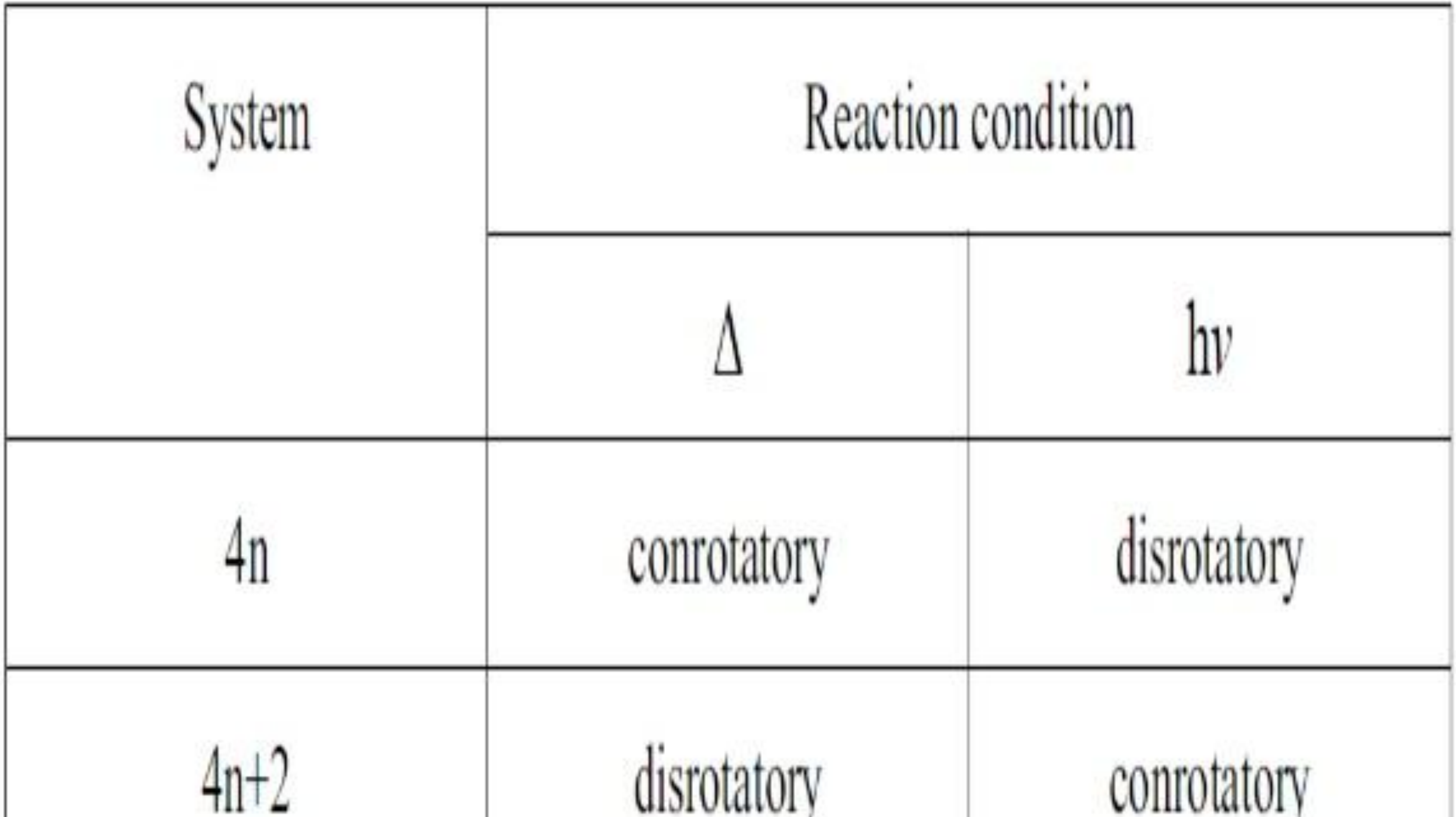
4n π-system for example interconversion of 1,3-butadiene and cyclobutene



In thermal condition ground state HOMO has terminal orbital with opposite phase, conrotatory motion lead to a bonding interaction and thus to the formation of cyclobutene while disrotatory movement results in an antibonding situation. In thermal electrocyclic reaction of



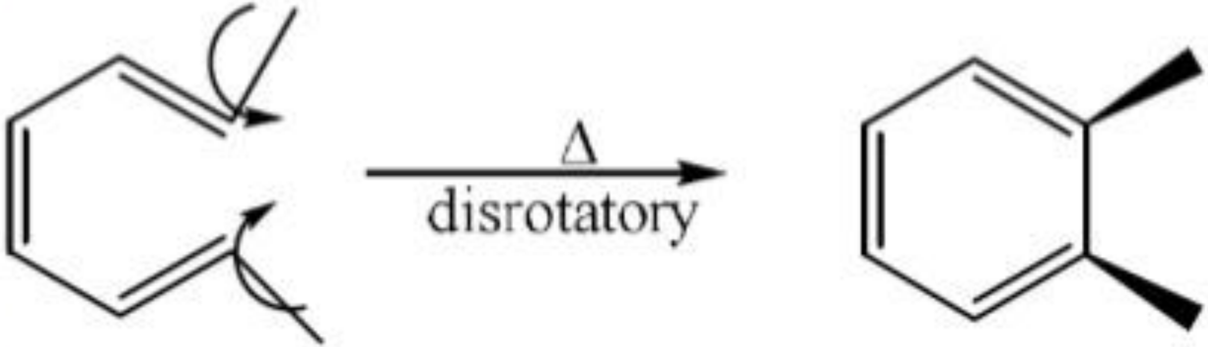
In the case of photochemical condition, ***irradiation of diene will result in the promotion of an electron into the orbital next higher energy level and ground state LUMO becomes the excited state HOMO which has terminal orbital with the same phase***. There is conrotatory motion leading to an antibonding situation, while disrotatory motion results in a bonding interaction and the formation



System	Reaction condition	
	Δ	hν
4n	conrotatory	disrotatory
4n+2	disrotatory	conrotatory

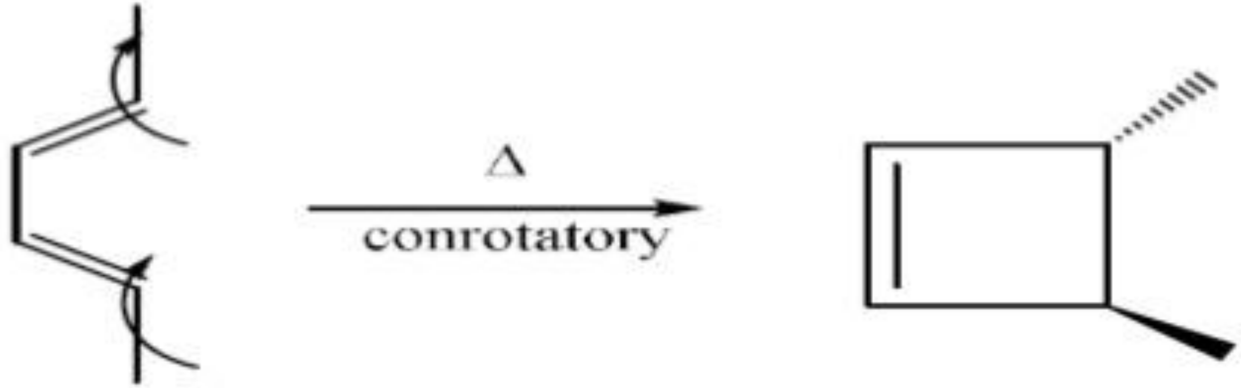
Electrocyclic reactions are completely stereo specific

- For example ***ring closure of (2E,4Z,6E)-2,4,6-octatriene*** yields a single product with *cis methyl groups* on the ring.



cis product only

- For example Cyclization of (2E,4E)-2,4-hexadiene with heat forms a cyclobutane with *trans methyl groups, whereas cyclization with light forms a* cyclobutane with *cis methyl groups.*

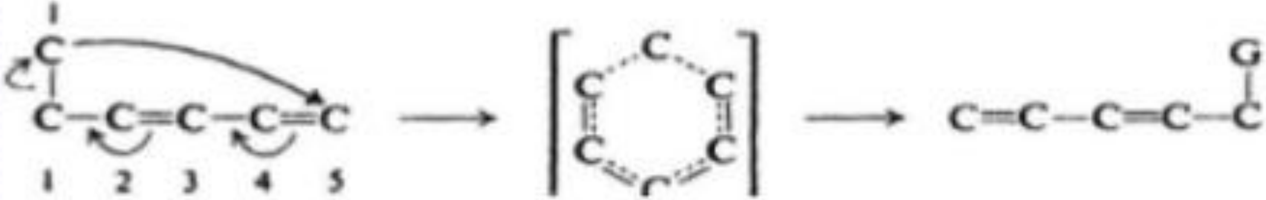


Sigmatropic rearrangements

A concerted reaction of the type.

In which a group migrates with its σ-*bond within a* π- *framework an one or a* polyene is called a sigmatropic reaction.

[1,3] sigmatropic reaction

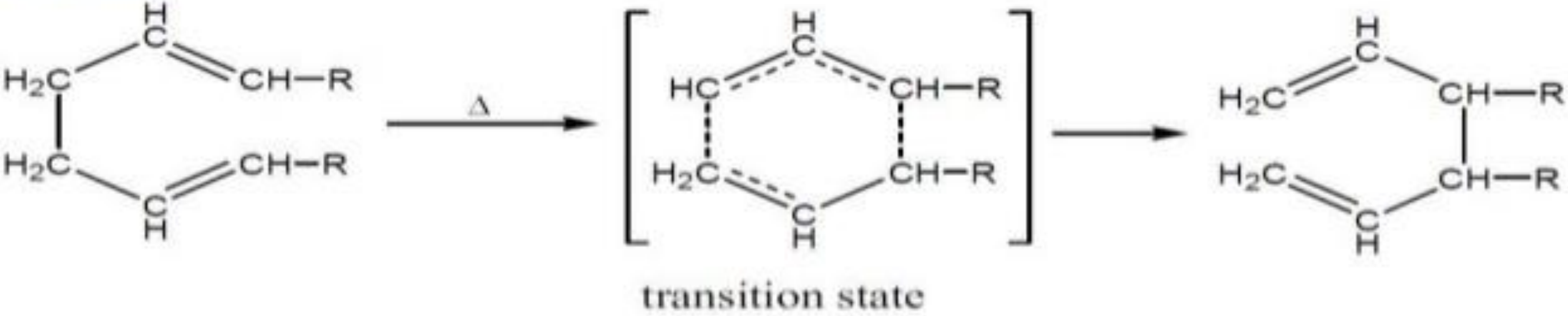


[1,5] sigmatropic reaction

3,3-Sigmatropic rearrangements

Sigmatropic rearrangements of order [3,3] are very common

Generally found in 1,5-hexadiene.

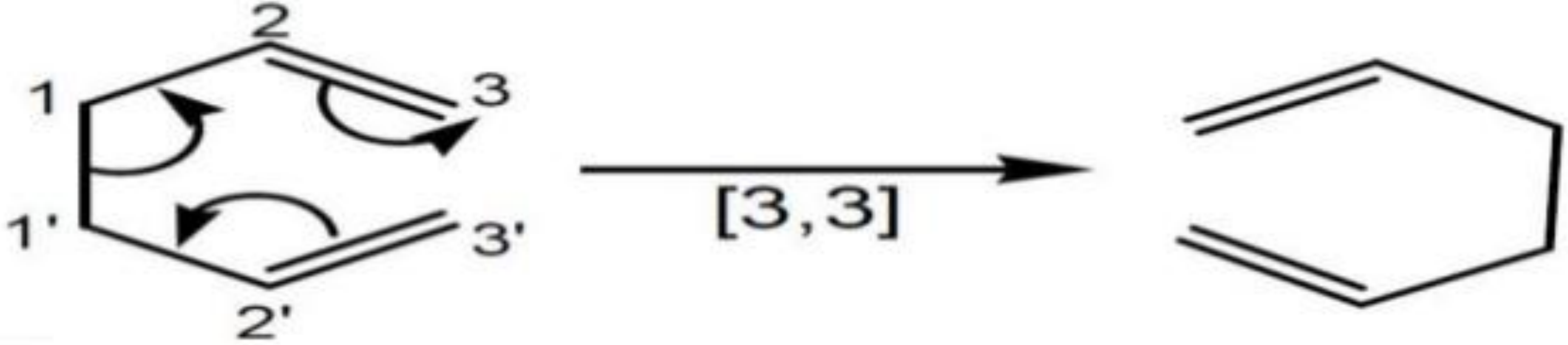


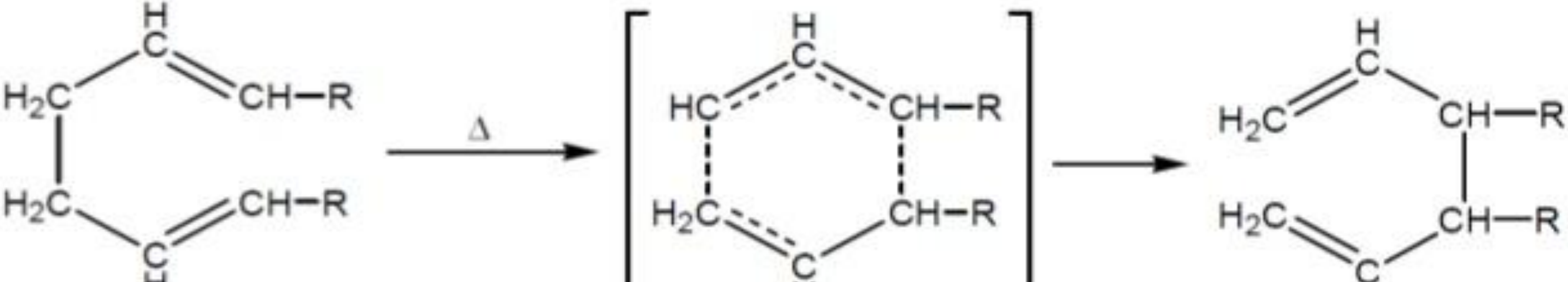
Sigmatropic Reaction of order [3,3]

1.Cope rearrangement
2.Aza-Cope rearrangement

Cope rearrangement

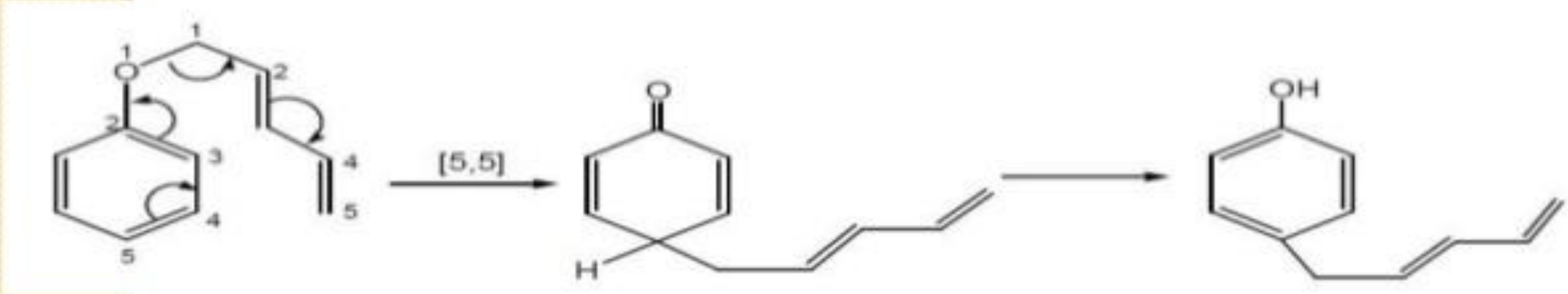
The thermal rearrangement of 1,5-diene through [3,3] sigmatropic shift is known as cope rearrangement.





[5,5] Sigmatropic Rearrangement

Rearrangement of 2,4-pentadienylphenyl ethers involves [5,5] sigmatropic rearrangement. It can be considered a homologous Claisen rearrangement



The benzidine rearrangement represents another example of a [5,5] sigmatropic rearrangement