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GENESIS TUTORIALS

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Pericyclic reactions

Pericyclic Reactions

- The reactions that are characterized by the making and breaking of two or more bonds in a single concerted step through cyclic transition state called Pericyclic reactions due to cyclic nature.
- They are initiated by heat or light
- These reactions are highly steriospecific in nature.

These reactions are generally of four types

(A) Electrocyclic reactions

(B) Cycloaddition reactions

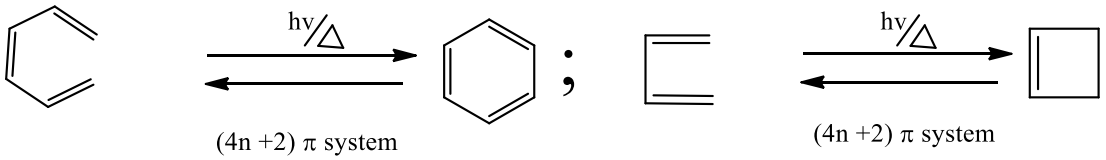
(C) Sigmatropic rearrangements.

(D) Group transfer (Not really Pericyclic reactions)

(A) **Electrocyclic reactions:-**

These reactions are

- Interamolecular
- Thermally and photochemically initiated
- Steriospecific and sterioselective
- Involves either formation of ring with generation of one sigma bond and consumption of one pie bond or reverse reaction can also be possible.



Frontier molecular orbital

HOMO–Highest occupied molecular orbital.

LUMO-Lowest unoccupied molecular orbital.

SOMO –Singly occupied molecular orbital.

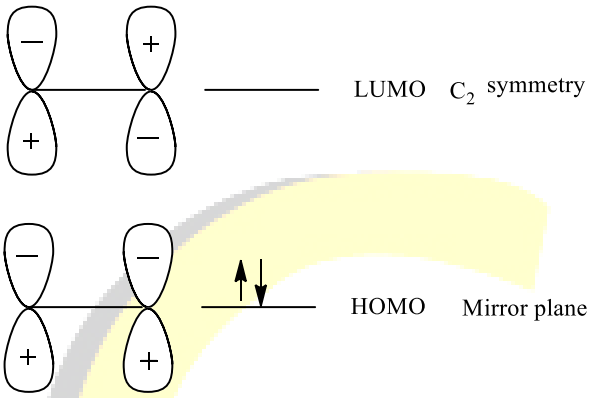
These terms were given by Woodward-Hoffmann.

Constructing MO diagram of polyene systems (Electronic Configuration):-

1. Although there are C-C and C-H sigma bonds present in the molecule, the π MOs can be constructed independently of them. Although there may be a change in the hybridization of carbon atoms during the course of a Pericyclic reaction, the MO levels of the sigma framework are relatively unaffected.

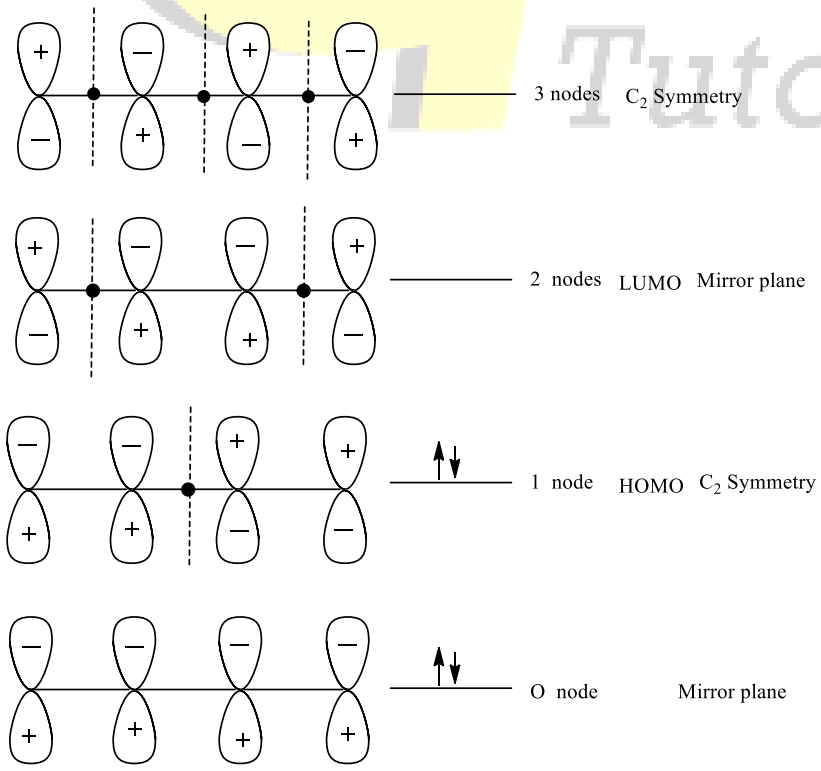
2. For a conjugated polyene system containing n π (n = even) electrons, there will be n/2 π bonding molecular orbitals that are filled MOs and n/2 antibording MOs that are empty in the ground state electronic configuration of the molecule.
3. The lowest energy MO has zero nodes, the next higher one has one node and the second higher have two nodes and so on.
4. The n^{th} M.O. will have (n-1) nodes.
5. The nodal points are found at the most symmetric points in a MO.

For ethylene:-



When orbitals are in same phase bonding takes place and molecular orbitals which are formed are called bonding molecular orbitals. These orbitals show mirror symmetry and when orbitals are in out phase then no bonding takes place and molecular orbital's which are formed are called anti-bonding molecular orbital's. These orbital have C_2 symmetry.

For 1, 3-butadiene:-



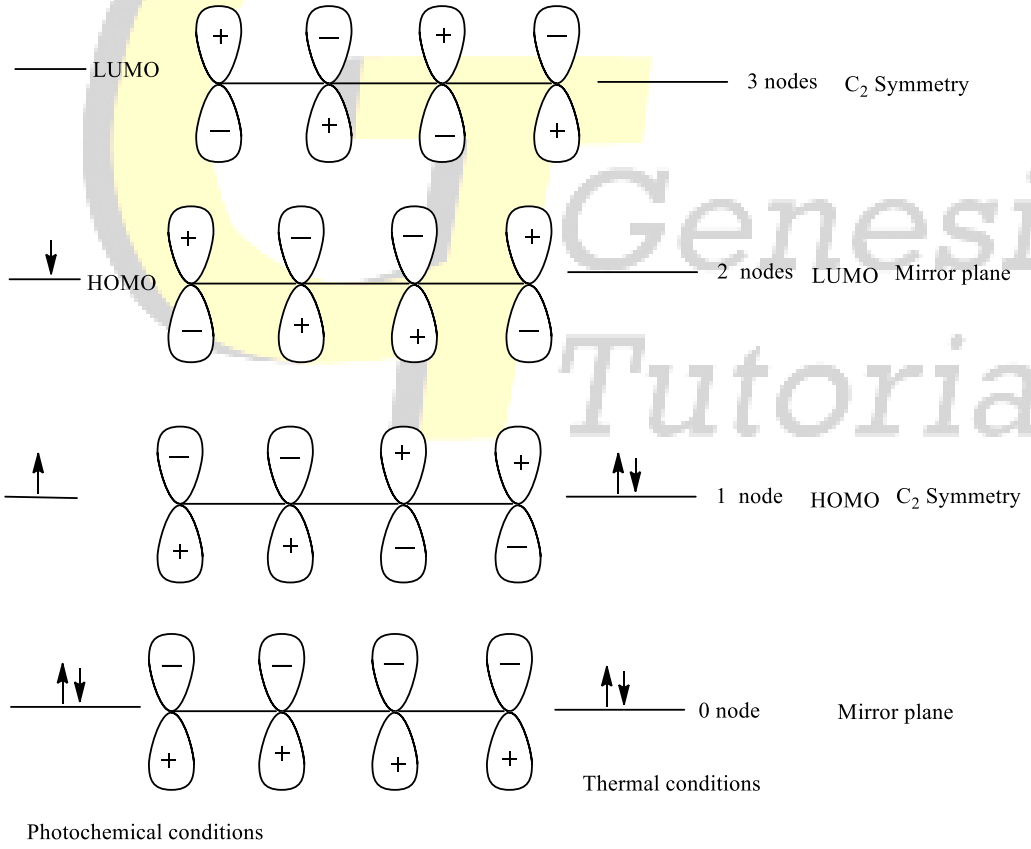
Points to ponder:-

- Number of nodes in a molecular orbital ψ_n is equal to (n-1)
- Molecular orbitals having zero or even number of nodes have mirror symmetry.
- Molecular orbitals having odd number of nodes have C_2 symmetry.

In this way we can be able to know the symmetry of any molecular orbital which can help us in Pericyclic reaction. The path by which it can proceed either thermally or photochemically.

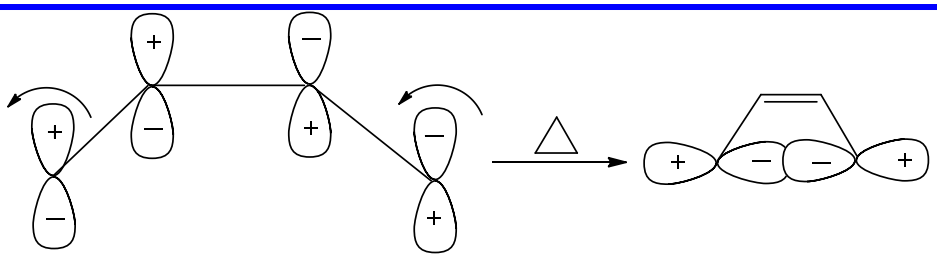
In Pericyclic reaction only symmetry allowed reactions are more favourable i.e. those orbitals which have same symmetry combine with each other.

Ground state & excited state:- In thermal condition orbital's are in ground state. When molecule is irradiated by photons then state is called excited state. In both thermal and photochemical conditions both ground state and excited state differs from each other. The state which is LUMO in thermal state becomes HOMO in excited state. So the condition in which reaction is taking place determines the stereochemistry of the product.

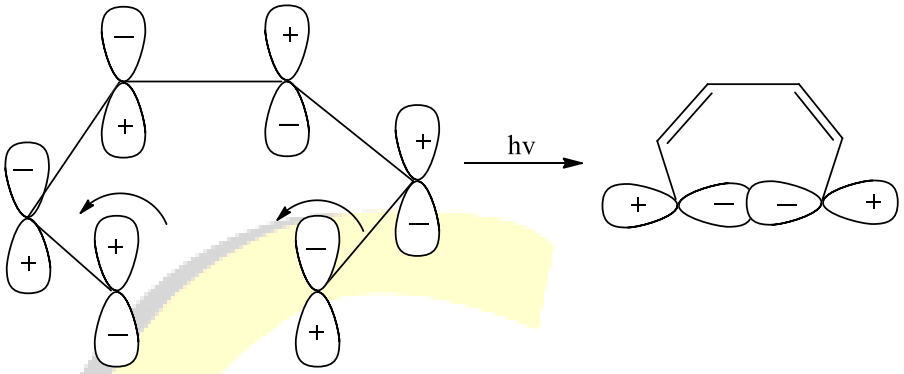


Conrotation and disrotation:-

When terminal orbitals in HOMO are in out of phase then they rotate in same direction for bonding. This is called conrotation.



(4n) π system



[4n +2] π system

Symmetry allowed process:-

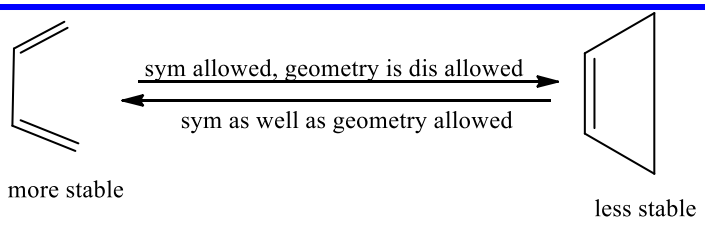
During Electrocyclic process orbitals rotate in such a way that orbitals of same symmetry can overlap, this is called symmetry allowed process.

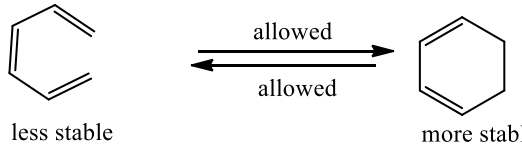
Selection rules for Symmetry allowed process

Condition	4n π	(4n +2) π
Thermal	Conrotation $\psi_{n/2}$ HOMO C_2 symmetry	Disrotation $\psi_{n/2}$ HOMO m symmetry
Photochemical	Disrotation $\psi_{n/2+1}$ HOMO m symmetry	Conrotaion $\psi_{n/2+1}$ HOMO C_2 symmetry

Geometry allowed process

During cyclisation if strained molecule is obtained then geometry in not allowed. If strain is minimum or released then geometry is allowed.

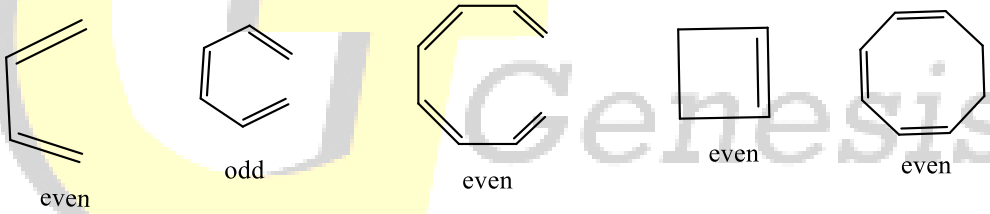




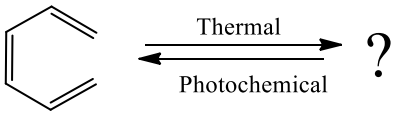
In some cases symmetry is allowed but reaction is not allowed due to geometrical strain (product is unstable). For reactions to take place symmetry as well as geometry should be allowed.

For solving problems related with Electrocyclic reactions follow the following steps.

- Count the number of π electrons or electron pairs. If conjugated system is given then simply count the number of π bonds. If cyclic system is there single σ bond which is formed by the use of π electron is also treated as π electron pair. So the result is electron pair counted may be odd or it may be even in number.



- Second step is to check whether the reaction is taking place in thermal or in photochemical conditions. Because this is the point which decides the symmetry of frontier molecular orbitals which take part in the reaction.



- Number of molecular orbitals formed is equal to number of atomic orbitals consumed.
- If even number of electron pairs are present in the molecule then $\psi_{n/2}$ with C_2 symmetry will be HOMO in thermal conditions and $\psi_{n/2+1}$ with mirror symmetry will be HOMO in photochemical conditions.
- If odd number of electron pairs are present in the molecule then $\psi_{n/2}$ with mirror symmetry will be HOMO in thermal conditions and $\psi_{n/2+1}$ with C_2 symmetry will be HOMO in photochemical conditions.
- Frontier orbitals with mirror symmetry show disrotatory motion during Electrocyclic and orbitals with C_2 symmetry show conrotatory motion during Electrocyclic reactions.

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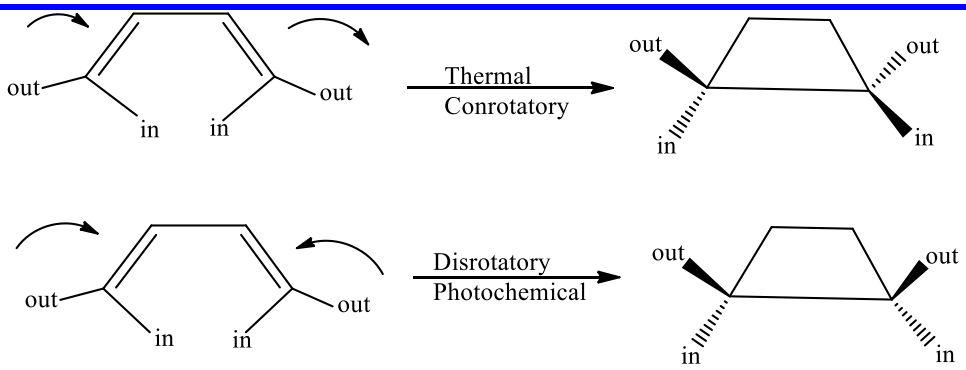
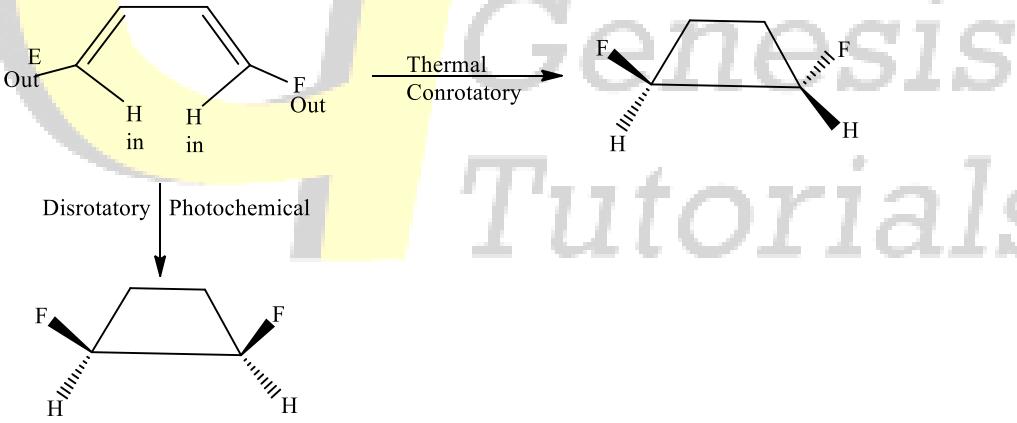


No of electron pairs	Thermal	Photochemical
Odd	Disrotatory	Conrotatory
Even	Conrotatory	Disrotatory

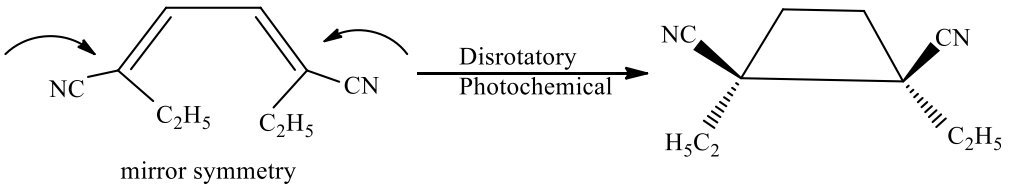
Determining the stereochemistry of product in Electrocyclic reactions.

- In conrotatory ring closing two out groups and two in groups are trans in relationship in the product or we can also say that out group is in cis relation with the in group.
- In disrotatory ring closing two out group are in cis relation with each other and two in group are in cis relation with each other in the product or we can say that one out group is in trans relation with one in group.



Examples

Problem1:-



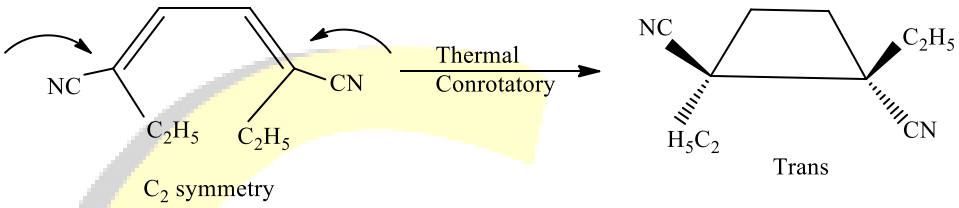
mirror symmetry

Explanation of the Process

- In this molecule first we look for the number of electron pair in the molecule number of electron pairs = 2 i.e. even number of electron pairs

- Then check for the condition of the reaction
- Reaction is taking place in photochemical condition so $\psi_{n/2+1}$ will be the HOMO of the molecule. Here n = 4(no of orbitals) so HOMO will be ψ_3, as we mentioned in the conditions that molecular orbital having even number of nodes have mirror symmetry ψ_3 have mirror symmetry. So according to the rules molecular orbitals having mirror symmetry undergo Electrocyclic reaction by disrotatory motion.
- Now the next question is of stereochemistry of the product. As mentioned in disrotatory motion two out groups are in cis relation with each other and similarly two in groups are also in cis relation with each other.

Problem 2:-



C_2 symmetry

Explanation of the process

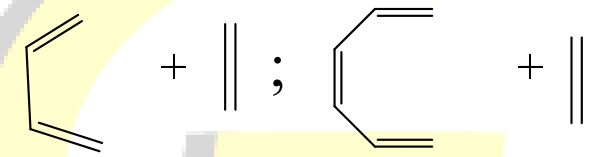
- In this molecule first look for the number of electron pair in the molecule no of electron pairs = 2 i.e. even number of electron pairs
- Then check the condition of the reaction
- Reaction is taking place in Thermal condition so $\psi_{n/2}$ will be the HOMO of the molecule. Here n = 4(no of orbitals) so HOMO will be ψ_2, as we mentioned in the conditions that molecular orbital having odd number of nodes have C_2 symmetry ψ_2 have C_2 symmetry. So according to the rules molecular orbitals having C_2 symmetry undergo Electrocyclic reaction by conrotatroy motion.
- Now the next question is of stereochemistry of the product. As mentioned in conrotatory motion two out groups are in trans relation with each other and similarly two in groups are also in trans relation with each other or we can say that out group is in cis relation with in group.

(B) **Cycloaddition reactions:-**

Cycloaddition reactions are those Pericyclic reactions in which after addition a ring is formed. In this reaction two σ bonds are gained at the cost of two π bonds. These reactions may be photochemically or thermally induced depending on the conditions of the reaction. Cycloaddition reactions are (2+2) π (4+2) π, (8+2) π additions etc.

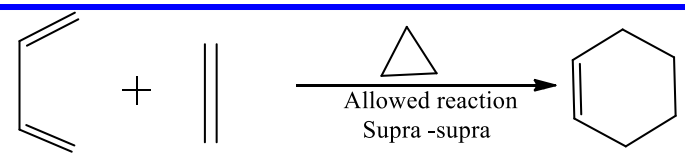
Cycloaddition reactions are both intermolecular and interamolecular. In this type of reaction two species having double bonds adds to each other. We can also apply the same type of mechanism on this type of reaction also. Whenever we are dealing with a Pericyclic reaction we should be aware about these things.

- First count the number of electron pairs in the molecule. Electron pairs can be odd or it can be even in number so this is the most important thing which is required for proposing a mechanism for Pericyclic reaction. There are few examples which are helpful for use in determining the number of electron pair in the molecule.

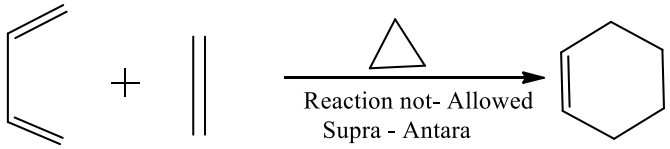


Odd electron species Even electron species

- Then check out the reaction conditions mentioned, it can be thermal or photochemical.
- When odd electron species is present it can undergo reaction in thermal conditions in superficial manner and antarafacial in photochemical conditions.
- When even electron species is present it can undergo reaction in thermal conditions in antarafacial manner and suprafacial in photochemical conditions.
- We know in case of cycloaddition reaction there are two species. One species is electron deficient or we can say that it contributes its LUMO for the reaction. The other species present is electron rich or we can say that it contributes its HOMO for the reaction.
- Now the last step is the symmetry criterion of the molecular orbitals. Check the symmetry of both type of frontier molecular orbitals taking part in the reaction i.e. HOMO & LUMO in a given condition if there symmetry matches with each other than the reaction is allowed steriochemically. Let's discuss an example before proceeding for the next step.

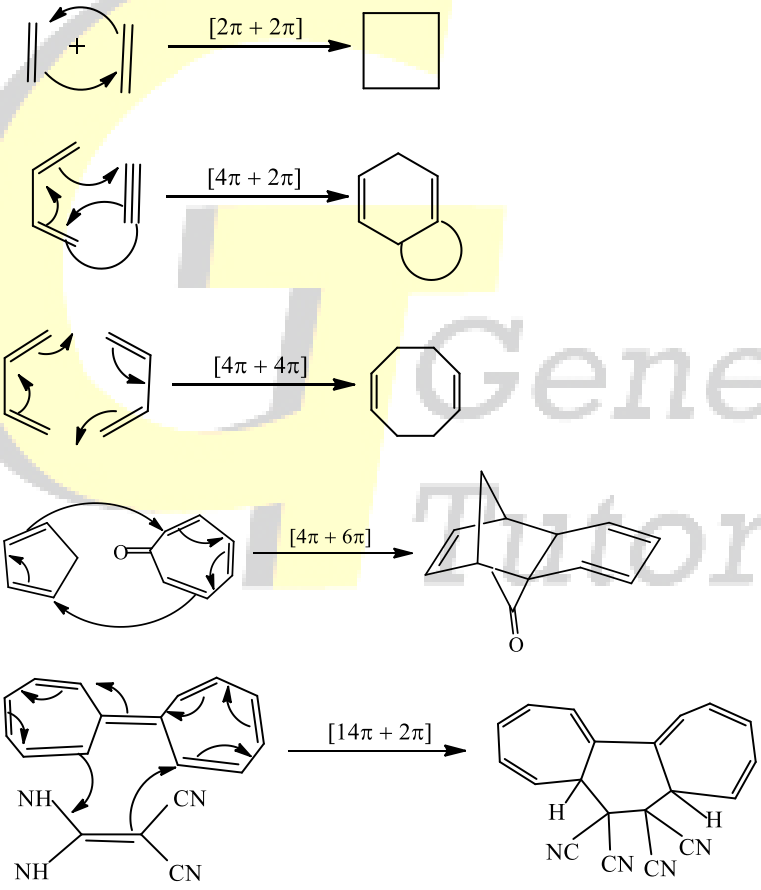


HOMO, C_2 symmetry LUMO, C_2 Symmetry



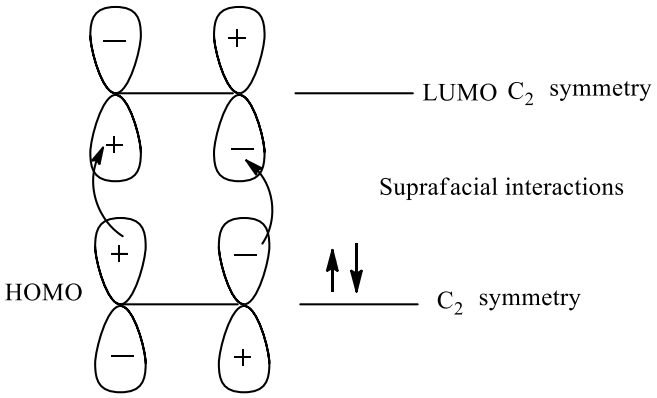
HOMO, C_2 symmetry LUMO, C_2 Symmetry

EXAMPLES OF CYCLOADDITION REACTIONS

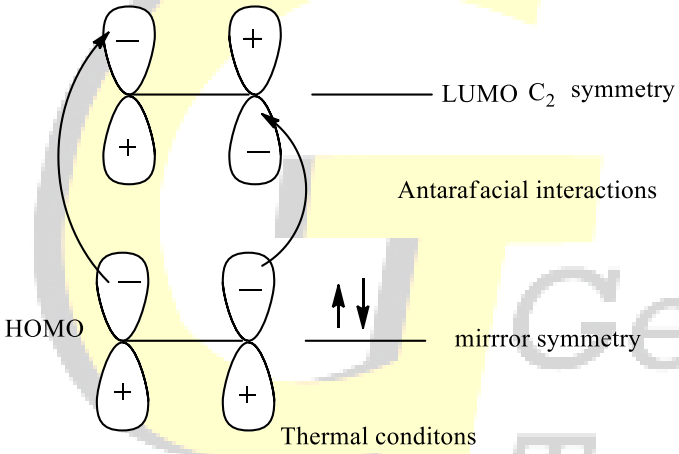


Terms used in Cycloaddition reactions:-

Suprafacial:- When orbitals join from the same side / face then it is Suprafacial interactions.



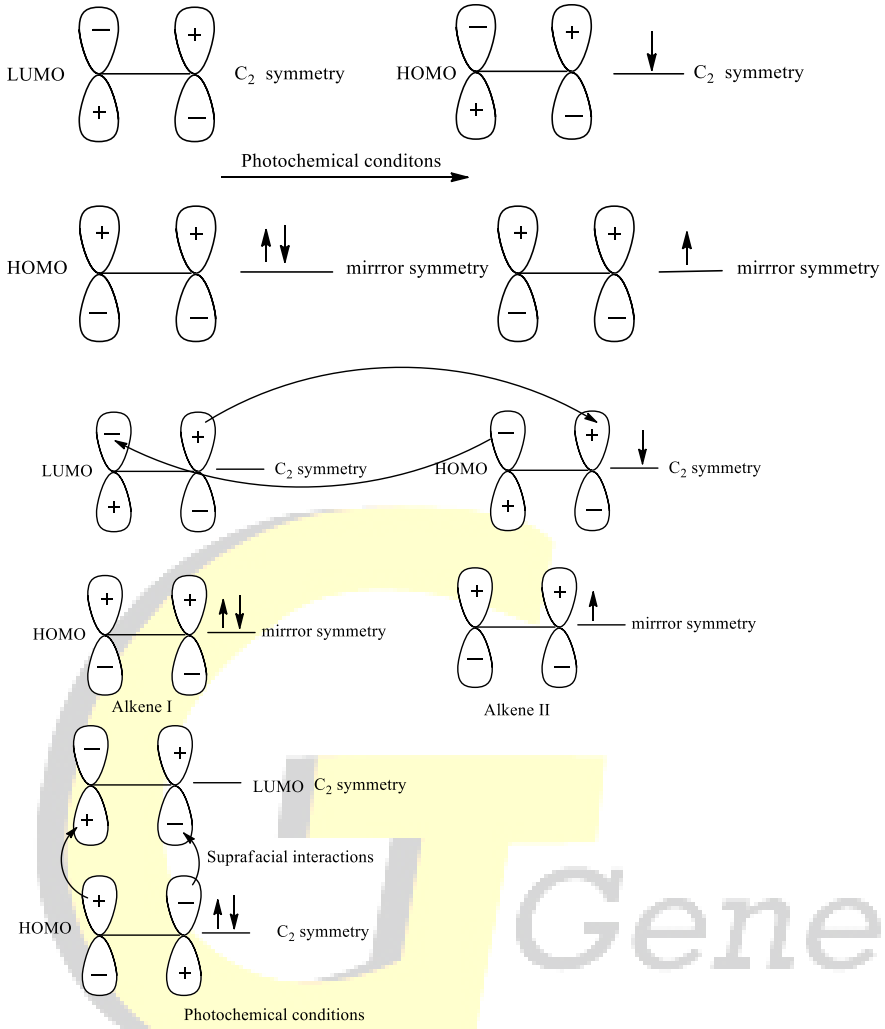
Antarafacial:- When orbital's join from opposite side / face then it is called as Antarafacial interaction.



- **(2+2) π Cycloaddition**

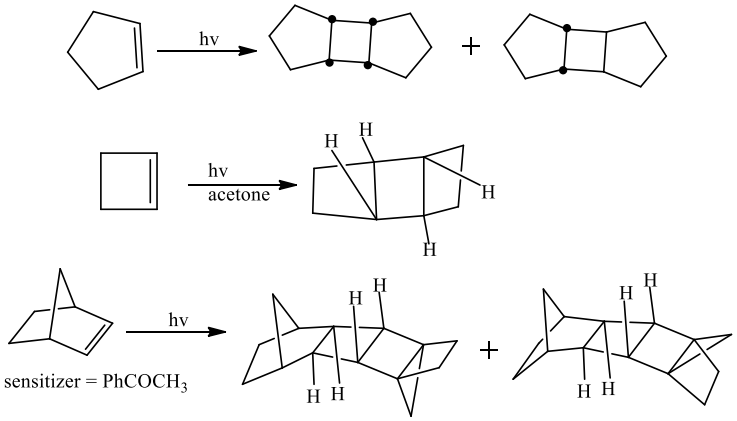
1. **Photochemical condition**

The concerted photochemical $[2\pi+2\pi]$ cycloaddition reaction is superficial on both the π systems. The dimerization of cis–and trans-2-butene have been reported to take place in a highly stereospecific manner.



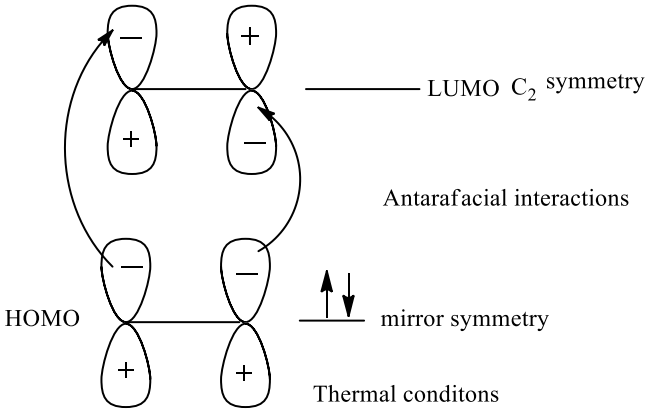
- Thus photochemical (2+2) π Cycloaddition is symmetry allowed process as LUMO of ground state is of same symmetry as that of HOMO of excited alkene.

$[2\pi+2\pi]$ Photocycloadditions of cyclic alkenes



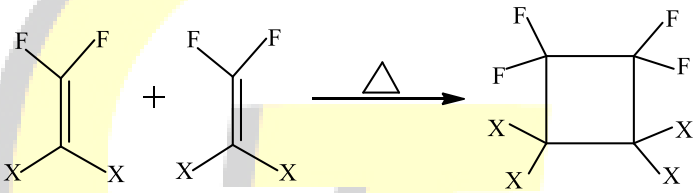
10 : 90

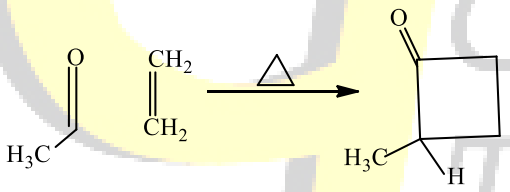
2. **Thermal condition**

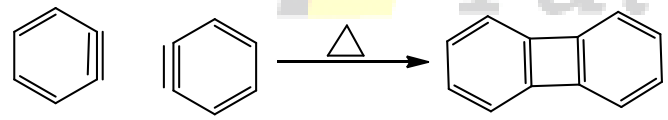


Interaction between different symmetry is called Antarafacial interaction. In thermal condition (2+2) addition is in between different symmetry orbital's so this process is not allowed symmetrically because of ring strain. Thus normal (2+2) cycloaddition reaction is only photochemically allowed thermally it is forbidden.

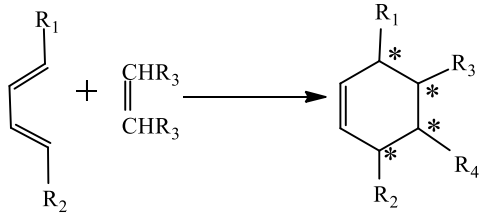
Exceptions which are thermally allowed in case of (2+2) system.

1. 

2. 

3. 

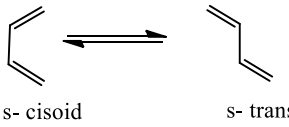
- **Diels-Alder Reaction**:- **[(4+2) Cycloaddition reactions]:-**
- Thermal cycloaddition between a cisoid conjugated diene and a dienophil, usually an olefin or an acetylene.
- Six membered ring is formed
- It is a concerted $[4\pi_s + 2\pi_s]$addition

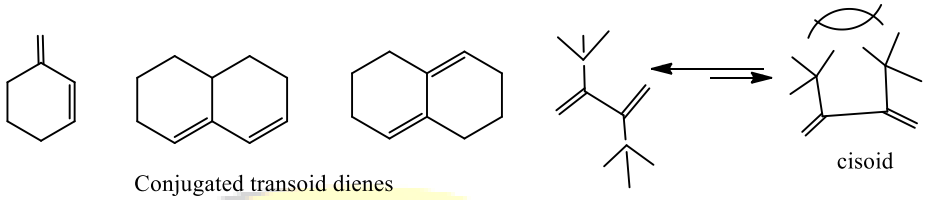


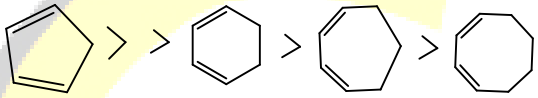
(4+2) Cycloaddition reaction is thermally allowed, photochemically it is not allowed. In this reaction as diene (4π) system is added with 2π electron system (dienophile) and from a closed compound.

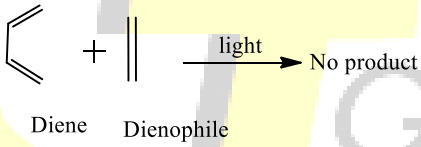
Diels Alder diene:-

- All systems having two double bonds are called dienes

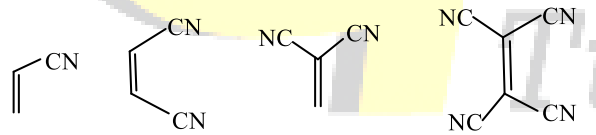


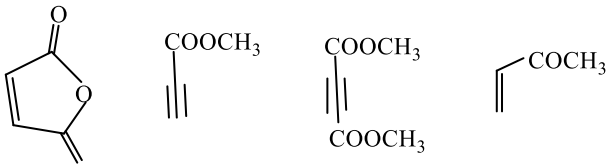


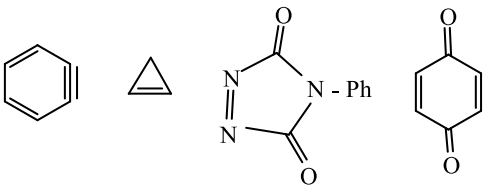

Order of reactivity of cyclic conjugated dienes



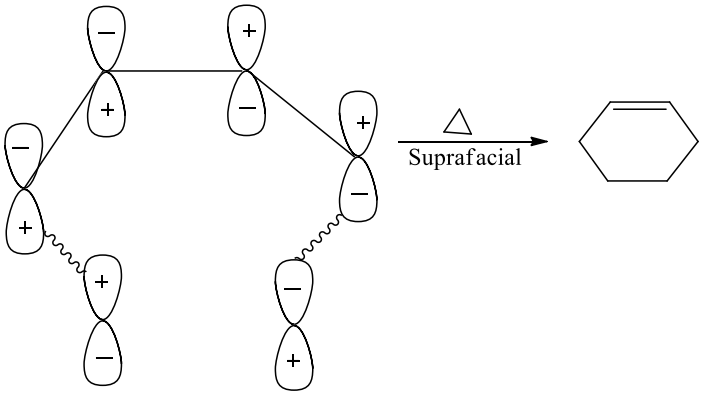
Diels Alder dienophiles





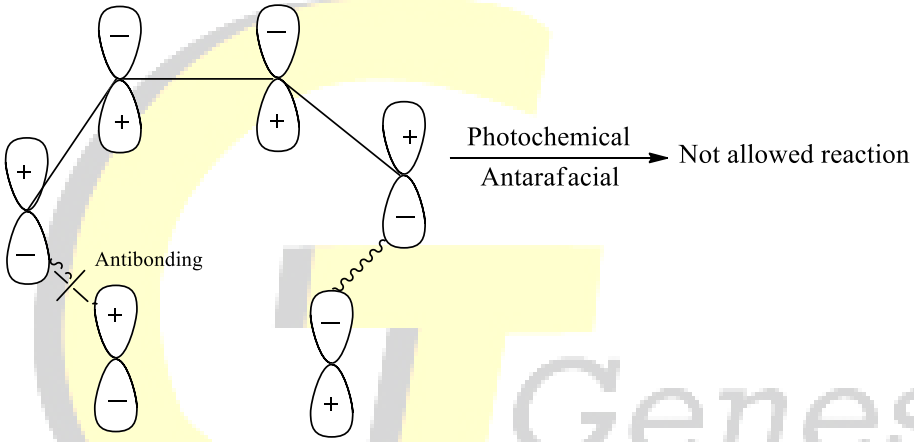


1. **Thermal conditions:-**



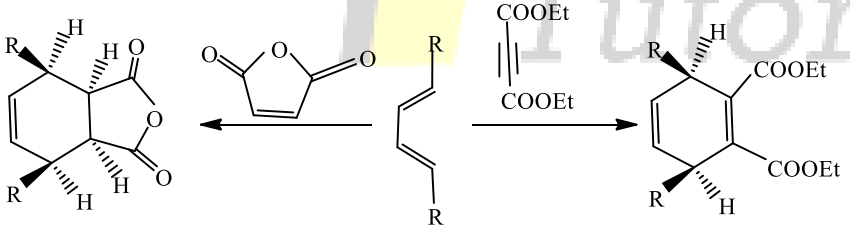
LUMO (C_2 symmetry) dienophile

1. **Photochemical conditions:-**

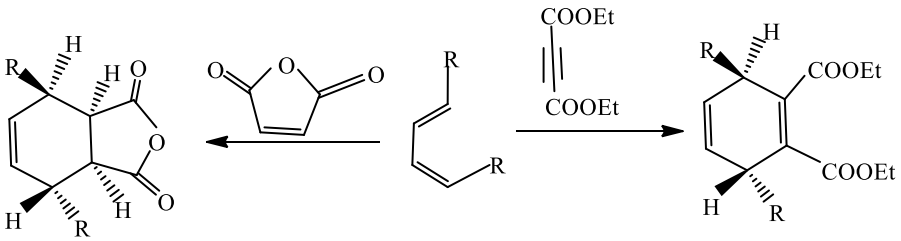


LUMO (C_2 symmetry) dienophile

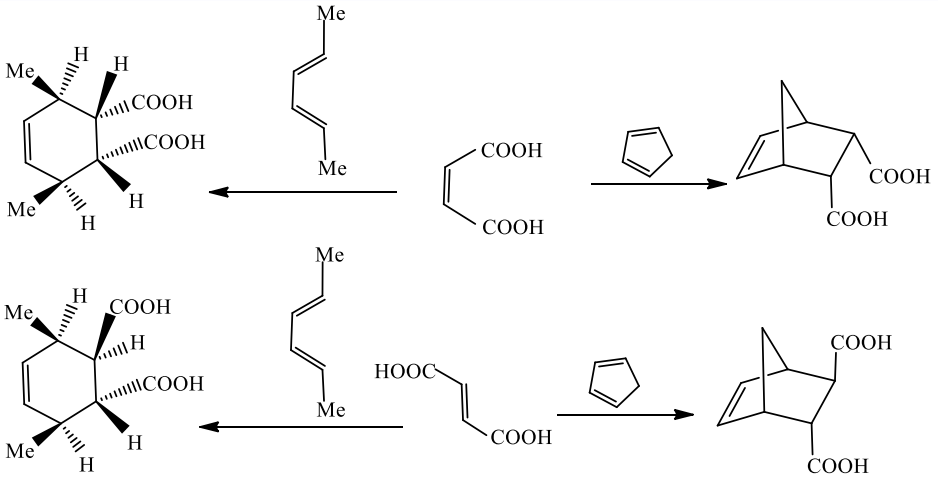
- **The "cis" rule:**



R = Me, Ph



R = Me, Ph

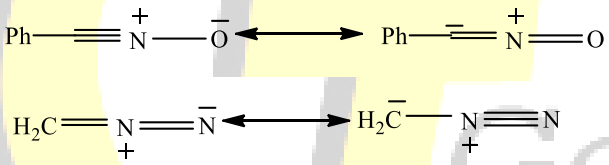


➢ **1,3-Dipolar cycloadditions**:-

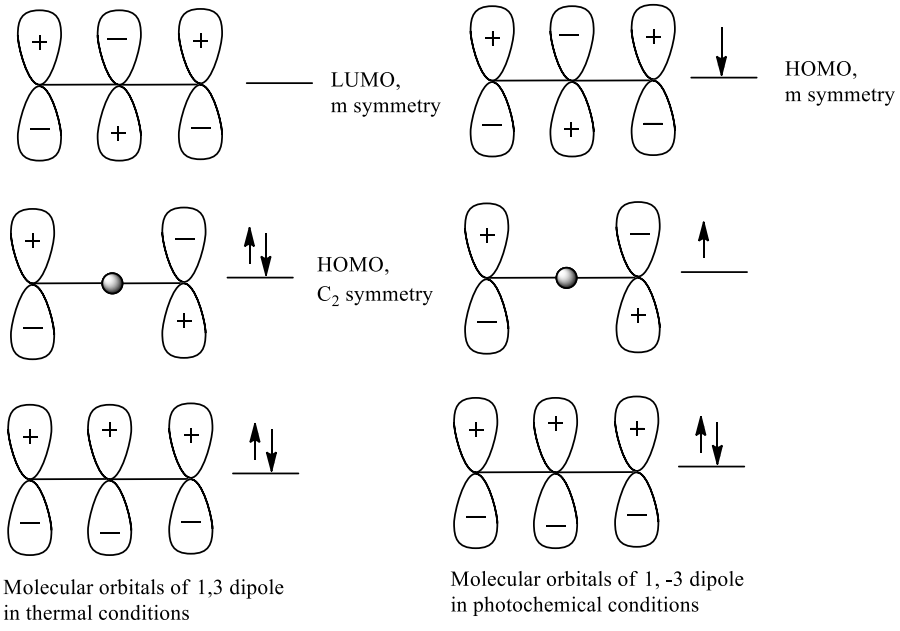
A large number of types of five membered ring may formed by the reaction of

"1,3–dipolar" compounds with unsaturated bonds (dipolarophiles) such as carbon carbon double bond, carbon oxygen double bond, carbon nitrogen triple bond. The 1, 3-dipolar components are compounds whose representation requires ionic structures which includes ones with charges on atoms bearing 1, 3- relationship,

Eg:-

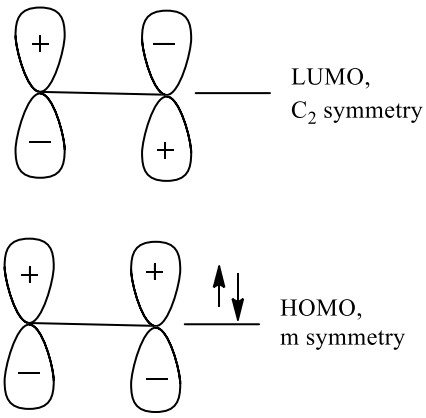


The 1, 3- dipolar is a structural variant of the diene component in the Diels-Alder reaction; in the dipolar compound, four π electrons are distributed over three atoms instead four in a diene. Moreover, the HOMO and LUMO of a 1, 3 dipole are of similar symmetry to those of a diene with respect to the two fold axis and to the mirror plane which bisects the molecule.

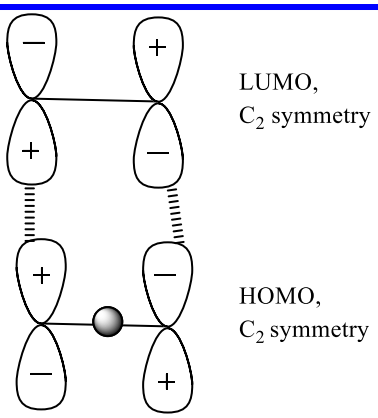


Molecular orbitals of 1,3 dipole in thermal conditions

Molecular orbitals of 1, -3 dipole in photochemical conditions



Molecular orbitals of dipolarophile in thermal conditoin

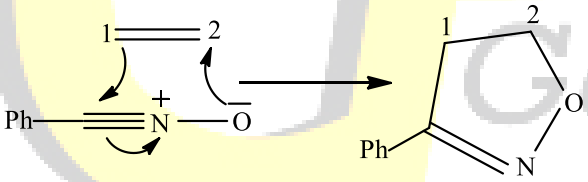


Reaction allowed in thermal conditions in suprafacial manner

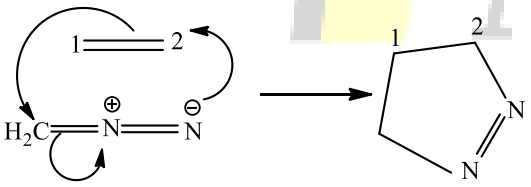
The same rules are applied to this reaction also, first count the number of electron pairs it may be either odd or even then check for the conditions mentioned. Check the molecular orbital symmetry of both the components. If symmetry is same then it is allowed stereiochemically if not then it is not allowed.

Whenever there is a formation of five membered heterocyclic ring it is always confirmed that there is involvement of 1, 3- dipolar reaction. Some examples are mentioned below.

- Nitrile oxides yield isoxazole derivatives,

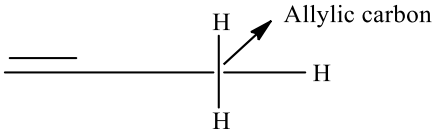


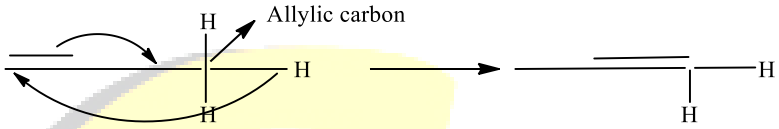
- Diazoalkanes yield pyrazole derivatives,



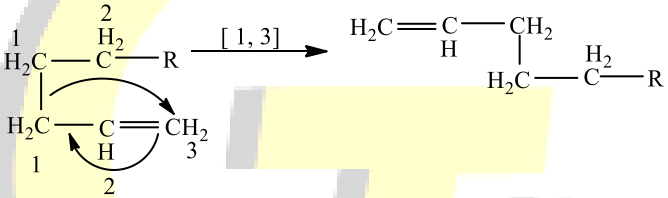
(C) Sigmatropic rearrangement:-

This rearrangement involves a concerted reorganization of electrons during which a group attached by a sigma bond migrates to the terminus of an adjacent π electron system. Sigmatropic rearrangement means movement of sigma bonds in allylic system. For sigmatropic rearrangement allylic carbon must be present. Sigmatropic rearrangement is always interamolecular in nature.

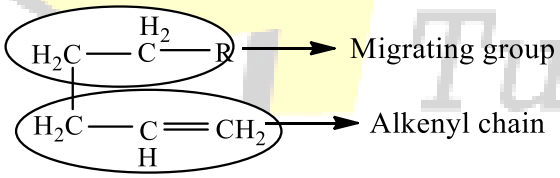




Numbering is done from allylic carbon.



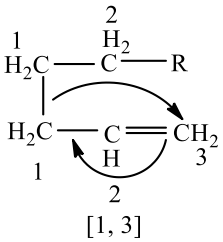
In sigmatropic rearrangement substrates can be divided in two parts; Alkenyl chain and migrating group. All substrates have at least one allylic carbon in Alkenyl for sigmatropic rearrangement.

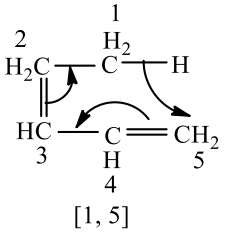


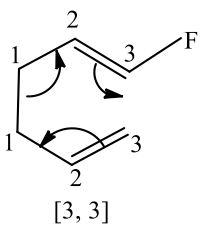
➢ Name of rearrangement

Sigmatropic rearrangement may be of following types

[1,3];[1,5];[1,7];[1,9][1,11][5,5];[3,3]


[1, 3]

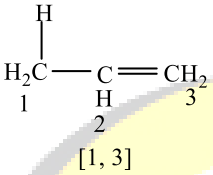

[1, 5]


[3, 3]

Mechanism of Sigmatropic rearrangement:-

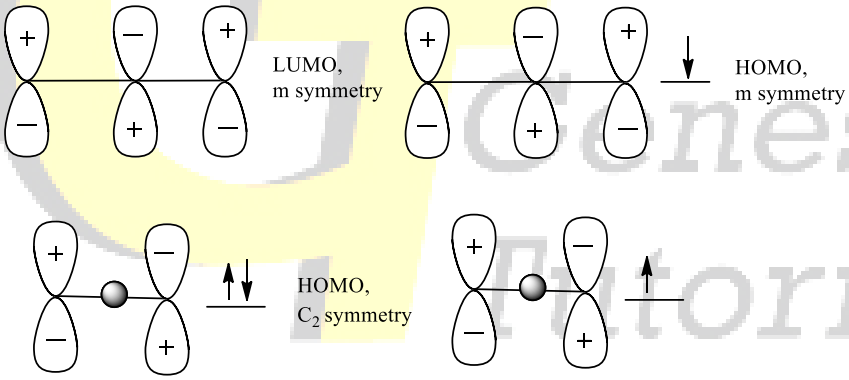
In Sigmatropic rearrangement reactions one group i.e. Alkenyl chain is treated as anionic species and migrating group is treated as cationic species. So, we can construct molecular orbitals for them in the same way as we discuss the construction of molecular orbitals in the beginning.

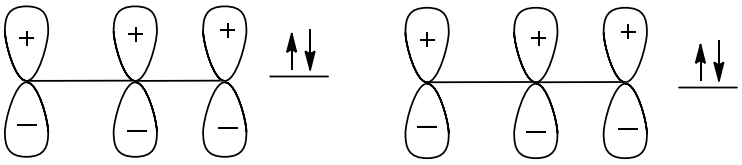
- Firstly count the no of electron pairs in the species. **For example:-** In the below given example there are 2 electron pairs present in case of sigmatropic rearrangements σ bond which is showing rearrangement is also considered as electron pair, So, one is the π bond and other is the σ which is counted as electron pairs.



[1, 3]

- Then check for the conditions in which reaction is taking place. It may be thermal or photochemical. The condition is the deciding factor for constructing the molecular orbital. As shown in the example given below orbital's of allyl anion for both thermal and photochemical conditions are different.





Molecular orbitals of allyl anion in thermal conditions

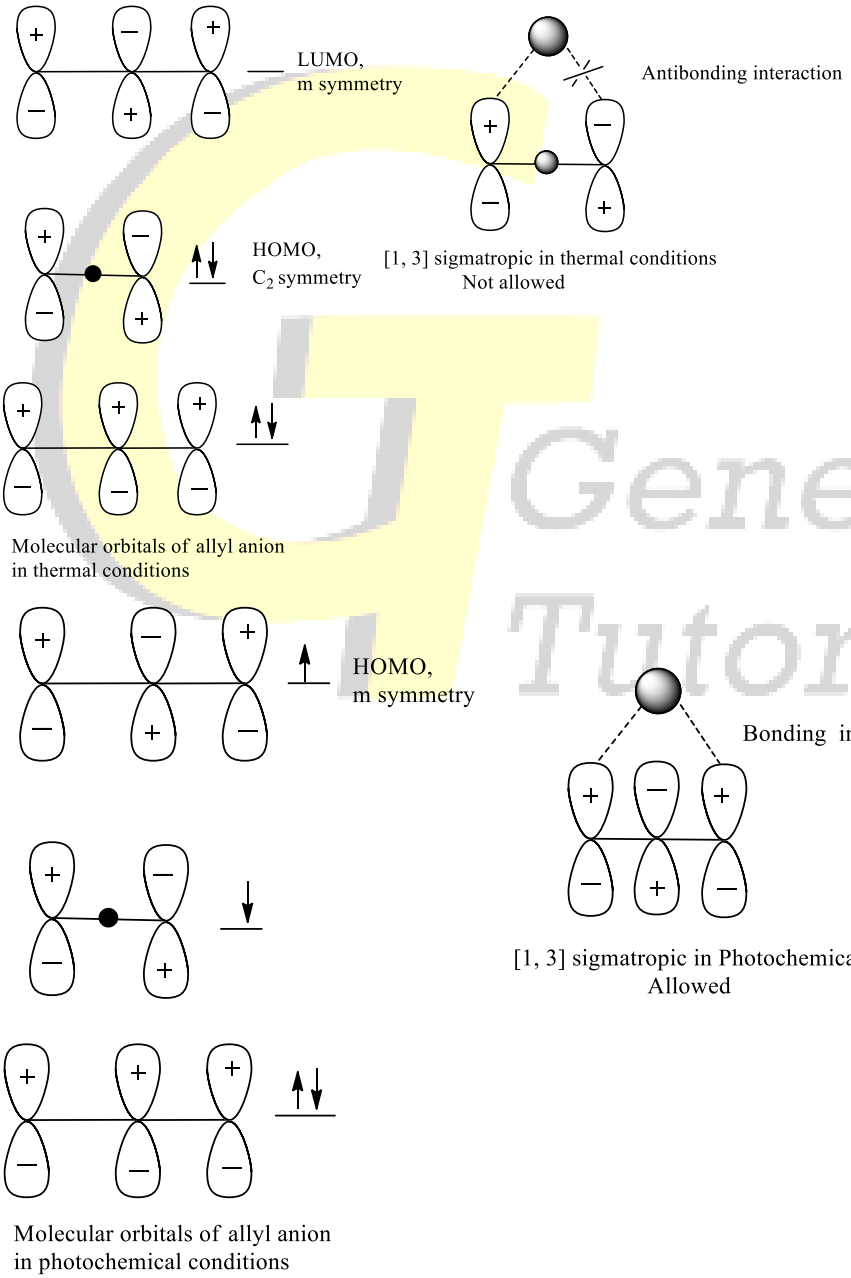
Molecular orbitals of allyl anion in photochemical conditions

- In the same way we can construct the molecular orbital of any species in any conditions.
- The next step is to apply the rule on counting the electron pair and the conditions mentioned.

No of electron pair	Thermal	Photochemical
Odd	Supra-supra	Supra-Antara
Even	Supra-Antara	Supra-supra

Now lets apply the above rules on an example any try to understand the concept behind Sigmatropic rearrangement reactions.

- **Even electron pair Svstem**



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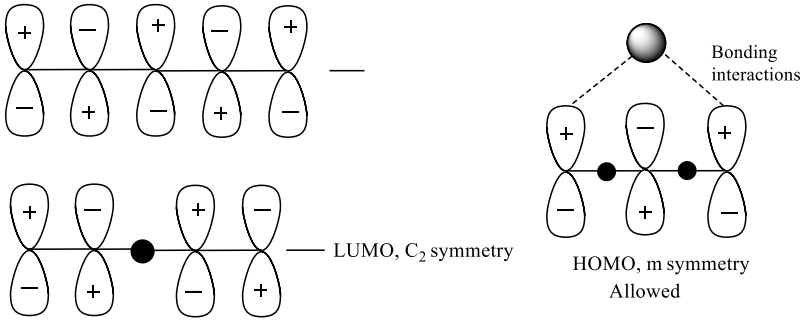
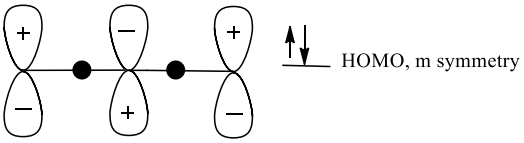
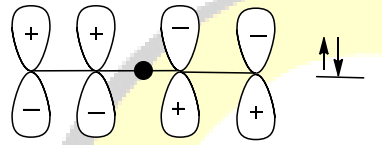
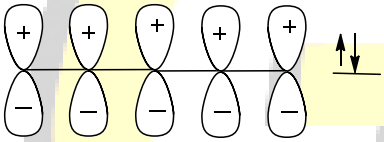
Contact: 8171000425, 7252022576
Web: www.genesis-tutorials.com
Email: info@genesis-tutorials.com

Odd electron pair system:-

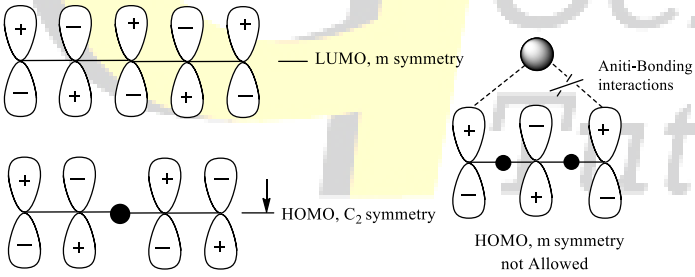


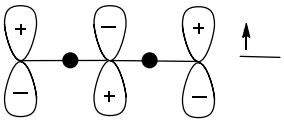


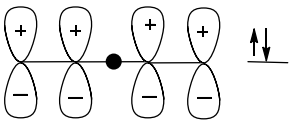


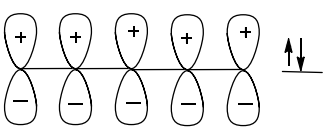


Molecular orbitals of Pentadienyl anion
in thermal conditions

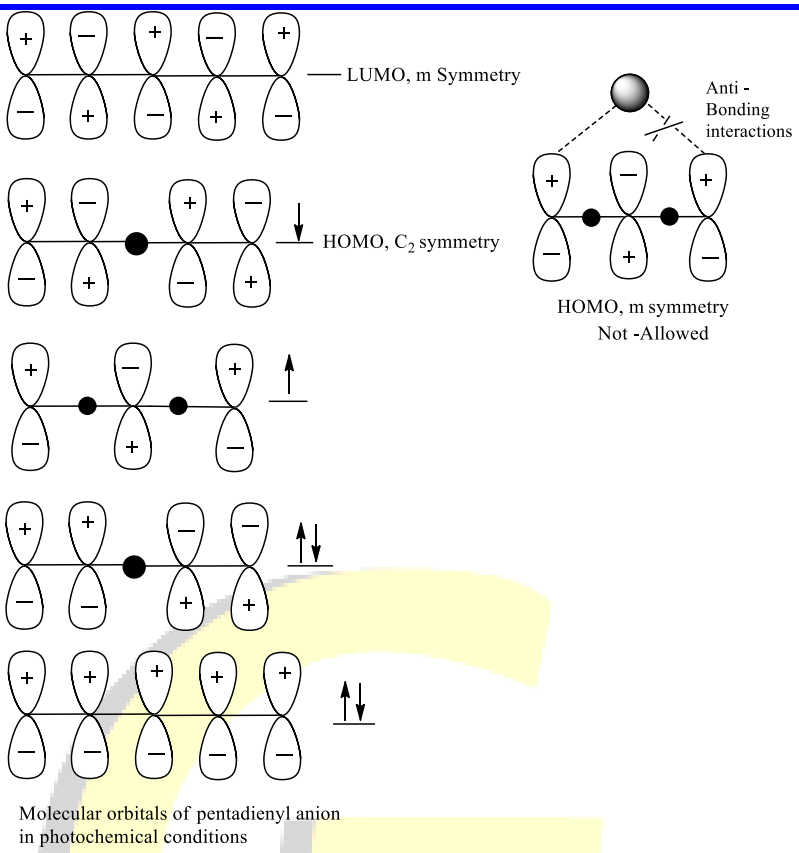








Molecular orbitals of Pentadienyl anion
in photochemical conditions

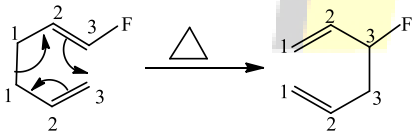


Molecular orbitals of pentadienyl anion in photochemical conditions

Examples of Sigmatropic rearrangement reactions

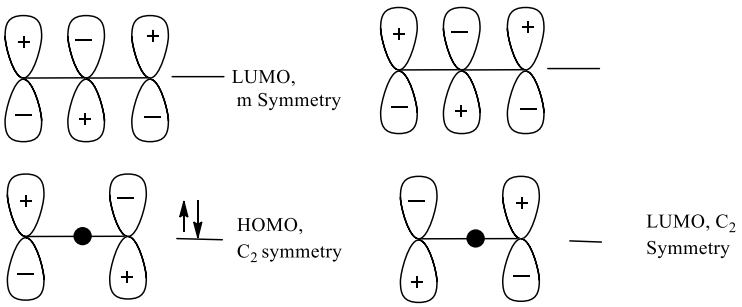
➢ Cope Rearrangement

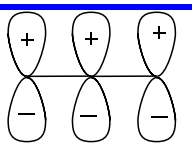
The most important sigmatropic rearrangements are the [3,3] process involving carbon–carbon bond. The thermal rearrangement of 1,5-dienes by [3,3] sigmatropy is called cope rearrangement. The reaction proceeds in the thermodynamically favoured direction.



[3, 3]

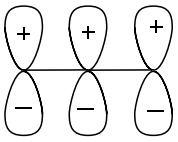
In the reaction one species is treated is anion and the other is cation. The total no of electron pairs participating in the reaction are 3 i.e. odd so according to the table mentioned above reaction containing odd electron pairs will be feasible or we can say it will be allowed stereiochemically in thermal conditions.





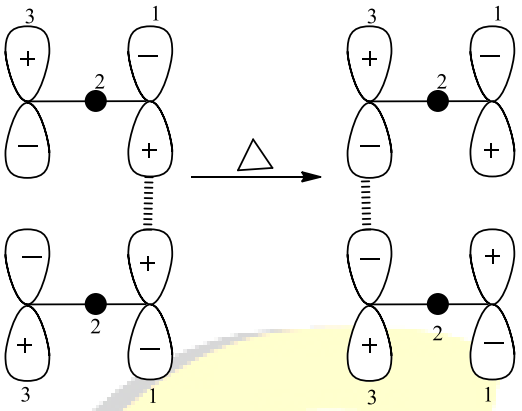
LUMO,
m Symmetry

Molecular orbitrals of allyl anion in thermal conditions



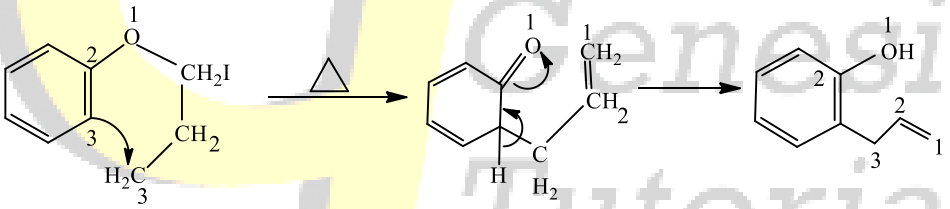
HOMO,
m symmetry

Molecular orbitrals of allyl cation in thermal conditions



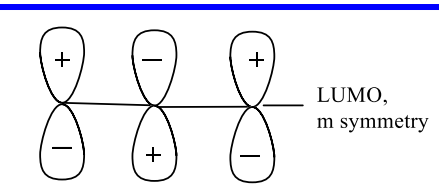
[3,3] Rearrangement allowed in thermal conditions

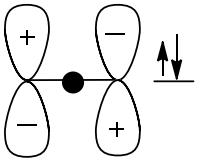
- **Claisen Rearrangement**
- Claisen Rearrangement is the first sigmatropic rearrangement which was discovered. The original Sigmatropic rearrangement occurs when allyl phenyl ether is heated without solvent. The product of the rearrangement is o – allyl phenol. The reaction proceeds in the thermodynamically favoured direction.

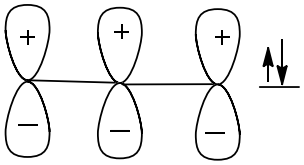


[3, 3] Rearrangement allowed in thermal conditions

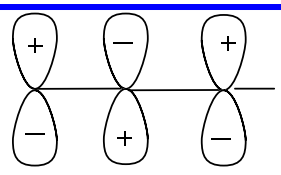
In the reaction one species is treated is anion and the other is cation. The total no of electron pairs participating in –the reaction are 3 i.e. odd so according to the toable mentioned above reaction containing odd electron pair will be feasible or we can say it will be allowed stereiochemically in thermal conditions.

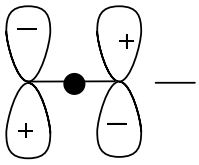


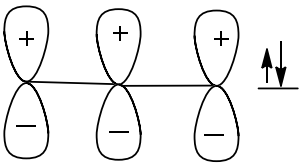




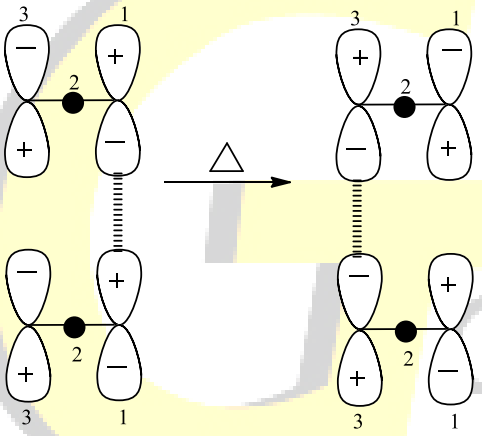
Molecular orbitals of allyl anion in thermal conditions







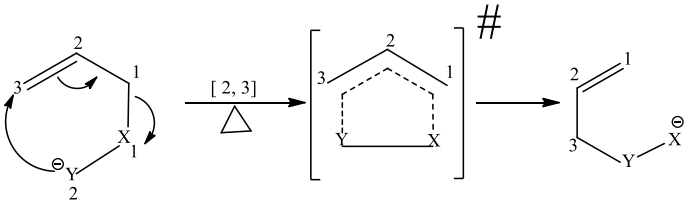
Molecular orbitals of allyl cations in thermal conditions



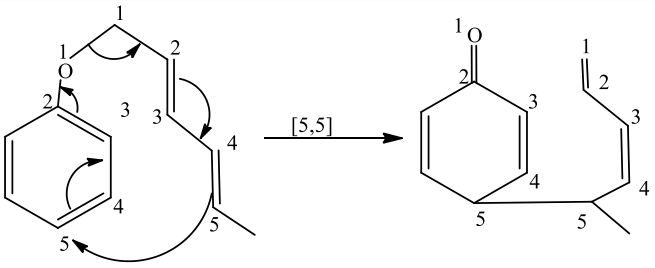
{3,3] Rearrangement allowed in thermal conditions

- **[2,3] Sigmatropic rearrangement**

All [3,3] Sigmatropic rearrangements have six-membered transition state. In case of [2,3] Sigmatropic rearrangement transition state should have five membered ring structure.[2,3] Sigmatropic rearrangements have many variants depending upon which atoms are present in the chain of five atoms. All atoms may be carbon but most have y (oxygen) and x (oxygen, nitrogen, sulphur and carbon)



- **[5,5] Sigmatropic rearrangement**

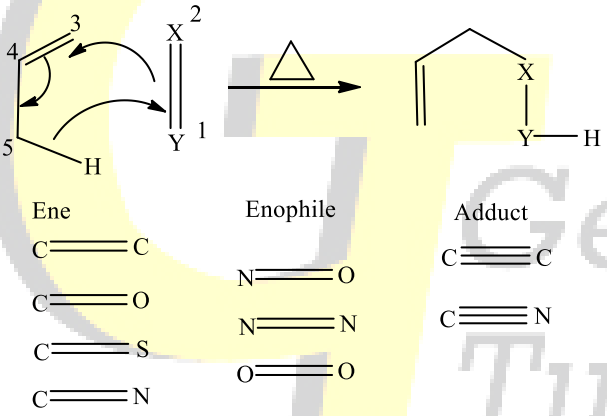


- This rearrangement is also feasible in thermal conditions. The number of electron pairs in this reaction is 5 i.e. odd so in thermal condition odd electron species undergo reaction superficially.

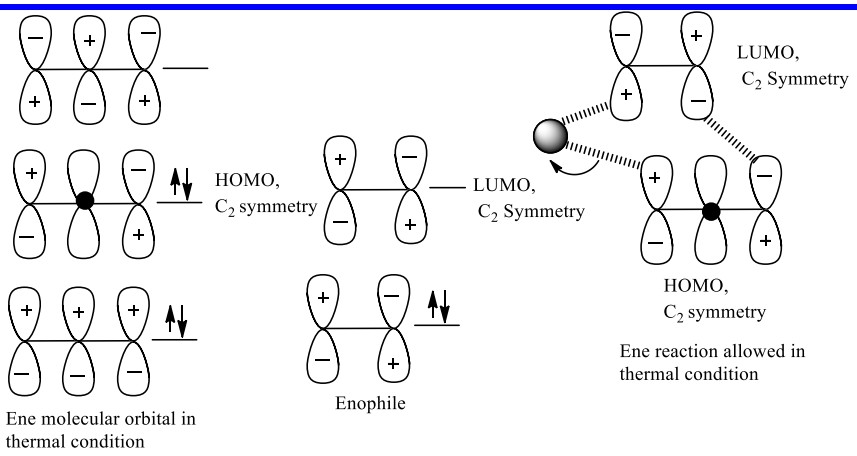
D. **Group transfer reactions/Ene reaction:-**

Ene reaction involves the thermal reaction of an alkene (called ene) having an allylic hydrogen with a compound having multiple bond (double or triple bonds) called enophiles.

During the reactions, transfer of allylic hydrogens (1, 5 migration of hydrogen), shift of allylic double bond and bonding between two unsaturated termini takes place to form 1:1 adduct.



In this reaction hydrogen atoms of allylic carbon moves from ene to enophile. In principle atom other than hydrogen from allylic carbon can move from ene to enophile. This reaction is favourable in the thermal condition because on applying Woodward-Hoffmann rule on ene reaction, we know that the no of electron pairs involved in the reaction is 3 i.e. odd so odd electron species show ene reaction under thermal condition in Suprafacial manner. In this ene is treated as electron rich and enophile is treated as electron deficient species.



No of electron pairs	Thermal	Photochemical
Odd	Supra-Supra	Supra-Antara
Even	Supra-Antara	Supra-Supra