Pericyclic. Mane, A.K. M.Sc.I.Y. II

1,3 butadiene into cyclobutane. [illegible] Δ/ hν

⑬ Explain stereochemistry of electrocyclic reacn ~~for~~ 4π system under Δ/hν condition by FMO method

① Explain the 1,3-dipolar cycloaddition reaction and chelotropic reactions with mechansim.

② What is sharpless Asymmetric epoxidn.

③. Explain the interconversion of cyclobutane $\xrightleftharpoons{\Delta/h\nu}$ 1,3 butadiene under thermal & hν condition by co-relation diagram method.

④ What are cycloaddition reaction & explain the cycloaddition between the two molecules of ethythene (2π + 2π) system.

⑤ Why on thermal reaction cis-3,4-dimethyl cyclobutane gives (2E,4Z) 2,4-hexadiene while trans isomer gives the (2E,4E) 2,4-hexadiene.

⑥ What are sigmatropic rearrangment & Explain 1,3-sigmatropic rearrangment by FMO & PMO.

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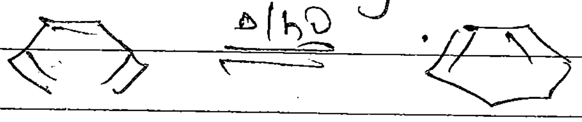
⑦ Construct corelation diagram & FMO method For following transformation. Predict whether these transformn are thermally or photochemically allowed



⑧ What do you understand by term suprafacial & antrafacial overlapping & Explain cycloaddn of 2π + 2π system is photochemically allowed process

⑨ What are sigmatropic rearrangment & explain cope & aza cope rearrangment with mechanism

⑩ Write a note i) chelotropic ii) 1,3 sigmatropic

⑪ With the help of FMO & PMO show that 2+2 cycloaddn reacn is photochemically allowed

⑫ With the help of corelation diagram, dielsalder reacn is a thermally allowed process

Pericyclic Reaction

- Pericyclic reactions are defined as the reaction that occur by a concerted cyclic shift of electrons
- These reactions are concerted means reactant bo are broken and product bonds are formed at the same time without intermediates.
- Pericyclic reactions involve a cyclic shift of ele-ns. The word pericyclic means around the circ
- Pericyclic reactions are characterised by a cyclic transition state involving the π-bonds
- The reaction are unaffected by solvent or cata-yst.
- Pericyclic reactions are induced by thermally (by heating) or photochemically (by irradiatin
- Pericyclic reactions are stereospecific.

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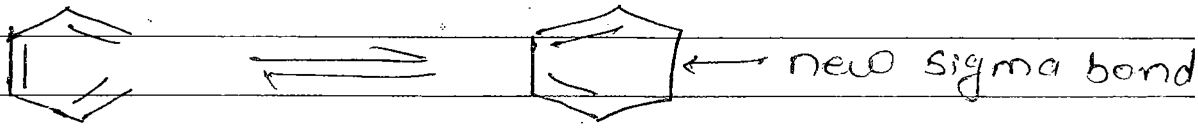


loss of one π
-bond & gain of 1 σ bond.

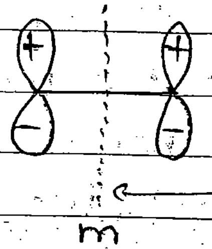
Symmetry in molecular orbital :→

A π-molecular orbital possesses either mirror plane symmetry or centre of symmetry: Both symmetries are not present together in a give molecular Orbital.

m-symmetry :→

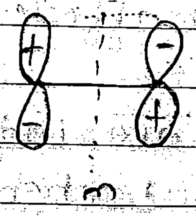
Some molecular orbitals have the symmetry about the mirror plane (m) which bisects the molecular orbitals and is perpendicular to the

Plane of the molecule.



mirror plane ⊥ar to the plane of the molecule.

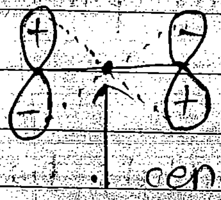
Both orbitals are mirror images to each other. hence in this MO there is plane of symmetry, abbreviated as m(S)



both orbitals are not mirror images to each other. thus in this MO there is mirror plane asymmetry, abbreviated as m(A)

C2 symmetry :-

The centre of symmetry is a point in the molecular axis from which if lines are drawn on one side and extended an equal distance on the other side, will meet the same phases of orbitals,



centre of molecular axis.

both orbitals are symmetrical with respect to center of the molecular axis. thus, in this MO there is centre of symmetry. abbreviated as C_2 (CS).

construction of π molecular orbitals :→

1) The number of molecular orbitals is always equal to the number of atomic p-orbitals. A π-electron system derived from the interactio of number of p-orbitals.

2) Half of the molecular orbitals are bonding molecular orbitals. and remaining half are antibonding molecular orbitals (ABMO's)

3) Number of p-orbitals equal to number of carbon atom upto conjugation.

4) The plus and minus signs used in drawing these orbitals indicate the phase of the wav function.

5) π Molecular orbitals abbreviated as ψ_1, ψ_2, ψ ψ_4.

6) The bonding MO of lowest energy ψ_1 has no node. each molecular orbital of increasin-ly higher energy has one additional node.

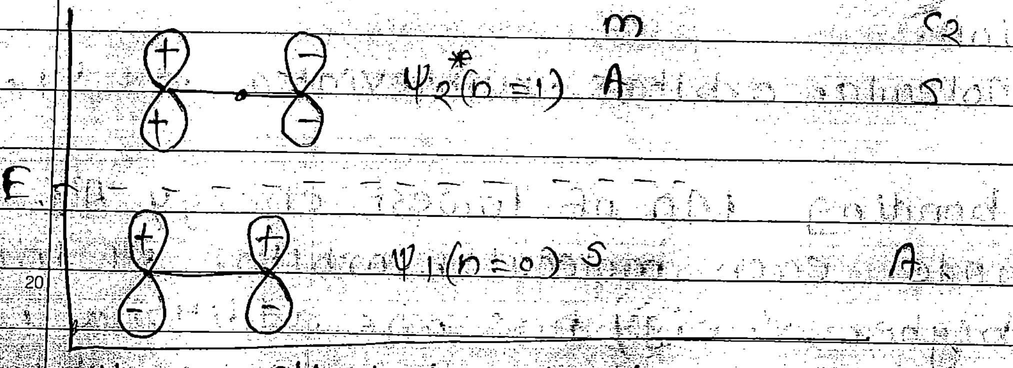
7) Node is the position where lobes changes it sign.

1) Frontier orbitals of ethylene :→

π -molecular orbitals of ethylene from the two p-atomic orbitals of the two carbons.

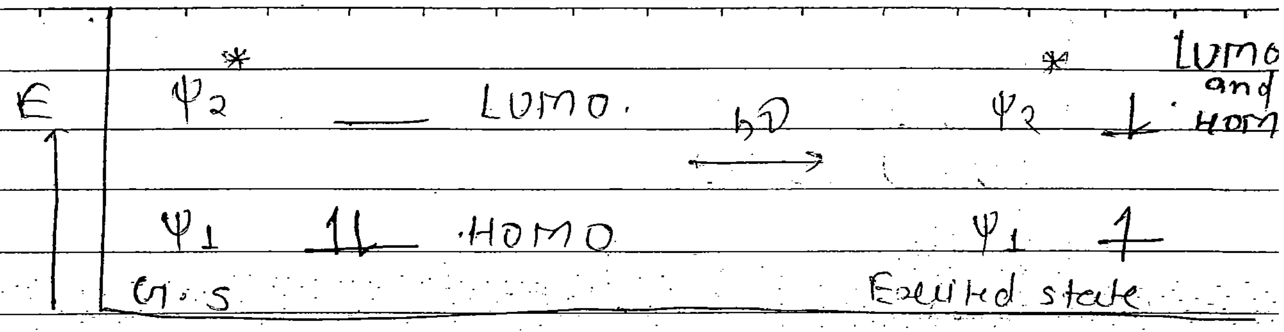
let us examine symmetry properties of π -orbitals of ethylene. in ground state and also in the excited state.

- The ground state π -orbital is symmetric (S) w.r.t. the mirror plane (m) & asymm -etric. w.r.t. C_2 axis.
- on the other hand, the antibonding orbital (ψ_2^*) π_2^* of ethylene is asymmetric w.r.t 'm' ~~the~~ and symmetric w.r.t. C_2 axis.
- The following diagram shows the symmetry properties of molecular orbital of ethylene.



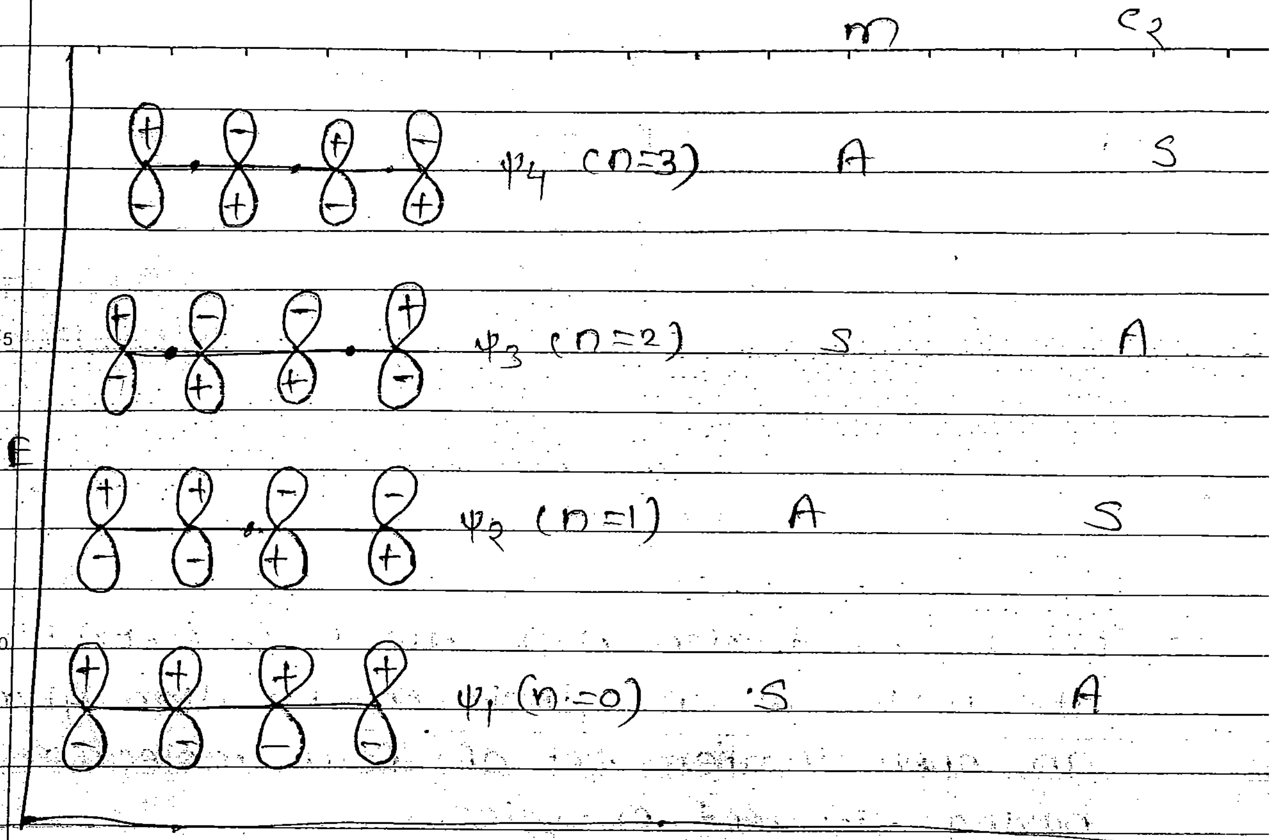
when ethylene absorbs a photon of proper wavelength a e^- is promoted from the Ground state to excited state.

- The orbital ψ_1 become HOMO and ψ_2^* become LUMO of the ground state.
- The species with the promoted e^- is excited state. The orbital ψ_2^* become HOMO as well as LUMO of the excited state.



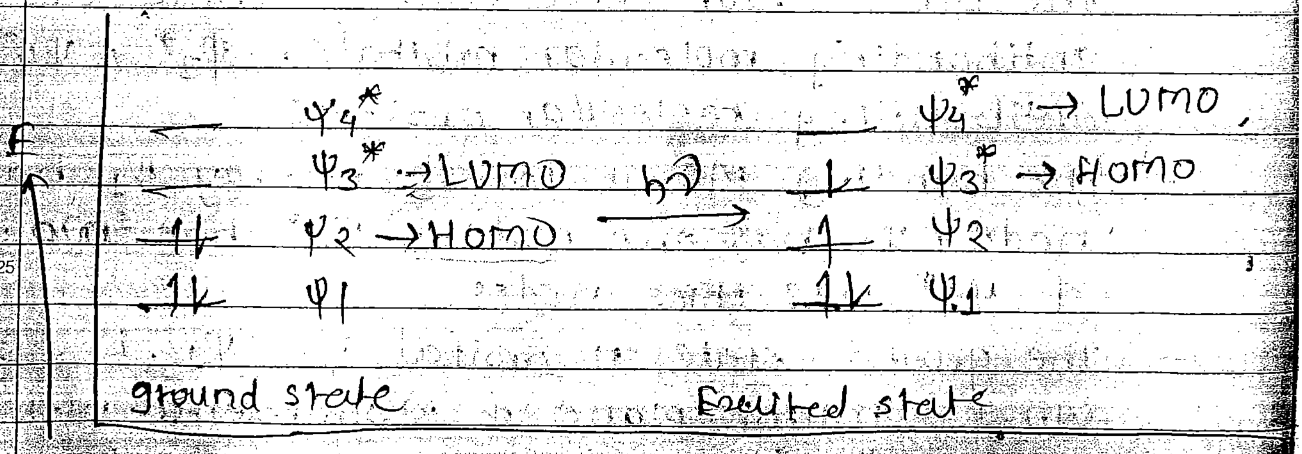
2) 1,3-butadiene :→

- In 1,3-butadiene there are four P-orbitals in the molecule and their combination gives us an approximation set of four molecular π-orbi having different energies.
- In 1,3-butadiene, four P orbitals are used in the formation of the π MO's, thus four π MO's results, which we shall abbreviate as ψ_1, ψ_2, ψ_3 & ψ_4.
- Half of the molecular orbitals have lower energy, These are called bonding molecular orbitals, ψ_1 & ψ_2 are bonding MO's.
- The other half have energy these are called antibonding molecular orbitals, ψ_3^*, ψ_4^* are antibonding molecular orbitals.
- The bonding MO of lowest energy ψ_1 has no node, ψ_2 has one node, ψ_3^* has two nodes & ψ_4^* has three nodes.
- The ground state π orbital i.e ψ_1 is symmetric w.r.t. mirror plane & asymmetric w.r.t. C2 axis. ψ_2 is asymmetric w.r.t. mirror plane and symmetric w.r.t. C2 axis



When 1,3-Butadiene absorbs a photon of proper wavelength an e^- is promoted from ground state to excited state.

- In the ground state ψ_2 is HOMO & ψ_3^* is LUMO. The orbital ψ_3^* becomes HOMO and ψ_4^* becomes LUMO of the excited state.



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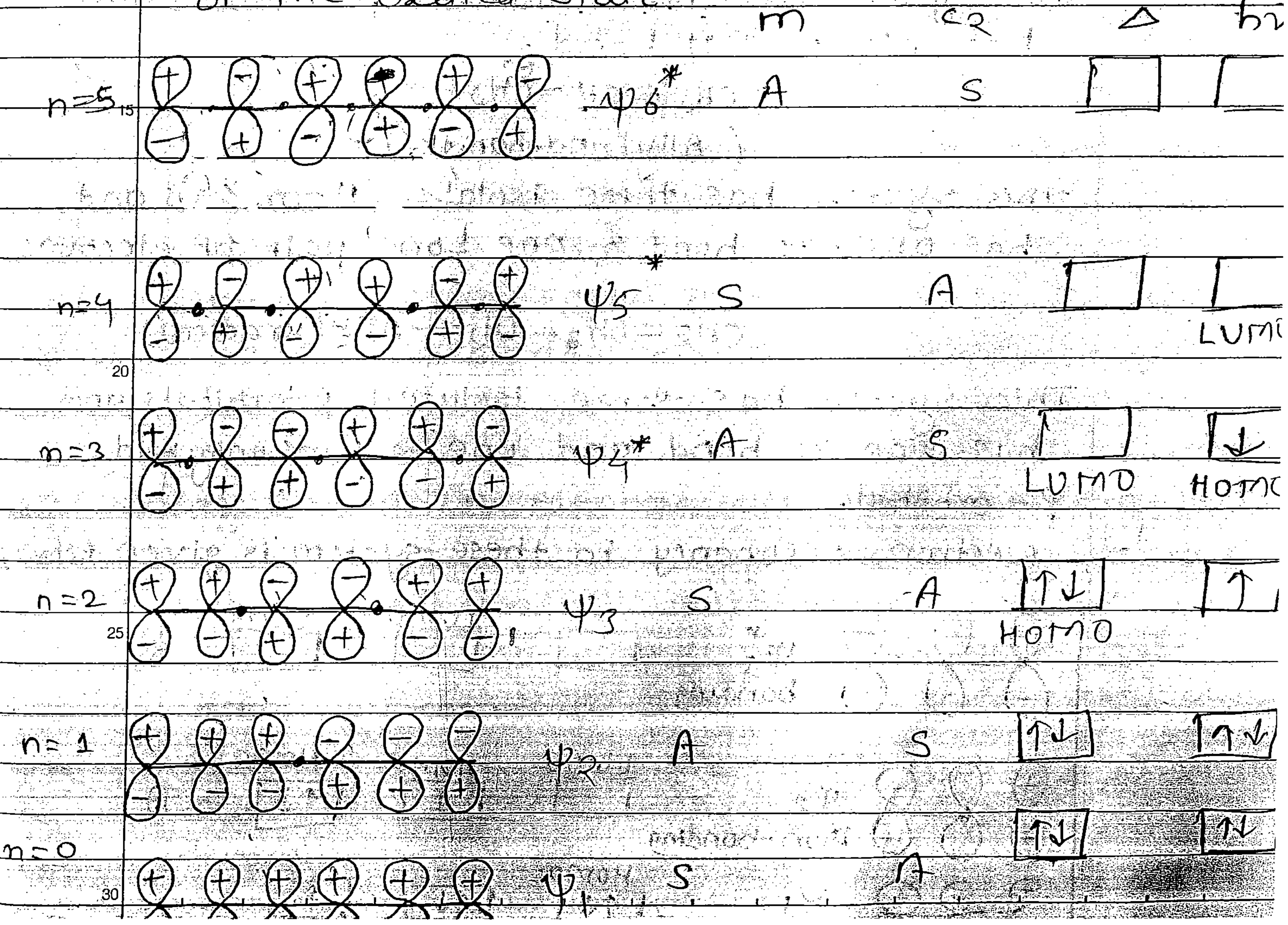
3 Frontier orbitals of 1,3,5 -hexatriene :→

- The six p electrons of hexatriene are occupied in th first three molecular orbitals. (ψ_1, ψ_2, ψ_3) while the remaing three higher energy molecule r orbitals (ψ_4, ψ_5, ψ_6) remain unaccupied in the ground state.
- In the ground state of 1,3,5-hexatriene. The orbital ψ_3 become Homo & ψ_4^* become LUMO the species with the promoted electron is an excited state of 1,3,5-hexatriene. The orbital ψ_4^* become HOMO and ψ_5^* become LUMO of the excited state.



4 Frontier orbitals of Allyl System :-

The allyl system (cation, anion or radical) has three carbon and three p-orbitals. hence, three molecular orbitals.

- Conjugated unbranched ions (cation & anions) and radical have an odd number of carbons. first member of these classes are allyl carbocation, allyl carbanion and allyl free radical.

$$CH_2 = CH_2 - \overset{\oplus}{C}H_2$$

(allyl carbocation)

This system has three isolated p-orbitals and has only one π bond.

$$CH_2 = CH - \overset{\ominus}{C}H_2$$

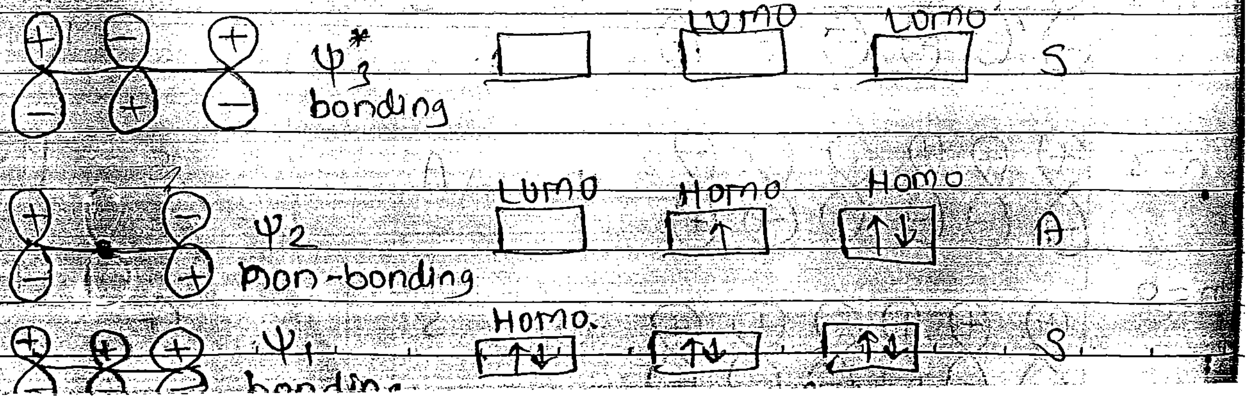
(Allyl carbanion)

This system has three isolated p-orbitals and has one π bond & one Lone pair of electrons

$$CH2 = CH_2 - \dot{C}H_2 \leftarrow \text{Allyl radical)}$$

This system has three isolated p-orbitals and has one π bond and one e^- in unhybrid p-orbital.

- Electron occupancy in these system is given below,



- The MO's of such species follow many of the same patterns as those of conjugated polyenes
- The MO's of allyl are shown in fig.
- this figure show two important differences between these MO's. and those of conjugated polyenes.
- first, one MO is neither bonding molecular orbit or antibonding molecular orbital but has the same energy as the isolated P-orbitals. this MO is called non-bonding molecular orbital.
- The non-bonding molecular orbital in the allylic system is ψ_2. The remaining MO's are bonding and antibonding MO's.
- second, in some of the MO's node pass through carbon atom.
- for example, in allyl free radical there is node on the central carbon atom of ψ_2;
- Notice that cations, anions and free radicals involving the same π-system have the same molecular orbitals, because all three species contain same number of P-orbitals. these species differe only in the no. of π-electrons as shown in electron occupancy column.

Theory of pericyclic reactions:-

- pericyclic reactions are defined as reactions that occur by concerted cyclic shift of e^-.
- Woodward and Hoffmann symmetry of molecular orbital that participate in the chemical reaction determines the course of the reaction. it is called as conservation of orbital symmetry

(maintain)

If symmetry is conserved during the course of the reaction then reaction will take place and process is known as symmetry allowed process.

If symmetry is not conserved during the course of the reaction the reaction is known as symmetry - forbidden process.

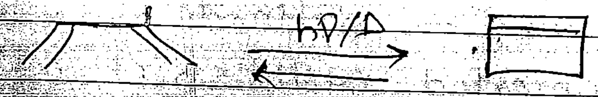
Classification of pericyclic reactions :→
There are four major types of pericyclic reactions,
① Electrocyclic reaction ② cycloaddition reaction
③ sigmatropic rearrangment ④ Group transfer reaⁿ.

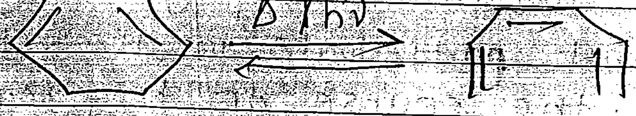
② Pericyclic reactions can be explained by three method.

a) frontier molecular orbital method (FMO)
[illegible] b) Perturbation molecular orbital. (PMO
c) Woodward - Hoffmann correlation diagram.

① Electrocyclic Reactions :→

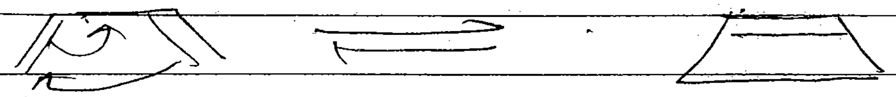
A electrocyclic reaction is the concerted interconversion of conjugated polyene and a cycloalkene. Electrocyclic reactions are induced either thermally or photochemically.





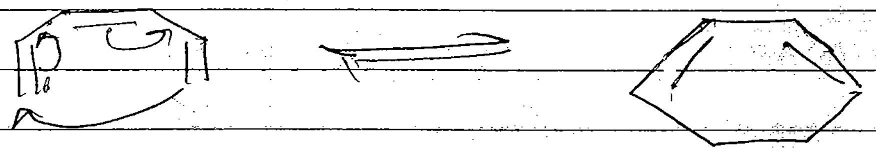
All electrocyclic reactions are reversible reactions. open-chain partner of the reaction is always a conjugated system where as cyclic partner may or may not contain conjugated system.

In electrocyclic reactions either a ring is formed with the generation of a new σ bond and the loss of a π bond (i.e gain of one σ bond and loss of one π-bond) or ring is broken with the loss of one σ bond and gain of one π bond.



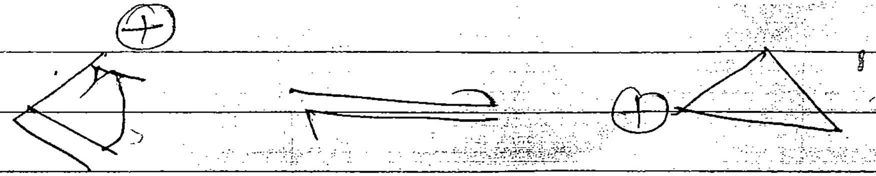
$4\pi e^-$

(loss of one π bond and gain of one σ bond)



$6\pi e^-$

(loss of one π bond and gain of one σ bond,



Formation of σ bond & loss of π bond

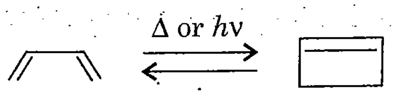
2

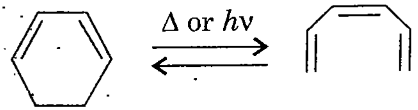
CHAPTER

Electrocyclic Reactions

2.1 INTRODUCTION

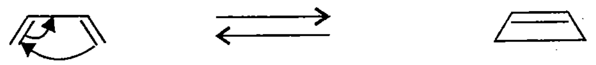
An electrocyclic reaction is the concerted interconversion of a **conjugated** polyene and a cycloalkene. Electrocyclic reactions are induced either thermally or **photochemically**.





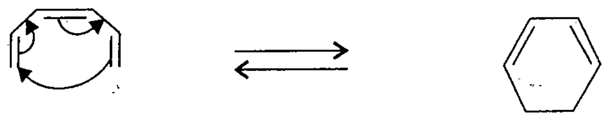
All electrocyclic reactions are reversible reactions. Open-chain **partner** of the reaction is always a conjugated system whereas cyclic partner may or may **not contain** conjugated system.

In electrocyclic reactions either a ring is formed with the **generation** of a new σ bond and the loss of a π bond (*i.e.*, gain of one σ bond and loss of one π bond) **or ring** is broken with the loss of one σ bond and gain of one π bond.



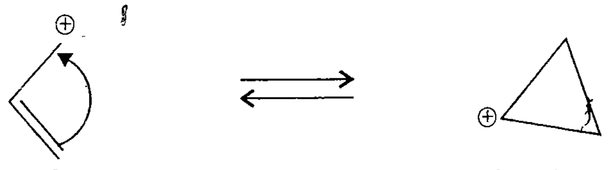
*k*π electrons
(*k* = 4)

(*k*π – 2) electrons + one
σ bond (loss of one π bond
and gain of one σ bond)



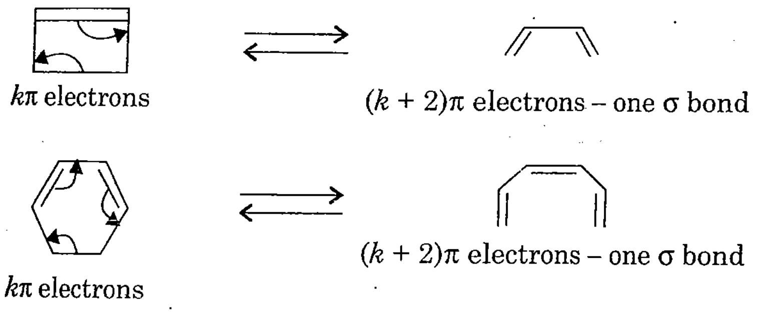
*k*π electrons
(*k* = 6)

(*k*π – 2) electrons + one σ bond



*k*π electrons

(*k*π – 2)π electrons + one σ bond



Thus electrocyclic reactions can be classified into two categories:

(*i*) Electrocyclic opening of the ring, and

(*ii*) Electrocyclic closure of the conjugated system.

In electrocyclic closure of the ring (or ring closing electrocyclic reaction) if the π system of the open-chain partner contains $k\pi$ electrons, the corresponding cyclic partner contains $(k - 2)\pi$ electrons and one additional σ bond. In ring opening electrocyclic reaction if ring partner contains $k\pi$ electrons, the open chain partner will contain $(k + 2)\pi$ electrons with the loss of one σ bond.

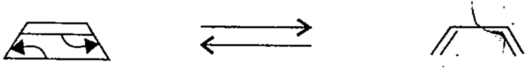
There are two possible stereochemistries for the ring-opening and ring-closing of electrocyclic reactions. They are:

1. Conrotatory process (or motion), and
2. Disrotatory process (motion).

2.2 CONROTATORY AND DISROTATORY MOTIONS IN RING-OPENING REACTIONS

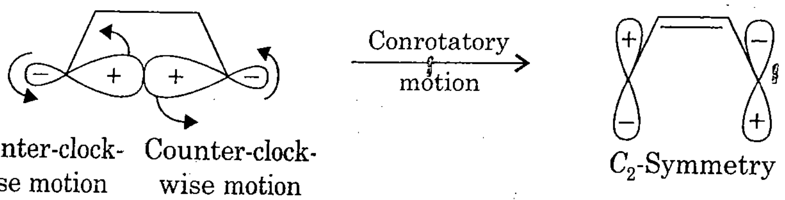
The most common example of the ring opening reaction is the conversion of cyclobutene to 1, 3-butadiene.

This conversion can only be possible if a σ (*sigma*) bond between C_3—C_4 of cyclobutene must break during the course of the reaction.



Ring opening reaction

This σ (*sigma*) bond may break in two ways. *First*, the two atomic orbital components of the σ (*sigma*) bond may both rotate in the same direction, clockwise or counter-clockwise. This process is known as **conrotatory motion** (Fig. 2.1).



Or

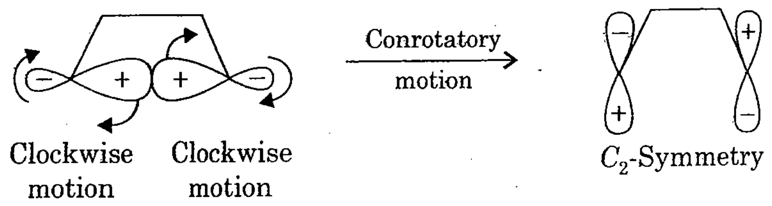


Fig. 2.1 Conrotatory ring-opening

Second, the atomic orbitals may rotate in opposite directions, one clockwise and the other counter-clockwise. This process of ring-opening is known as **disrotatory motion** (Fig. 2.2).

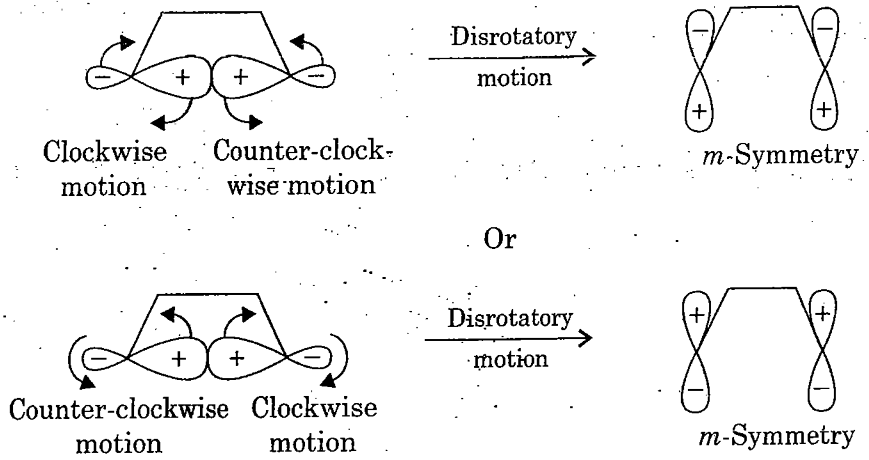


Fig. 2.2 Disrotatory ring-opening

The substituents present on the carbons of the rotating orbitals may also rotate in the direction of the rotating orbitals. Thus in the conrotatory motion substituents rotate in the same direction (Fig. 2.3) and in disrotatory motion substituents rotate in the opposite directions (Fig. 2.4).

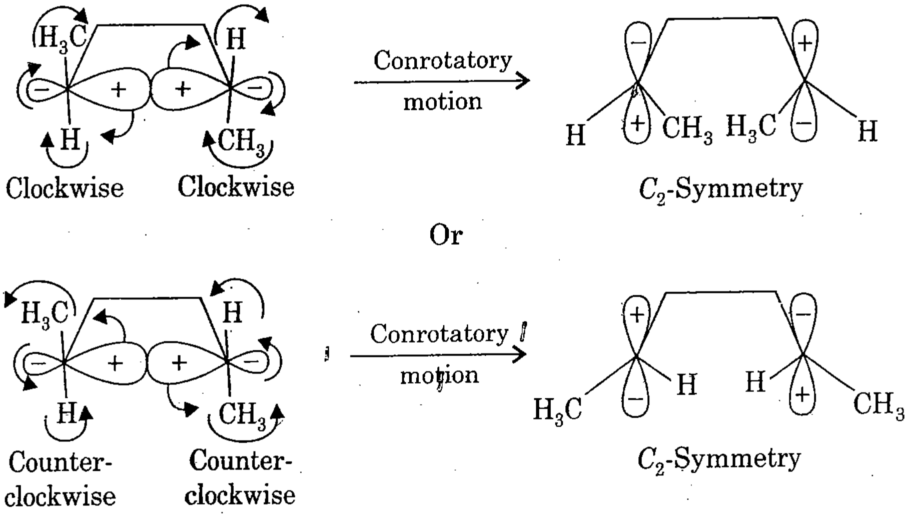


Fig. 2.3 Conrotatory ring-opening, orbitals and groups migrate in the same direction

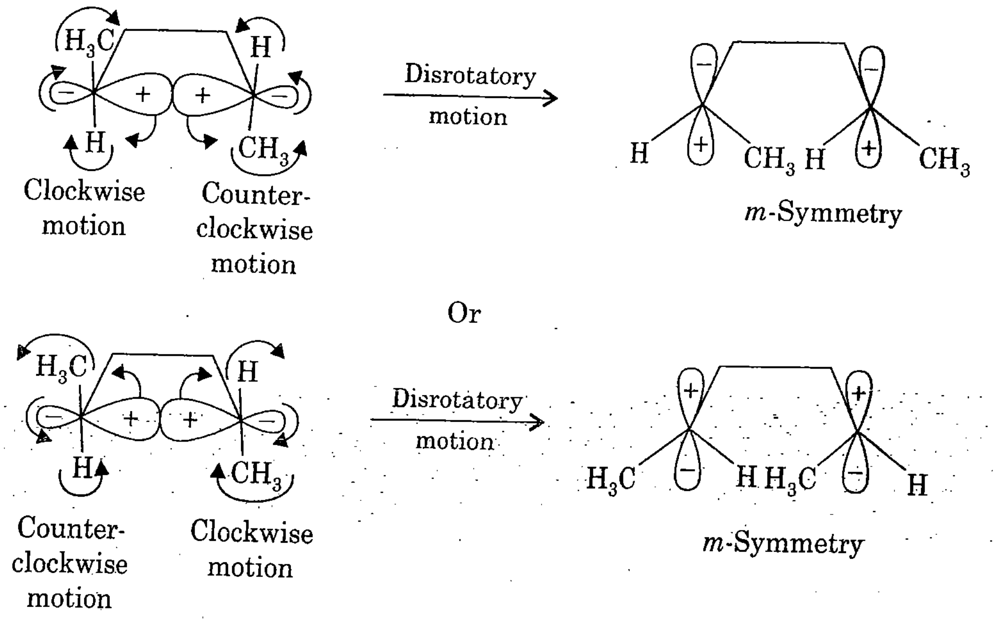
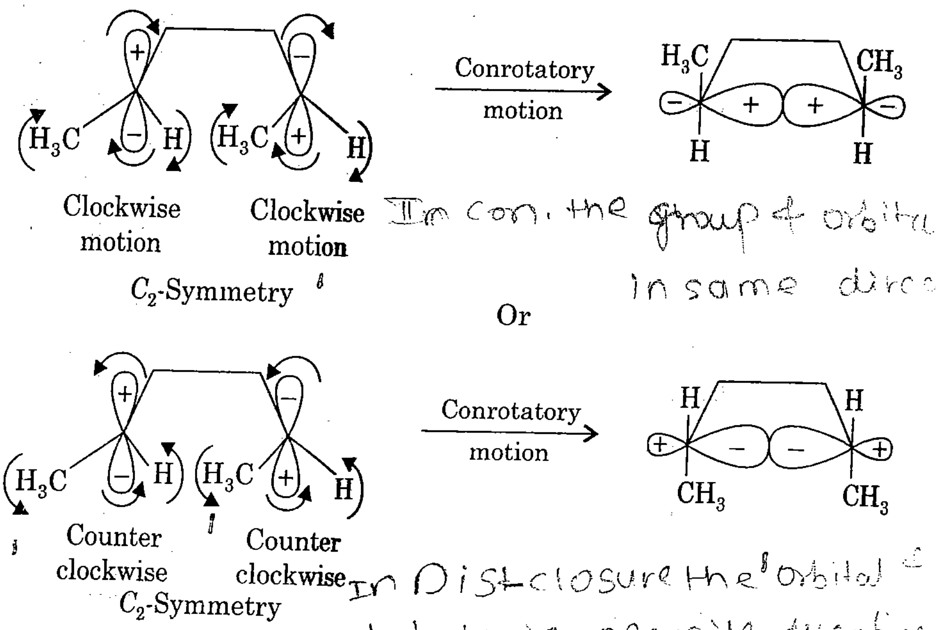


Fig. 2.4 Disrotatory ring-opening, orbitals and groups migrate in the opposite directions

2.3 CONROTATORY AND DISROTATORY MOTION IN RING-CLOSING REACTIONS

When an electrocyclic reaction takes place, the carbon at each end of the conjugated π system must turn in a concerted fashion so that the p orbitals can overlap (and rehybridised) to form σ bond that closes the ring. This turning can also occur in two stereochemically distinct ways.

In a conrotatory closure the orbitals and groups of the two carbon atoms turn in the same direction, clockwise or counter-clockwise (Fig. 2.5).



In con. the group & orbital rotate in same direction,

In Dis-closure the orbital & groups rotate in opposite direction

Fig. 2.5 Conrotatory closure of the ring

In a disrotatory closure the orbitals and groups of the two carbon atoms turn in the opposite direction, one clockwise and other counter-clockwise (Fig. 2.6).

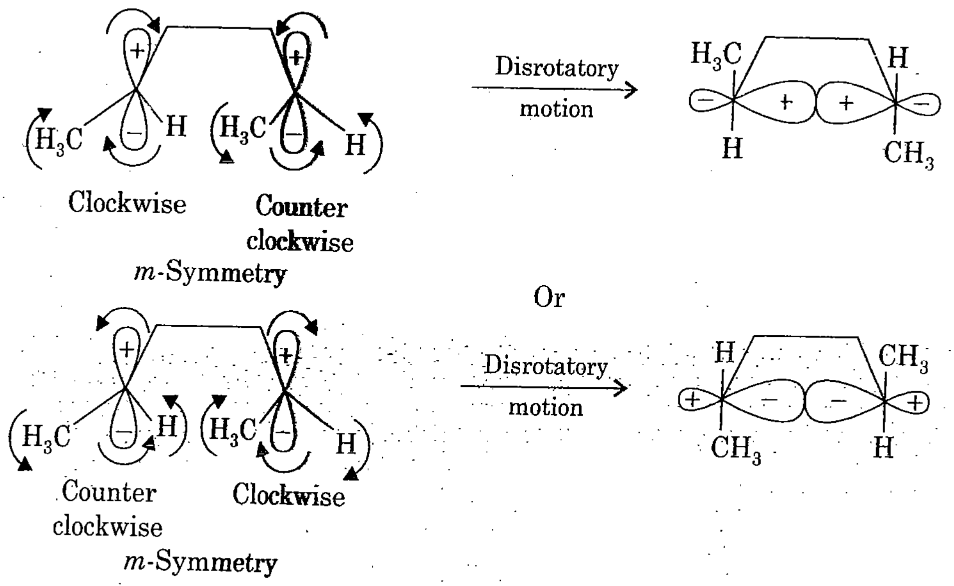


Fig. 2.6 Disrotatory ring-closure

From these examples it is clear that **orbitals having *m*-symmetry always give disrotatory motion.** (Fig. 2.4 and Fig. 2.6) whereas **orbitals having C_2-symmetry give conrotatory motion** (Fig. 2.3 and Fig. 2.5).

The reason behind this rule can be easily understood by recalling that overlap of wave functions of the same sign is bonding (and symmetry allowed reaction) whereas overlap of wave functions of opposite sign is antibonding (and symmetry forbidden process).

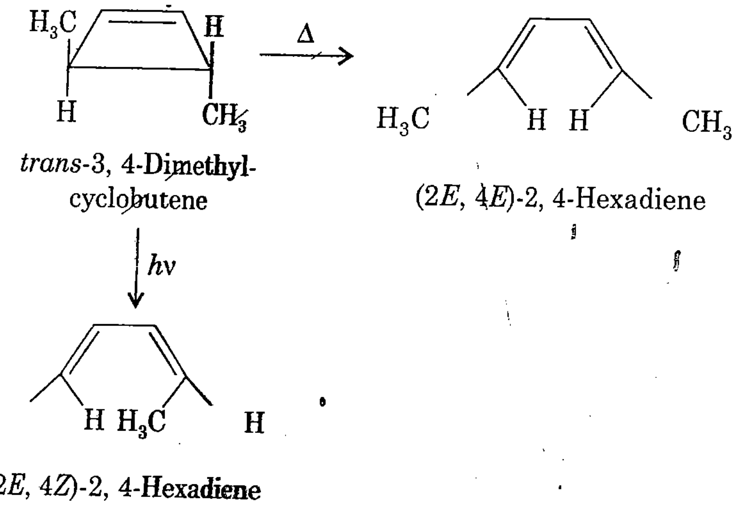
Electrocyclic reactions are highly stereospecific. An intriguing feature about electrocyclic reactions is that the stereochemistry of the product is dependent on whether the reaction is thermally **induced or photo-induced.**

2.3.1 Open Chain Conjugated System having 4nπ Conjugated Electrons

Let us consider the simplest example in which a cyclobutene derivative opens to a 1, 3-butadiene derivative, *i.e.*, open-chain conjugated system has **4*n* conjugated π electrons.**

In thermal condition *trans*-3, 4-dimethylcyclobutene gives (2*E*, 4*E*)-2, 4-hexadiene. Thus, this reaction is completely stereospecific.

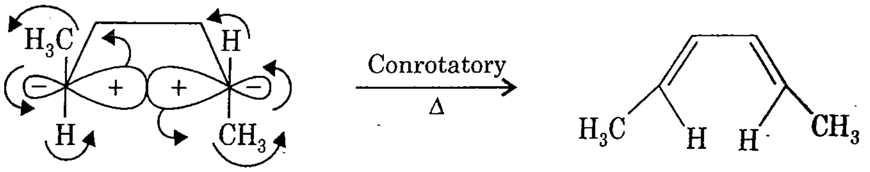
In the photochemical condition the same substrate gives (2*E*, 4*Z*)-2, 4-hexadiene. In this case too, the reaction is completely stereospecific. Thus the reaction can be performed thermally or photochemically, and under either condition the reaction is completely stereospecific.



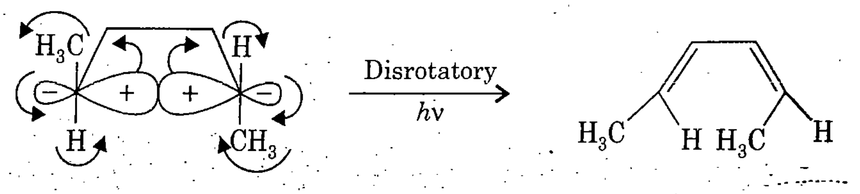
...(1)

...(2)

Stereochemistry of the thermal reaction-1 (of the $4n\pi$ system) **can only** be explained if process should be conrotatory.



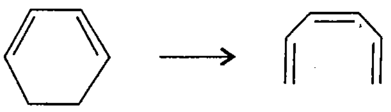
Stereochemistry of the photochemical reaction-2 (of the $4n$, π **system**) can only be explained if process should be disrotatory.



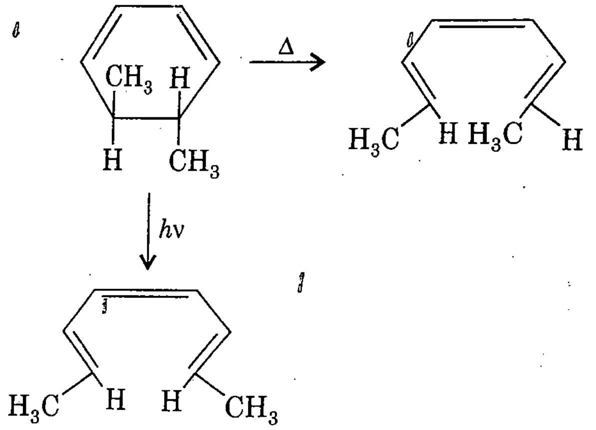
From the above two examples it is clear that **thermally induced electrocyclic reaction involving $4n\pi$ conjugated electrons require conrotatory motion and photochemically induced electrocyclic reaction require disrotatory motion.**

2.3.2 Open Chain Conjugated System having (4n + 2)π Conjugated Electrons

The simplest example of this category is the ring-opening of 1, 3-cyclohexadiene into 1, 3, 5-hexatriene.



In thermal condition 5, 6-*trans*-dimethyl-1, 3-cyclohexadiene is converted exclusively to (2*E*, 4*Z*, 6*Z*)-2, 4, 6-octatriene. In the photochemical condition the same substrate is converted exclusively to (2*E*, 4*Z*, 6*E*)-2, 4, 6-octatriene.



...(3)

...(4)

These two conversions are also highly stereospecific. Stereochemistry of these two reactions (*i.e.*, reaction-3 and 4) can only be explained if process is **disrotatory** in thermal condition and conrotatory in photochemical condition.

On the basis of these experimental results the stereochemistry of electrocyclic reactions can be summarised by noting that thermally induced electrocyclic reactions involving $4n\pi$ electrons require conrotatory motion. Under similar conditions, electrocyclic reactions involving $(4n + 2)\pi$ electrons follow disrotatory motion. Similarly, photo-induced electrocyclic reactions involving $4n\pi$ electrons require disrotatory motion. Under similar conditions, electrocyclic reactions involving $(4n + 2)\pi$ electrons follow conrotatory motion.

A summary of the type of motion to be expected from different polyenes under thermal and photochemical conditions is shown in Table 2.1.

Table 2.1

Number of π electrons	*Condition (mode of activation)*	*Motion*
$4n$	(*i*) Thermal (*ii*) Photochemical	Conrotatory Disrotatory
$4n + 2$	(*i*) Thermal (*ii*) Photochemical	Disrotatory Conrotatory

The above experimental results can be explained by the four theories given for pericyclic reactions.

2.4 FRONTIER MOLECULAR ORBITAL (FMO) METHOD

A methodology for quickly predicting whether a given pericyclic reaction is allowed by examining the symmetry of the highest occupied molecular orbital (HOMO) (in case of unimolecular reaction) and, if the reaction is bimolecular, the lowest unoccupied molecular orbital (LUMO) of the second partner.

Thus, electrocyclic reaction is analysed by HOMO of the open chain partner because reaction is unimolecular reaction. The stereochemistry of an electrocyclic process is determined by the symmetry of the highest occupied molecular orbital (HOMO) of the open chain partner, regardless of which way the reaction actually runs. In thermal condition HOMO is always ground state HOMO whereas in photochemical condition HOMO is always first excited state HOMO.

If the highest occupied molecular orbital has *m* symmetry, the process will be disrotatory. On the other hand, if HOMO has C_2-symmetry then the process will be conrotatory (Table 2.2).

Table 2.2

Symmetry in HOMO	*Mode of rotation*
m-Symmetry	Disrotatory
C_2-Symmetry	Conrotatory

For any electrocyclic reaction there are two conrotatory and two disrotatory modes of ring cleavage and ring closure. The two conrotatory modes can give same or different products. Similarly, the two disrotatory modes can also give the same or different products.

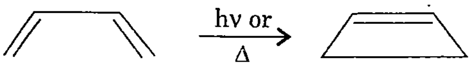
[illegible]
Δ/hν condition by FMO method

Now we are in a position to consider specific examples of the **application** of the FMO method.

Q. With the FMO & corelation explain interconversion of 1,3 butadien into cyclobutene under Δ/hν.

2.4.1 Cyclisation of 4nπ Systems

1. Electrocyclic ring-closure reaction given by butadiene: 1, 3-butadiene is the first member of the conjugated polyene having 4nπ electrons.



Thermal-induced cyclisation: When 1, 3-butadiene is heated, reaction takes place from the ground state. The electrons that are used for the σ (*sigma*) bond **formation** are in the HOMO (ψ_2 in this case). Pertinent *p* orbitals in ground state HOMO has C_2-symmetry. For the new σ (*sigma*) bond to form, rotation must be conrotatory. Disrotatory **motion** would not place the in-phase lobes together.

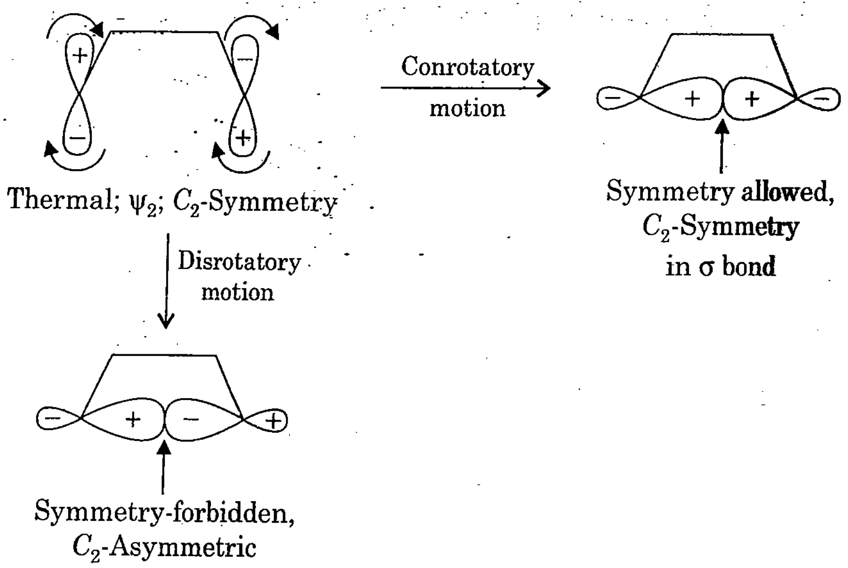
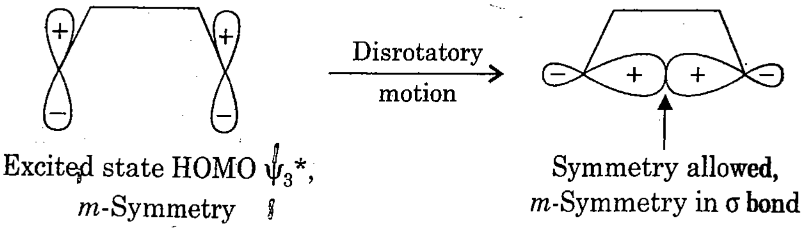


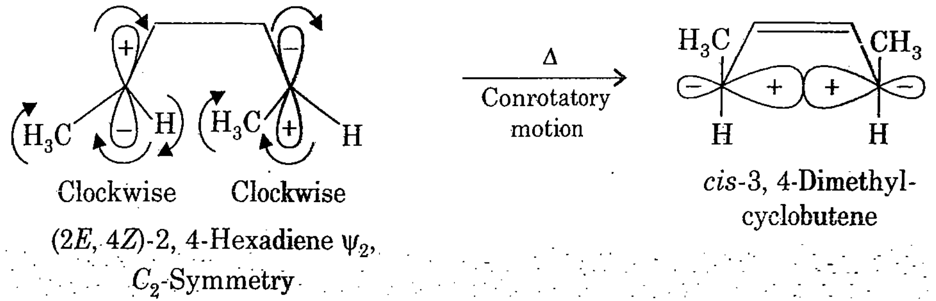
Photo-induced cyclisation: In photo-induced cyclisation, the **first** excited HOMO of 1, 3-butadiene is ψ_3^* which has *m* symmetry. For the new σ (*sigma*) **bond** to form, rotation must be disrotatory.



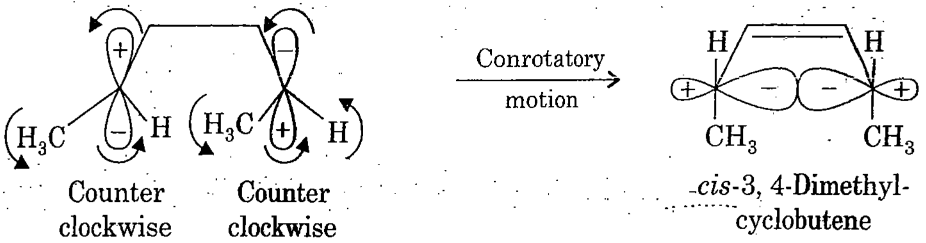
Let us return to (2*E*, 4*Z*)-2, 4-hexadiene to see why the *cis*-3, 4-dimethylcyclobutene results from the thermal cyclisation and the *trans*-isomer from the **photo** cyclisation.

Stereochemistry

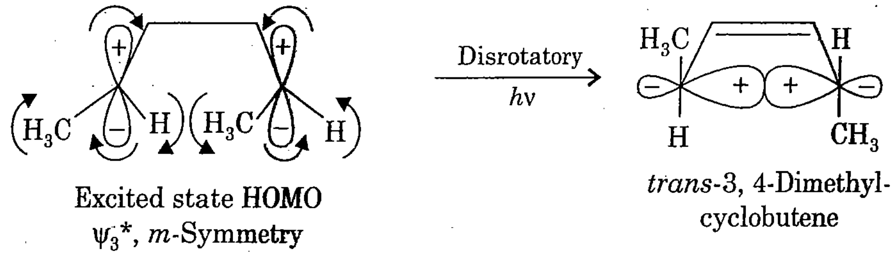
In the case of the thermal cyclisation the ground state **HOMO** is ψ_2 which has C_2-symmetry. Thus, conrotatory motion is required for σ (*sigma*) bond **formation**. Both methyl groups rotate in the same direction, as a result they end up on the same side of the ring or *cis* is the product.



Or

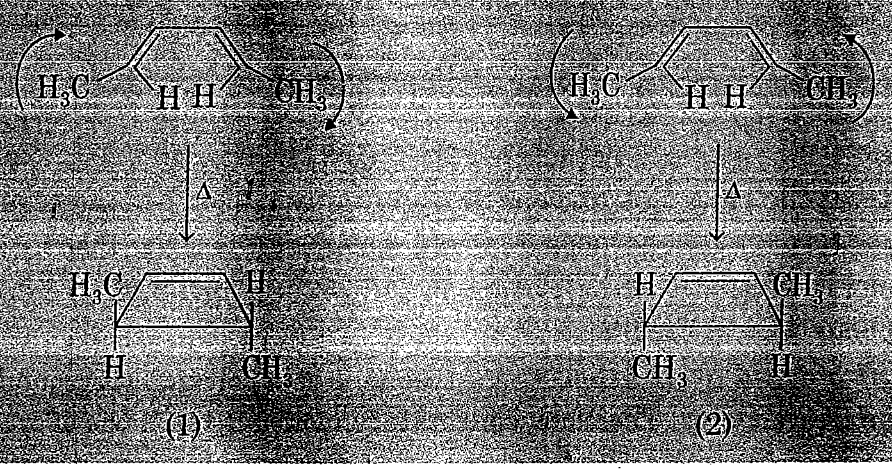


In the case of photocyclisation the excited state HOMO is ψ_3^* which has *m*-symmetry. Thus, disrotatory motion is required for the σ bond formation. In disrotatory motion, one of the methyl groups, rotates up and the other rotates down. The result is that both methyl groups are *trans* in the product.



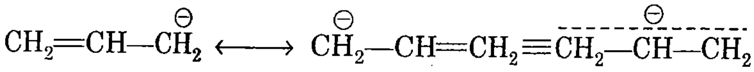
Problem 1: *Show both conrotatory processes for the thermal electrocyclic conversion of (2E, 4E)-2,4-hexadiene into 3,4-dimethylcyclobutene. Explain why the two processes are equally alike?*

Solution: The two different conrotatory motions are as follows:

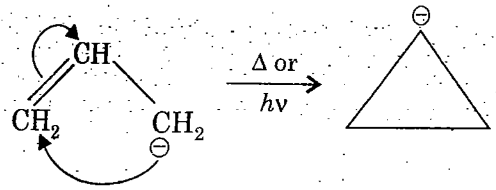


They are equally likely because they [(1) and (2)] are enantiomeric. Enantiomers have equal energies. Enantiomeric pathways have identical energies at all points and therefore identical rates.

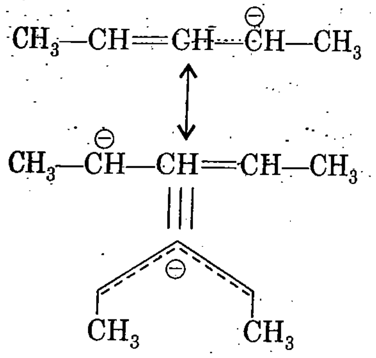
2. Electrocyclic ring-closure given by allyl carbanion: Allyl carbanion is also a $4n\pi$ conjugated system.



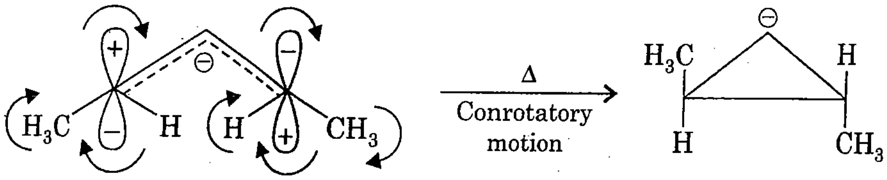
$$CH_2{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}CH_2 \equiv \overset{\ominus}{\overline{CH_2{-}CH{-}CH_2}}$$



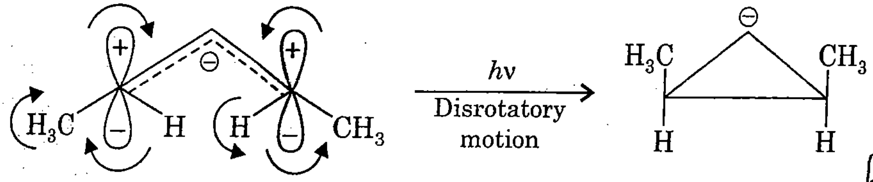
HOMO of the allyl carbanion in the ground state is ψ_2 which has C_2-symmetry. Therefore, conrotatory motion is the mode of cyclisation in the thermal condition.



$$CH_3{-}CH{=}CH{-}\overset{\ominus}{C}H{-}CH_3 \updownarrow \; CH_3{-}\overset{\ominus}{C}H{-}CH{=}CH{-}CH_3$$



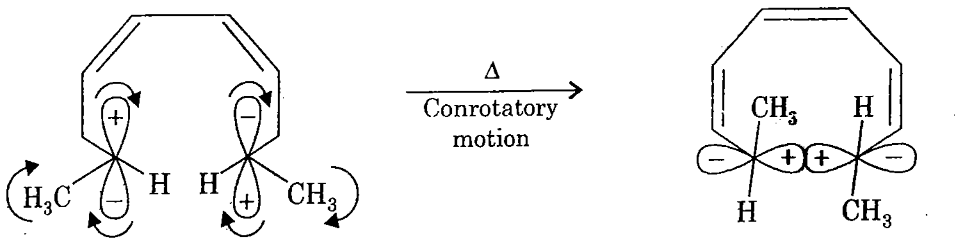
In case of photocyclisation, the excited HOMO is ψ_3* which has m-symmetry. Thus, disrotatory motion is required for σ (*sigma*) bond formation.



3. Electrocyclic ring-closure reaction given by 1, 3, 5, 7-octatetraene: 1, 3, 5, 7-octatetraene and its derivatives contain $4n\pi$ conjugated electrons.

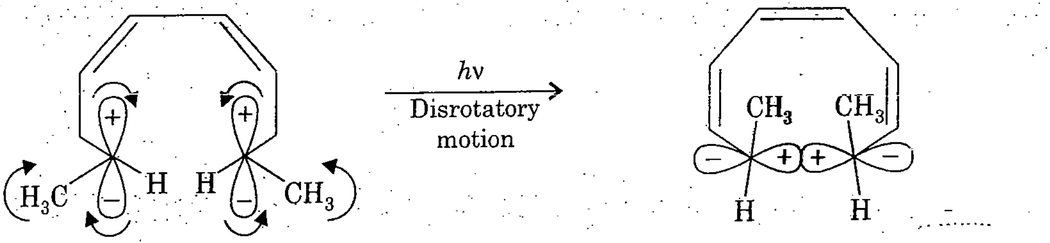
Consider the electrocyclic ring-closure of (2*E*, 4*Z*, 6*Z*, 8*E*)-2, 4, 6, 8-decatetraene in thermal and photochemical conditions.

Thermal-induced cyclisation: The tetraene is a $4n$ polyene. Its ground state HOMO is ψ_4 which has C_2-symmetry. Therefore, conrotatory motion is the mode of cyclisation.



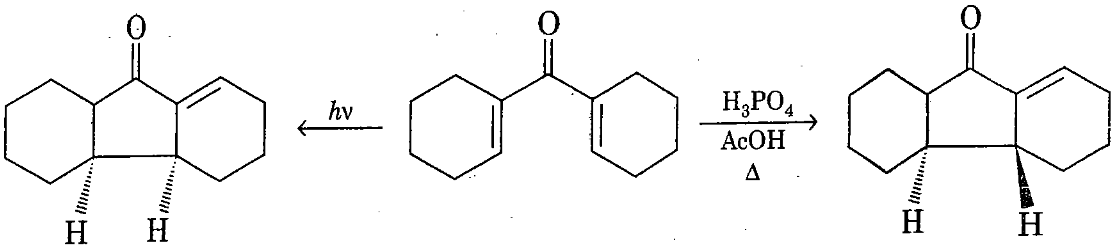
trans-7, 8-Dimethyl-1, 3, 5-cyclotriene

Photo-induced cyclisation: In case of photo-induced cyclisation the excited state HOMO is ψ_5^* which has *m*-symmetry. Thus disrotatory motion is the mode of cyclisation.

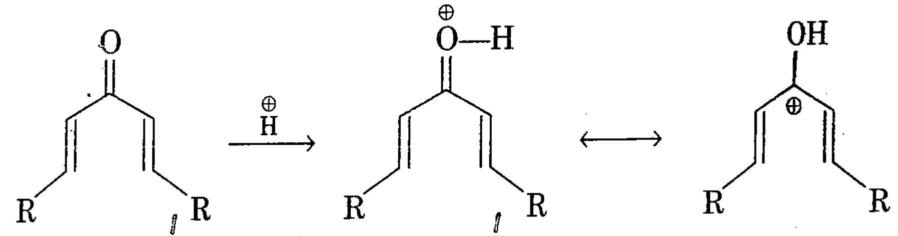


cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene

4. Nazarov cyclisation: Nazarov cyclisation is given by 1, 4-pentadiene-3-one and its derivatives. The product of the reaction is cyclopentenone. The reaction is conrotatory electrocyclic ring-closure under thermal condition and disrotatory ring-closure under photochemical conditions.



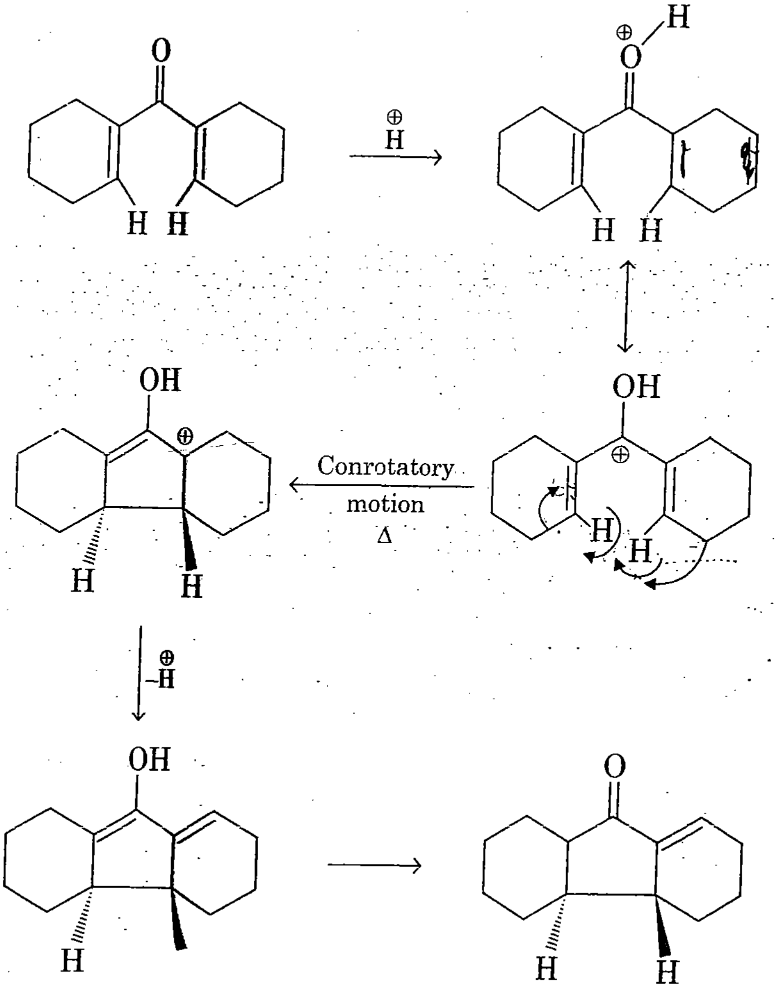
Nazarov cyclisations require acid. Under acidic condition the substrate converts into cation which has 4π conjugated electrons.



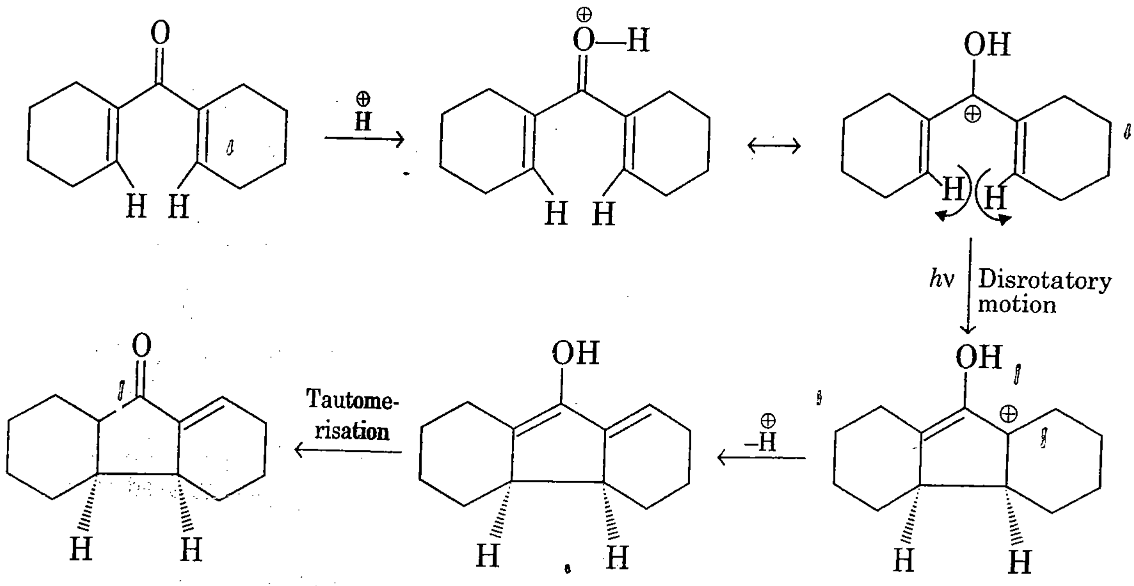
Under thermal condition, the motion is conrotatory and under photochemical conditions, the motion is disrotatory because the conjugated system has (4*n*)π conjugated electrons.

Zero/odd [illegible] – [illegible]
even [illegible] – [illegible]

The reaction under thermal condition



The reaction under photochemical conditions



Q Why on thermal condⁿ cis-3,4-dimethyl cyclobutane give (2E,4Z) 2,4 hexadiene while trans gives (2E,4E) 2,4 hexad

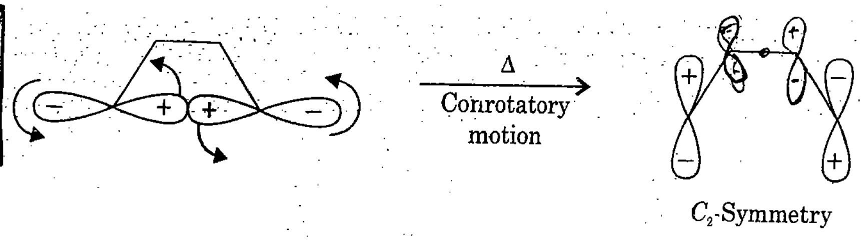
2.4.2 Electrocyclic Ring-Opening in which Polyene has 4nπ Electrons

Conversion of cyclobutene to butadiene

(A) ***Thermal-induced ring opening:*** In the ring-opening reactions stereochemistry of the product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of butadiene and its derivative will be ψ_2 which has C_2-symmetry. The cyclobutene ring must open in such a fashion that the σ bond orbitals transform into the HOMO of the product having C_2-symmetry. To get C_2-symmetry in the product HOMO, motion should be conrotatory in the ring opening of the reaction. even

ψ_1

Even — C2
odd/zero — m



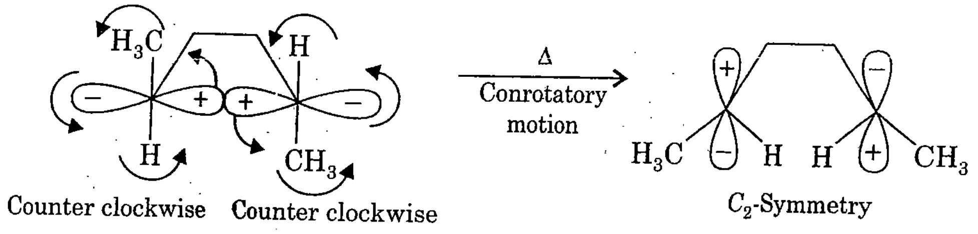
C_2-Symmetry

Thus, if the open-chain polyene has 4nπ electrons then the process is always *conrotatory* in thermal condition whether the reaction is ring-closure or ring opening.

Let us take the stereochemistry of the ring opening of *trans*-3, 4-dimethylcyclobutene.

There is possibility of two modes of conrotatory motion, counter clockwise and clockwise motions.

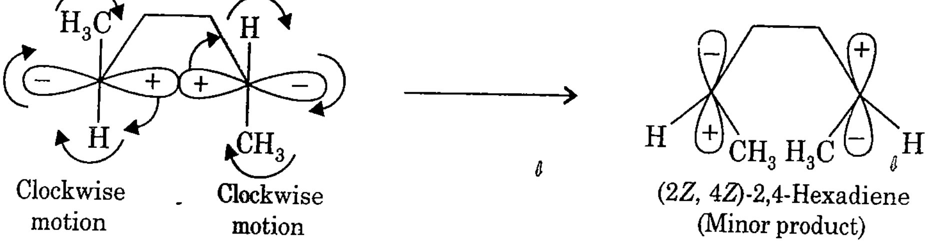
(*i*)



C_2-Symmetry

(2*E*, 4*E*)-2,4-Hexadiene (Major product)

(*ii*)

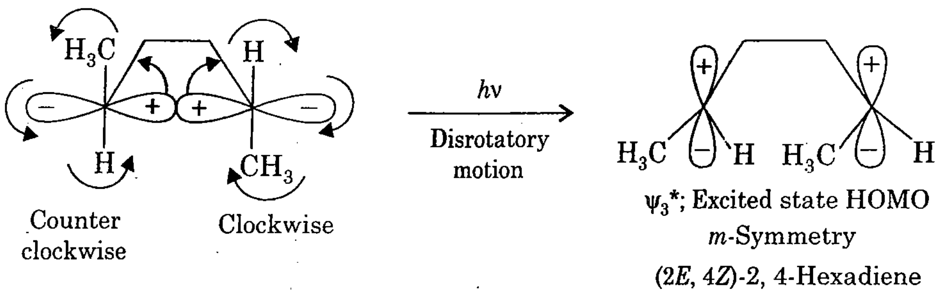


(2*Z*, 4*Z*)-2,4-Hexadiene (Minor product)

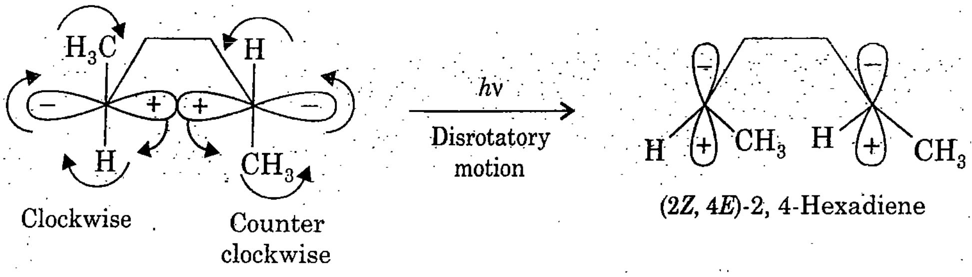
Thus, the thermal process is conrotatory with two products possible in the above case. The conrotation in the second case (clockwise rotation) leads to severe steric interactions between two methyl groups. This interaction is avoided in the first process (rotation is counter clockwise) in which two methyl groups move away from each other, and this is the favoured process.

(B) ***Photo-induced ring opening:*** The photo state HOMO of the open chain butadiene and its derivative will be ψ_3^* which has *m*-symmetry. Thus, the cyclobutene ring must open in such a fashion that the σ bond orbitals transform into the excited state HOMO of the product having *m*-symmetry. To get *m*-symmetry in excited state HOMO of the product, motion should be disrotatory in the ring-opening of the reaction. There is also possibility of two modes of disrotatory motion.

(i)



(ii)

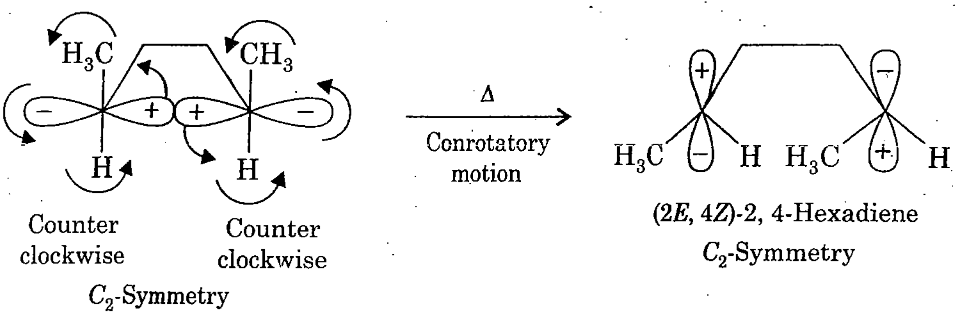


Thus, photo-induced process is disrotatory with either possible disrotation giving same product.

Let us take the conversion of *cis*-3, 4-dimethylcyclobutene into 2, 4-hexadiene.

Thermal ring-opening

(i)



(ii)

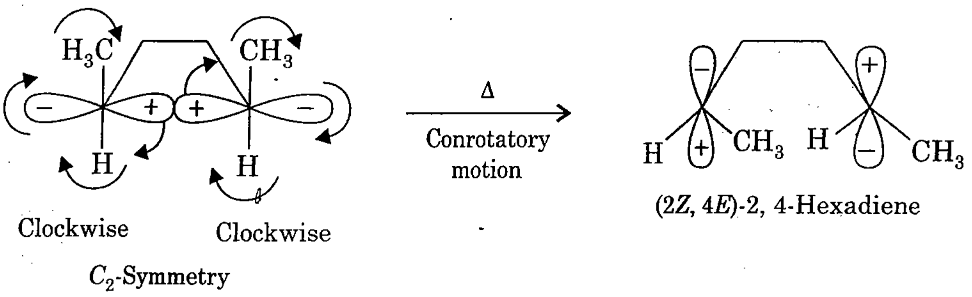
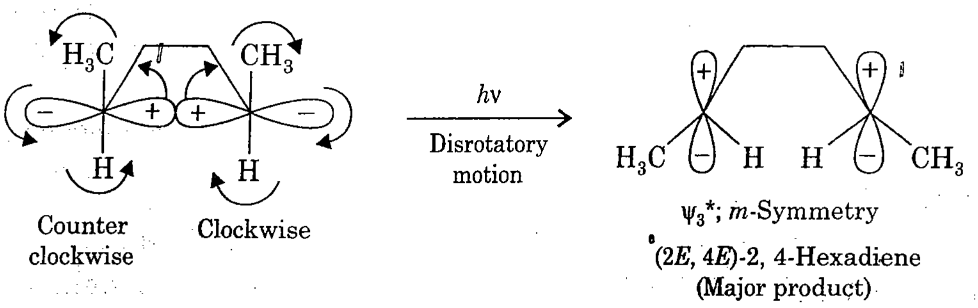
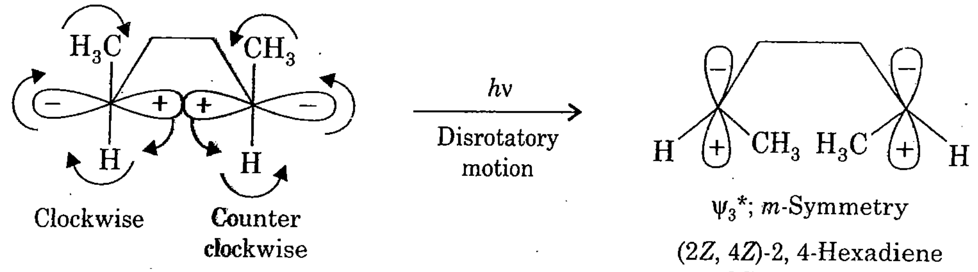


Photo-induced ring-opening

(i)



(ii)



ψ_3*; *m*-Symmetry

(2*Z*, 4*Z*)-2, 4-Hexadiene

(Minor product)

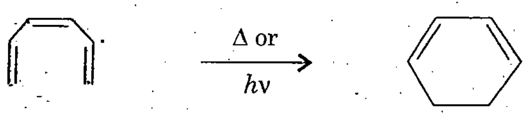
In case of *cis*-3, 4-dimethylcyclobutene, the thermal process is conrotatory with either possible conrotation giving the same product. The photochemical process is disrotatory with two possible products.

Q Interconversion of 1,3,5 hexatrien ⇌ 1,3 cyclc hexadien under Δ/hν by Fmo method

2.4.3 Cyclisation of (4n + 2)π Systems

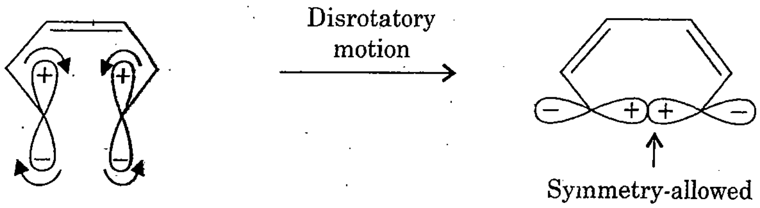
1. Electrocyclic ring-closure reaction given by 1, 3, 5-hexatriene

1, 3, 5-Hexatriene is the most common example of the polyene having $(4n + 2)\pi$ conjugated electrons.



1, 3, 5-Hexatriene 1, 3-Cyclohexadiene

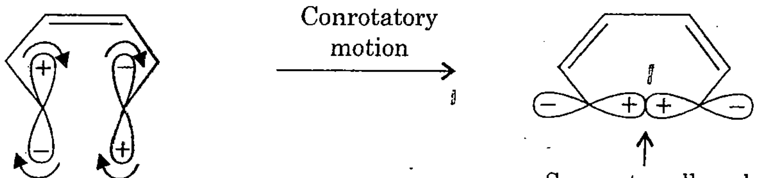
(A) ***Thermal-induced cyclisation:*** ψ_3 is the ground state HOMO of 1, 3, 5-hexatriene which has *m*-symmetry. Therefore, the thermal cyclisation proceeds by disrotatory motion.



ψ_3, Ground state HOMO *m*-Symmetry

Symmetry-allowed (*m*-Symmetry)

(B) ***Photo-induced cyclisation:*** When an electron of 1, 3, 5-hexatriene is promoted by photon absorption, ψ_4* becomes the HOMO. This excited state HOMO has C_2-symmetry. Therefore, photo-induced cyclisation proceeds by conrotatory motion.

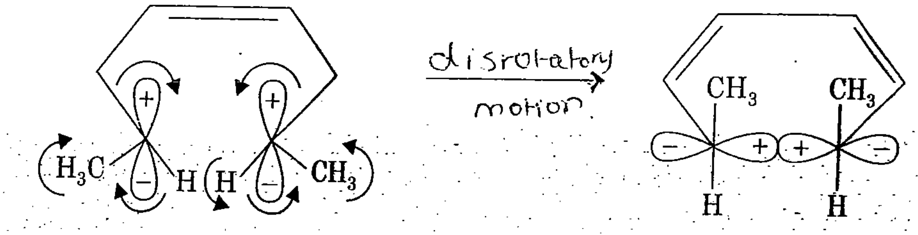


ψ_4*; Excited HOMO (C_2-Symmetry)

Symmetry-allowed (C_2-Symmetry)

Consider the stereochemistry of the thermal and photo-induced closure of (2*E*, 4*Z*, 6*E*)-2, 4, 6-octatriene to 5, 6-dimethyl-1, 3-cyclohexadiene.

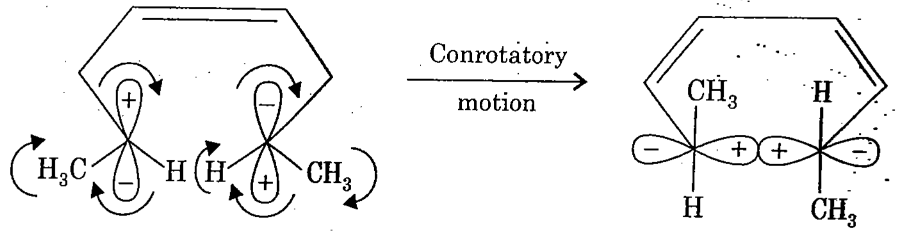
(A) ***Thermal-induced cyclisation:*** In the case of the thermal induced cyclisation, the ground state HOMO is ψ_3 which has *m*-symmetry. Thus, disrotatory motion is required for sigma bond formation. In disrotatory motion substituents rotate in the opposite directions.



ψ_3, Ground state HOMO
(*m*-Symmetry)

cis-5, 6-Dimethyl-1, 3-cyclohexadiene

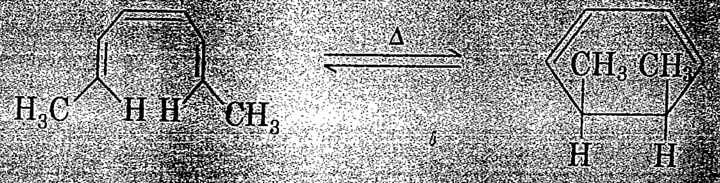
(B) ***Photo-induced cyclisation:*** In case of photo-induced cyclisation, the excited state HOMO is ψ_4^* which has C_2-symmetry. Therefore, conrotatory motion is required for σ (*sigma*) bond formation. In conrotatory motion substituents rotate in the same direction.



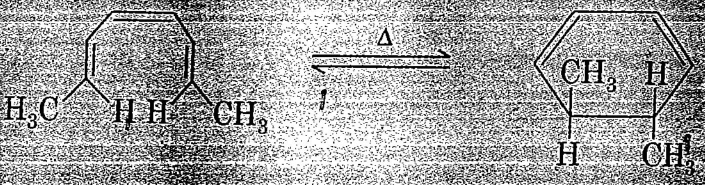
trans-5, 6-Dimethyl-1, 3-cyclohexadiene

Problem 2: *Which one of the following electrocyclic reactions should occur readily by a concerted mechanism?*

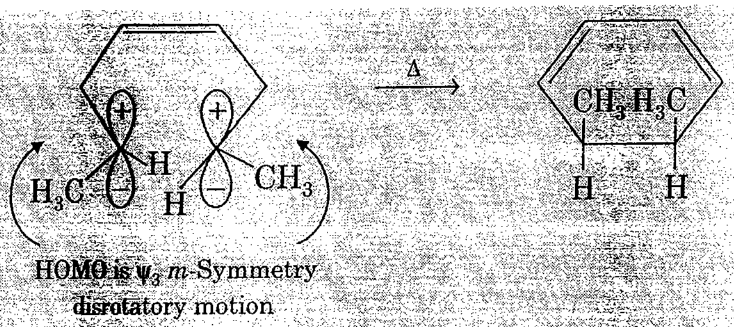
Reaction 1



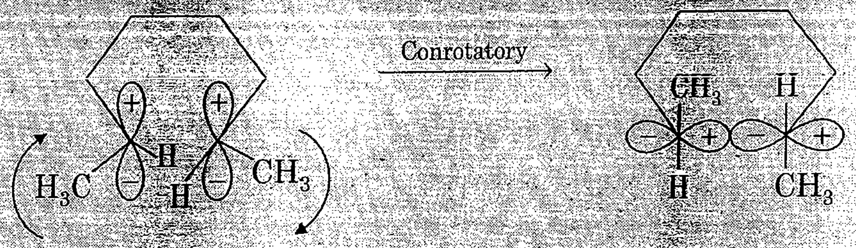
Reaction 2



Solution: Reaction 1 is a disrotatory reaction involving $(4n + 2)\pi$ electrons because this will give *cis* product. This reaction is allowed reaction. This reaction, therefore, can occur readily by a converted mechanism.

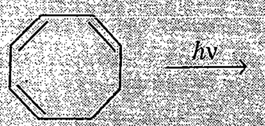


Reaction 2 is a conrotatory reaction involving $(4n + 2)\pi$ electrons because conrotatory motion will give *trans* product. It does not allow because the reaction is symmetry forbidden reaction,

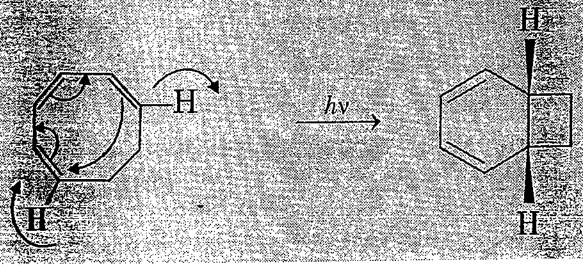


Thus, the reaction does not occur readily.

Problem 3: *Complete the following reaction and give stereochemistry of the product.*



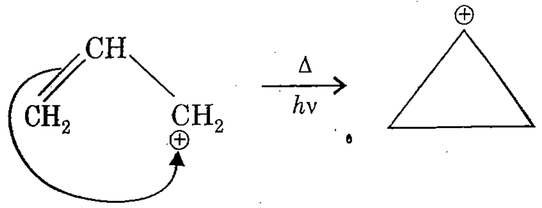
Solution: Reaction is photo-induced reaction. Reactant has $(4n + 2)\pi$ electrons. Its excited HOMO is ψ_4^* which has C_2-symmetry. Thus, motion is conrotatory motion.



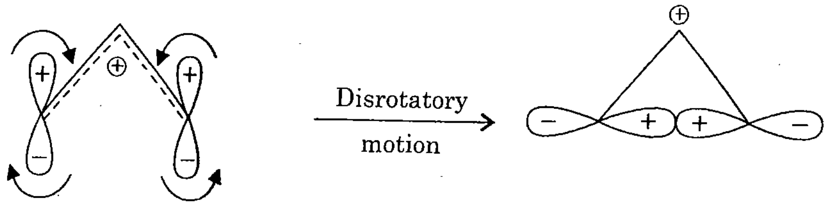
2. Electrocyclic ring-closure reaction given by allyl carbocation

Allyl carbocation contains $(4n + 2)\pi$ conjugated electrons.

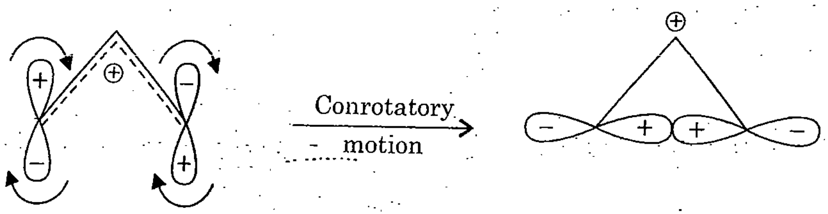
$$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2 \equiv \overset{\oplus}{\overline{CH_2{-}CH{-}CH_2}}$$



(A) ***Thermal-induced cyclisation:*** HOMO of the allyl carbocation in the ground state is ψ_1 which has m-symmetry. **Therefore**, disrotatory motion is the mode of cyclisation in the thermal condition.



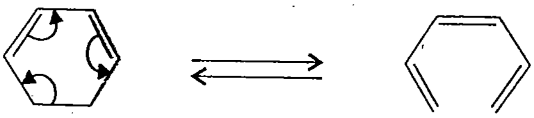
(B) ***Photo-induced cyclisation:*** HOMO of the allyl carbocation in the excited state is ψ_2 which has C_2-symmetry. Thus, **conrotatory** motion is required for σ (*sigma*) bond formation.



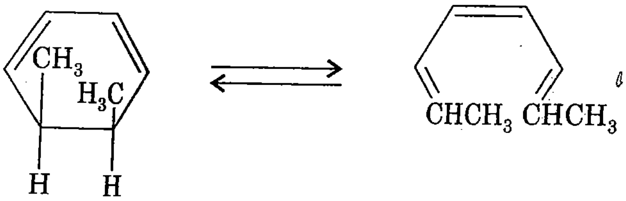
2.4.4 Electrocyclic Ring-opening in which Polyene has $(4n + 2)\pi$ Electrons

1. Conversion of 1, 3-cyclohexadiene to 1, 3, 5-hexatriene system

The most common example of this class is the conversion of 1, 3-cyclohexadiene to 1, 3, 5-hexatriene.

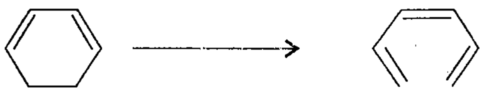


Let us take the example of the ring opening of a *cis*-5, 6-dimethyl-1, 3-cyclohexadiene into 2, 4, 6-octatriene.



(A) ***Thermal ring-opening:*** As mentioned earlier that in the ring opening reactions stereochemistry of product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of the triene will be ψ_3 which has m-symmetry. The cyclohexadiene ring therefore, must open in such a fashion that σ bond orbitals transform into the ground state HOMO of the product having m-symmetry. To get m-symmetry in the HOMO of the product, motion should be disrotatory in the ring opening of the reaction.

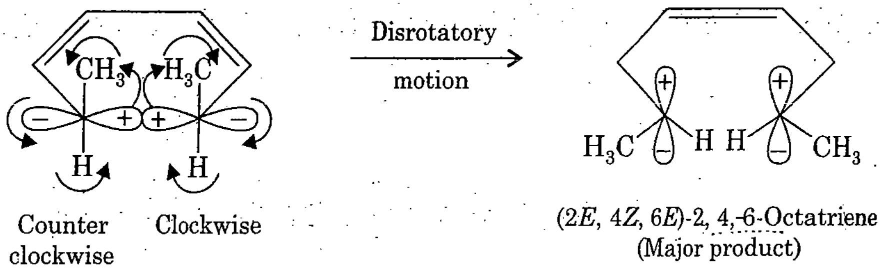
The above results can be obtained in short as follows:



Ground state HOMO is ψ_3 which has *m*-symmetry. Therefore, motion is disrotatory

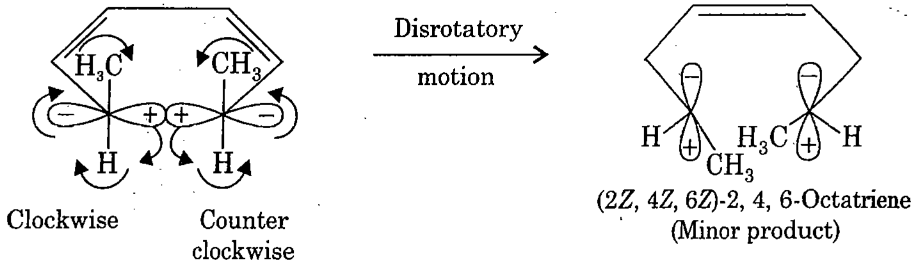
Two modes of disrotatory motions can take place as follows:

(*i*)



(2*E*, 4*Z*, 6*E*)-2, 4, 6-Octatriene
(Major product)

(*ii*)



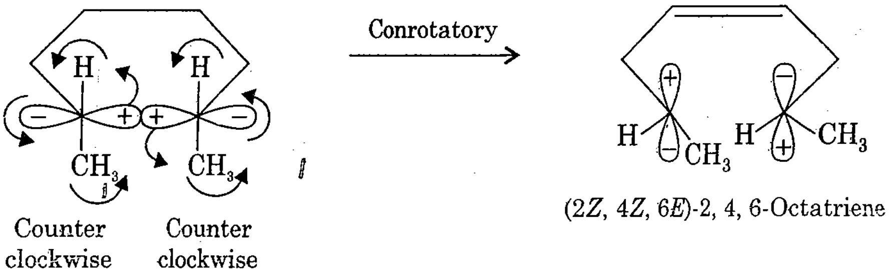
(2*Z*, 4*Z*, 6*Z*)-2, 4, 6-Octatriene
(Minor product)

Thus, the thermal process is disrotatory with two possible products, one is major and the other is minor due to the steric reasons.

(B) ***Photo-induced ring-opening:*** The photo state HOMO of the triene system is ψ_4^* which has C_2-symmetry. To get C_2-symmetry in the product, motion should be conrotatory in the ring opening reaction.

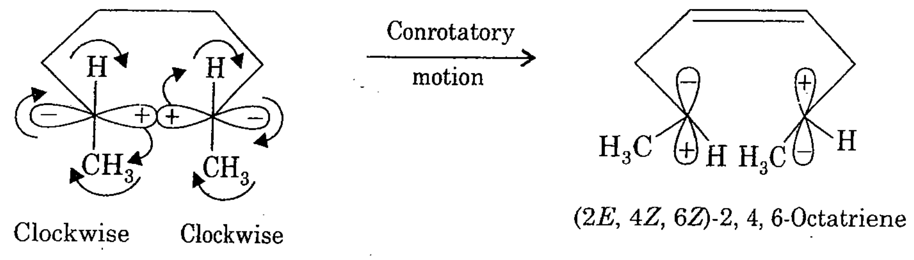
Consider the two modes of conrotatory motions:

(*i*)



(2*Z*, 4*Z*, 6*E*)-2, 4, 6-Octatriene

(*ii*)



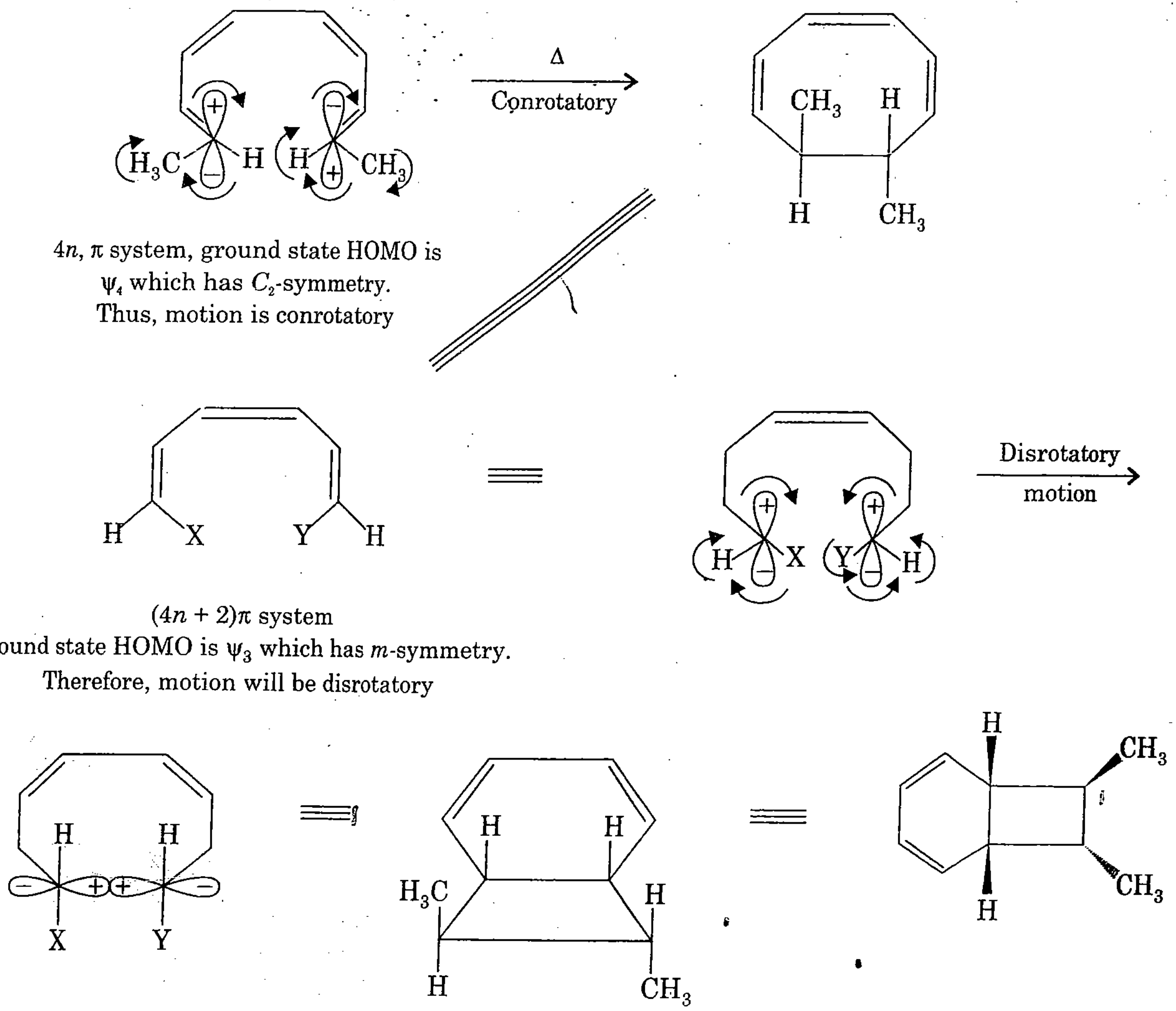
(2*E*, 4*Z*, 6*Z*)-2, 4, 6-Octatriene

In this case either possible conrotation giving the same product.

2. Thermal electrocyclic reaction given by (2*E*, 4*Z*, 6*Z*, 8*E*)-2, 4, 6, 8-decatetraene

The thermally induced electrocyclic reaction of (2*E*, 4*Z*, 6*Z*, 8*E*)-2, 4, 6, 8-decatetraene provide elegant examples of electrocyclic reactions.

The starting tetraene forms a cyclooctatriene at room temperature. The tetraene is a 4*n* polyene; therefore, conrotatory motion is the expected mode of cyclisation. Indeed the *trans*-7, 8-dimethyl-1, 3, 5-cyclooctatriene is the product of this initial cyclisation. When this cyclooctatriene is heated above room temperature, another electrocyclic ring closure occurs. However, the cyclooctatriene is a (4*n* + 2)π polyene; therefore, this thermally induced electrocyclic reaction proceeds with disrotatory motion, and a *cis* ring junction is formed.



4*n*, π system, ground state HOMO is ψ_4 which has C_2-symmetry.
Thus, motion is conrotatory

(4*n* + 2)π system
Ground state HOMO is ψ_3 which has *m*-symmetry.
Therefore, motion will be disrotatory

Correlation diagram :→

The diagram that shows the similarity in energ and symmetry between relevant reactant and product orbitals is called orbital correlation diagram or simply correlation diagram.

- This method can be used for any pericyclic reaction, but is usually utilised only for electrocyclic reactions.

Correlation diagram is based on the fundamental rule of the conservation of orbital symmetry as proposed by Woodward & Hoffmann.

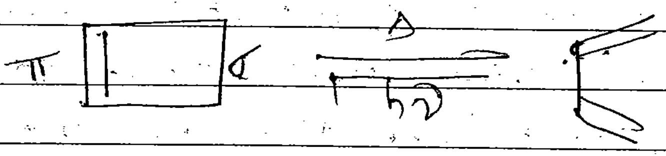
- According to this rule orbital symmetry must be conserved (maintain) throughout the course of reaction in concerted reaction
- This means that a symmetric orbital in the starting material must transform into a symmetric orbital in the product & asymm-etric orbital must transform into an asymmetric orbital.
- The orbitals that correlate are connected by lines ~~there~~ keeping that there is correlation betⁿ orbitals of same symmetr having minmum energy difference.
- The diagram is constructed as follows.
- in separate columns orbitals of reactant & Product are listed in their order of relativ energies, each orbital is classified on the basis of the symmetry elements retained at all points along the reaction coordinate.

lines are drawn bet^n the reactant & product orbitals connecting the lowest energy orbitals of the same symmetry type.
The following two conclusions can be correlation diagram:

i) Thermal transformation is symmetry allowed reaction when the ground state orbitals of the reactant correlate with ground state orbitals of the product.

ii) Photochemical transformation is symmetry allowed when first excited state orbitals of the reactant correlate with first excited state orbitals of the product.

Correlation Diagram of the Electrocyclic reaction in which polyene has $4n\pi$ electrons.



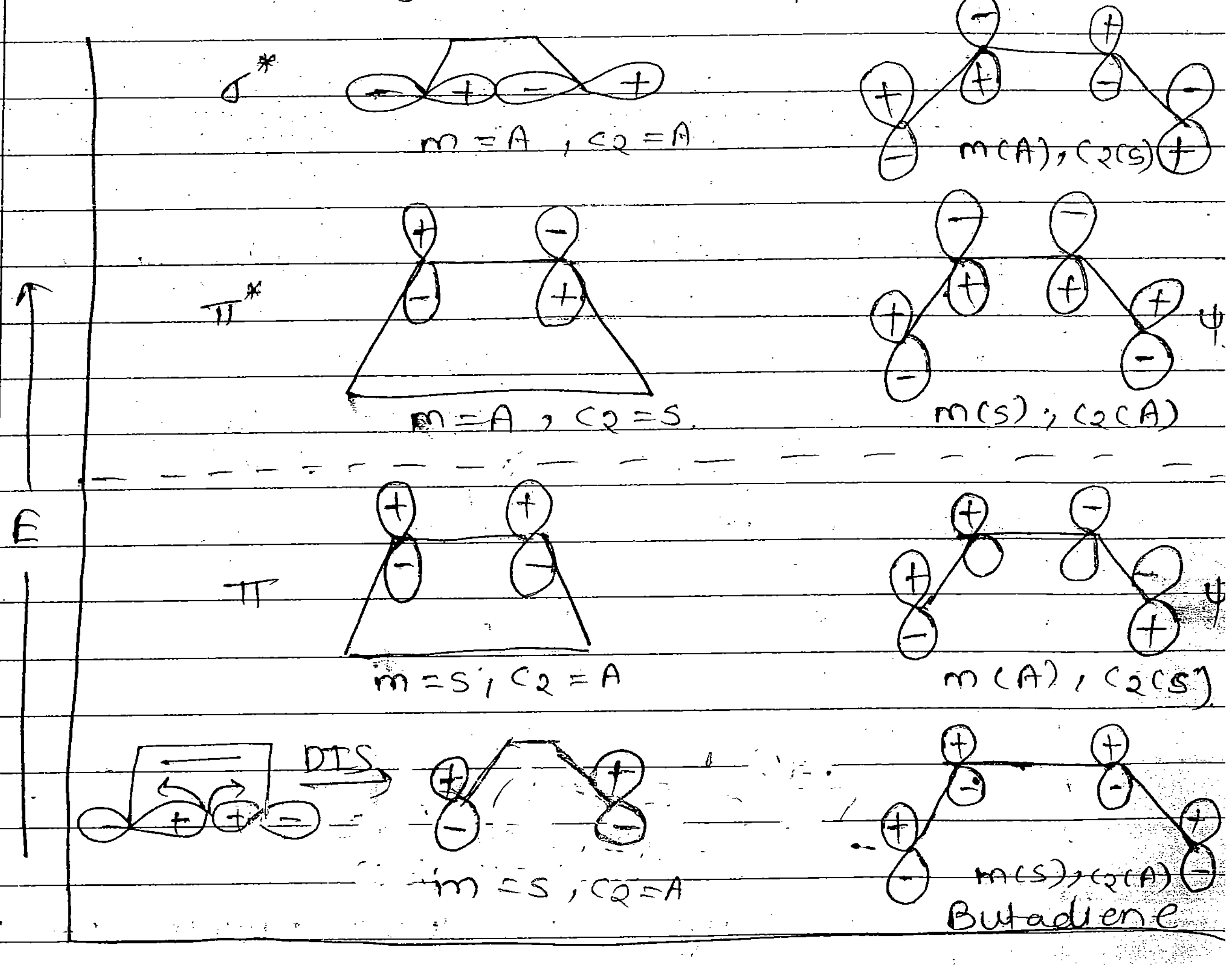
Transformation of cyclobutene to 1,3-butadien in this interconversion ring opening (or ring closing) may be conrotatory or disrotatory.
- The orbitals that undergo direct changes in cyclobutene are σ, π & the related antibonding orbitals, σ^* & π^*, these orbitals pass on to the four π molecular orbitals of butadien viz. ψ_1, ψ_2, ψ_3^*, ψ_4^*.
For corelation diagram all these orbitals are listed in order of increasing energy along with their mirror plane (m) & C_2-symmetric

a) under thermal condition :→

i) Let us first analyse a disrotatory opening o
cyclobutene under thermal condition.

- In a disrotatory opening always plane symmetry is maintained through the transfor
-ation.

- correlation diagram can be represented as :→



In the above correlation diagram σ which is G.S. orbitals of cyclobutene correlate with ψ_1 which is ground state MO of 1,3 butadiene.

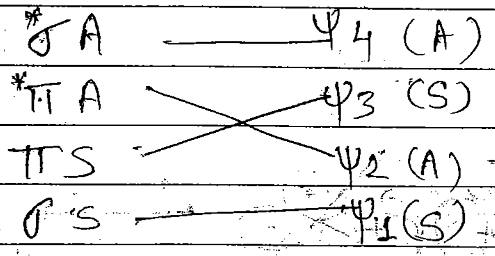
π which is another ground state of MO of cyclobutene does not correlate with ψ_2 which is another ground state MO of 1,3 butadiene but it correlate with ψ_3^* which is an excited state antibonding orbital.

Thermal transformation takes place only when G.S. MO's of the reactant correlate with G.S MO of the product in their symmetry properties but in this interconversion by disrotations there is no such type of correlation betn their symmetry properties

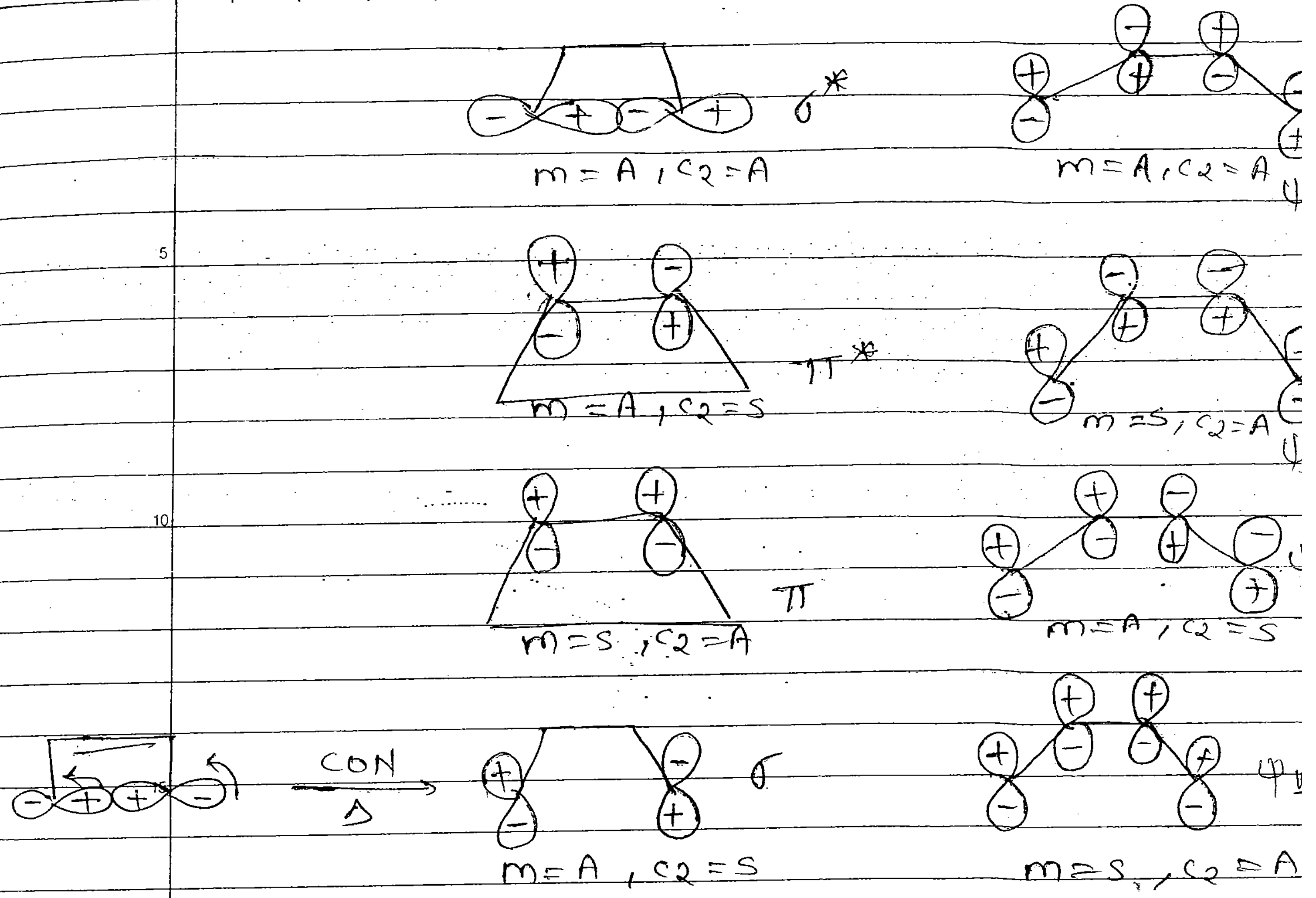
Hence thermal transformation of cyclobutene to butadiene by disrotation process is symmetry forbidden (not allowed).

$$\sigma^2 \pi^2 \underset{dis}{\overset{\Delta}{\cancel{\rightleftharpoons}}} \psi_1^2 \psi_2^2 .$$

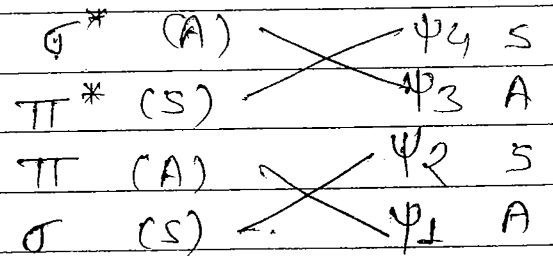
This correlation can also be represented as



ii) let us analyse the ring opening (or ring closing by con rotation in which C_2 axis of symmetry is maintained throughout the transformation.



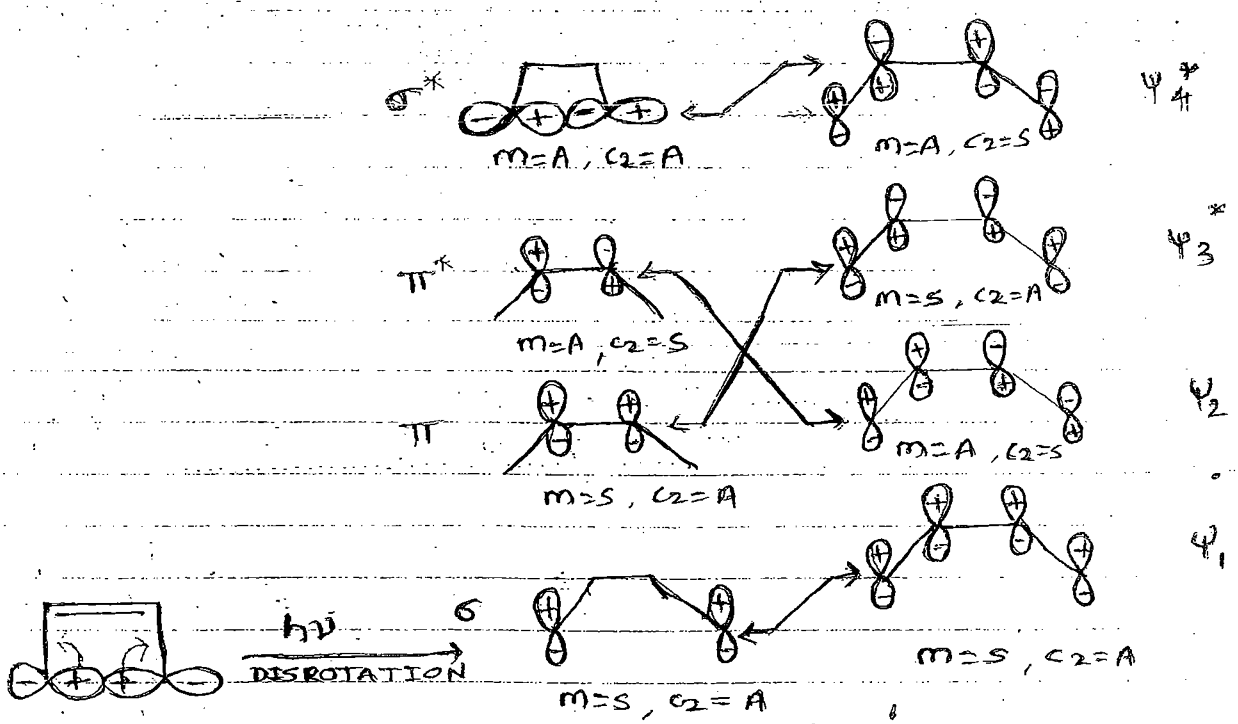
This correlation can also be represented as



The above correlation diagram shows that G.S MO's $\sigma^2 \pi^2$ of cyclobutene correlate with G.S. state MOs $\psi_1^2 \psi_2^2$ of 1,3 - butadiene. Hence transformation of cyclobutene to 1,3 - butadiene under thermal condⁿ by conrotation is symmetry allowed process.

c) Let us analyse transformation of cyclobutene to 1,3-butadiene under photochemical condiation by by dissotation in which plane of symmetry is maintained throughout the transformation.

The correlation diagram can be shown as —



This correlation diagram can also be represented as —

$$\begin{tikzcd}
\sigma^* \; A \arrow[r, leftrightarrow] & \psi_4^* \; A \\
\pi^* \; A \arrow[dr, leftrightarrow] & \psi_3^* \; S \\
\pi \; S \arrow[ur, leftrightarrow] & \psi_2 \; A \\
- \; \sigma \; S \arrow[r, leftrightarrow] & \psi_1 \; S
\end{tikzcd}$$

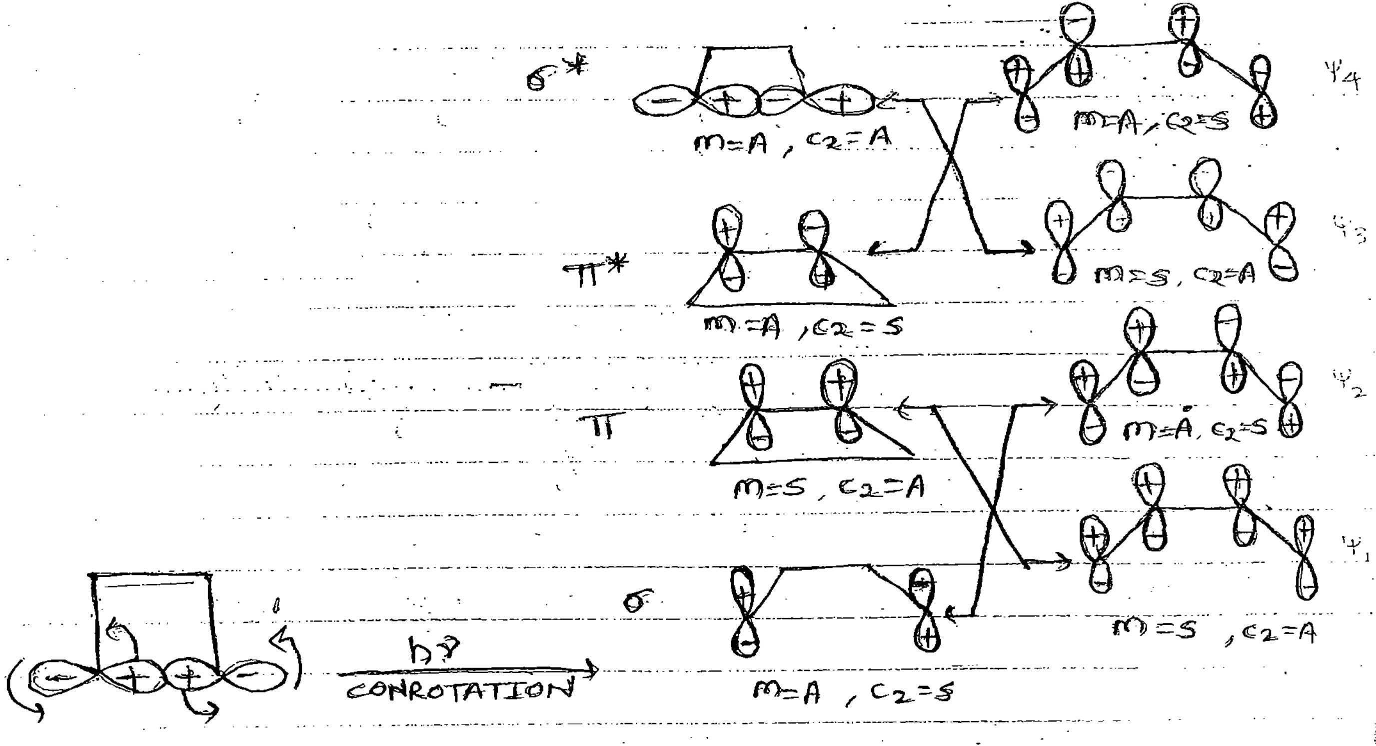
on irradiation with UV rays one electron from π orbital gets promoted to π*. Hence first excited state of cyclobutene becomes $\sigma^2 \pi^1 \pi^{*1}$.

first excited state of cyclobutene $\sigma^2\pi^1\pi^{*1}$ correlate with first excited state of butadiene $\psi_1^2\psi_2^1\psi_3^1$ in their symmetric properties. Hence this transformation under hν condition by disrotation is symmetry allowed process.

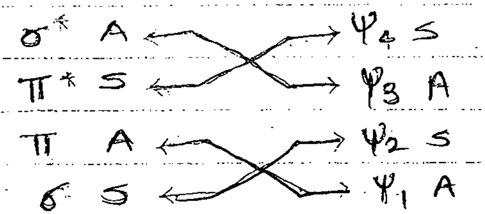
$$\sigma^2\pi^1\pi^{*1} \xrightarrow[\text{DIS}]{\Delta} \psi_1^2\psi_2^1\psi_3^1$$

d] Let us analyse the transformation of cyclobutene to butadiene under photochemical condition in which C_2 axis of symmetry is maintained through out the transformation.

The correlation diagram can be shown —



The correlation can also be represented as



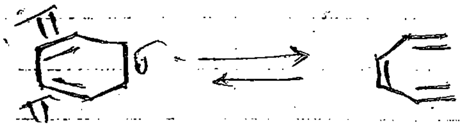
48000
14500
25500

On irradiation with UV rays one electron from π-orbital is promoted to π*. Hence first excited state of cyclobutene becomes $\sigma^2\pi^2\pi^{*1}$. The above correlation diagram shows that first excited state of cyclobutene $\sigma^2\pi^1\pi^{*1}$ correlates with the excited state of butadiene $\psi_1^2\psi_2^1\psi_4$. But ψ_4 is second higher excited state. Hence this interconversion under the photochemical condition by con rotation is symmetry forbidden.

All above are in ~~arg~~ agreement with Woodward - Hofmann selection rule for electrocyclic pericyclic reaction for 4π system.

II] 4π+2 system :→

Corelⁿ as well as pm



Interconversion of cyclohexadiene to 1,3,5-hexatriene is an example of 4π+2 system.

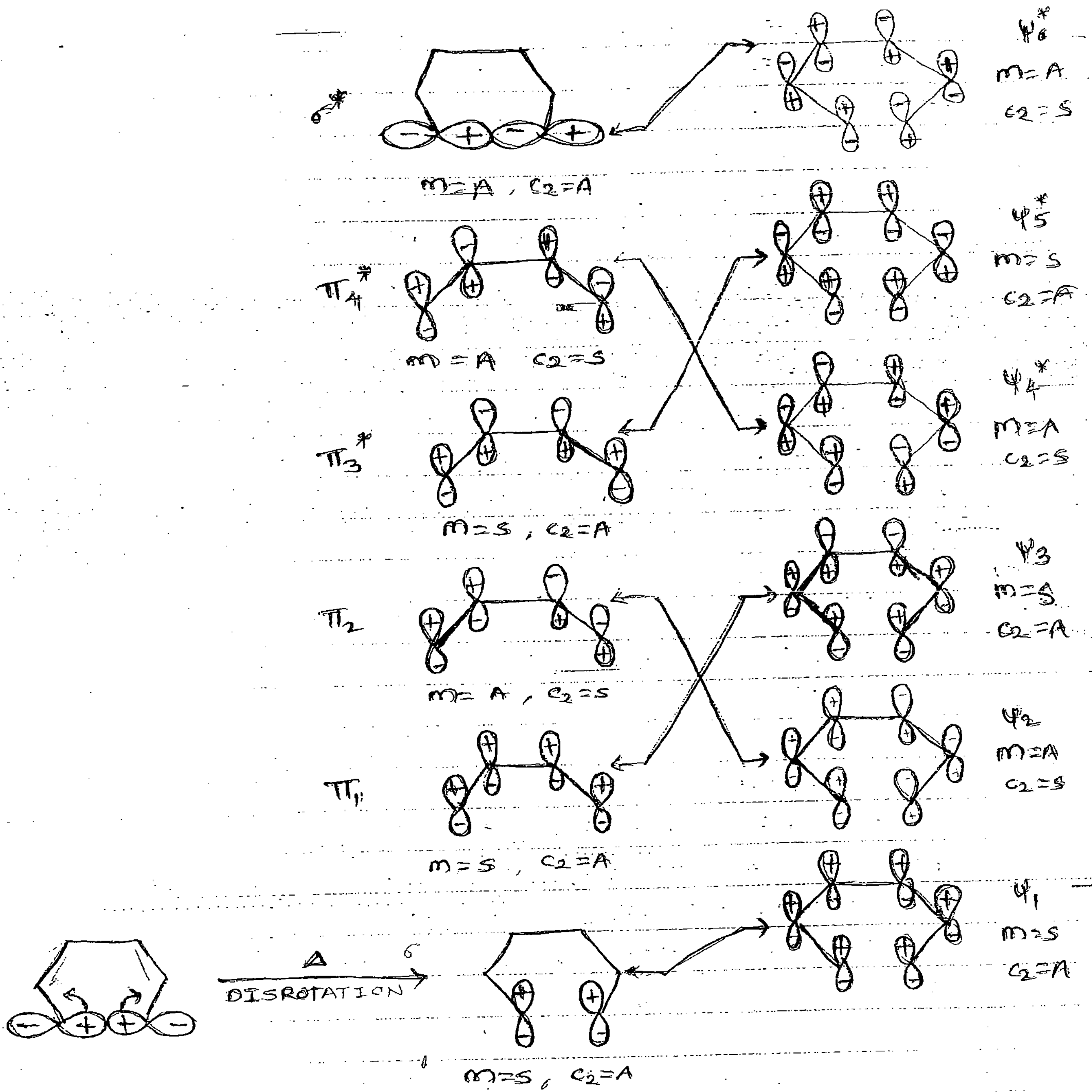
— In this interconversion σ, π_1, π_2 bonding MOs and $\sigma^*\pi_3\pi_4$ antibonding MOs of cyclohexadiene and $\psi_1\psi_2\psi_3$ bonding MOs as well as $\psi_4\psi_5\psi_6$ antibonding MOs of 1,3,5-hexatriene are involved.

a] Let us analyse ring opening (or ring closing) of cyclohexadiene under thermal condiation by disrotation in which plane of symmetry is maintained throughout the transformation.

correlation diagram of symmetry properties of cyclohexadiene and 1,3,5-hexatriene can be represented as —

Dis-rotation (m) plane of symm

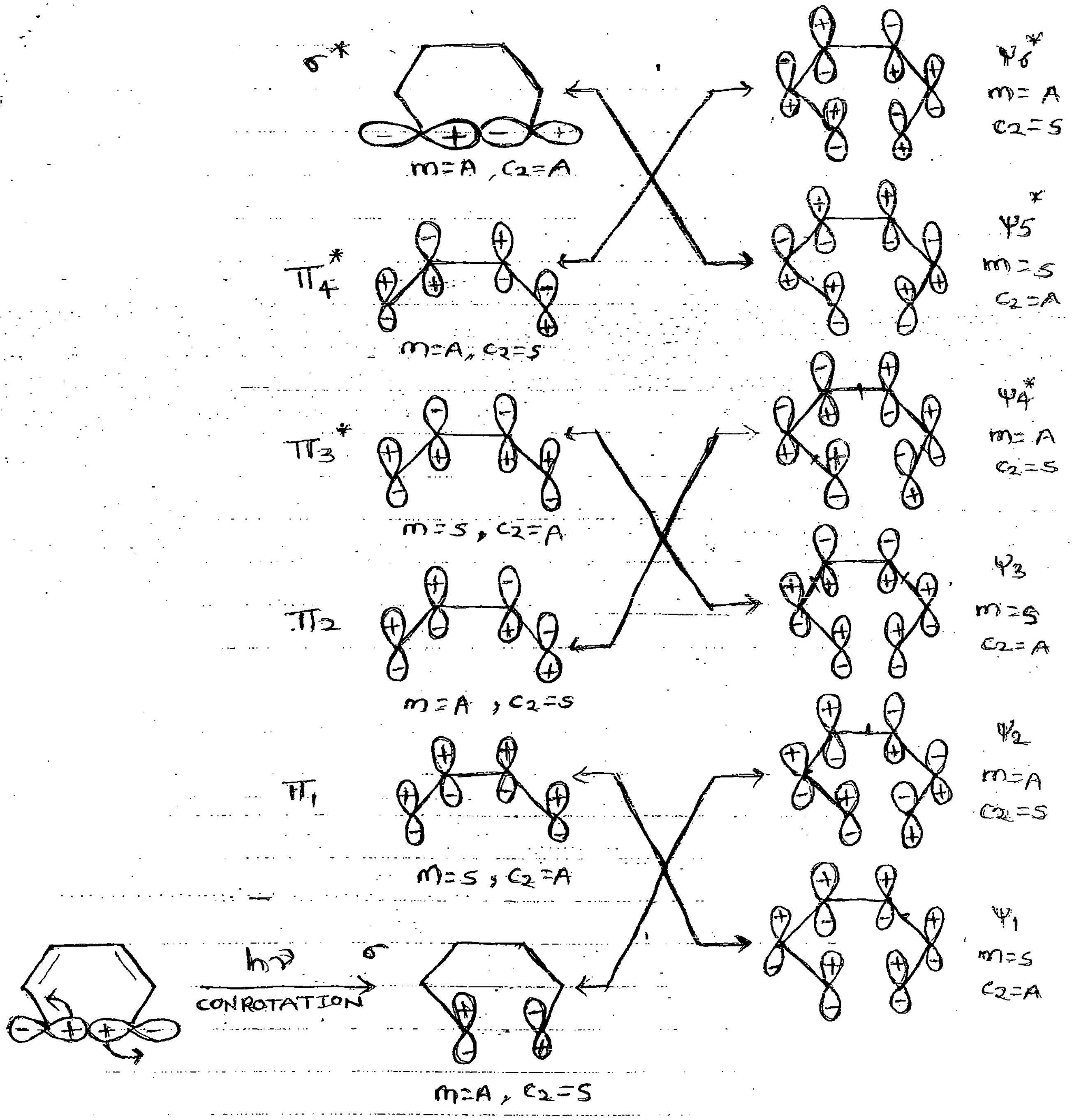
con-rotation (C_2) ~~Pto~~ axis of symm



The above correlation diagram shows that under thermal condiation ground state orbital of cyclohexadiene $\sigma^2\pi_1^2\pi_2^2$ correlates with ground state orbitals of 1,3,5-hexatriene $\psi_1^2\ \psi_2^2\ \psi_3^2$ w.r.t 'm' symmetry. Hence this interconversion under thermal condiation by disrotation is symmetry allowed process.

b] Let us analyse ring opening of cyclohexadiene under photochemical condiation by correlation in which c_2 axis of symmetry is maintained.

The correlation diagram can be shown —

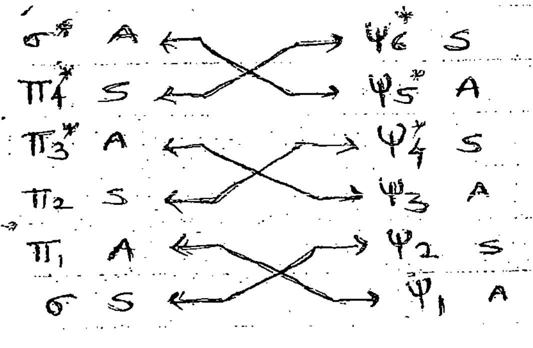


on irradiation with uv rays one electron from π-bonding orbital is promoted to π_3^*. Hence first excited state of cyclohexadiene becomes $\sigma^2\pi_1^2\pi_2^1\pi_3^1$, This first excited state of cyclohexadiene correlate with the first excited state of 1,3,5-hexatriene $\psi_1^2\psi_2^2\psi_3^1\psi_4^1$

$$\sigma^2\pi_1^2\pi_2^1\pi_3^1 \xrightarrow[\text{CONROTATION}]{h\nu} \psi_1^2\psi_2^2\psi_3^1\psi_4^1$$

Hence this interconversion under photochemical condition by conrotation is symmetry allowed process.

This correlation can also be represented as -



The above facts are in agreement with the woodward - Hofmann selection rules for $4\pi+2$ system.

	Δ	hν
4n	con	dis
4n+2	dis	con

	con	dis
T T	T	C
C C	T	C
T C	C	T
C T	C	T

3) Huckel-Mobius Method or Perturbation molecular orbital (PMO) method,

- Another method for quickly predicting whether a given reaction is allowed by examining the cyclic array of orbitals at the transition state of the pericyclic reaction.
- Huckel rule of aromaticity states that a mono-cyclic, planar, conjugated system is aromatic. if it has $(4n+2)\pi$ conjugated or delocalised electrons and consequently stable in ground state.
- similarly monocyclic plannar, conjugated system is anti-aromatic if it has $(4n)\pi$ conjugated or delocalised electrons. this system is unstabl in ground state. However, further calculation shows that these rules are reversed by the presence of a node in the array of atomic orbitals. Thus, system with $(4n+2)\pi e^-$ & a nod is antiaromatic while system with $(4n)\pi e^-$ & a node is aromatic

Thus, system has no node then:

$(4n+2)\pi$ electrons → aromatic → stable in G

$(4n)\pi$ electrons → antiaromatic → unstable in G.S

Similarly, system having a node then

$(4n)\pi e^-$ → aromatic → stable in ground stat

$(4n+2)\pi e^-$ → antiaromatic → unstable in G.S

If system has no node then it is called Huckel system and array is called Huckel array.

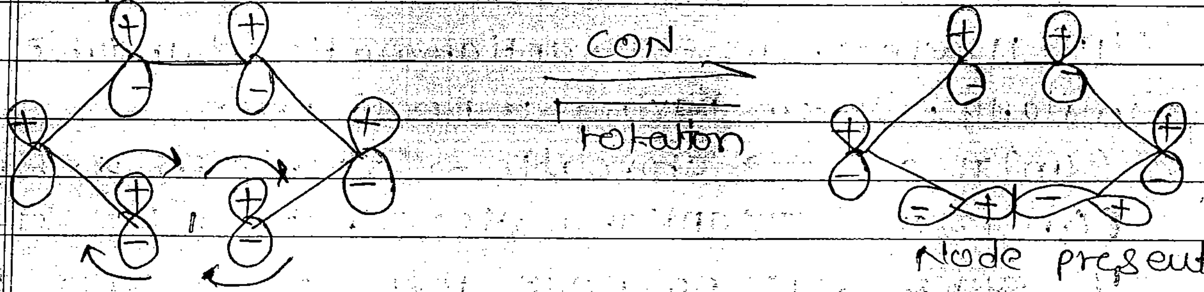
- similarly, if system has node then it is called Mobius system and array is called mobius array.

Application of these rules to pericyclic reactions led to the generalisation that thermal reactions takes place via aromatic transition state (i.e $(4n+2)\pi$ electrons having no node or $(4n)\pi$ electrons having one node]

- whereas Photochemical reaction proceed via antiaromatic transition state. [i.e $(4n)\pi$ e⁻ having no node or $(4n+2)\pi$ electrons having one node.]
- A cyclic transition state is said to be aromatic or iso conjugated with the corresponding aromatic system.
- Pericyclic reactions can be classified as aromatic or antiaromatic based on either Huckel or Mobius system.
- According to the concept of aromatic and antiaromatic of cyclic π-electron system, the predictions for thermal or Photochemical Pericyclic reaction can be summarized.
- Let us consider the following electrocyclic reaction.

① i.e:- 1,3,5-hexatriene ⇌ cyclohexadiene

<u>contotatory motion</u> :→

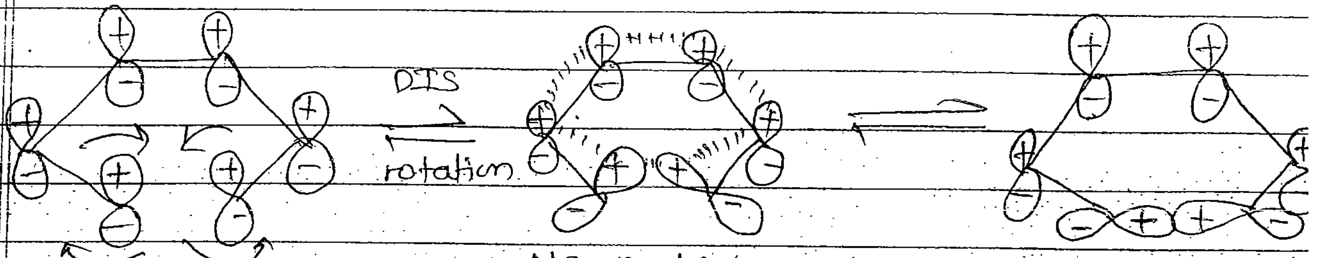


conrotatory ring closure of 1,3,5-hexatriene system

- The number of nodes = 1
- Array of orbital arrangments :- Mobius
- number of π-electrons = 6
- The system is Antiaromatic according to Mobius.

and therfore. , it is photochemically allowed.

Distotatory motion :→



No node in T.S

~~an~~ distotatory ring closure of 1,3,5 hexatriene system.

The number of node = 0

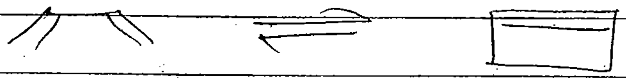
Array of orbital arrangement : Huckel.

number of π electrons = 6

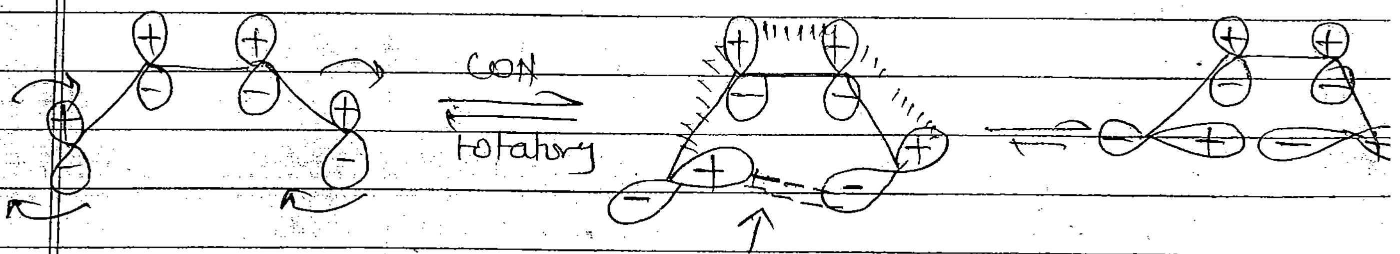
This system is aromatic according to Huckel and therefore, it is thermally allowed

② similarly for,

1,3-butadiene ⇌ cyclobutene



conrotatory motion :→



Note in T.S.

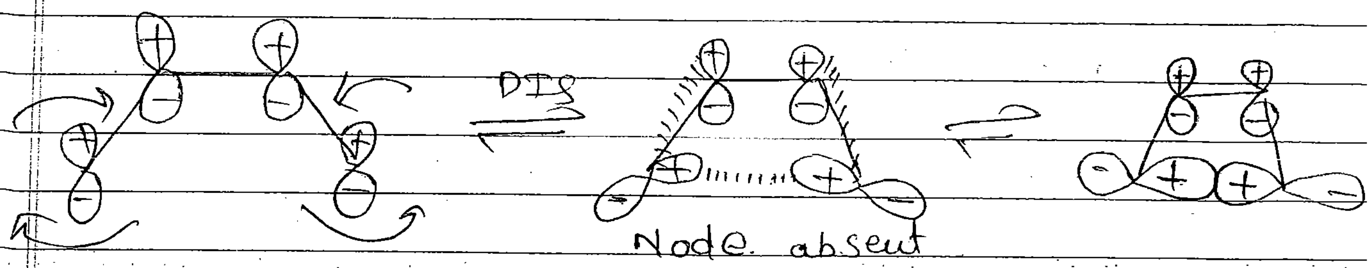
conrotatory ring closure of 1,3-butadien system.

The no. of nodes : 1

Array of orbital arrangements : Mobius.

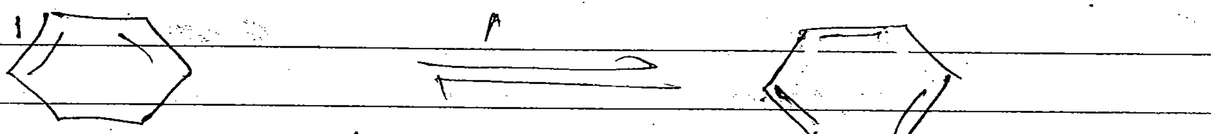
Number of π electrons = 4.

The system is aromatic according to Mobius and therefore. it is thermally allowed disrotatory motion :→



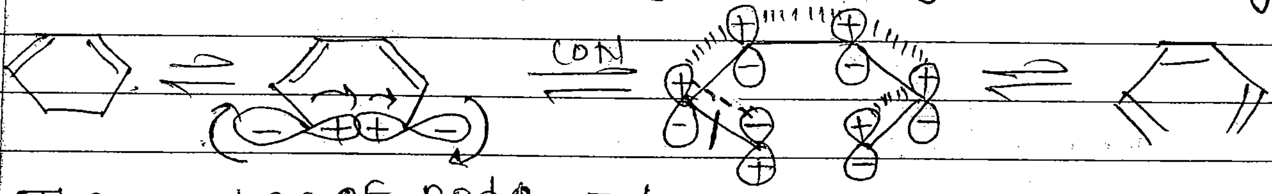
disrotatory ring closure of 1,3-butadiene system
The number of node = 0
Array of orbital arrangement : Huckel , number of π electrons = 4.
The system is antiaromatic according to Huckel and therefore , Photochemically allowed.

③



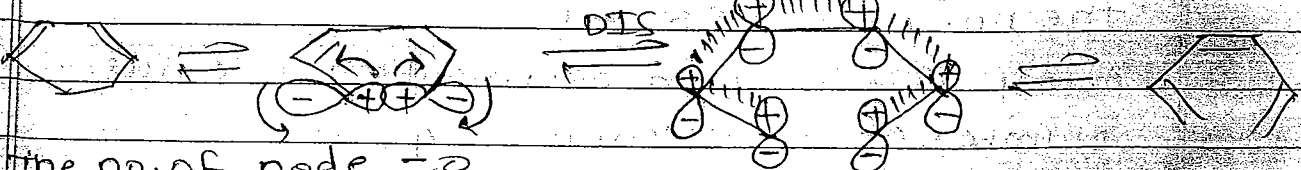
1,3-cyclohexadiene 1,3,5-Hexatriene

conrotatory motion :→
conrotatory ring opening of 1,3-cyclohexadiene system



The number of node = 1
Array of orbital arrangment :: Mobius ..
number of π electrons = 6.
The system is Antiaromatic according to Mobius and therefore , Photochemically allowed

Disrotatory motion : →

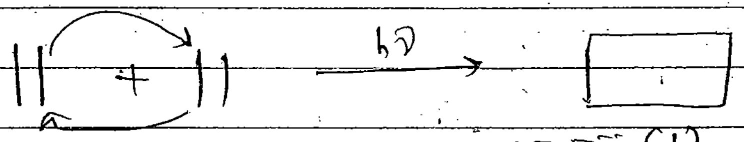


The no. of node = 0 No node
Array of orbital = Huckel

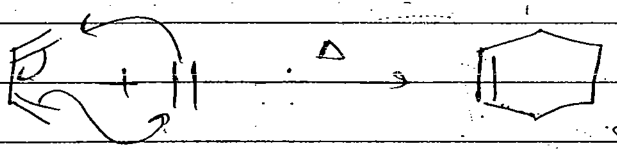
Cycloaddition Reaction :→

Introduction :→

- A cycloaddition is a reaction in which two unsaturated molecules undergo an addition reaction to yield a cyclic product.
- In this reaction there is loss of two π bonds of the reactants and gain of two σ bond in the product;



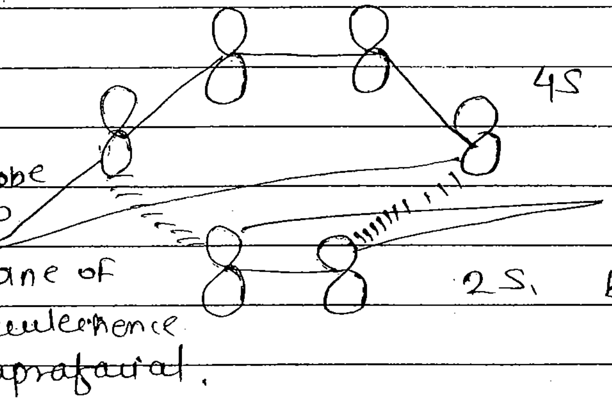
loss of two π bond & gain of two σ bonds.
---- (1)



loss of two π bonds & gain of two σ bonds.
---- (2)

The reaction in eq^n (1) is a [2+2] cycloaddition reaction because the reaction involves two electrons from one reacting component & also two electrom from the other. The reaction in eq^n (2) is a [4n+2π] cycload

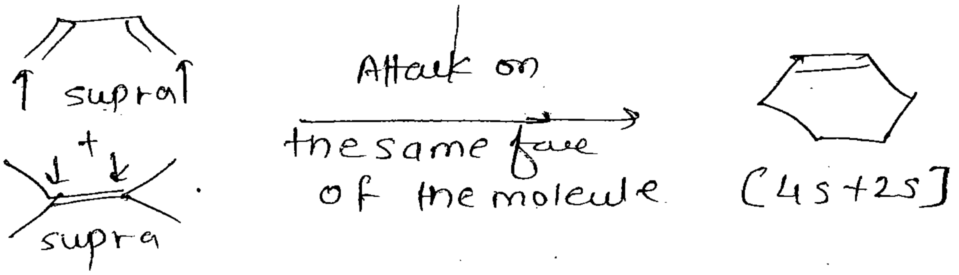
- The stereochemical mode is given by a subscript 's' or 'a' which indicates whether the addition occurs in a supra or antara mode on each unit.
- If reaction occurs across the same face of π system the reaction is said to be suprafacial with respect to that π system, The suprafacial add^n is nothing more than a syn add^n.



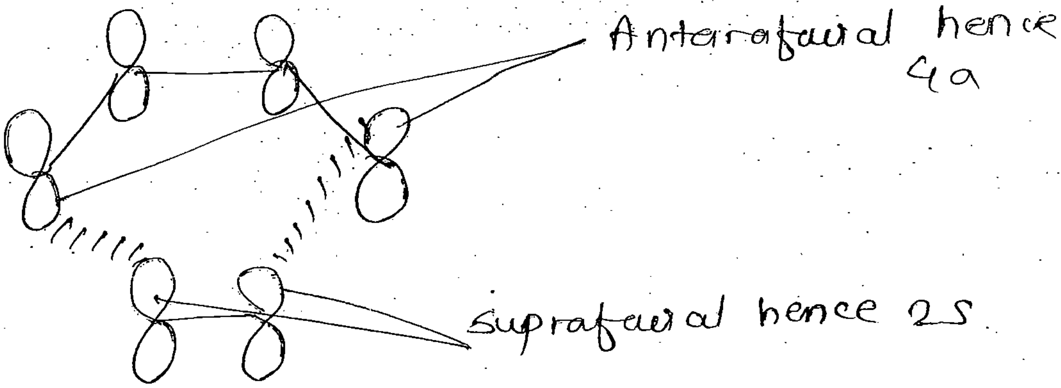
both lobe are below the plane of moleculehence suprafacial.

both lobes are above the plane of the molecule or both lobes are in same Plane, hence suprafacial

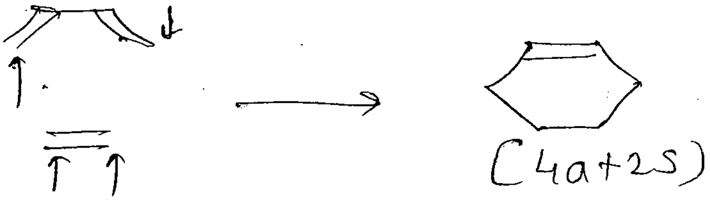
This add^n reaction is thus [4s+2s] cycloadd^n rea^n.
This can also represented as follows.



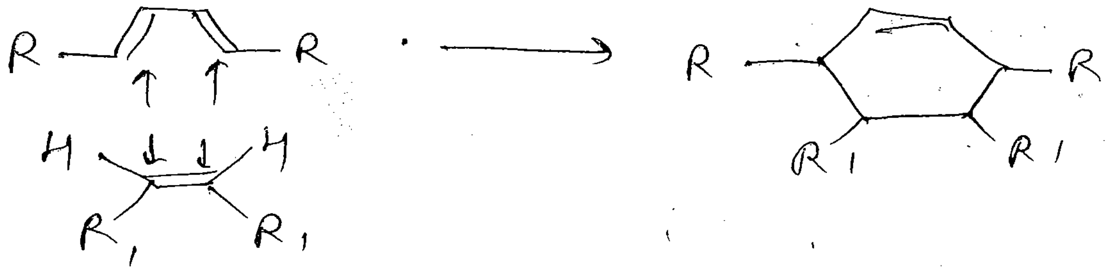
If the reaction bridges opposite faces of a π system ~~It~~ is said to be antarafacial. An antarafacial add^n is just an anti addition



This mode of add^n rea^n is thus [4a+2s] cycloadd^n rea^n
this can be represented as



Almost all cycloaddition reactions are supra-facial on both components.



Theory of cycloaddition reaction : FMO method
for a cycloaddition between two components to occur, there must be bonding overlap between the p-orbitals at the terminal carbons at each π electron system.

- overlap can occur between Ground state HOMO o one component and Ground state LUMO of another component under thermal condition
- and overlap can occur between first excited stat HOMO of one component and Ground state LU under Photochemical condition.

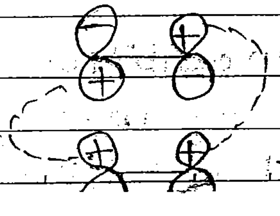
I) [2+2] cycloaddition reactions :→

a) Thermal induced [2+2] cycloaddition reaction :→

under thermal condition ψ_1 represent HOMO of one ethylene molecule. LUMO of another ethylen molecule under thermal condition is represente by ψ_2

- overlapping betn HOMO of one ethylene molecu (ψ_1) and LUMO of another ethylene molecule takes place by supra-antra process which is symmetrically forbidden.

Hence cycloaddition reaction betn two ethylene molecule under thermal condition is not possible

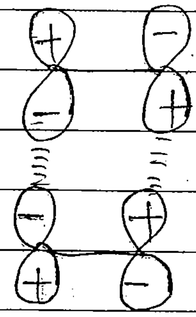

→ ψ_2 LUMO of one molecule, C_2 symmet
→ ψ_1 HOMO of other mol., m symmet

For bonding, the phase of the overlapping must be same. Hence thermally induced [2+2] cycloaddition is said to a symmetry Forbidden

B) Photo-induced [2+2] cycloaddition :→

- under photochemical condition one electron of ψ_1 of one ethylene molecule is promoted to ψ_2.

Hence under photochemical condition ψ_2 become HOMO and ψ_2 is LUMO of another molecule

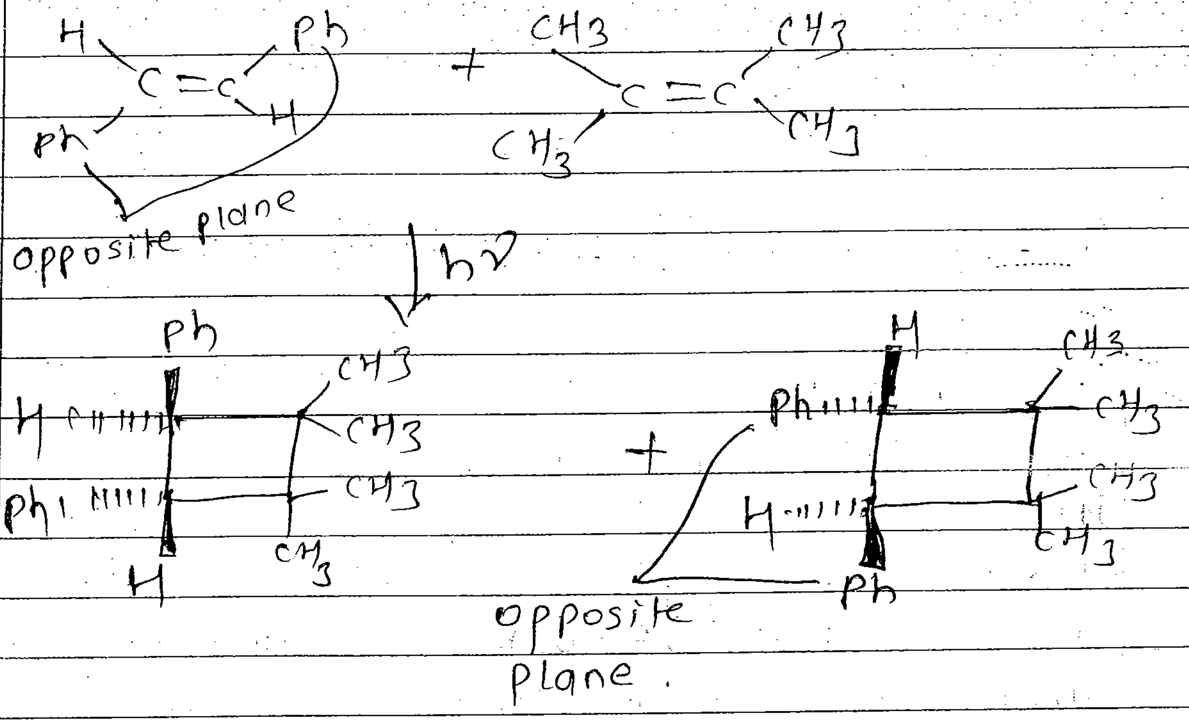


- for cycloaddition reaction both HOMO & LUMO should have same symmetry ∴
- overlapping bet^n HOMO of one ethylene molecule and LUMO of another ethylene molecule takes place by supra - supra process which is symmetrically allowed.
- Hence cycloaddition rea^n bet^n two ethylene molecule takes place under photochemical condition.

- Hence for (2+2) system cycloaddition rea^n under thermal cond^n is supra-supra symmetry Forbidden & under photochemical rea^n ..

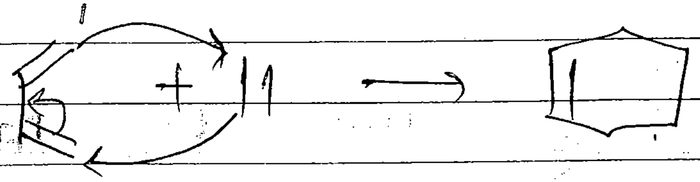
Stereochemistry :→

Stereochemical integrity is maintained in cyclo -addition reaction because. the reaⁿ is concerte



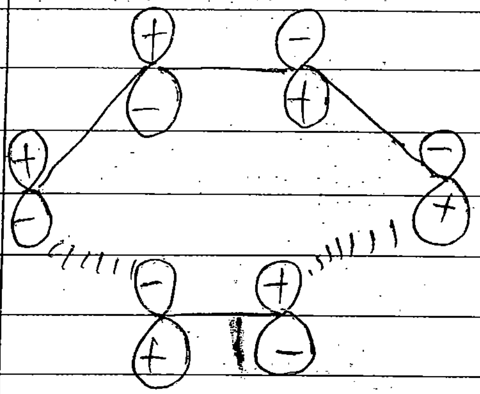
II) [4+2] cycloaddition reaction :→(diel's-Alder

The best example of this type is diels -Alder reaction bet^n 1,3-butadiene (diene) and ethylene (dienophile) to form cyclohexan (adduct).



a) under thermal condition :→

under thermal condition HOMO of 1,3 butadien can be represented by ψ_2 while LUMO of ethylene can be represented by π_2 overlaping betn these MOs is supra-supra



HOMO ψ_2, C_2 symmetry

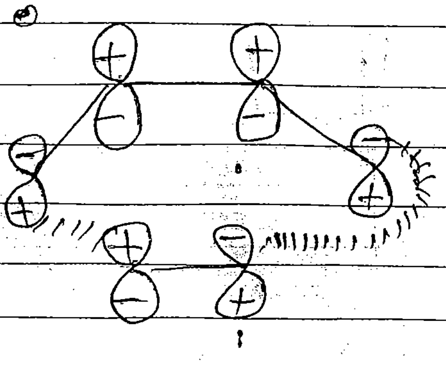
LUMO π_2 C_2 symmetry

for cycloaddition reaⁿ both Homo & Lumo should have same symmetry, Hom & Lumo have same symmetry hence cycloaddition reaction betⁿ 1,3-butadiene and ethylene under thermal condition is symmetry allowed process.

b] under photochemical condition :→

on iradiation with U.V light one e⁻ excite from ψ_2 of 1,3 butadiene to ψ_3.

- Hence ψ_3 becomes Homo & Lumo of ethylene can be represented by π_2.



HOMO ~~ψ3~~ ψ3 ~~m~~ symmetry

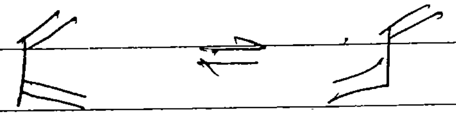
LUMO ~~of~~ π_2 ~~m~~ C_2 symmetry

overlapping betn these two Mos is supra-an
hence cycloaddition rean betn 1,3 - butadiene
and ethylene under photochemical condition
is symmetry forbidden condition.

No. of e⁻	Mode of activation	Allowed Stereoche
4nπ(2+2)	Photochemical	supra-supra
(4n+2)π	Thermal	supra-supr

stereochemistry of the Diels-Alder rean.

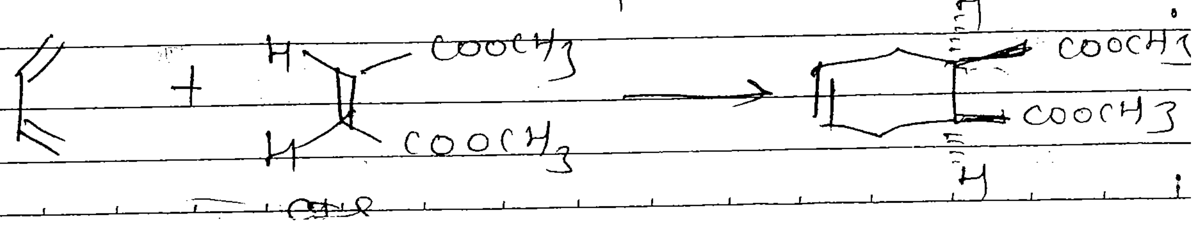
a] The diene must be in the conformation (S-c that permits the end of the conjugated syste to react the doubly bonded carbon of the dienophile.

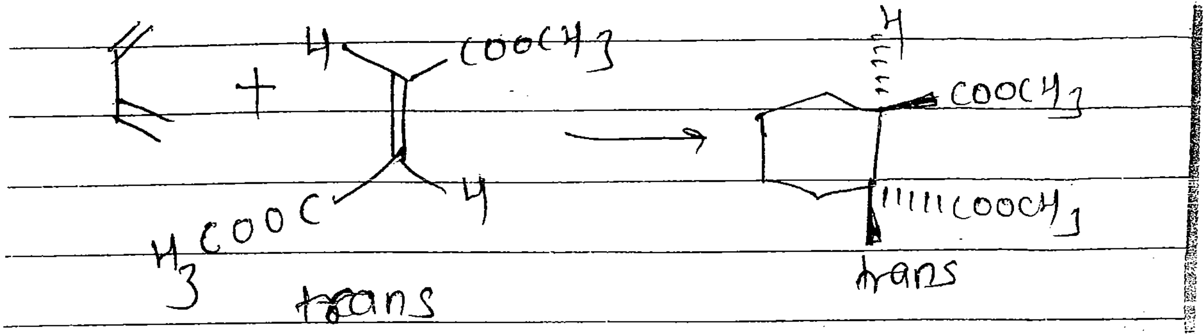


S-cis S-Trans

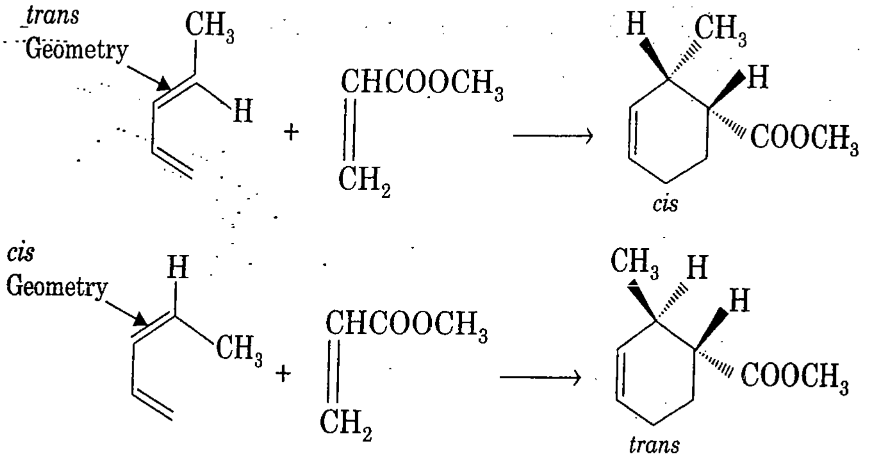
ⓑ stereochemistry of the dienophile :-

- The Diels-Alder rean is stereospecific.
- Substituents that are cis in the dienophile remain cis in product.
- Substituents that are trans in the dienophi remain trans in the product.

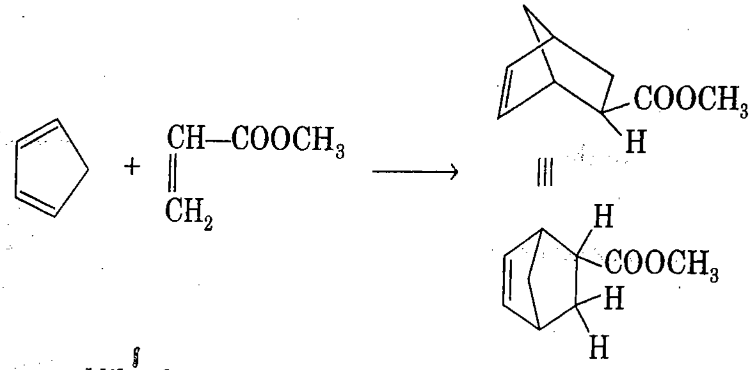




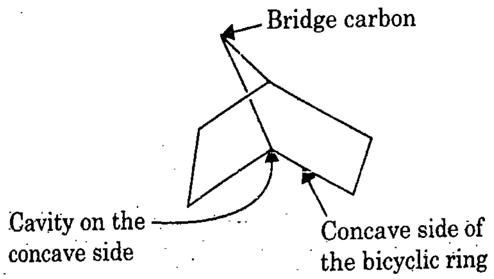
We also need to consider the stereochemistry in the product of the substituents on the diene relative to those on the dienophile. If *trans* 1, 3-pentadiene reacts with methyl propenoate we know that in the product the methyl and ester groups could be either *cis* or *trans*. It is found, in fact, that the *cis* product is formed from *trans* diene and the *trans* product is formed from *cis* diene.

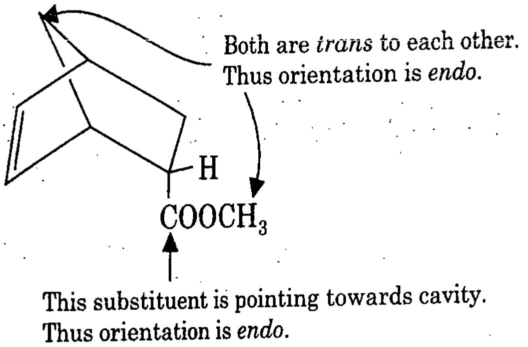


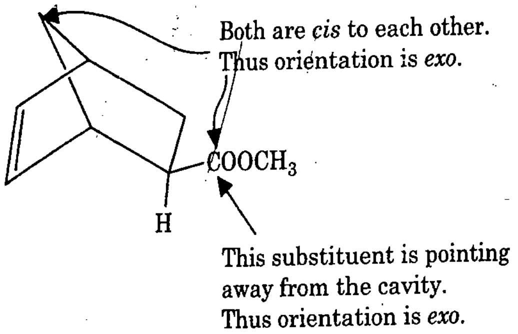
(*iii*) ***Endo*** **and** ***Exo*** **stereochemistry:** The Diels-Alder reaction will produce a bicyclic ring system if the diene is monocyclic. Cyclic dienes are particularly reactive in Diels-Alder reaction because the two double bonds are held in an *s-cis* conformation in five or six-membered rings. This can be seen in the reaction of 1, 3-cyclopentadiene with methyl propenoate.



When a compound like this is synthesised, we introduce another stereochemical question. What will be the relative stereochemistry of the methylene bridge and the substituent (in this case $COOCH_3$)? Will they be *cis* or *trans* to one another? Asking these questions is the same as asking whether the substituent will be *endo* or *exo* in the product. An orientation is said to be *endo* meaning that the substituent is *trans* to the bridge carbon or substituent projects into the cavity on the concave side of the bicyclic ring. Similarly, an orientation is said to be *exo* meaning that the substituent is *cis* to the bridge carbon or substituent projects out of the cavity on the concave side of the bicyclic ring.

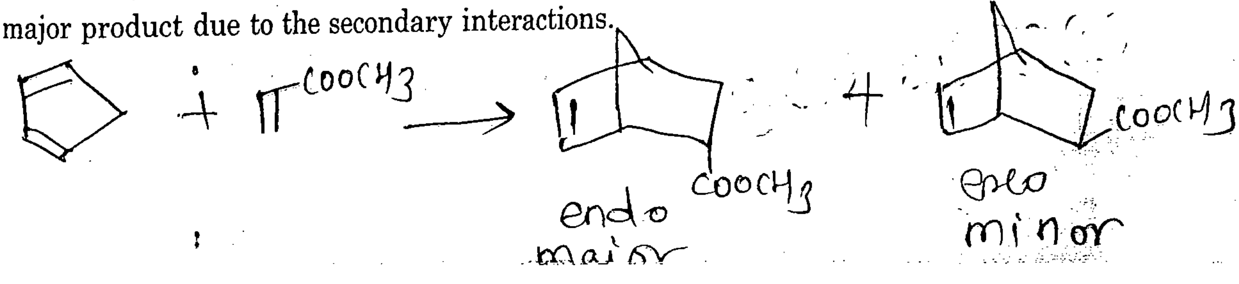






(The *exo* product is expected to be more stable than the *endo* product for steric reasons. In *exo* product, the *exo* substituent points away from the more congested part, *i.e.*, bicyclic ring but in *endo* product the *endo* substituent points towards the more congested part. Thus steric repulsion in *endo* is more than in *exo*. Due to this reason, *exo* is expected to be more stable than *endo*.)

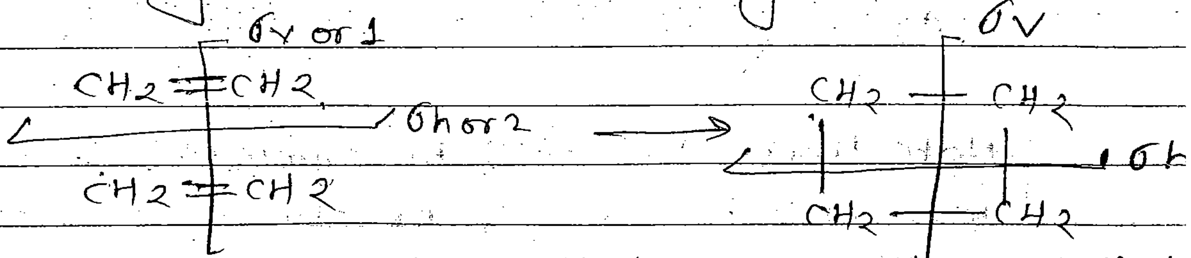
But in practice it has been found that if the diene has a π bond in its electron-withdrawing group then the *endo* product is more stable than the expected *exo* product. This stereochemical preference for the *endo* position is often called the *endo rule*. The reaction of 1, 3-butadiene with methyl propenoate produces three times as much as *endo* as *exo* product. Endo product is major product due to the secondary interactions.



correlation diagram method :→

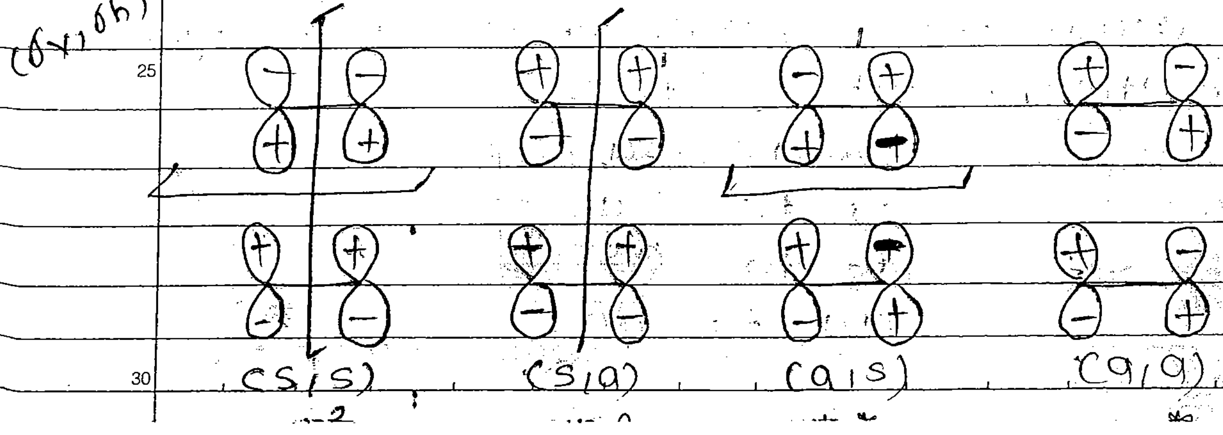
I) (2+2) π system :→

orbital symmetry arguments make useful predictions about Concerted cycloaddition reaction Whic is suprafacial - suprafacial. Consider the [$\pi 2s + \pi$ cycloaddition of ethylene molecules in parallel planes approaching each other Vertically.

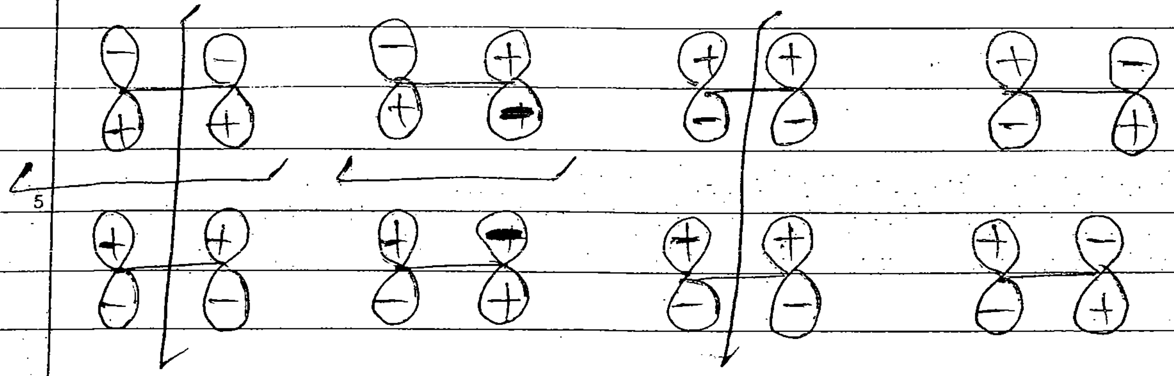


two ethylene molecules approching each other vertical & suprafacial - suprafacial,

This system Contains Vertical & horizontal plane of Symmetry (i.e. mirror plane of symmetry) denoted by σv (or 1) and σh (or 2) which are useful in characterising the orbitals. In the transformation of ethylene molecules to cyclobutane we are mainly Concerned with the four π orbitals of two ethylene molecules & the four σ orbitals of cyclobutane. Let us first take the σv & σh in two ethylene molecules.



Now Let us take the σ_v & σ_h in cyclobutane



(s,s) (a,s) (s,a) (a,a)

σ_1^2 σ_2^2 σ_3^* …… σ_4^* (σ_v, σ_h)

Note that more will be symmetry in the system less will be energy of the system for π as well as σ orbital.

Energy of π system is as follows in increasing order.

ss sa as aa

Energy of σ system is as follows in increasing order.

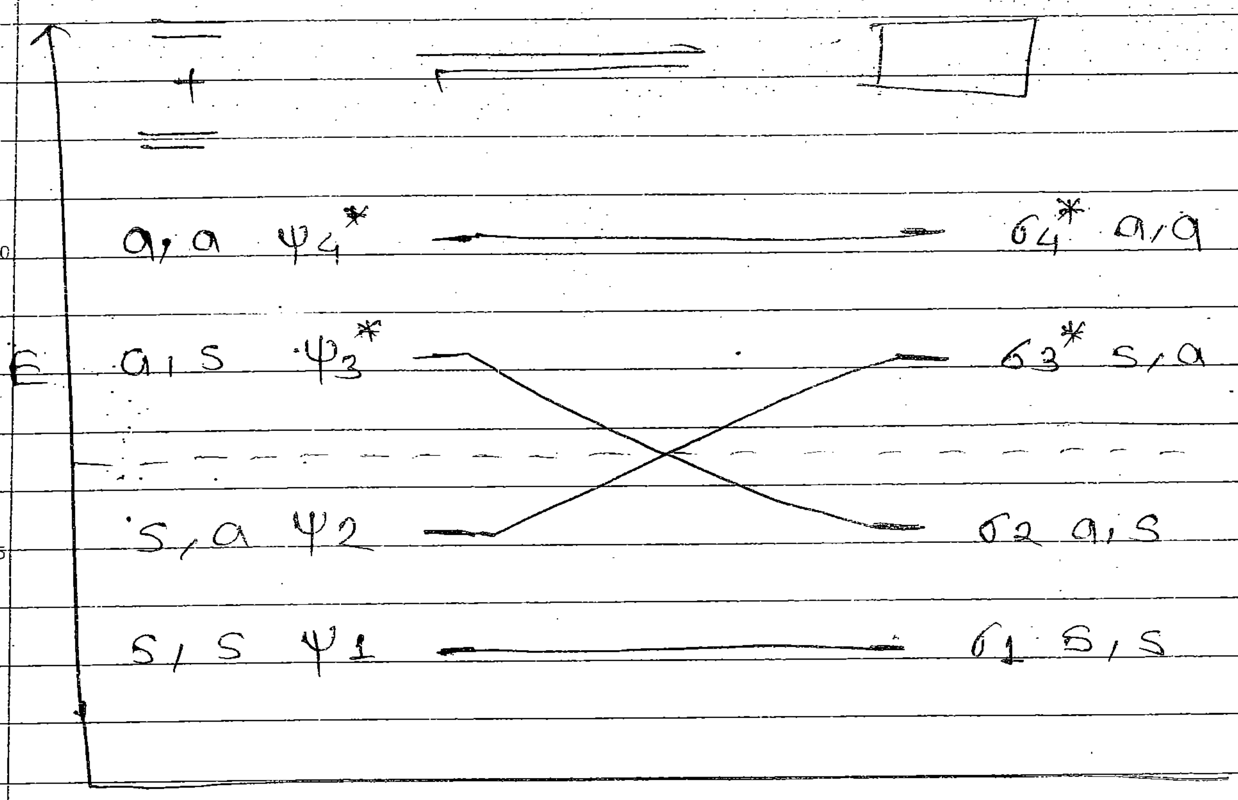
ss as sa aa

~~Lowest energy orbital.~~

We can now complete by correlating energy levels feeding the orbitals in the starting material into orbitals of the same symmetry in the product ss to ss

sa to sa
sa to sa
as to as
aa to aa

on the basis of the above information, a correlation diggram may be drawn in which the levels of like symmetry are connected by lines.



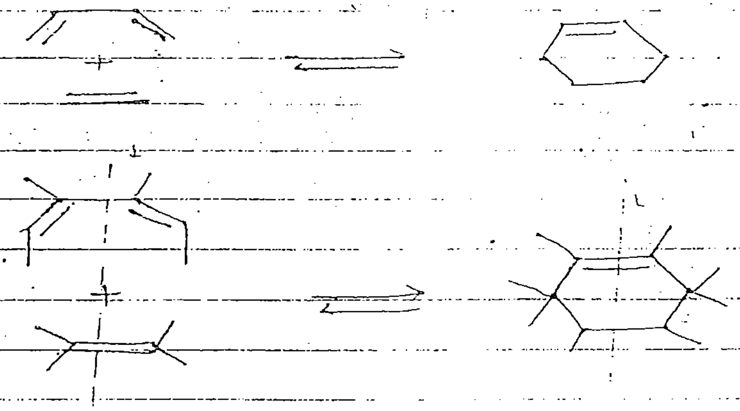
correlation dia. for cycloadd^n of ethylene into cyclobutane

The correlation dia. shows that ground state of MO's of two ethylene molecules $\pi_1^2 \pi_2^2$ correlate with $\sigma_1^2 \sigma_1^*$ but σ_1^* is the first excited state. Hence cycloadd^n reaction between two ethylene molecule is symmetry forbidden.

under Photochemical condition one electron from π_2 get promoted to π_1^*. Hence first excited state of two ethylene molecule becomes $\pi_1^2 \pi_2^1, \pi_1^{*1}$. The above correlation dia. shows :

that this first excited state $\pi_1^2, \pi_2^1, \pi_1^{*1}$ of two ethylene molecules correlate with the first excited state of cyclobutane $\sigma_1^2, \sigma_2^1, \sigma_3^{*1}$. Hence the cycloaddiation reaⁿ betⁿ two ethylene molecules under photochemical condiation is symmetry allowed. These facts are in agreement with the Woodward - Hofmann selection rule for (2+2)π system cycloaddition reaction.

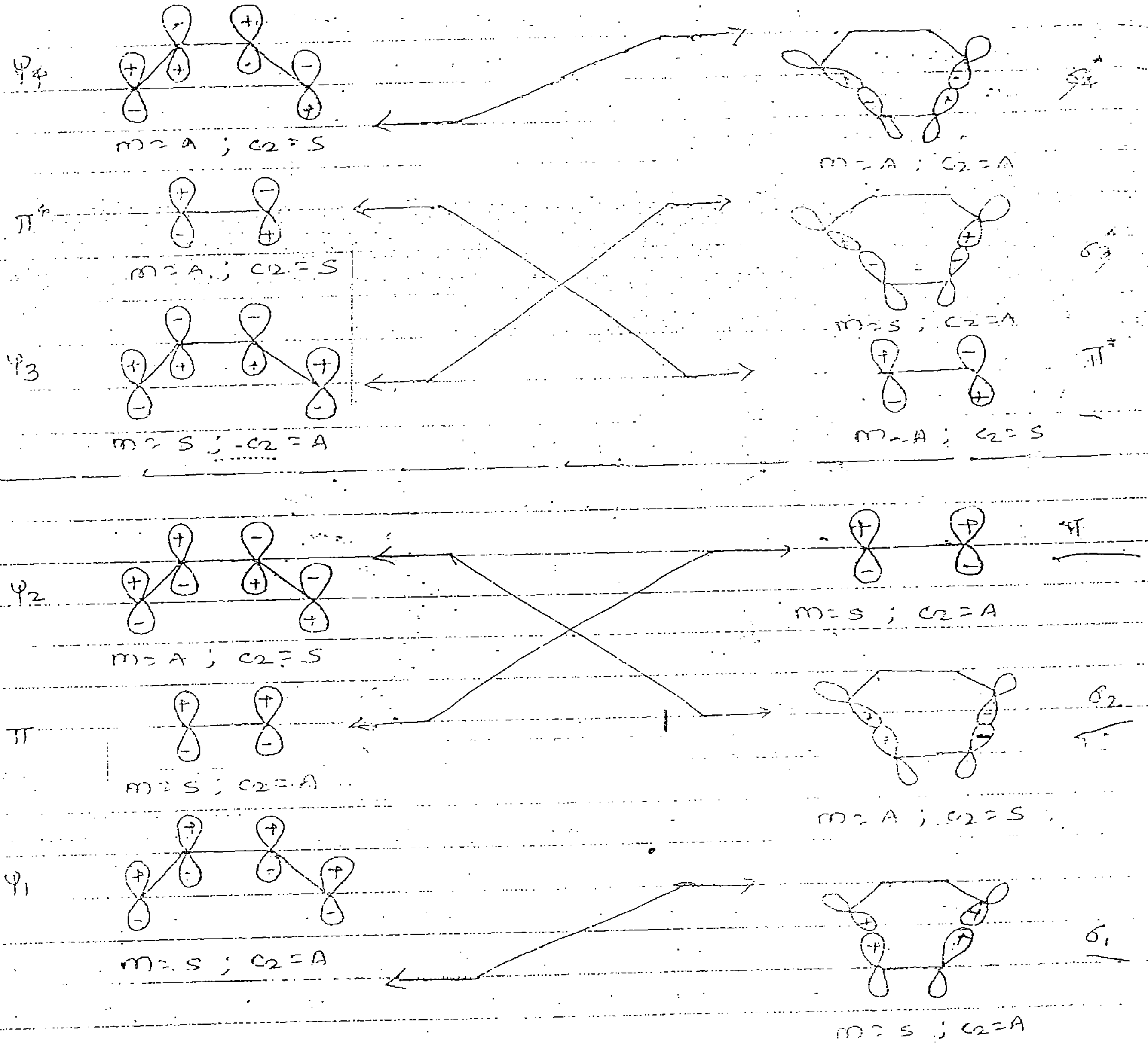
II] (4+2) π system :→



a] Under Thermal condiation :→

In this cycloaddiation reaⁿ, three π ground state orbitals (2π ground state orbitals of 1,3 buta-diene + one π ground state orbital of ethylene) of reactants (1,3 butadiene + ethylene) and there respective antibonding π* orbitals, two σ ground state orbitals and one π orbital of cyclohexene (product) and there respective antibonding orbitals are involved. For correlation diagram vertical plane of symmetry of these MOs is considered, correlation diagram can be represented as follows :-

Diagram shows that ground state orbitals ($\psi_1^2 \pi^2 \psi_2^2$) of 1,3 butadiene & ethylene correlate with ground state orbitals ($\sigma_1^2 \sigma_2^2 \pi_3^2$) of cyclohexene. Hence under thermal condition this addition reaⁿ is symmetry allowed. It is in agreement with the Woodward - Hoffmann selection rule.



$$\psi_1^2 \pi^2 \psi_2^2 \longrightarrow \sigma_1^2 \sigma_2^2 \pi^2$$

b] Under photochemical condition →

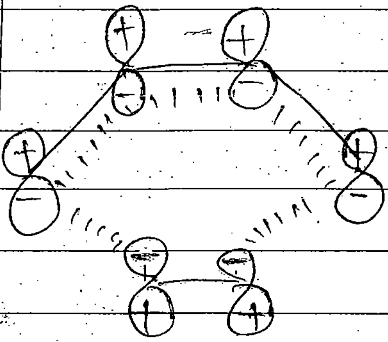
On the other hand on irradiation with UV light, one electron from ψ_2 gets promoted to ψ_3. Hence first excited state of reactants becomes $\psi_1^2 \pi^2 \psi_2^1 \psi_3^1$ which does not correlate with first excited state of product i.e. $\sigma_1^2, \sigma_2^2 \pi^1, \pi^{*1}$

$\psi_1^2 \pi^2 \psi_2^1 \psi_3^1 \longrightarrow$ ~~$\sigma_2^2 \pi^1$~~ $\sigma_1^2\ \sigma_2^2\ \pi\ \sigma_3^*$

Hence under photochemical condition, this condition reaction is symmetry forbidden.

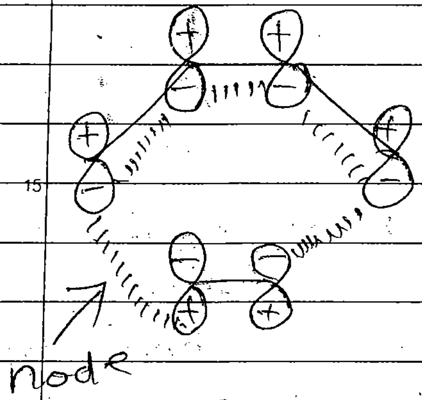
II) 4+2 cycloaddition : →

S-S : →



The no. of node = 0
Array of orbital arrangment = Hucke
no. of π e⁻ = 6
The system is Aromatic accordi
to Huckel & therfore therm
-ally allowed

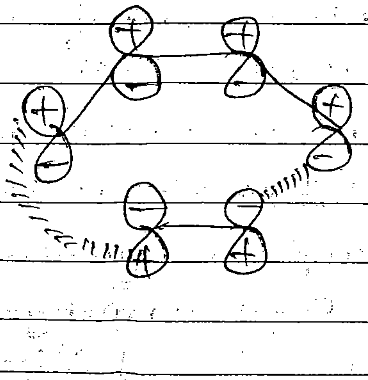
S-a : →



The no. of node = 1
Array of orbital arrangment - Mobiu
no. of π e⁻ - 6
The system is Antiaromatic accordi
to Mobius & therefore Photoche
-mically allowed

a-s : →
simillarly a-s is Mobius antiaromatic therefore
photochemically allowed

a-a

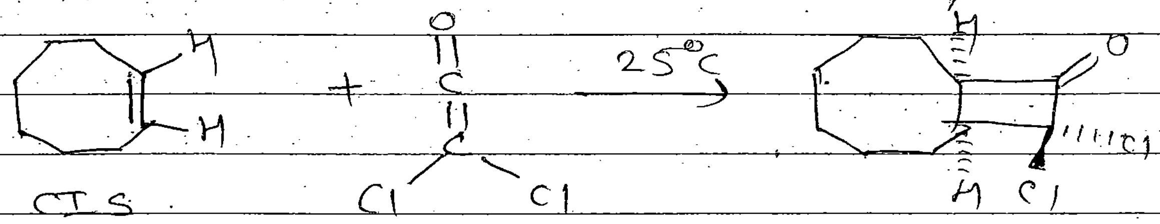


The no. of node = 0
Array of orbital arrangment = Huckel
no. of π e⁻ = 6
The system is Aromatic according
to Huckel & therefore thermally
allowed

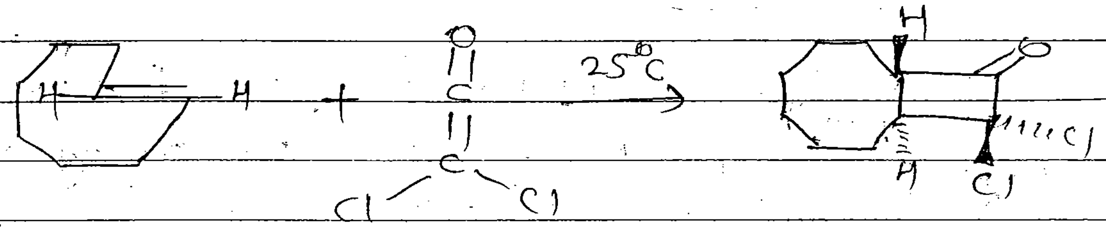
[2+2] cycloaddition of Ketene :→

- Let us first take some addition of Ketene with alkene.

The reaction is syn addition and geometry of reactant is maintained in the product.



Both H' are cis



H' are trans.

Both hydrogens are trans

In the give two examples stereochemistry of reactant is maintained in the product. These two reactions are pericyclic [2+2] cycloaddition reactions and thermally allowed reactions.

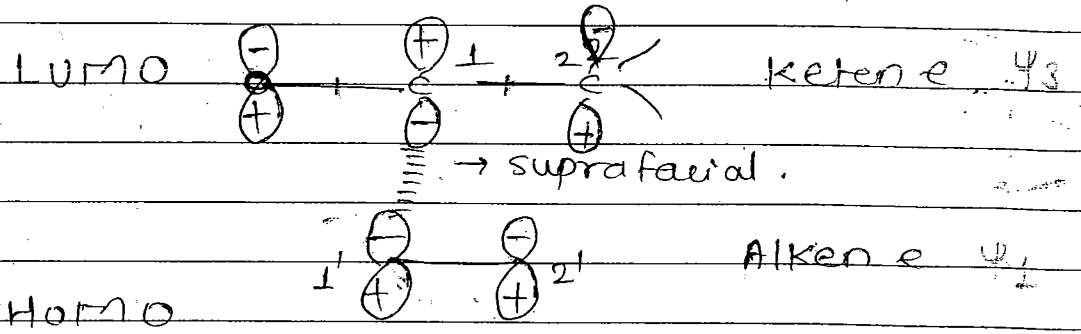
- We know that [2+2] cycloaddition is photochemical reaction and supra-suprafacial.

- If reaction is thermally allowed then reaction should be suprafacial - antarafacial reaction.

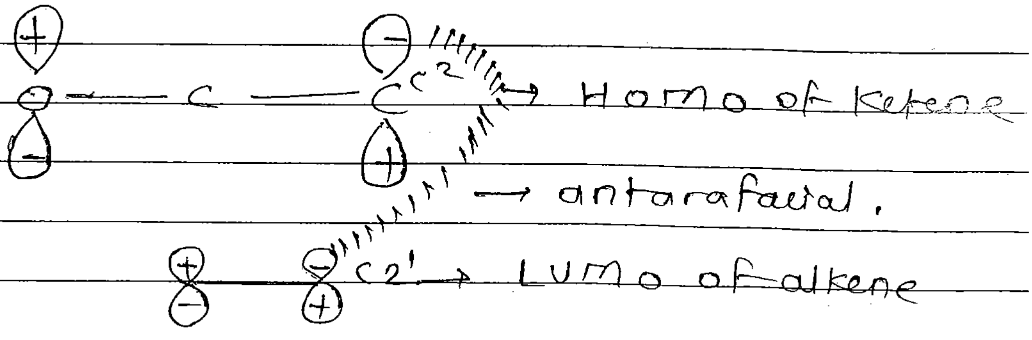
- The explaination for this is that it is suggested that two molecules approach each other at right angles for overlapping in an antarafacial sense of the ketene.

FMO method for [2+2] ketene cycloaddition :-

The FMO treatment shows that the bond formation between C-1 & C-1' develops mainly from the interaction of the LUMO of ketene (π^* of C=O) and HOMO of alkene. and the bond between C2 & C2' develops mainly from the interaction of HOMO ketene (ψ_2) and LUMO of the alkene.

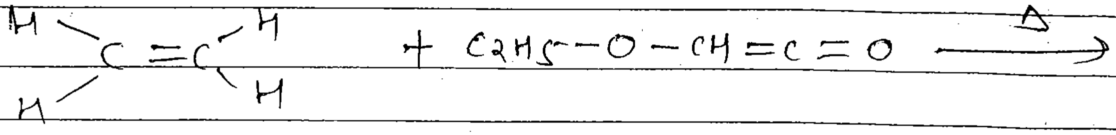


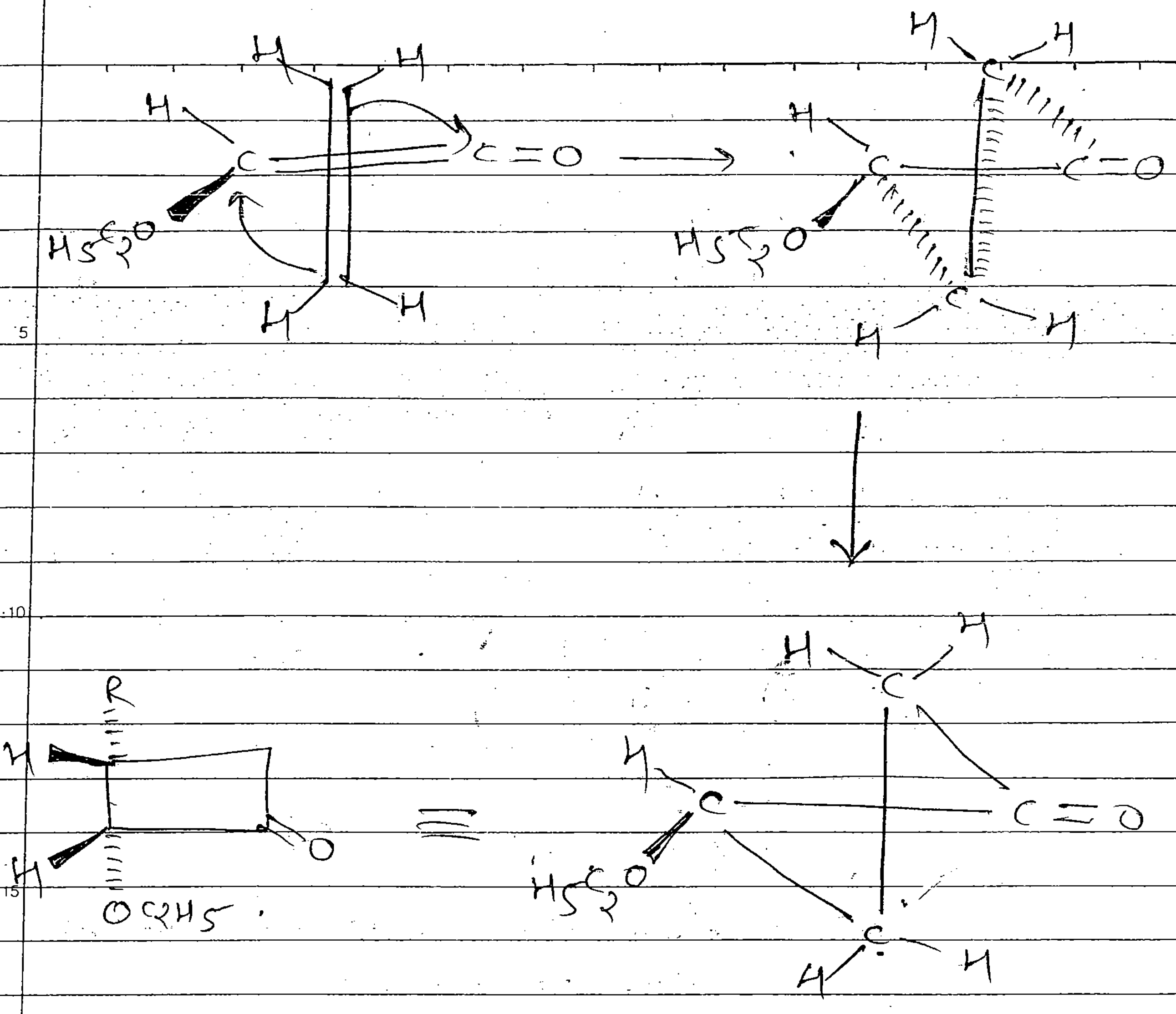
Bond formation betn C-1 of ketene & C-1' of alkene.



Bond formation between C-2 of ketene & C-2' of alkene.

The reaction can be represented as follows




H
H
H
C
C=O
H₅C₂O
H
H
H
H
H
C
C–O
H₅C₂O
C
H
H
H
H
C
H
C
C=O
H₅C₂O
C
H
H
≡
R
H
H
O
OC₂H₅