Pericyclic Reaction
(part 2)

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Pericyclic reaction:

- Concerted (This means that all the electron reorganization takes place in a single step. Therefore, there is one transition state and no intermediate)
- cyclic transition state of breaking and forming bonds
- no electrophiles, nucleophiles, or radicals
- very stereospecific
- energy supplied by heat, Δ, thermolysis or pyrolysis or light, hν, photolysis
- In general, not catalyzed by Lewis acid

The configuration of the product formed in a pericyclic reaction depends on:

- ✓ The configuration of the reactant
- ✓ The number of conjugated double bonds or pairs of electrons in the reacting system
- ✓ The reaction condition i.e whether the reaction is a thermal reaction or a photochemical reaction

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A pericyclic reaction is a reaction in which bondsare formed or broken at the termini of one or moreconjugated π systems

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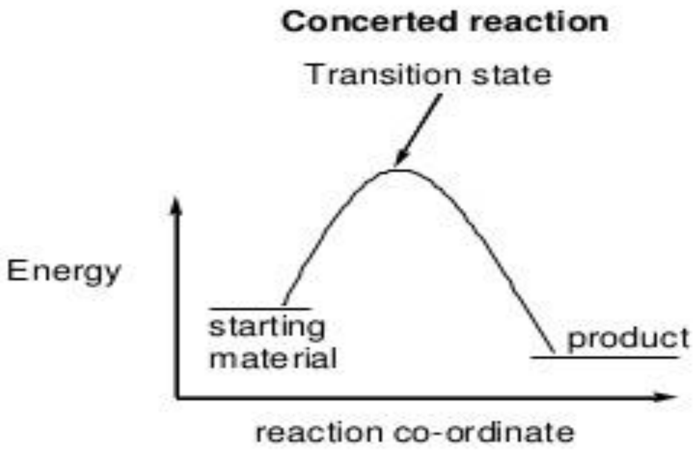
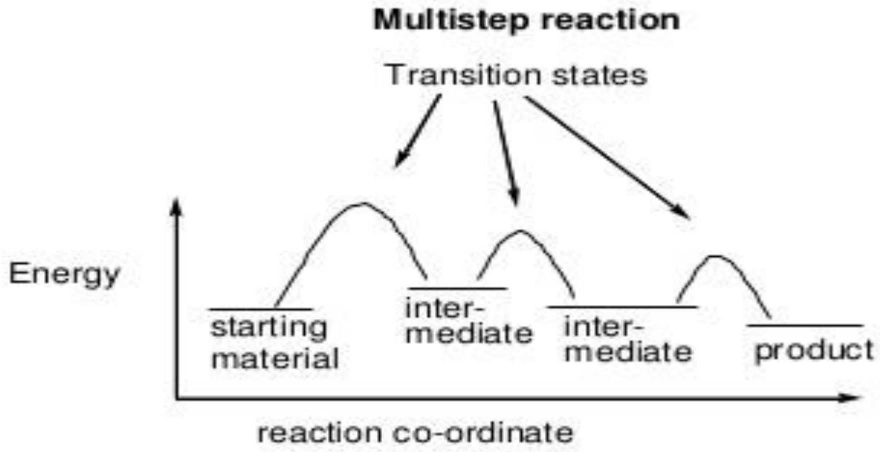
Pericyclic reactions are "Any concerted reaction in which bonds are formed or broken in a cyclic transitions state”. (electrons move around in a circle).

i.e. there is a single transition state from start to finish, in contrast to a stepwise reaction.





.*Angew. Chem. Int. Edit.* **1969**, 8(5),343-348.

Classes of Pericyclic Reactions

There are four major classes of pericyclic reactions:

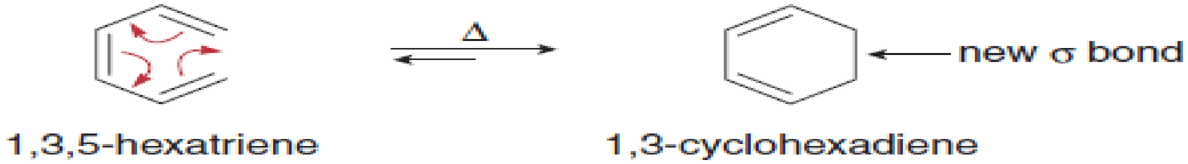
- Electrocyclic reactions (ring openings or ring closings),
- Cycloadditions
- Sigmatropic rearrangements and
- Cheletropic reactions.

Electrocyclic reaction:

An electrocyclic ring-opening reaction is a reaction in which a σ bond of a cyclic reactant is cleaved to form a conjugated product with one more π bond.

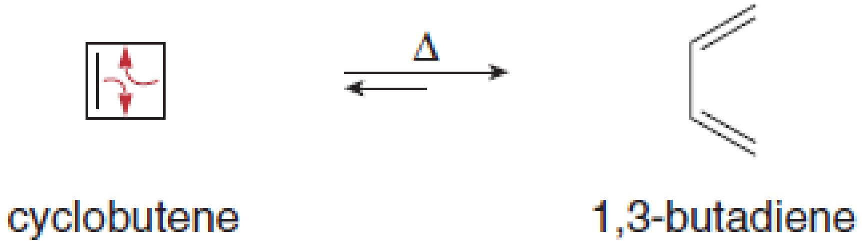
A striking feature of thermal electrocyclic reactions that proceed by concerted mechanisms is their high degree of stereospecificity. Thus when cis-3,4-dimethylcyclobutene is heated, it affords only one of the three possible cis-trans isomers of 2,4-hexadiene, namely, cis,trans-2,4-hexadiene:

Ring-closing reaction



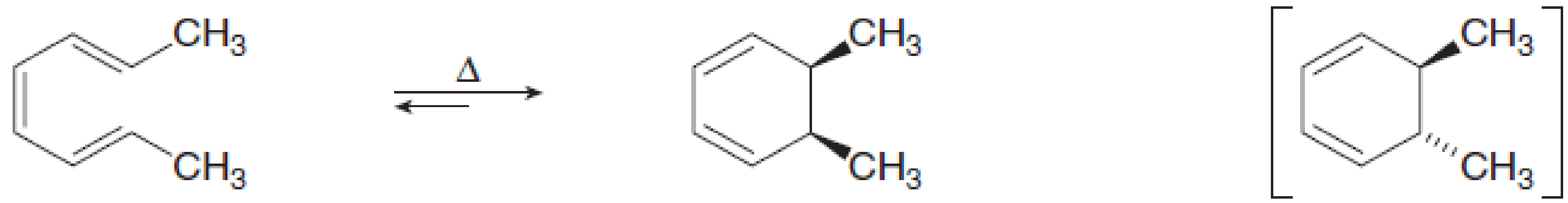
An electrocyclic ring closure is an intramolecular reaction that forms a cyclic product containing one more σ bond and one fewer π bond than the reactant.

Ring-opening reaction



Stereochemistry and Orbital Symmetry

Electrocyclic reactions are completely stereospecific. For example, ring closure of (2*E*,4*Z*,6*E*)-2,4,6-octatriene yields a single product with cis methyl groups on the ring. Ring opening of *cis*-3,4-dimethylcyclobutene forms a single conjugated diene with one *Z* alkene and one *E* alkene.

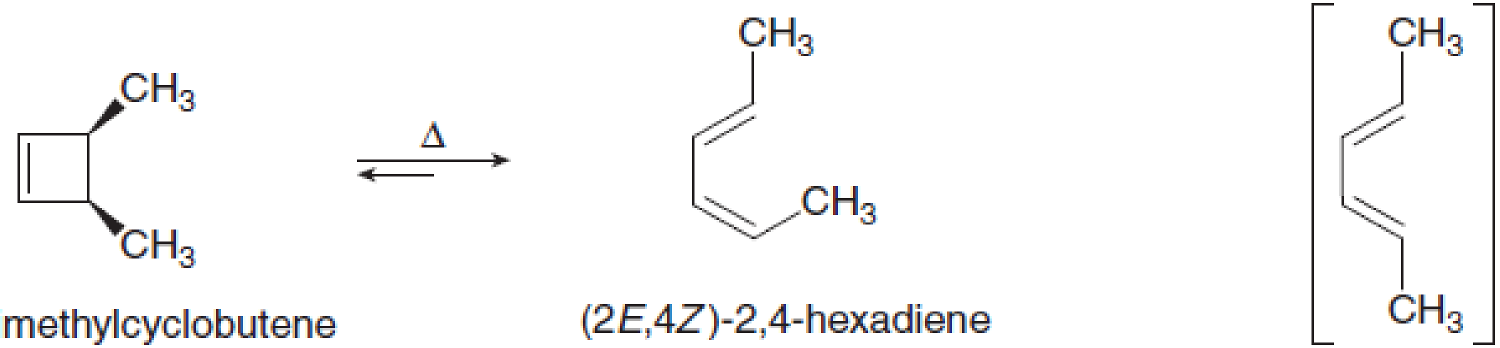


(2*E*,4*Z*,6*E*)-2,4,6-octatriene

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

cis product only

NOT formed

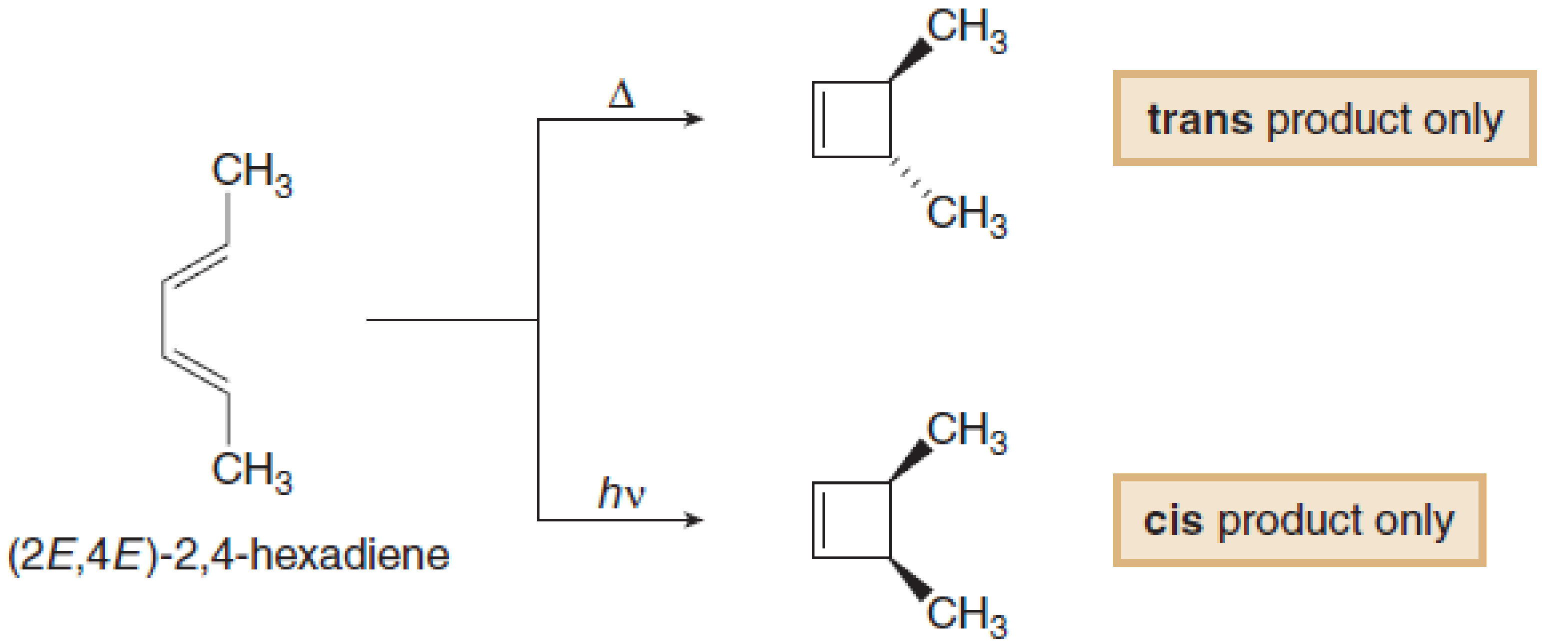


cis-3,4-dimethylcyclobutene

(2*E*,4*Z*)-2,4-hexadiene

(2*E*,4*Z*) diene only

NOT formed



To understand these results, we must focus on the HOMO of the acyclic conjugated polyene that is either the reactant or product in an electrocyclic reaction. In particular, we must examine the *p* orbitals on the terminal carbons of the HOMO, and determine whether like phases of the orbitals are on the same side or on opposite sides of the molecule.

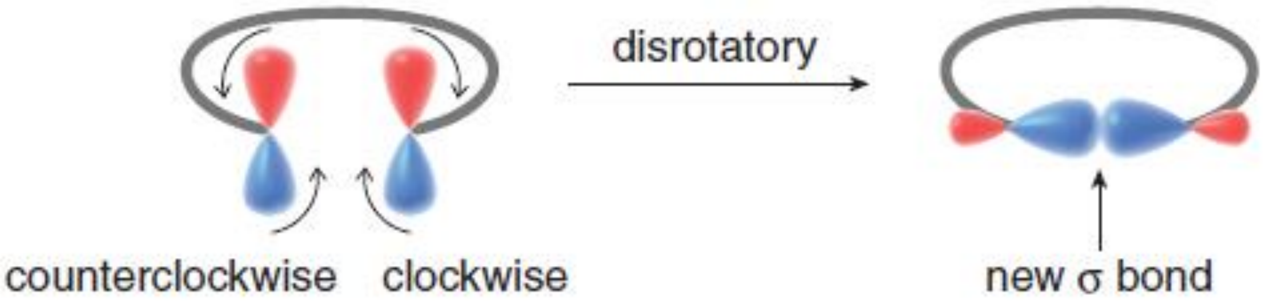
like phases on the same side

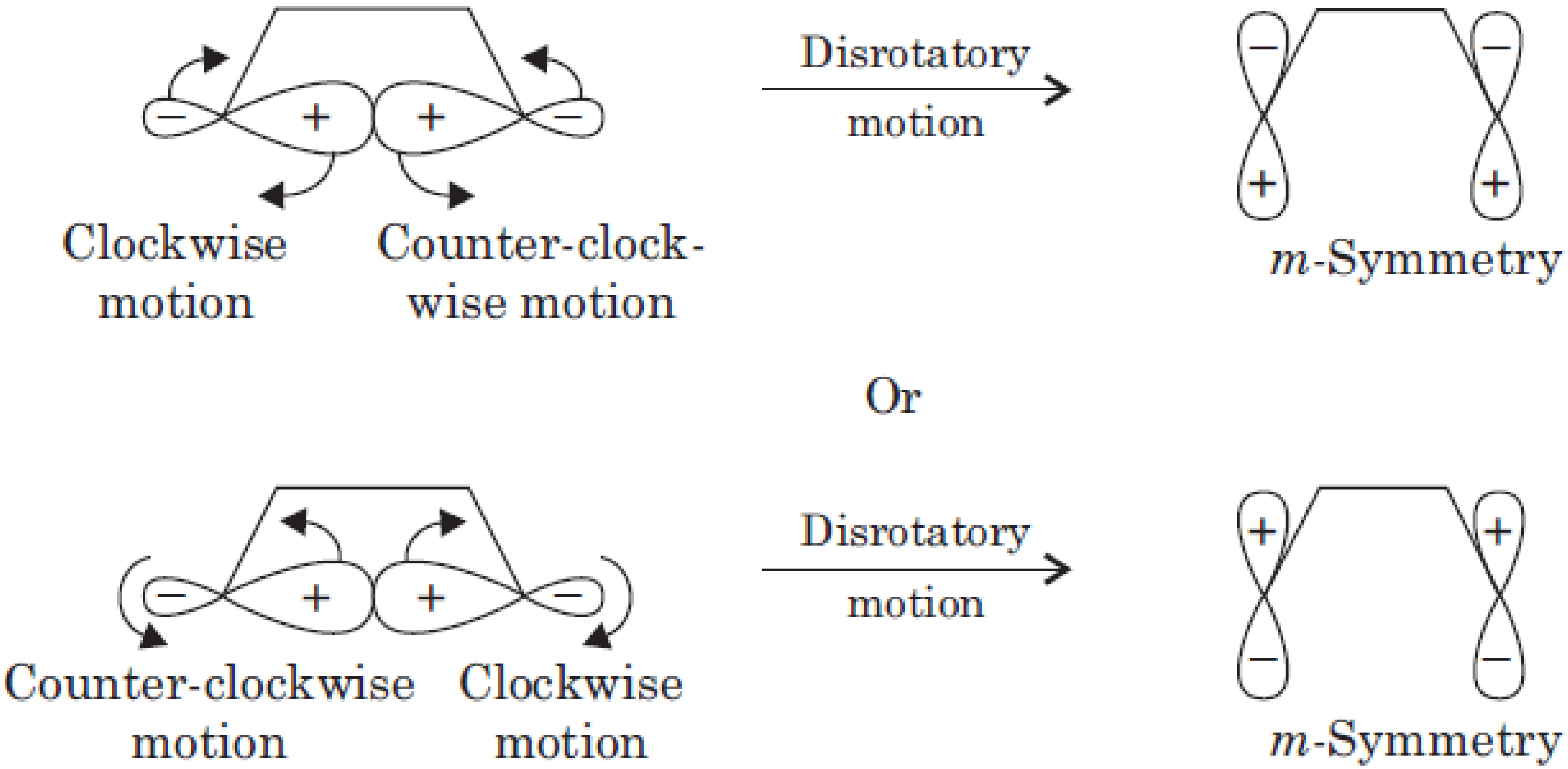
like phases on opposite sides

- An electrocyclic reaction occurs only when like phases of orbitals can overlap to form a bond. Such a reaction is *symmetry allowed.*
- An electrocyclic reaction cannot occur between orbitals of opposite phase. Such a reaction is *symmetry forbidden.*

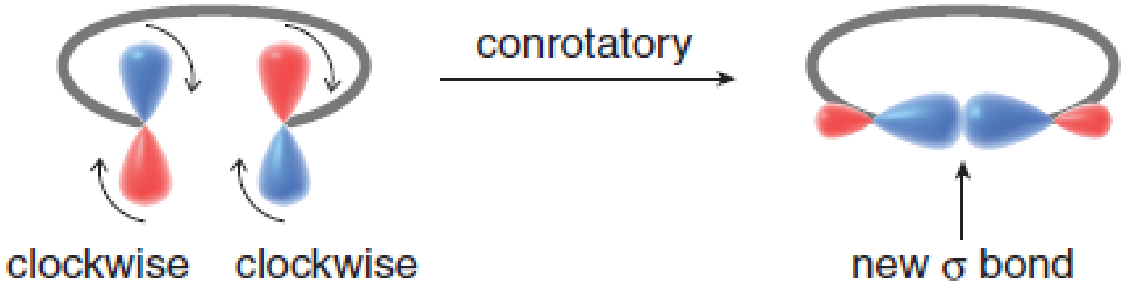
To form a bond, the *p* orbitals on the terminal carbons must rotate so that like phases can interact to form the new σ bond. Two modes of rotation are possible.

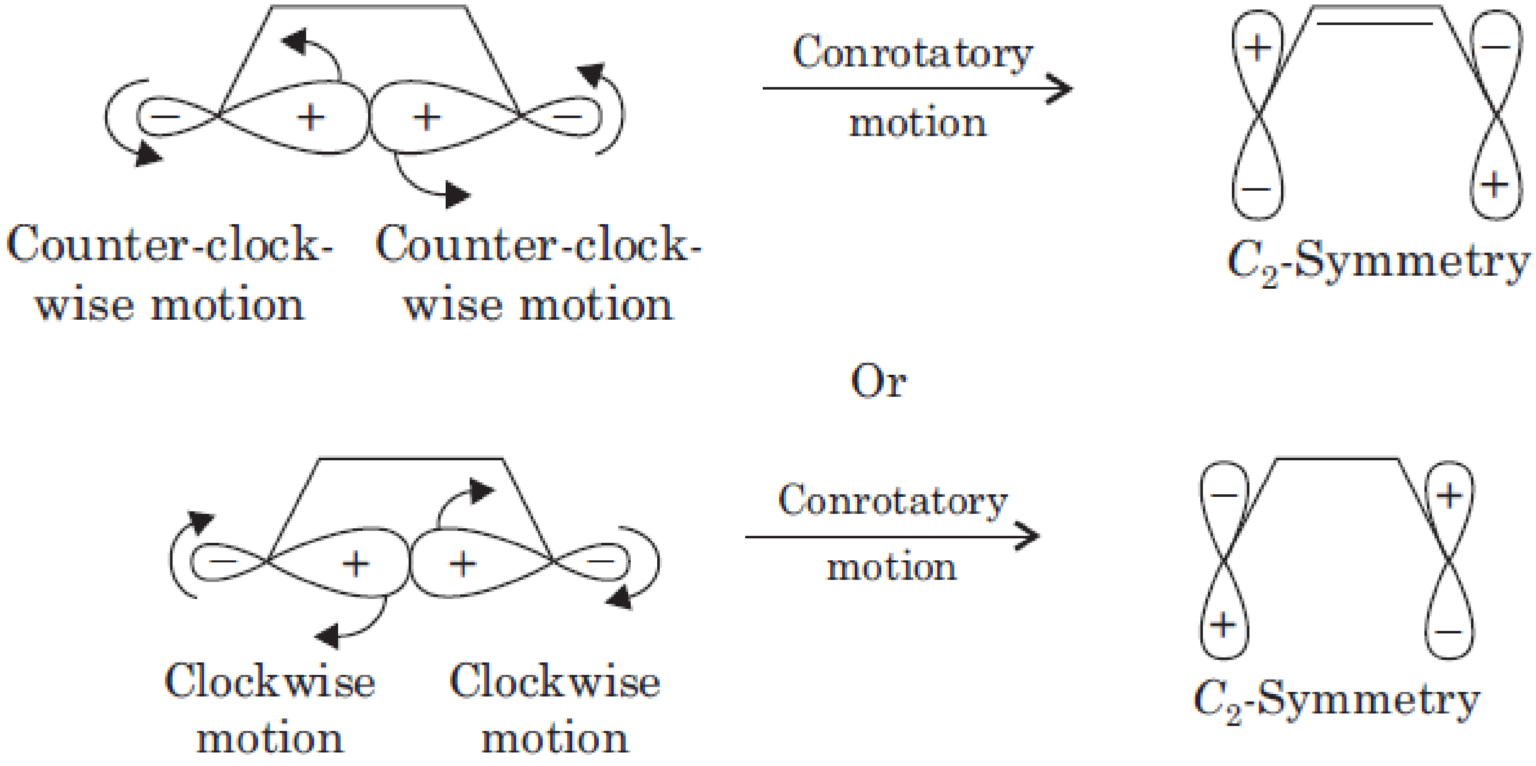
- When like phases of the *p* orbitals are on the same side of the molecule, the two orbitals must rotate in opposite directions—one clockwise and one counterclockwise. Rotation in opposite directions is said to be *disrotatory.*

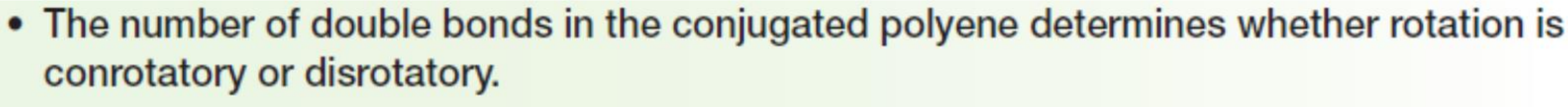



−
+
+
−
Clockwise motion
Counter-clock-wise motion
Disrotatory motion
−
−
+
+
m-Symmetry
Or
−
+
+
−
Counter-clockwise motion
Clockwise motion
Disrotatory motion
+
+
−
−
m-Symmetry

- When like phases of the *p* orbitals are on opposite sides of the molecule, the two orbitals must rotate in the same direction—both clockwise or both counterclockwise. Rotation in the same direction is said to be *conrotatory*.



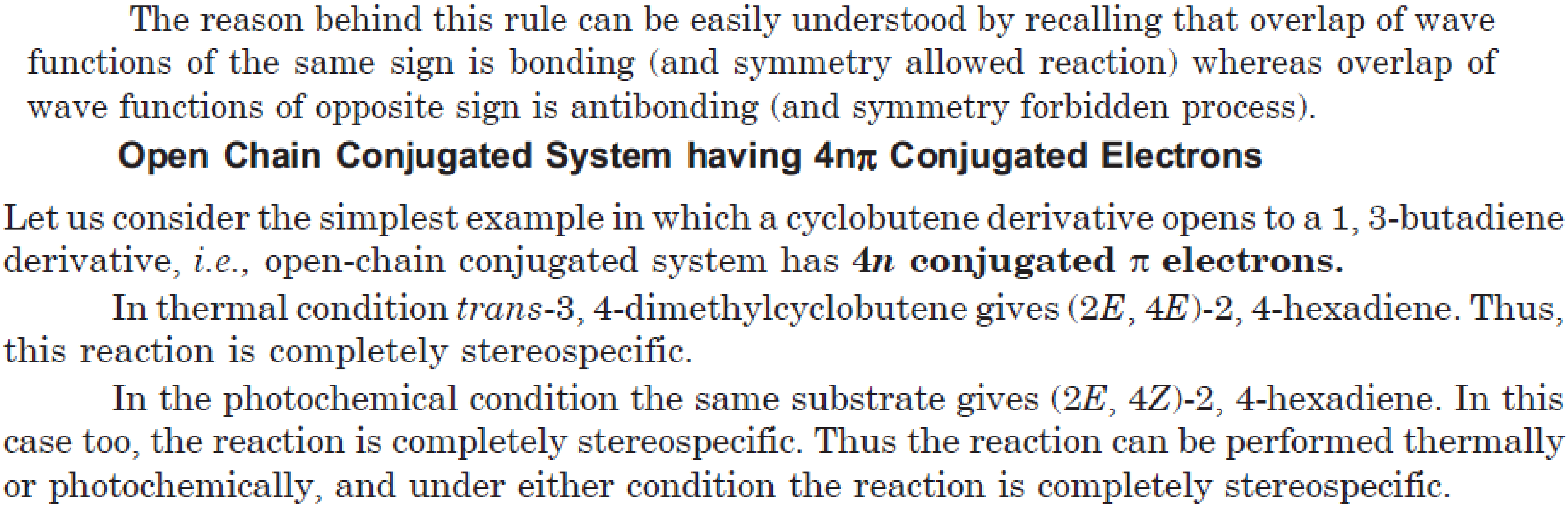




- The number of double bonds in the conjugated polyene determines whether rotation is conrotatory or disrotatory.

- The orbital symmetry also determines the mode of rotation

Orbitals having m symmetry always give disrotatory motion and having C_2 symmetry gives conrotatory motion.



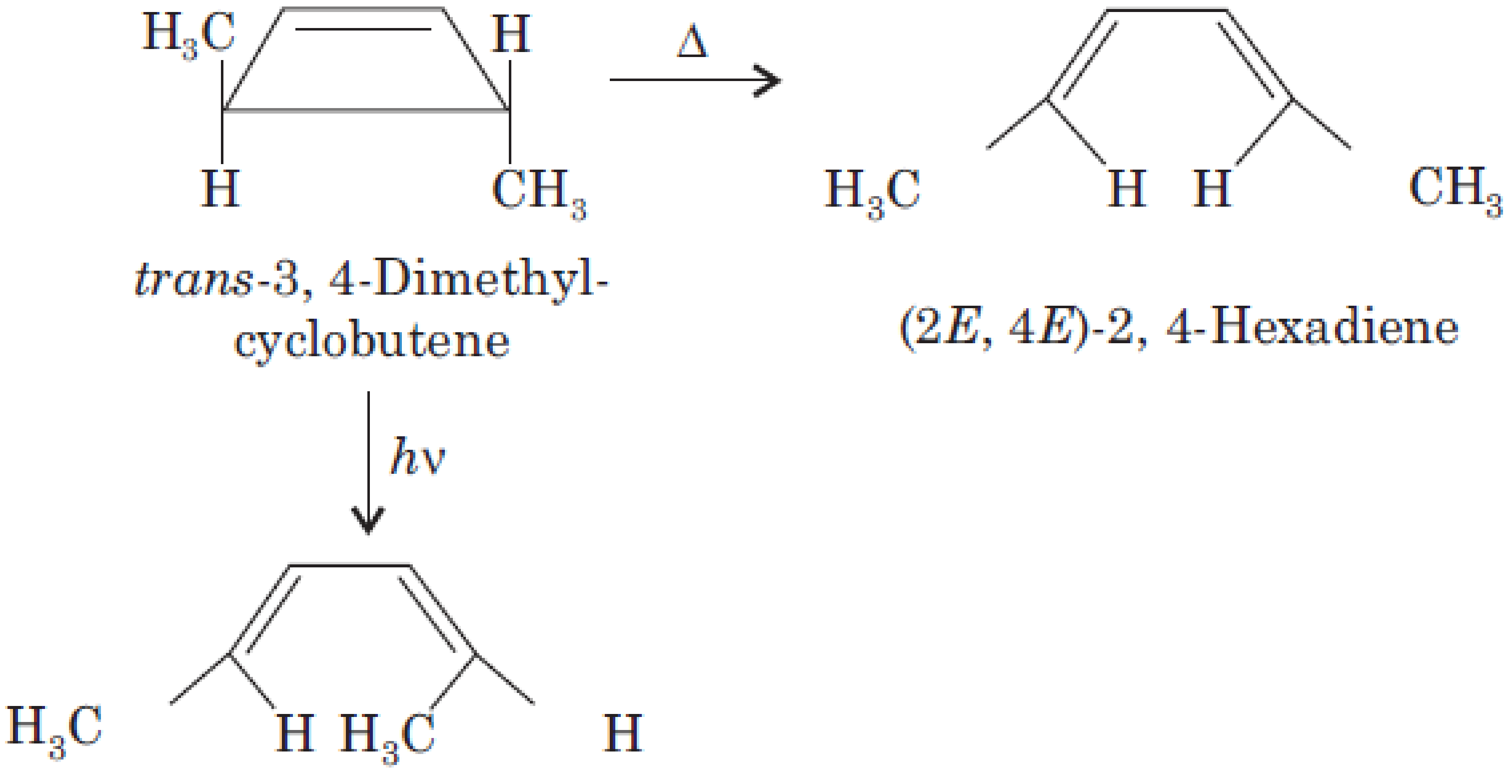
The reason behind this rule can be easily understood by recalling that overlap of wave functions of the same sign is bonding (and symmetry allowed reaction) whereas overlap of wave functions of opposite sign is antibonding (and symmetry forbidden process).

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.

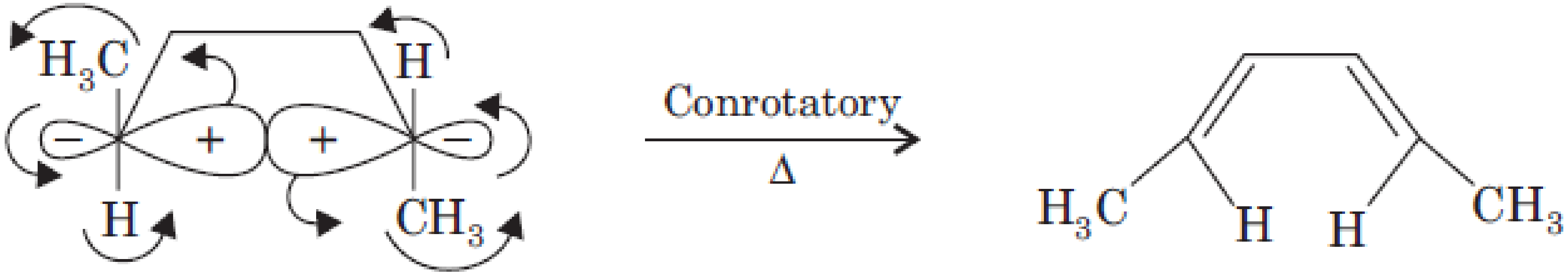


trans-3, 4-Dimethylcyclobutene

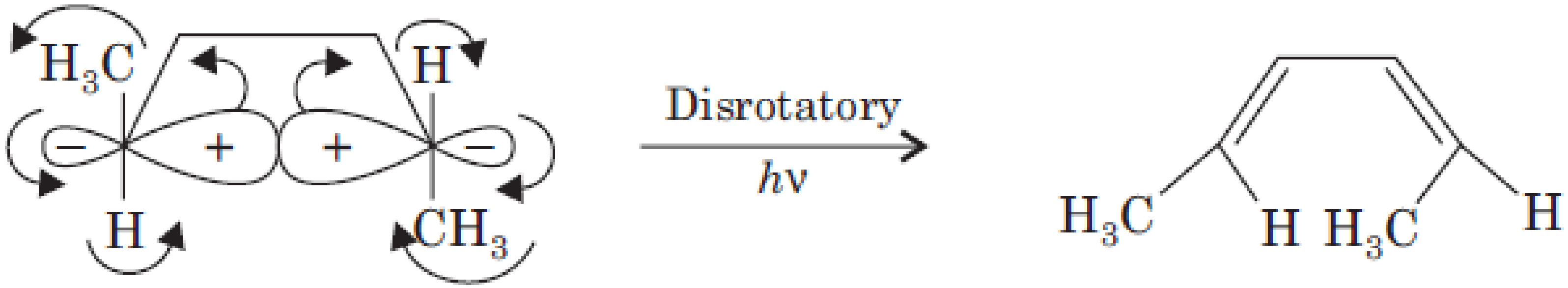
(2*E*, 4*E*)-2, 4-Hexadiene ...(1)

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

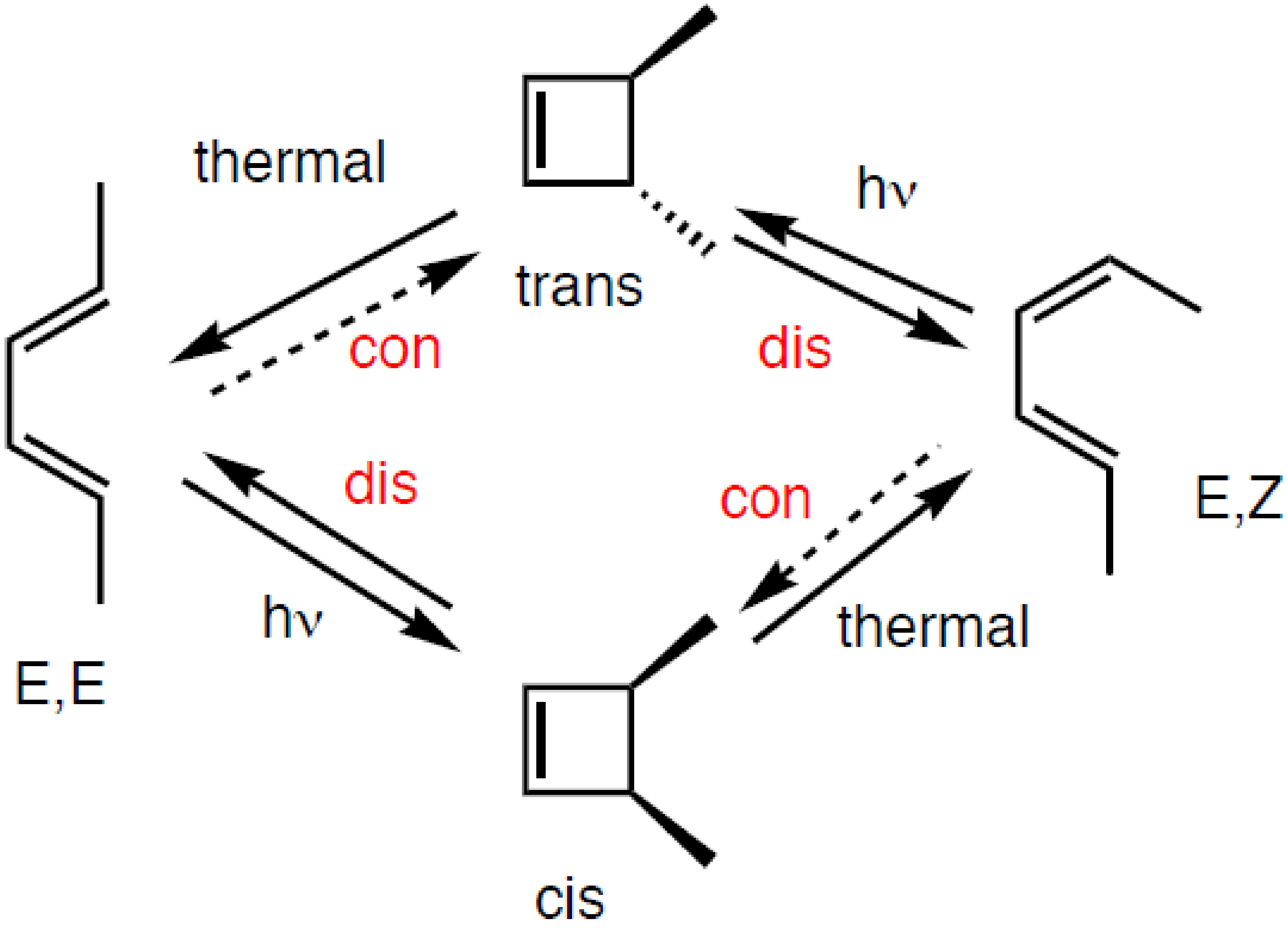
Stereochemistry of the thermal reaction-1 (of the $4n\pi$ system) can only be explained if process should be conrotatory.



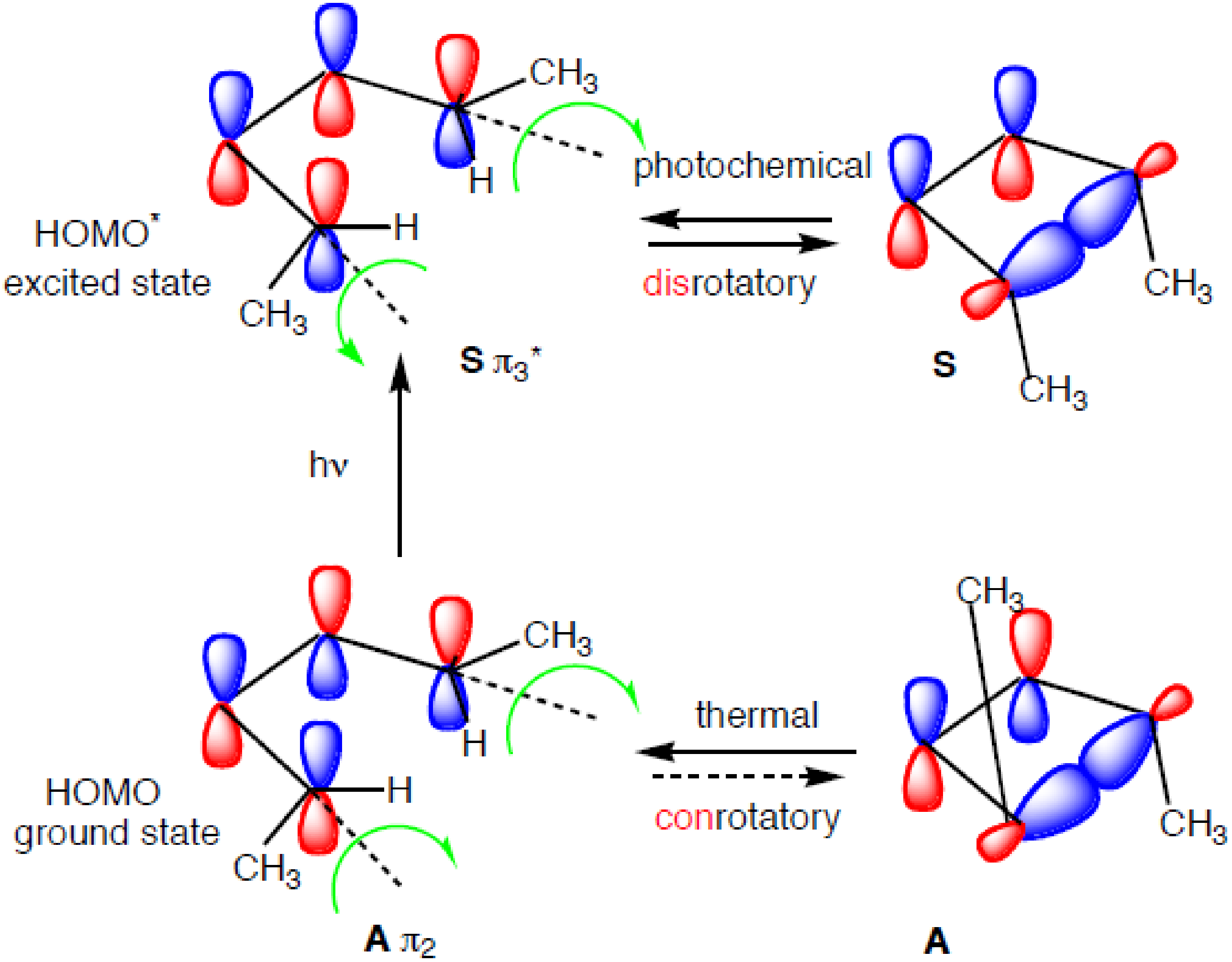
Stereochemistry of the photochemical reaction-2 (of the $4n$, π system) can only be explained if process should be disrotatory.



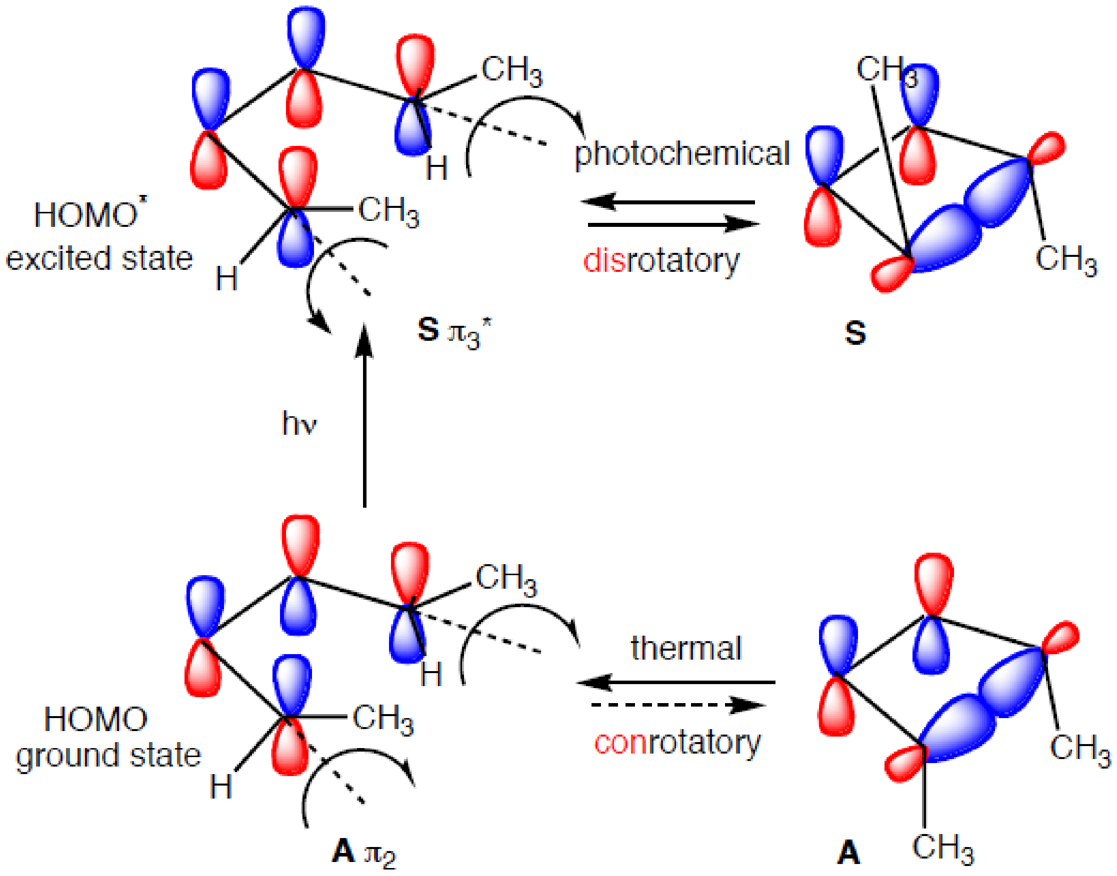
1,3-Butadiene-Cyclobutene



(*E,E*)-1,3-Butadiene-Cyclobutene



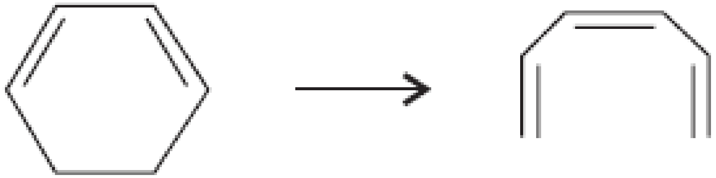
(*E*,*Z*)-1,3-Butadiene-Cyclobutene



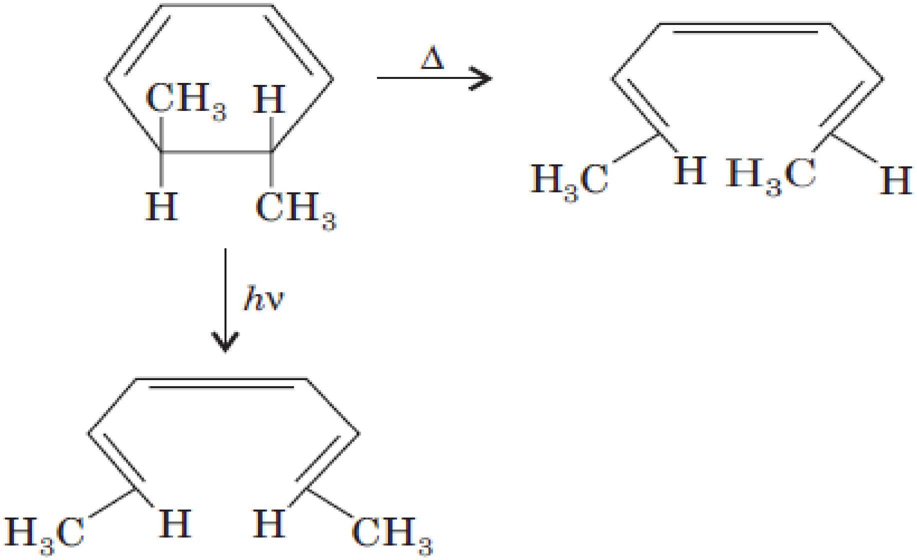
From the above two examples it is clear that **thermally induced electrocyclic reaction involving $4n\pi$ conjugated electrons require conrotatory motion and photochemically induced electrocyclic reaction require disrotatory motion.**

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.



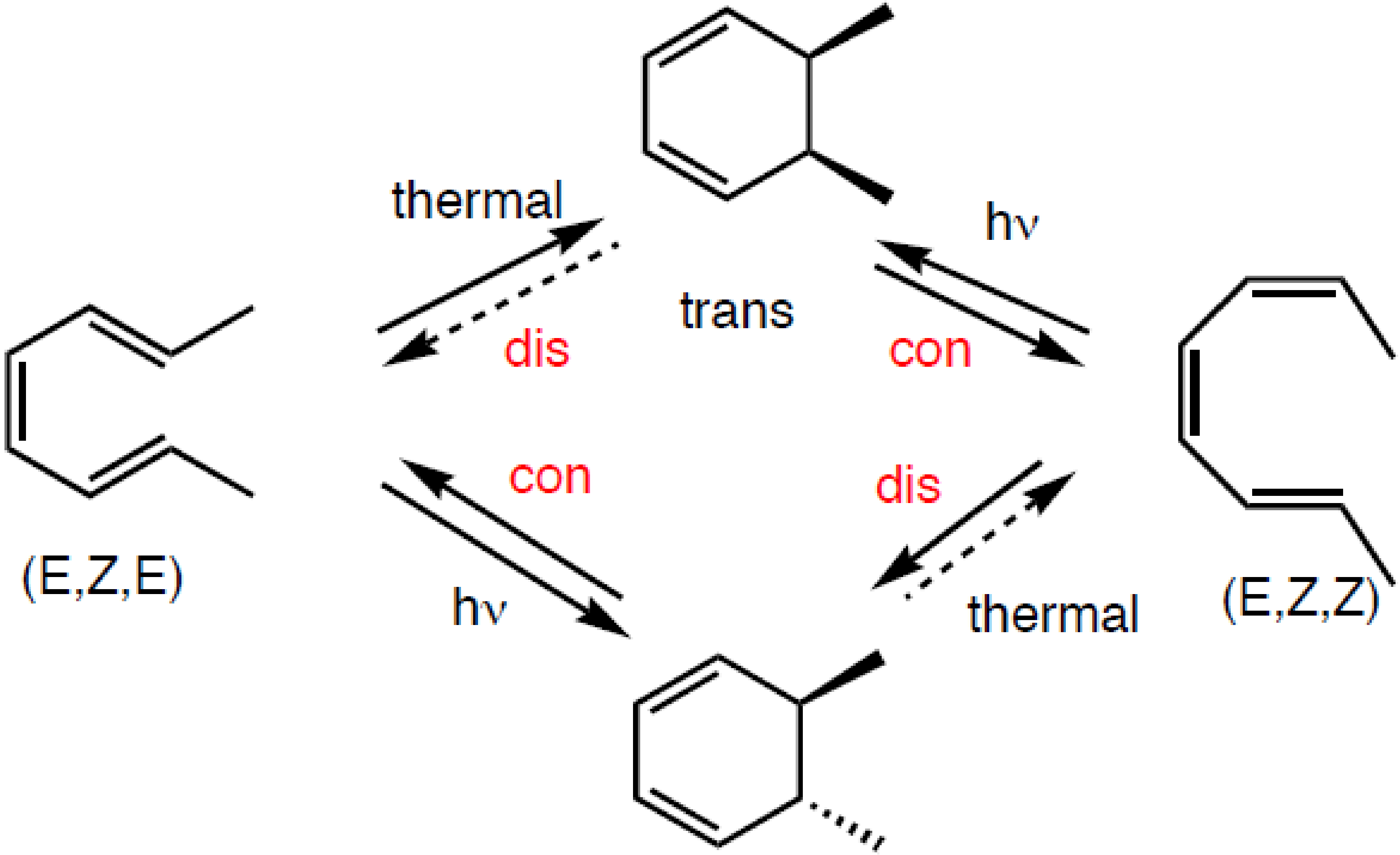
In thermal condition 5, 6-*trans*-dimethyl-1, 3-cyclohexadiene is converted exclusively to (2*E*, 4*Z*, 6*Z*)-2, 4, 6-octatriene. In the photochemical condition the same substrate is converted exclusively to (2*E*, 4*Z*, 6*E*)-2, 4, 6-octatriene.



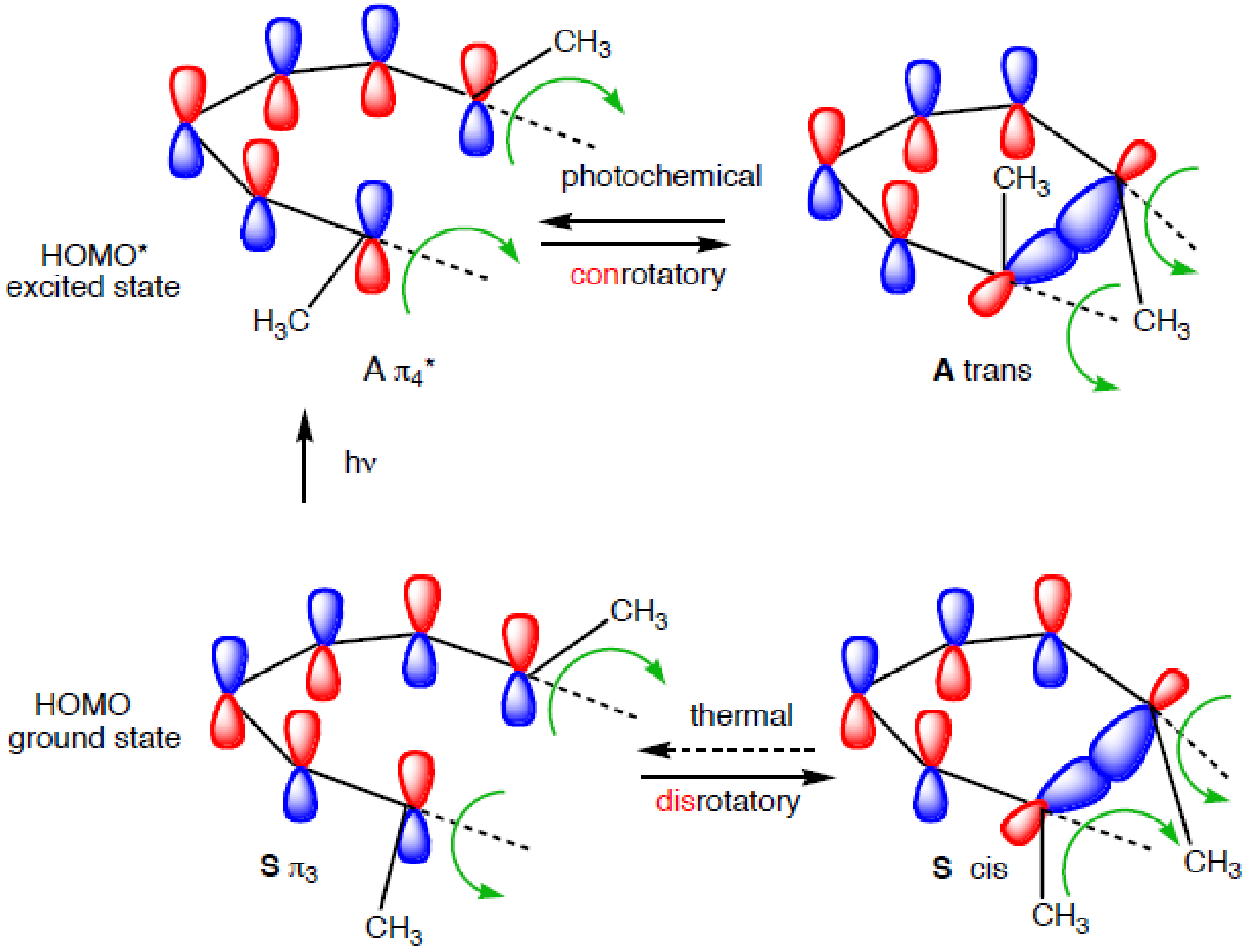
...(3)

...(4)

(*E*,*Z*,*E*)-1,3,5-Hexatriene-Cyclohexadiene



(*E*,*Z*,*E*)-1,3,5-Hexatriene-Cyclohexadiene Orbitals

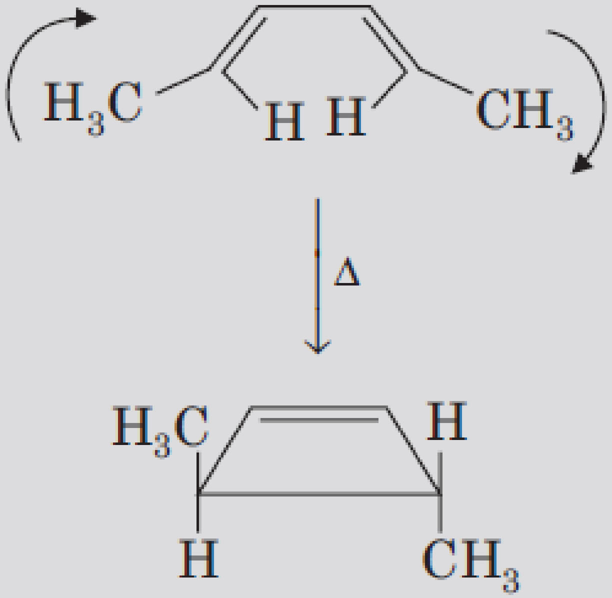


These two conversions are also highly stereospecific. Stereochemistry of these two reactions (*i.e.*, reaction-3 and 4) can only be explained if process should be disrotatory in thermal condition and conrotatory in photochemical condition.

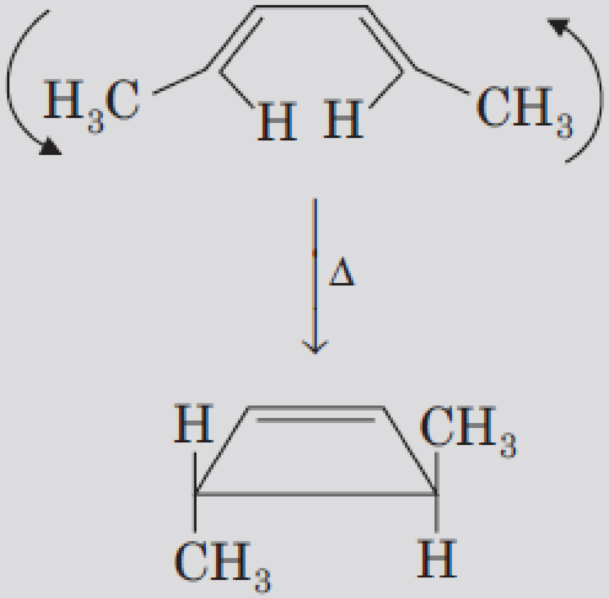
Number of π electrons	*Condition (mode of activation)*	*Motion*
$4n$	(*i*) Thermal (*ii*) Photochemical	Conrotatory Disrotatory
$4n + 2$	(*i*) Thermal (*ii*) Photochemical	Disrotatory Conrotatory

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:



(1)

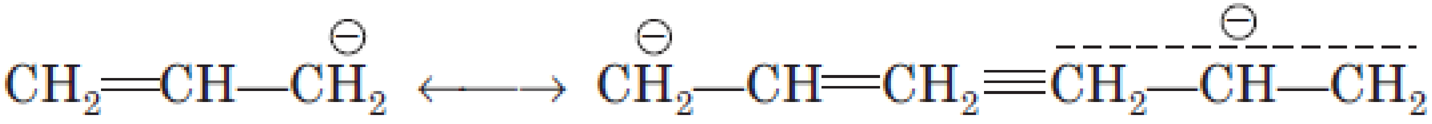


(2)

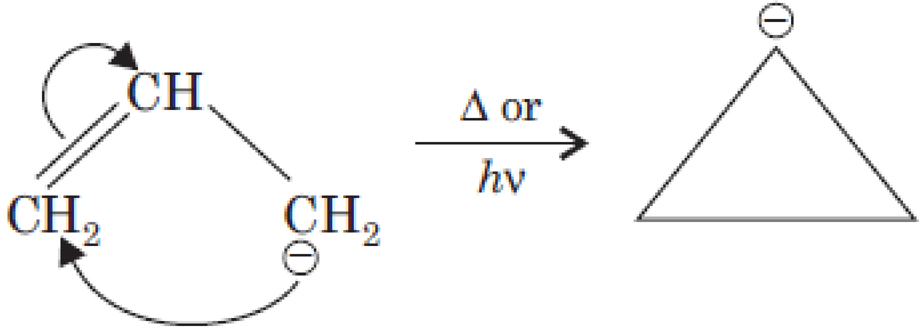
They are equally likely because they [(1) and (2)] are enantiomeric. Enantiomers have equal energies. Enantiomeric pathways have identical energies at all points and therefore identical rates.

Electrocyclic ring-closure given by allyl carbanion:

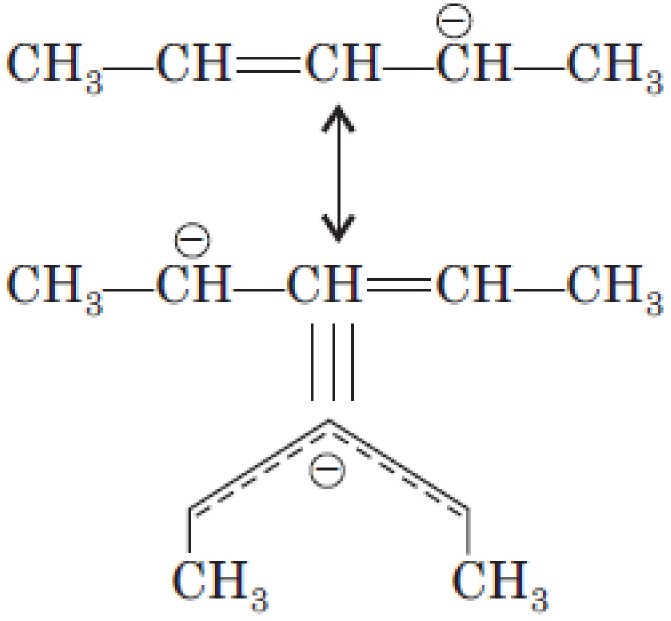
Allyl carbanion is also a 4n π conjugated system……

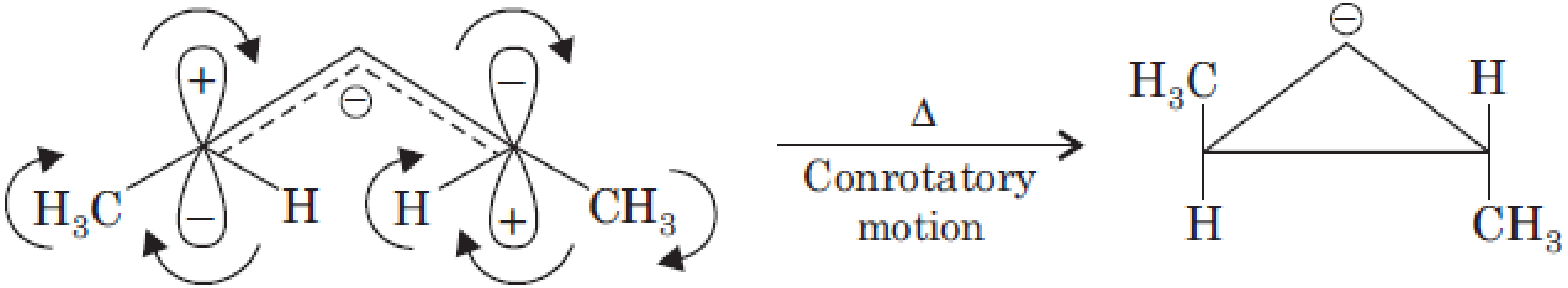


$$\mathrm{CH_2{=}CH{-}\overset{\ominus}{C}H_2} \longleftrightarrow \mathrm{\overset{\ominus}{C}H_2{-}CH{=}CH_2} \equiv \overset{\ominus}{\overline{\mathrm{CH_2{-}CH{-}CH_2}}}$$

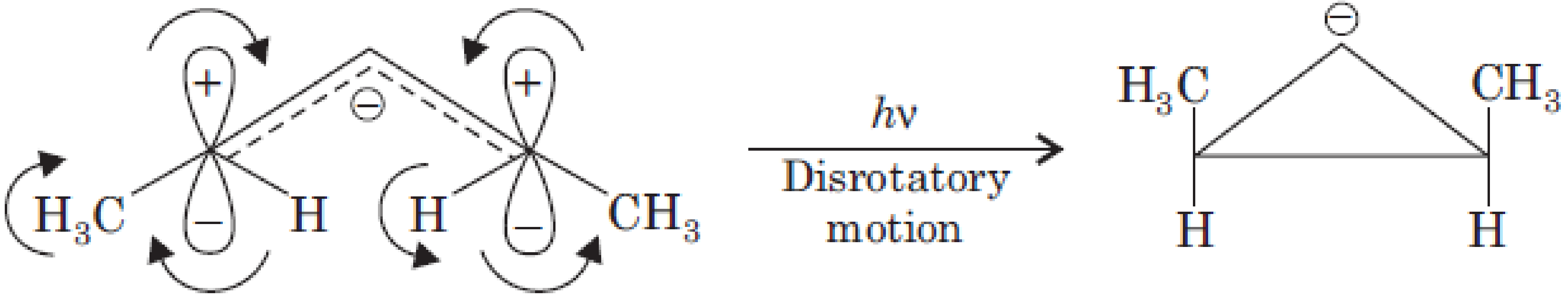


HOMO of the allyl carbanion in the ground state is ψ_2 which has C_2-symmetry. Therefore, conrotatory motion is the mode of cyclisation in the thermal condition.





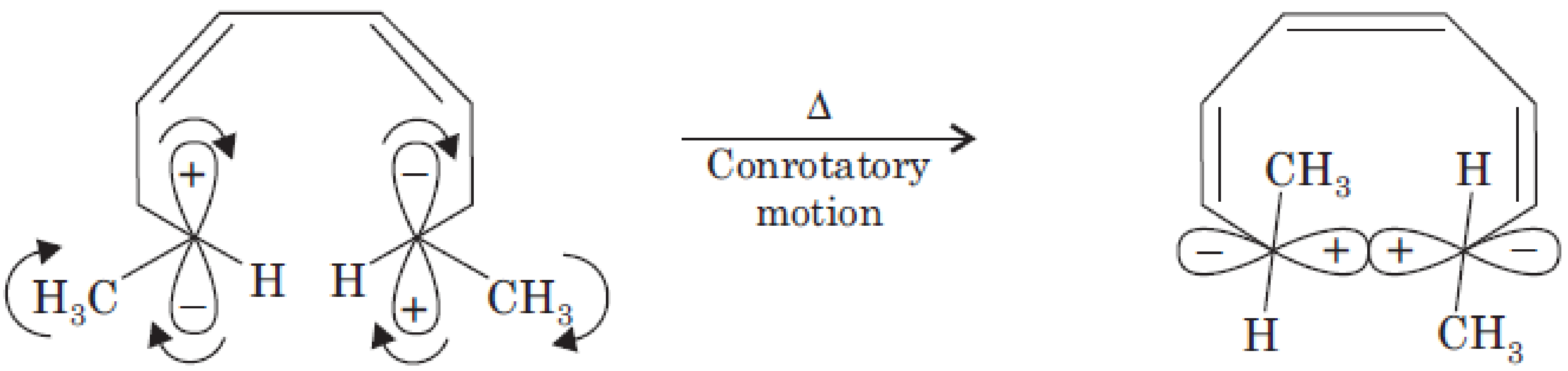
In case of photocyclisation, the excited HOMO is ψ_3^* which has *m*-symmetry. Thus, disrotatory motion is required for σ (*sigma*) bond formation.



Electrocyclic ring-closure reaction given by 1, 3, 5, 7-octatetraene:

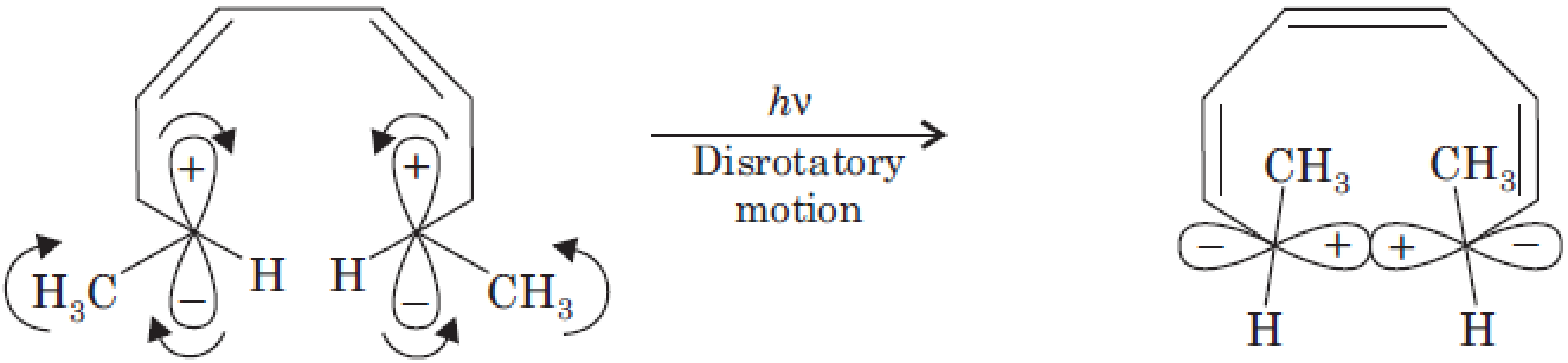
This compound and its derivative is considered as 4n π conjugated system

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.



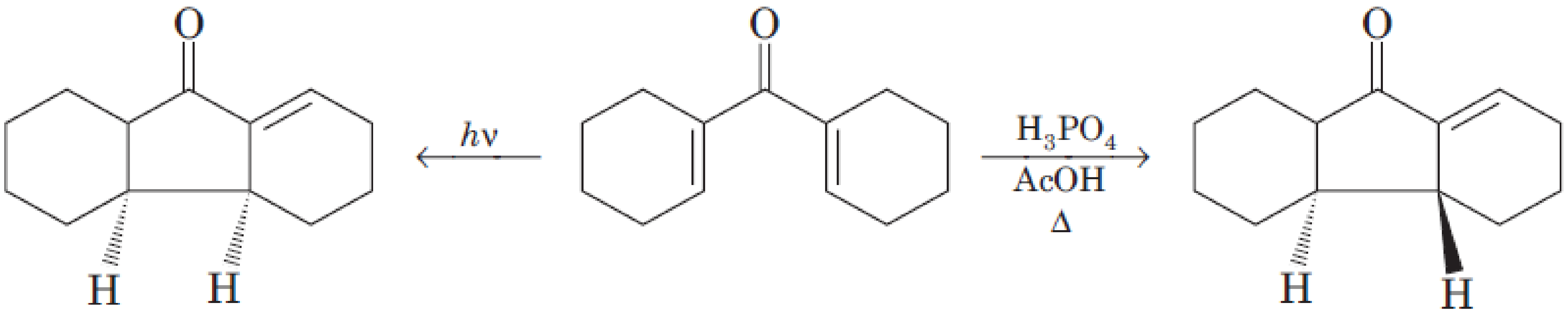
trans-7, 8-Dimethyl-1, 3, 5-cyclotriene

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.

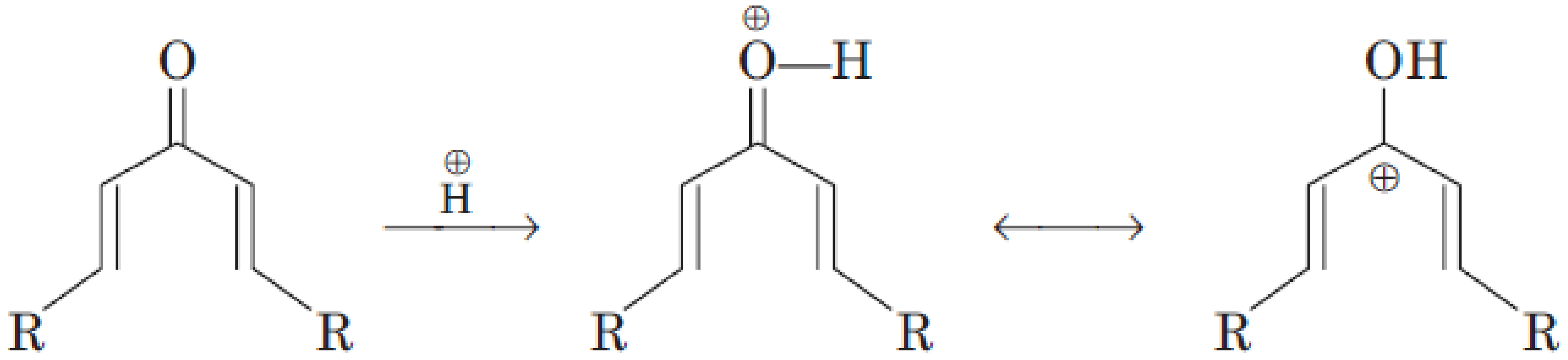


cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene

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.

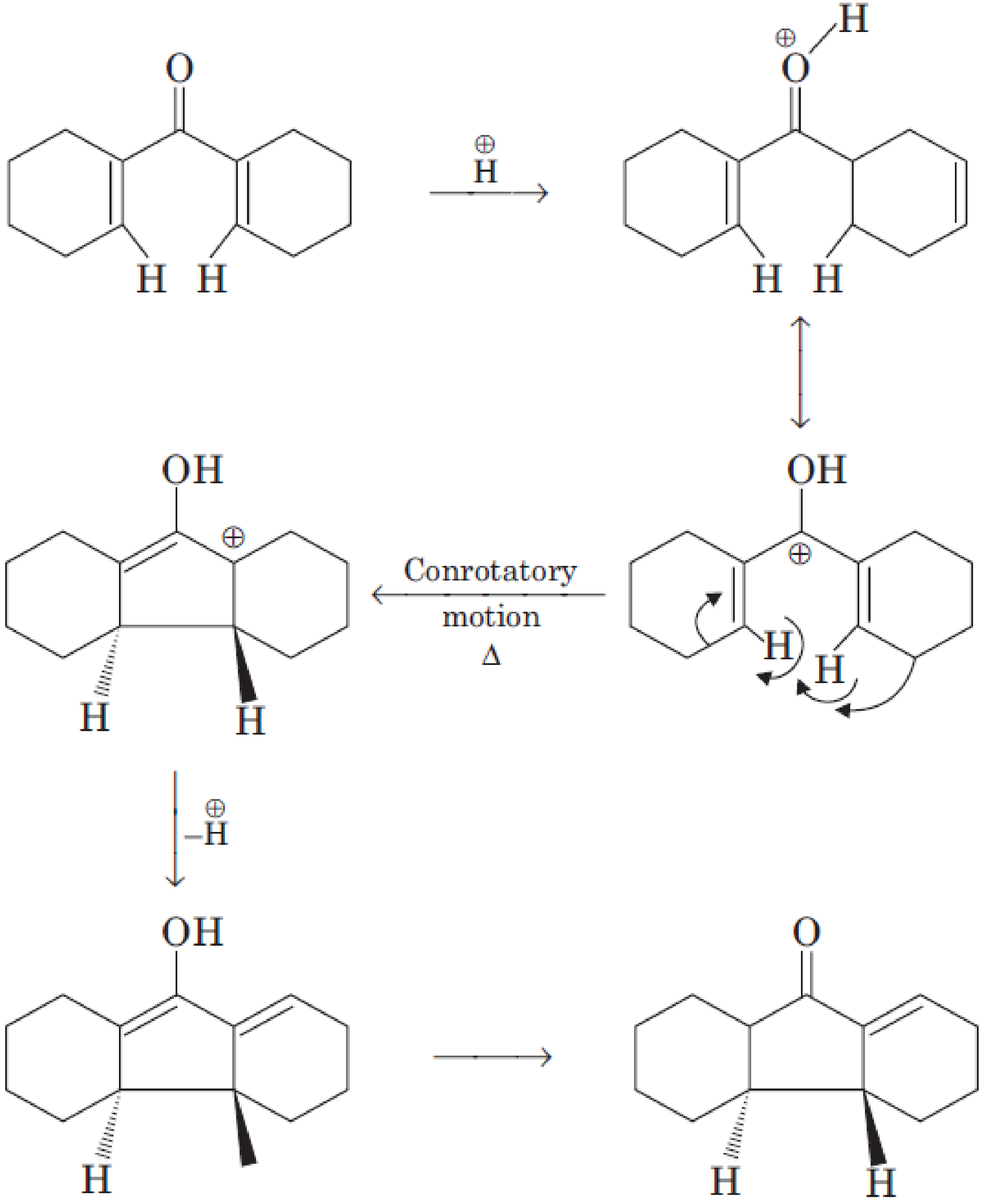


Nazarov cyclisations require acid. Under acidic condition the substrate converts into cation which has 4π conjugated electrons.

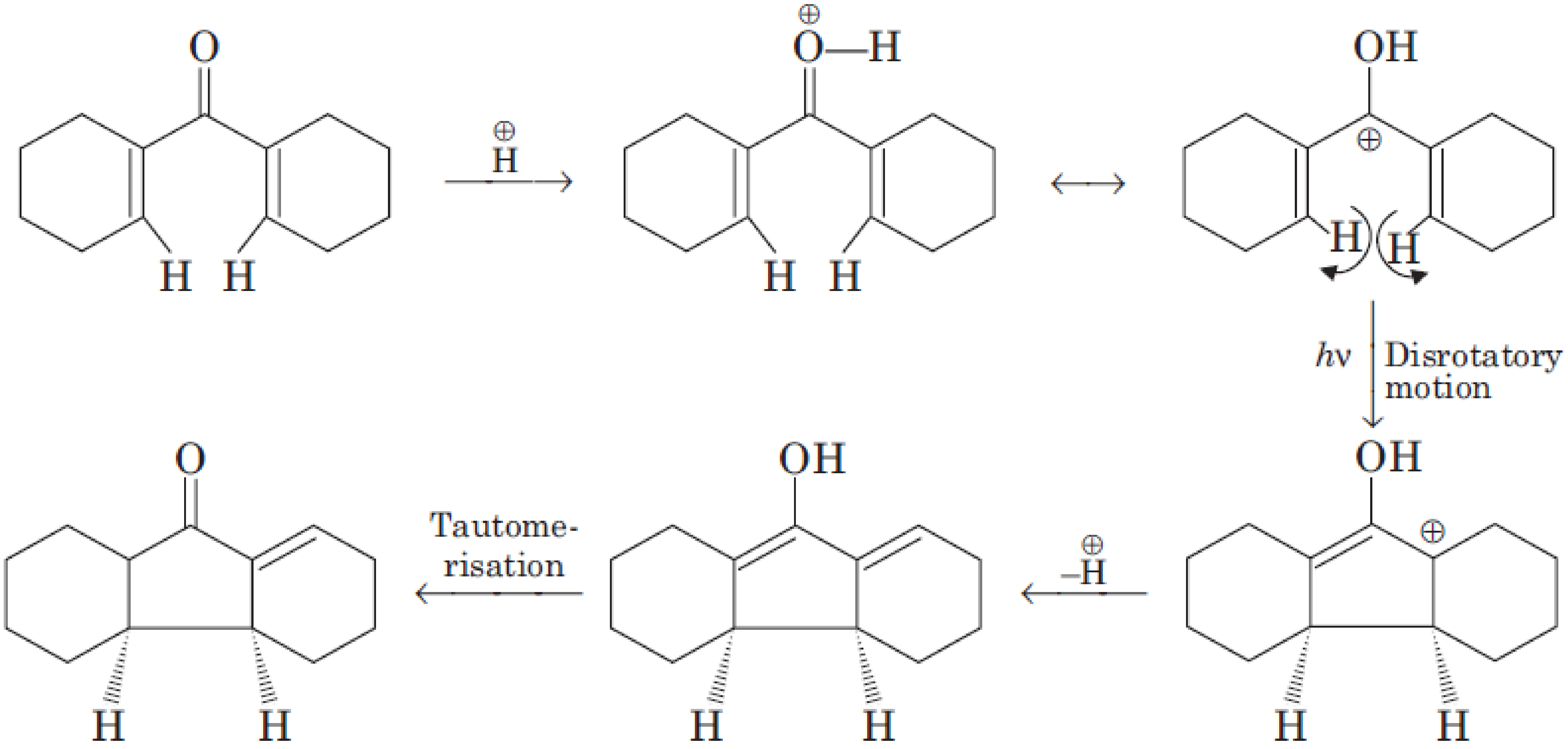


Under thermal condition, the motion is conrotatory and under photochemical conditions the motion is disrotatory because the conjugated system has $(4n)\pi$ conjugated electrons.

Under thermal condition:

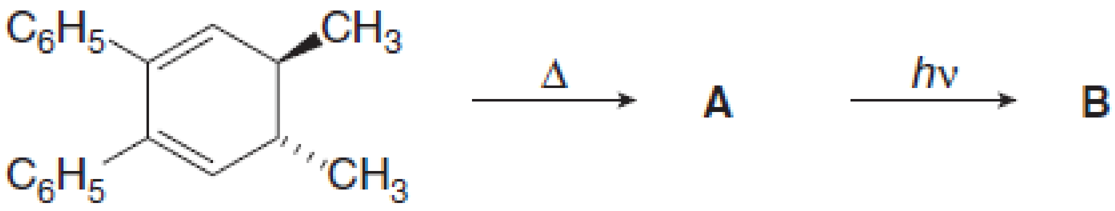


Under photochemical condition:



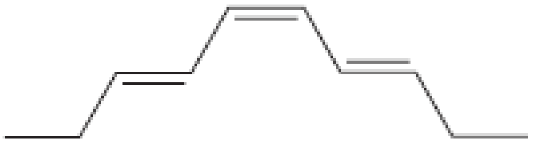
Solve the following problems…..

1. Identify **A** and **B** in the following reaction sequence. Label each process as conrotatory or disrotatory.

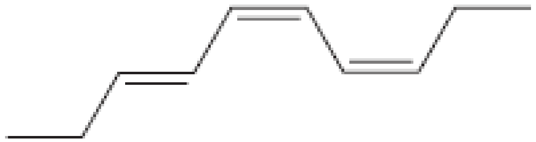


2. Draw the product formed when each triene undergoes electrocyclic reaction under [1] thermal conditions; [2] photochemical conditions.

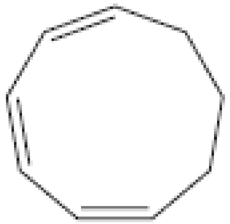
a.



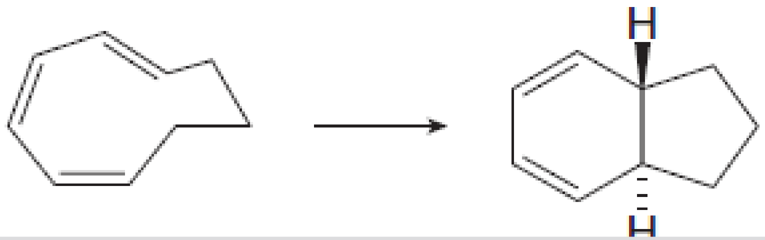
b.



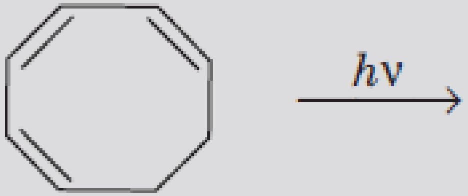
3. What product would be formed by the disrotatory cyclization of the given triene? Would this reaction occur under photochemical or thermal conditions?



4. Consider the following electrocyclic ring closure. Does the product form by a conrotatory or disrotatory process? Would this reaction occur under photochemical or thermal conditions?



5. *Complete the following reaction and give stereochemistry of the product.*



Hints: