

# **CYI101**

## **Common CHEMISTRY(Organic)**

**Stereochemistry: Pericyclic reactions**

Definitions, Classifications, Electrocyclic Reactions

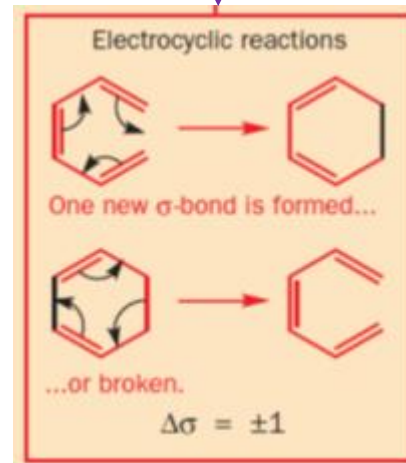
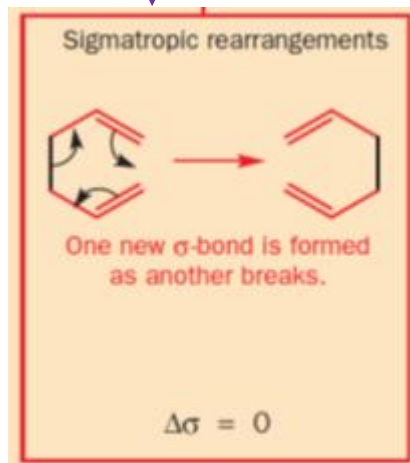
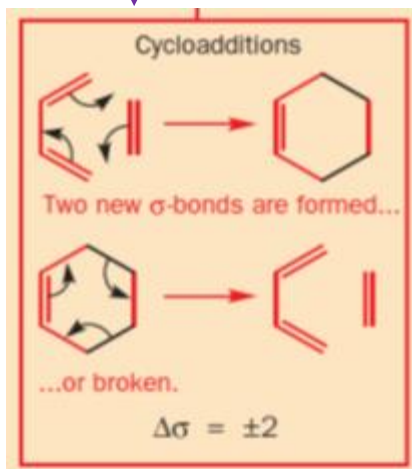
# Pericyclic Reactions: Definitions, Classifications

Pericyclic reaction involves a cyclic redistribution of bonding electrons through a concerted process.

A **pericyclic reaction** is a type of organic reaction wherein the transition state of the molecule has a *cyclic geometry*, the reaction progresses in a *concerted fashion*, and the *bond orbitals involved in the reaction overlap* in a continuous cycle at the transition state.

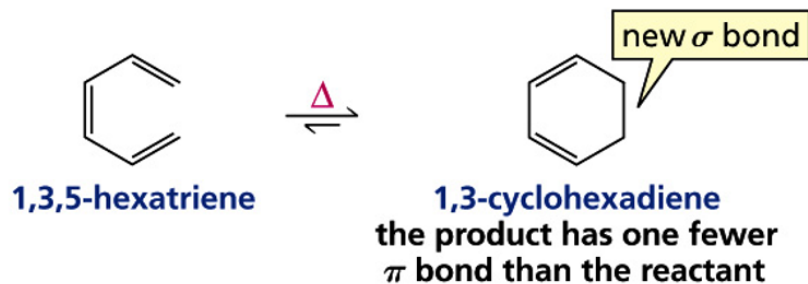
The three principle classes of pericyclic reactions are termed: **Cycloaddition**, **Electrocyclic**, and **Sigmatropic**

*Types of Pericyclic Reactions: are distinguished by the number of  $\sigma$ -bonds made or broken*

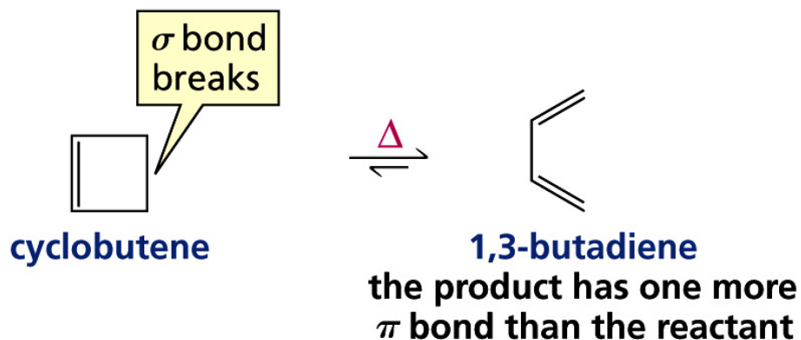


# Pericyclic Reactions: *Electrocyclic Reaction*

an electrocyclic reaction



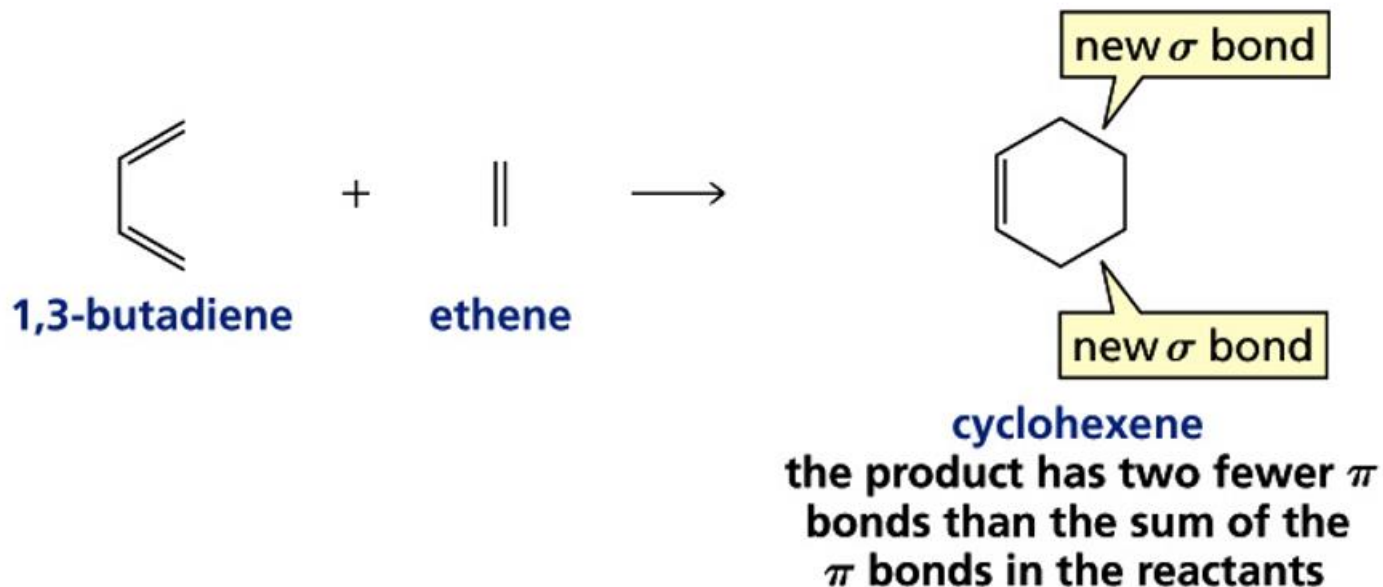
An intramolecular reaction in which a new  $\sigma$  bond is formed between the ends of a conjugated  $\pi$  system



Electrocyclic Reactions Are Reversible

# Pericyclic Reactions: *Cycloaddition Reaction*

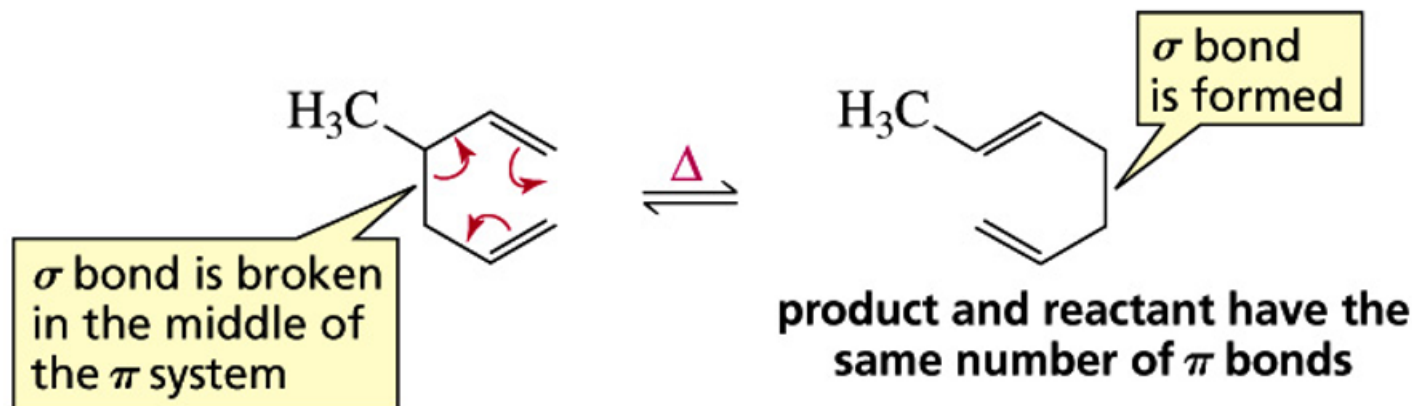
a cycloaddition reaction



**Two different  $\pi$  bond-containing molecules react to form a cyclic compound**

# Pericyclic Reactions: *Sigmatropic Reaction*

sigmatropic rearrangements



**A  $\sigma$  bond is broken in the reactant, a new  $\sigma$  bond is formed in the product, and the  $\pi$  bonds rearrange**

## Pericyclic Reactions: *Important Facts*

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- The electrocyclic reactions and sigmatropic rearrangements are intramolecular reactions
- The cycloaddition reactions are usually intermolecular reactions

### Common features among the three pericyclic reactions

- Concerted reactions
- Highly stereoselective
- Not affected by catalysts

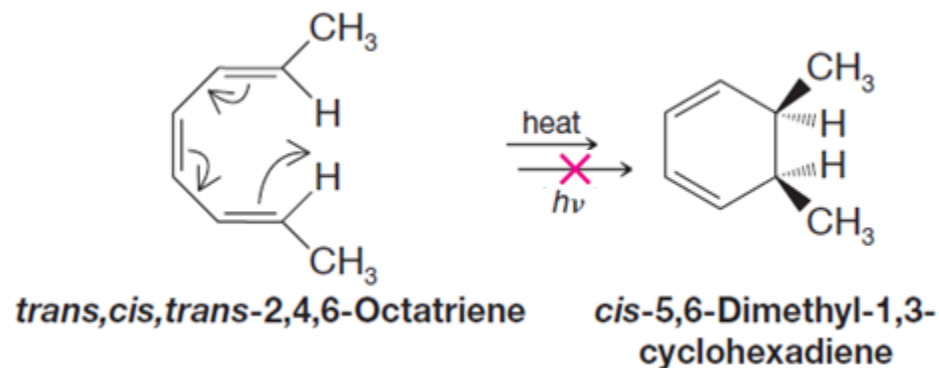
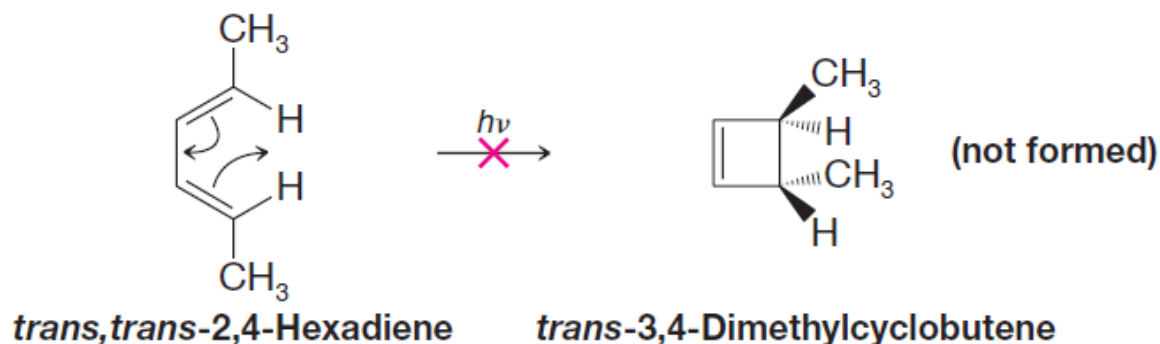
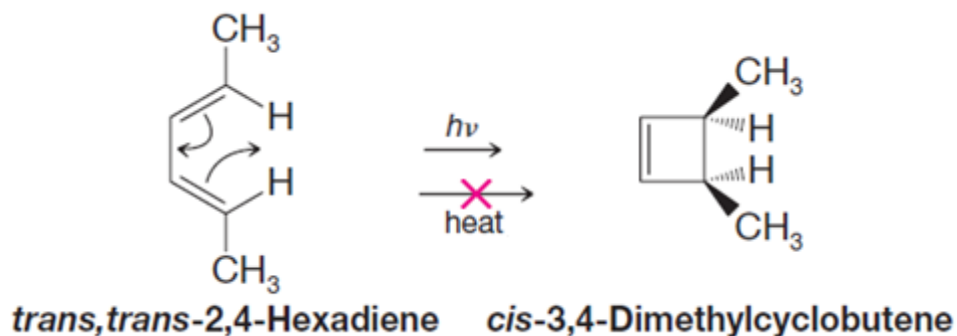
# Electrocyclic Reaction: *Characteristic Features*

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Electrocyclic reactions have several characteristic features:

1. They require only heat or light for initiation.
2. Their mechanisms do not involve radical or ionic intermediates.
3. Bonds are made and broken in *a single concerted step involving a cyclic transition state*.
4. The reactions are *stereospecific*.

# Electrocyclic Reaction: *Stereospecific*





## **Mechanism:** *Frontier Molecular Orbitals (FMO) Approach*

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

# Guidelines of Electrocyclic Reaction: *W-H Rules*

## Woodward-Hoffmann Rule:

- A *thermal electrocyclic* reaction involving  $4n \pi$  electrons (where  $n = 1, 2, 3, \dots$ ) proceeds with *conrotatory motion*; the *photochemical* reaction proceeds with *disrotatory motion*.
- A *thermal electrocyclic* reaction involving  $(4n + 2) \pi$  electrons (where  $n = 0, 1, 2, \dots$ ) proceeds with *disrotatory motion*; the *photochemical* reaction proceeds with *conrotatory motion*.

**TABLE D.1 WOODWARD-HOFFMANN RULES FOR ELECTROCYCLIC REACTIONS**

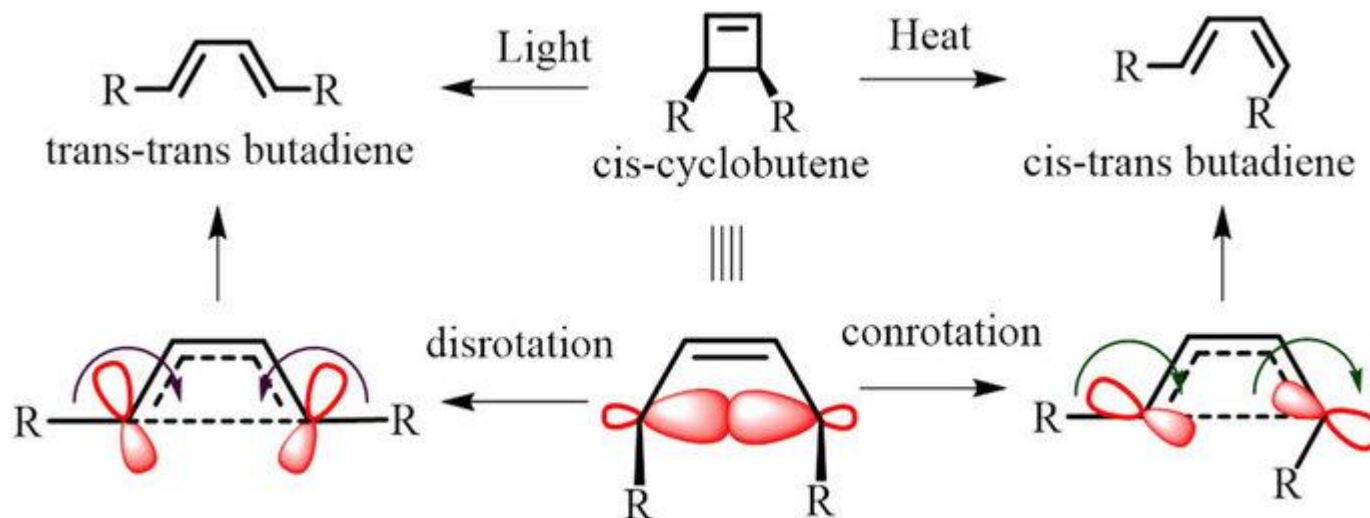
Number of $\pi$ Electrons	Motion	Rule
$4n$	Conrotatory	Thermally allowed, photochemically forbidden
$4n$	Disrotatory	Photochemically allowed, thermally forbidden
$4n + 2$	Disrotatory	Thermally allowed, photochemically forbidden
$4n + 2$	Conrotatory	Photochemically allowed, thermally forbidden



*Simple Single Rule: “4-Con-Tha”*

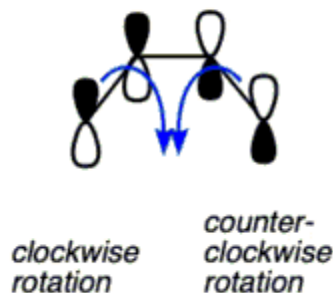


# Mode of Rotation: *Conrotatory* vs *Disrotatory*

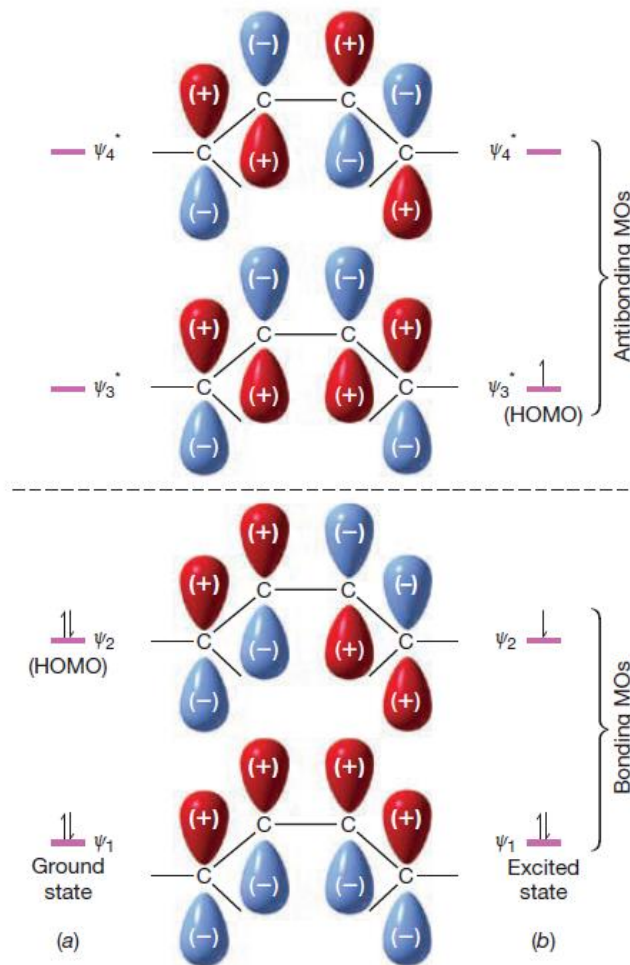


**What if both lobes rotate in the opposite direction?**

If both lobes rotate in the opposite direction, there will not be constructive orbital overlap and no bond can form.



# Frontier Molecular Orbitals (FMO): $4\pi e$ -Systems

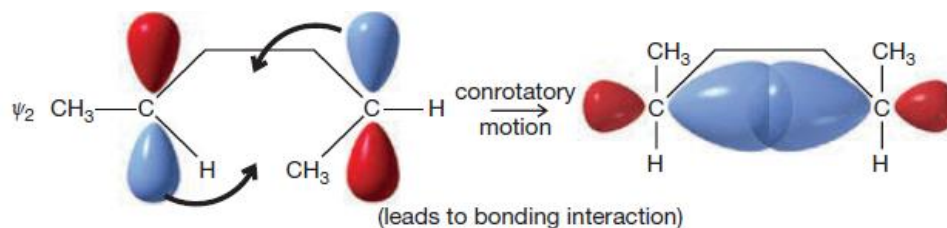
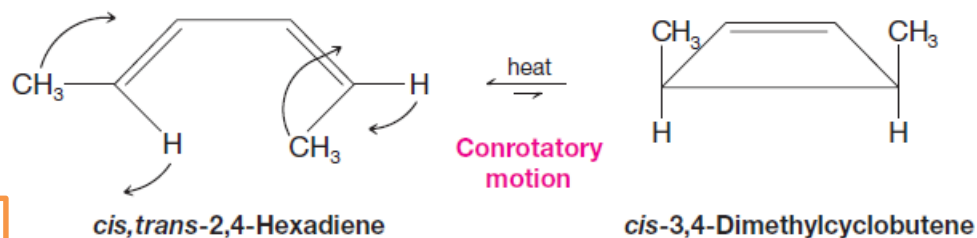


$\psi$  = LCAO (Linear combination of Atomic orbitals)

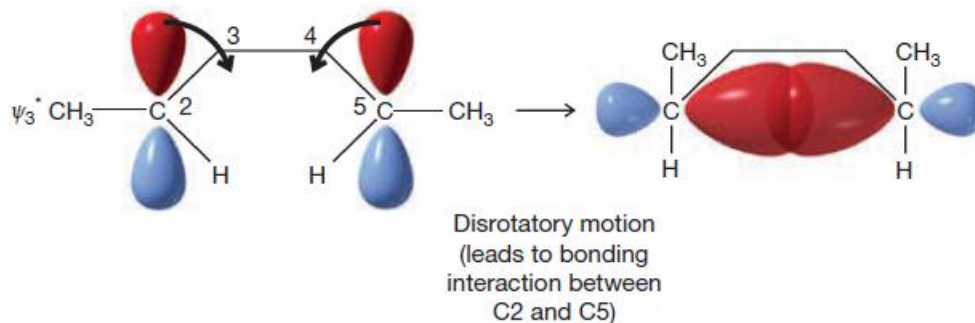
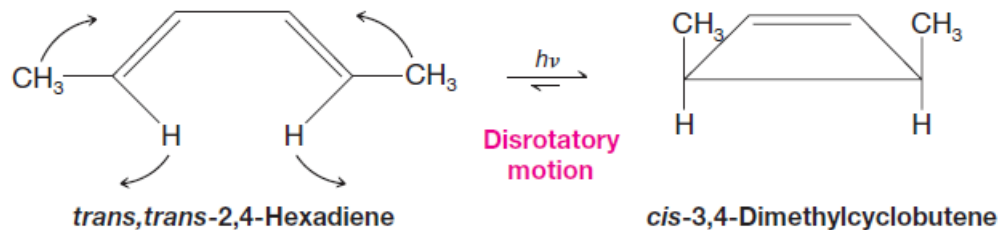
**FIGURE D.1** The  $\pi$  molecular orbitals of a 2,4-hexadiene (other parts of the formula omitted for clarity). (a) The electron distribution of the ground state. (b) The electron distribution of the first excited state. (The first excited state is formed when the molecule absorbs a photon of light of the proper wavelength.) Notice that the orbitals of a 2,4-hexadiene are like those of 1,3-butadiene shown in Fig. 13.4.

# Electrocyclic Reaction: $4\pi e^-$ -Systems

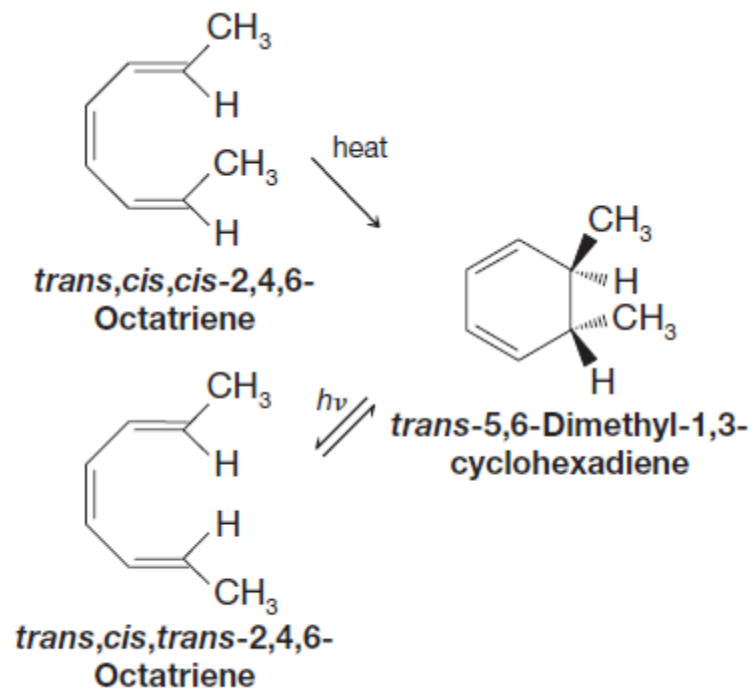
## Thermal



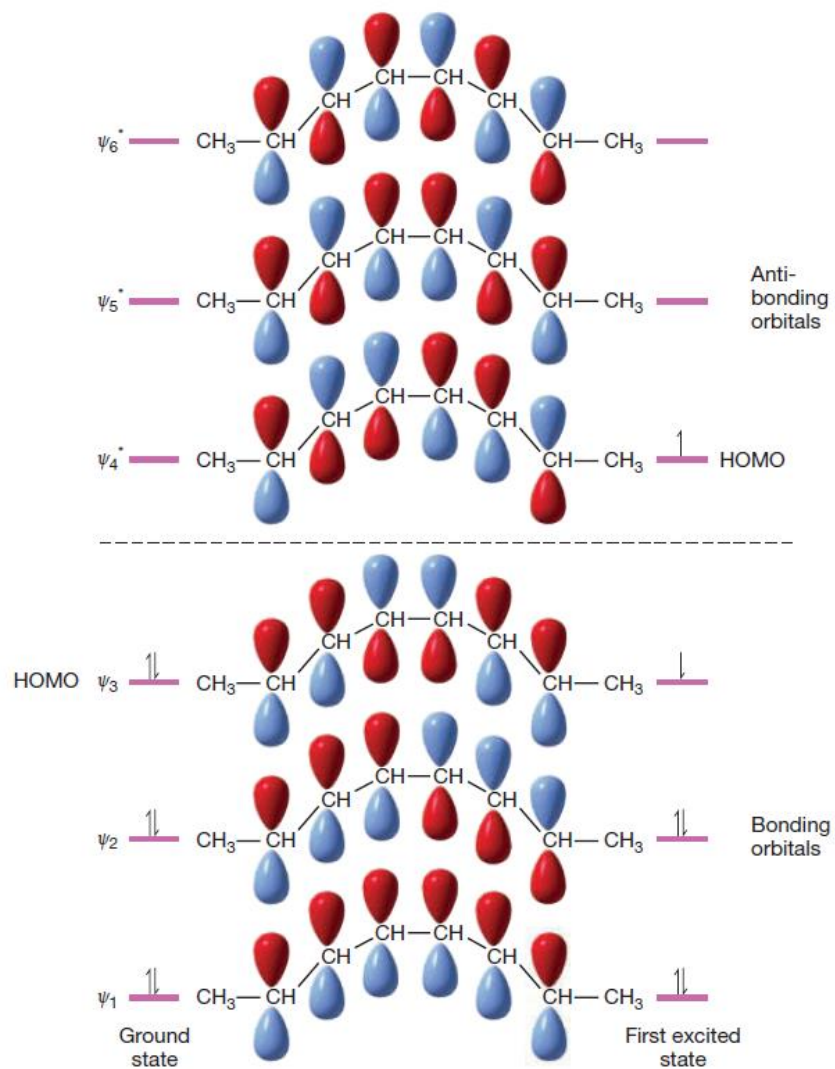
## Photochemical



# Electrocyclic Reaction: $6\pi$ -Systems

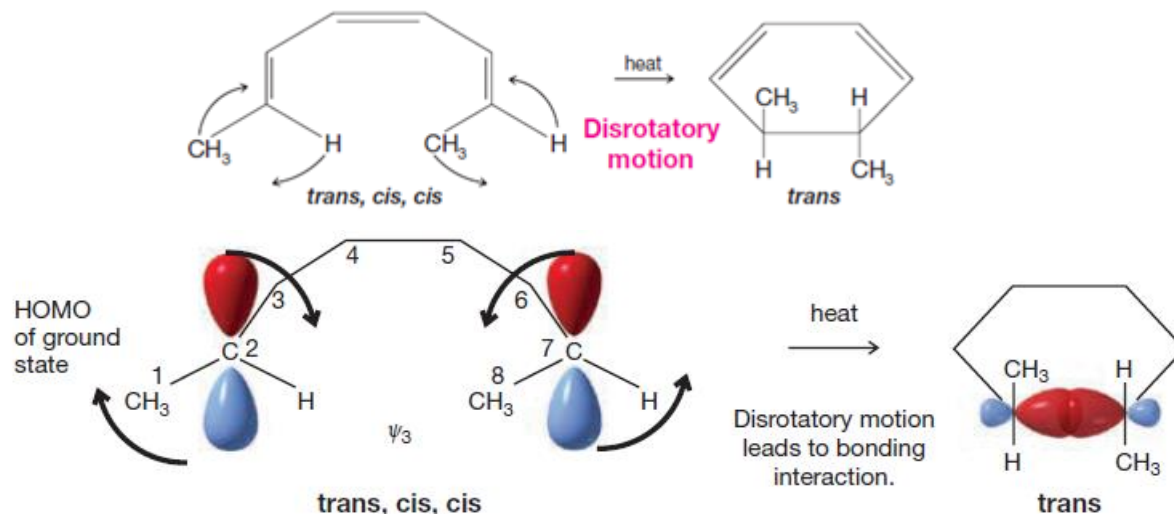


# Frontier Molecular Orbitals: $6\pi$ -System

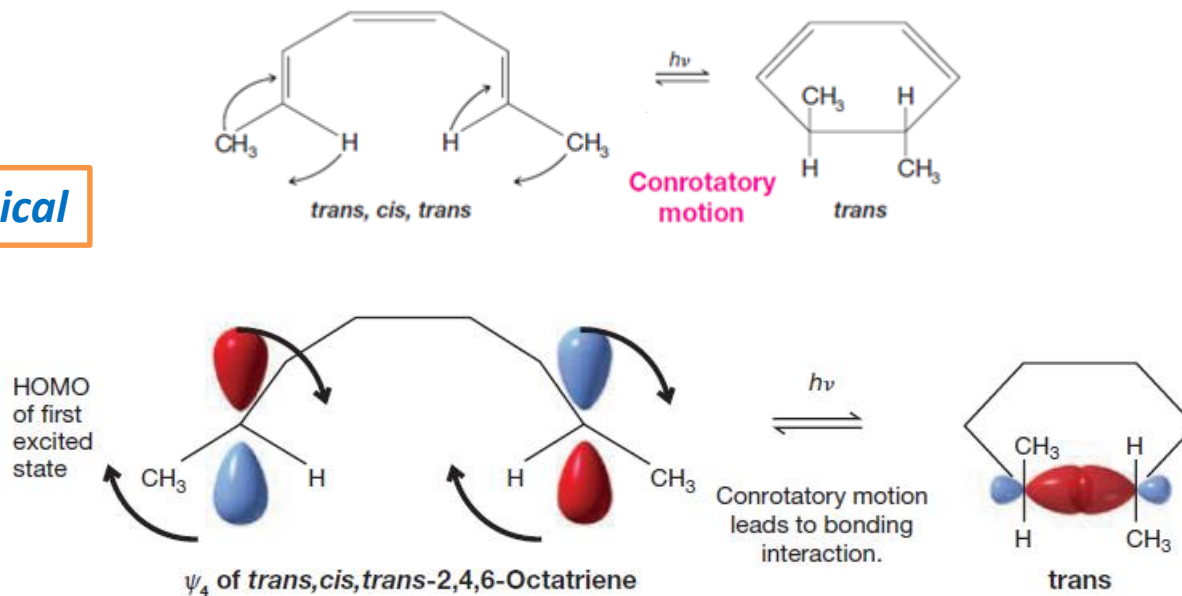


# Electrocyclic Reaction: $6\pi$ -Systems

## Thermal



## Photochemical



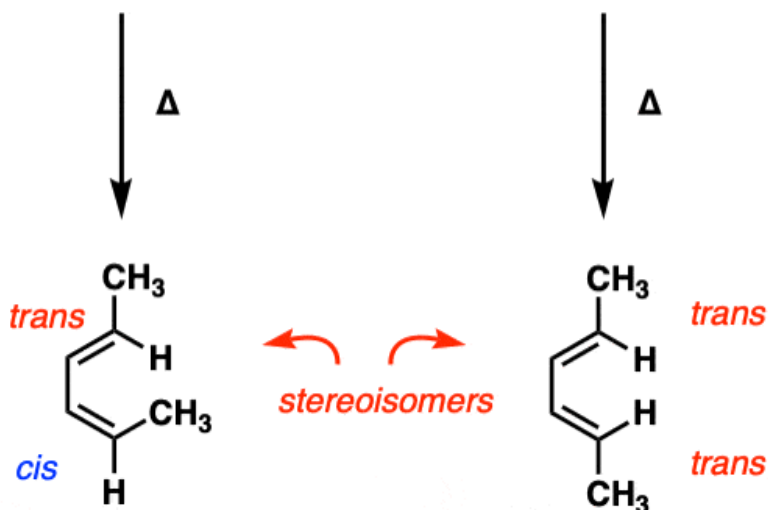


## Electrocyclic Reactions Are Stereospecific

*cis*- and *trans*- 3,4-dimethylcyclobutene are stereoisomers



The products of their electrocyclic ring-opening reactions are also stereoisomers.



Electrocyclic ring-opening and ring-closing reactions are **stereospecific**; the stereochemistry of the products can be predicted from knowing the stereochemistry of the reactants.