

M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry



II. Pericyclic Reactions
3. Electrocyclic Reaction
(FMO Method)



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II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatory and disrotatory motion, $4n$ and $(4n+2)$ systems, Cycloaddition reaction: $[2+2]$ and $[4+2]$ cycloaddition reaction, Cycloaddition of ketones, Secondary effects in $[4+2]$ cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

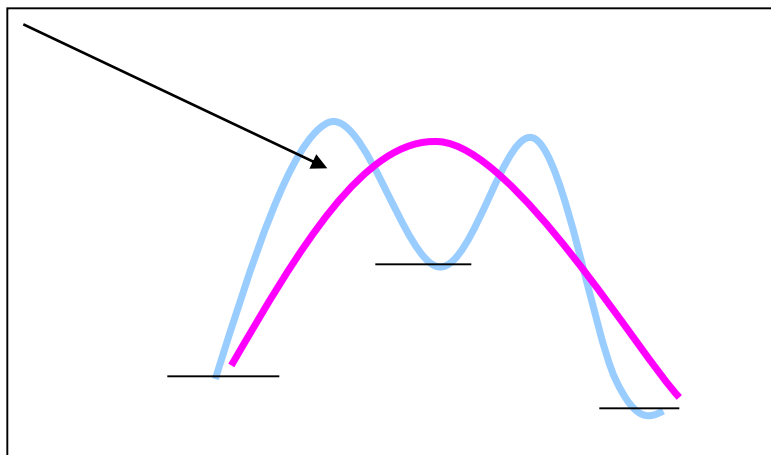
Sigmatropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, $[3,3]$ -, $[1,5]$ -, $[2,3]$ -, $[4,5]$ -, $[5,5]$ -, and $[9,9]$ -Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

Coverage:

Electrocyclic reactions: Conrotatory and disrotatory motion, $4n$ and $(4n+2)$ systems

Pericyclic Reactions

- Involves several simultaneous bond-making breaking process with a cyclic transition state involving delocalized electrons
- The combination of steps is called a **concerted process** where intermediates are skipped



Molecular Orbitals of Conjugated π Systems

- **A conjugated diene or polyene has alternating double and single bonds**
- **Bonding MOs are lower in energy than the isolated p atomic orbitals and have the fewest nodes**
- **Antibonding MOs are higher in energy**

1,3,5-Hexatriene

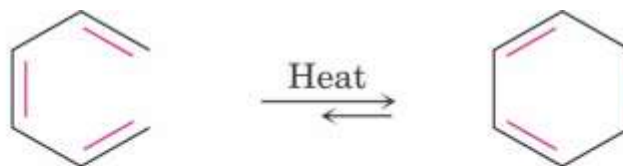
- **Three double bonds and six π MOs**
- **Only bonding orbitals, ψ_1 , ψ_2 , and ψ_3 , are filled in the ground state**
- **On irradiation with ultraviolet light an electron is promoted from ψ_3 to the lowest-energy unfilled orbital (ψ_4^*)**
- **This is the first (lowest energy) excited state**

Molecular Orbitals and Pericyclic Reactions

- If the symmetries of both reactant and product orbitals match the reaction is said to be *symmetry allowed* under the Woodward-Hoffmann Rules (these relate the electronic configuration of reactants to the type of pericyclic reaction and its stereochemical imperatives)
- If the symmetries of reactant and product orbitals do not correlate, the reaction is *symmetry-disallowed* and there are no low energy concerted paths
- Fukui's approach: we need to consider only the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), called the frontier orbitals

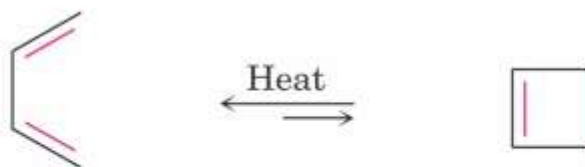
Electrocyclic Reactions

- These are pericyclic processes that involves the cyclization of a conjugated polyene
- One π bond is broken, the other π bonds change position, a new σ bond is formed, and a cyclic compound results
- Gives specific stereoisomeric outcomes related to the stereochemistry and orbitals of the reactants



A conjugated triene

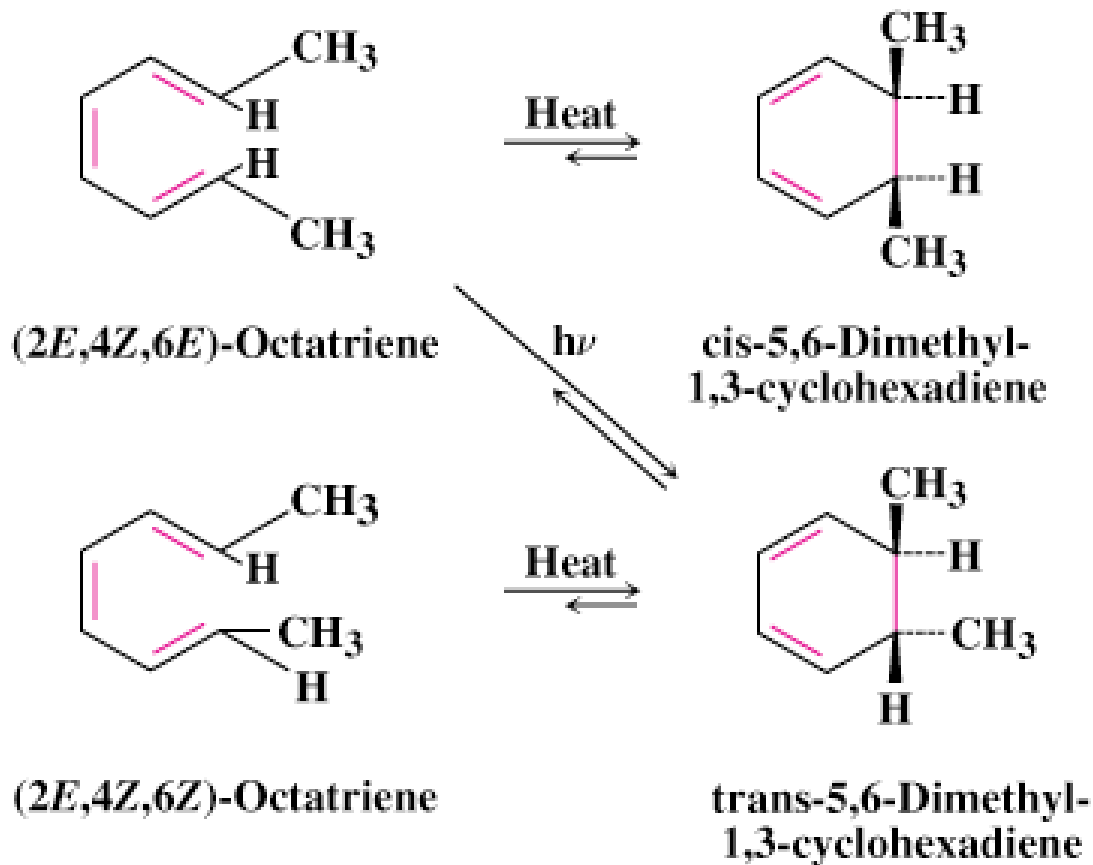
A cyclohexadiene



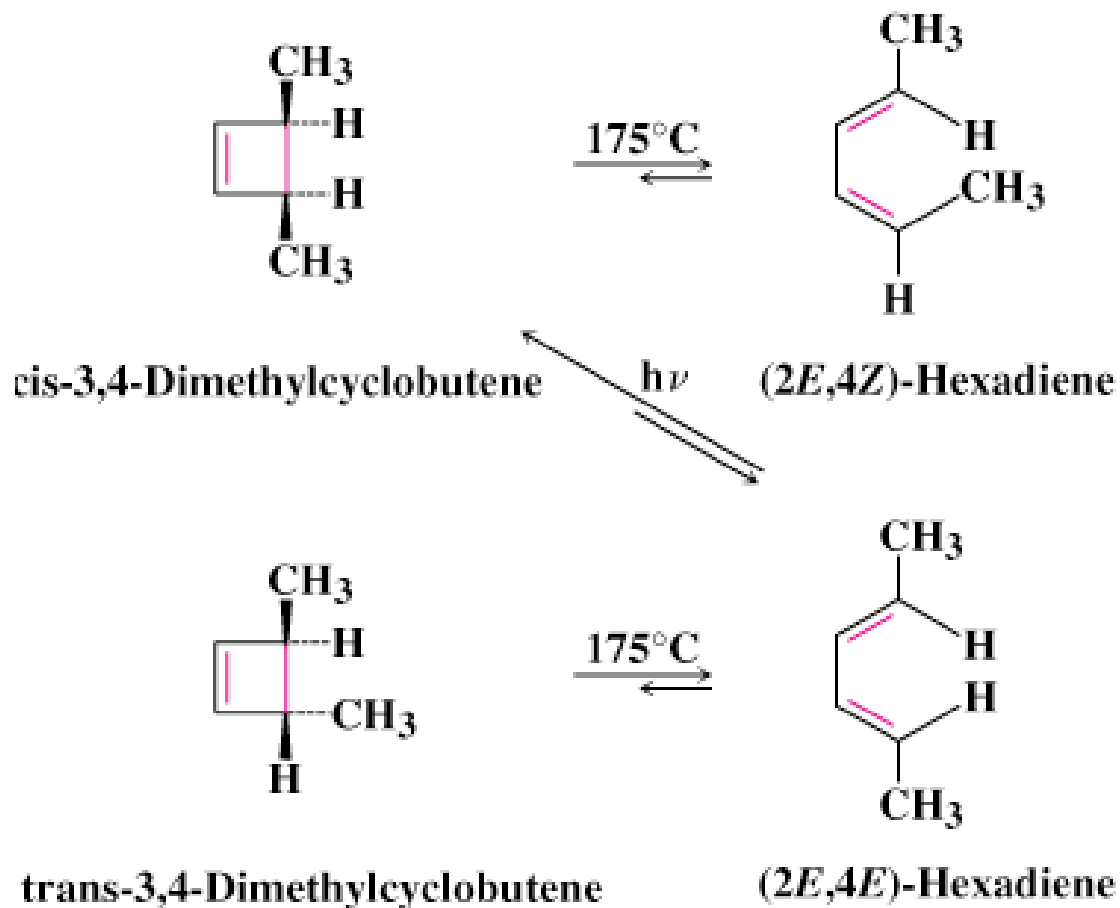
A conjugated diene

A cyclobutene

Example: Electrocyclic Interconversions With Octatriene

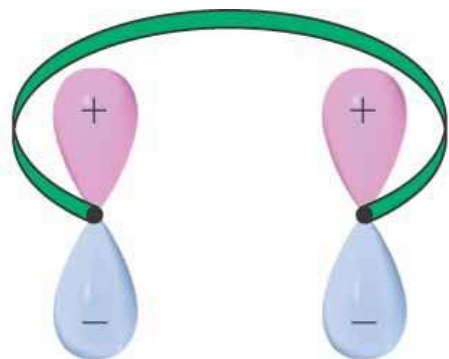


Example: Electrocyclic Interconversions with Dimethylcyclobutene



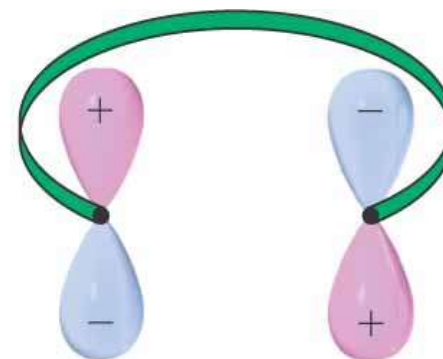
The Signs on the Outermost Lobes Must Match to Interact

- The lobes of like sign can be either on the same side or on opposite sides of the molecule.
- For a bond to form, the outermost π lobes must rotate so that favorable bonding interaction is achieved



Like lobes on same side

OR



Like lobes on opposite side

Disrotatory Orbital Rotation

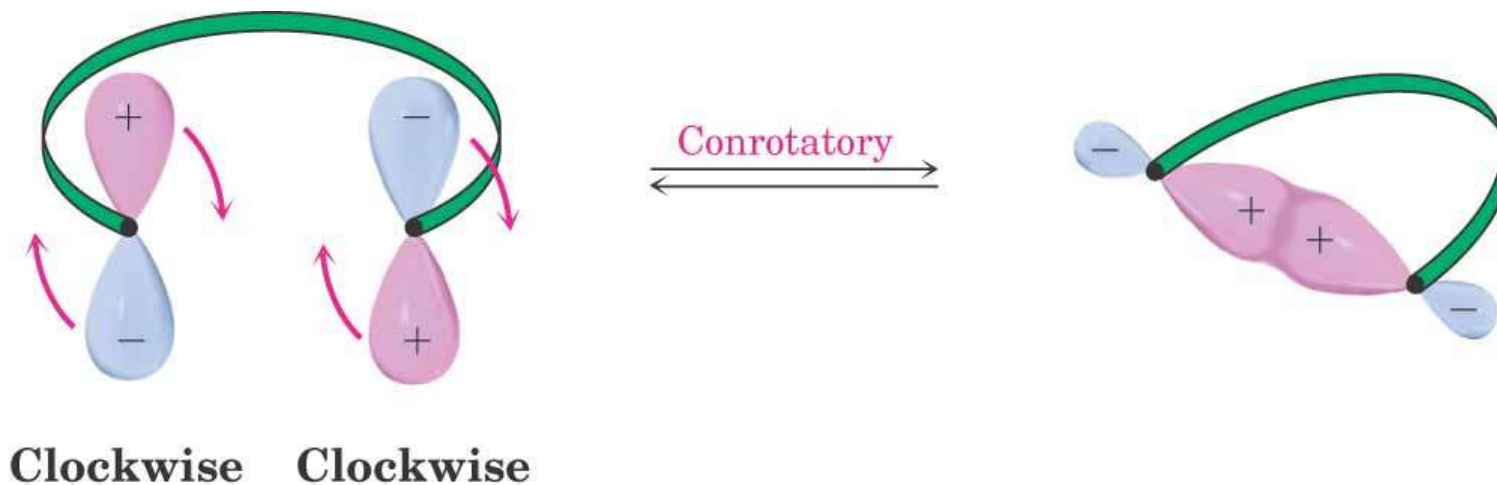
- If two lobes of like sign are on the same side of the molecule, the two orbitals must rotate in opposite directions—one clockwise, and one counterclockwise
- Woodward called this a disrotatory (dis-roh-tate'-or-ee) opening or closure



Clockwise Counterclockwise

Conrotatory Orbital Rotation

- If lobes of like sign are on opposite sides of the molecule: both orbitals must rotate in the same direction, clockwise or counterclockwise
- Woodward called this motion conrotatory (con-roh-tate'-or-ee)

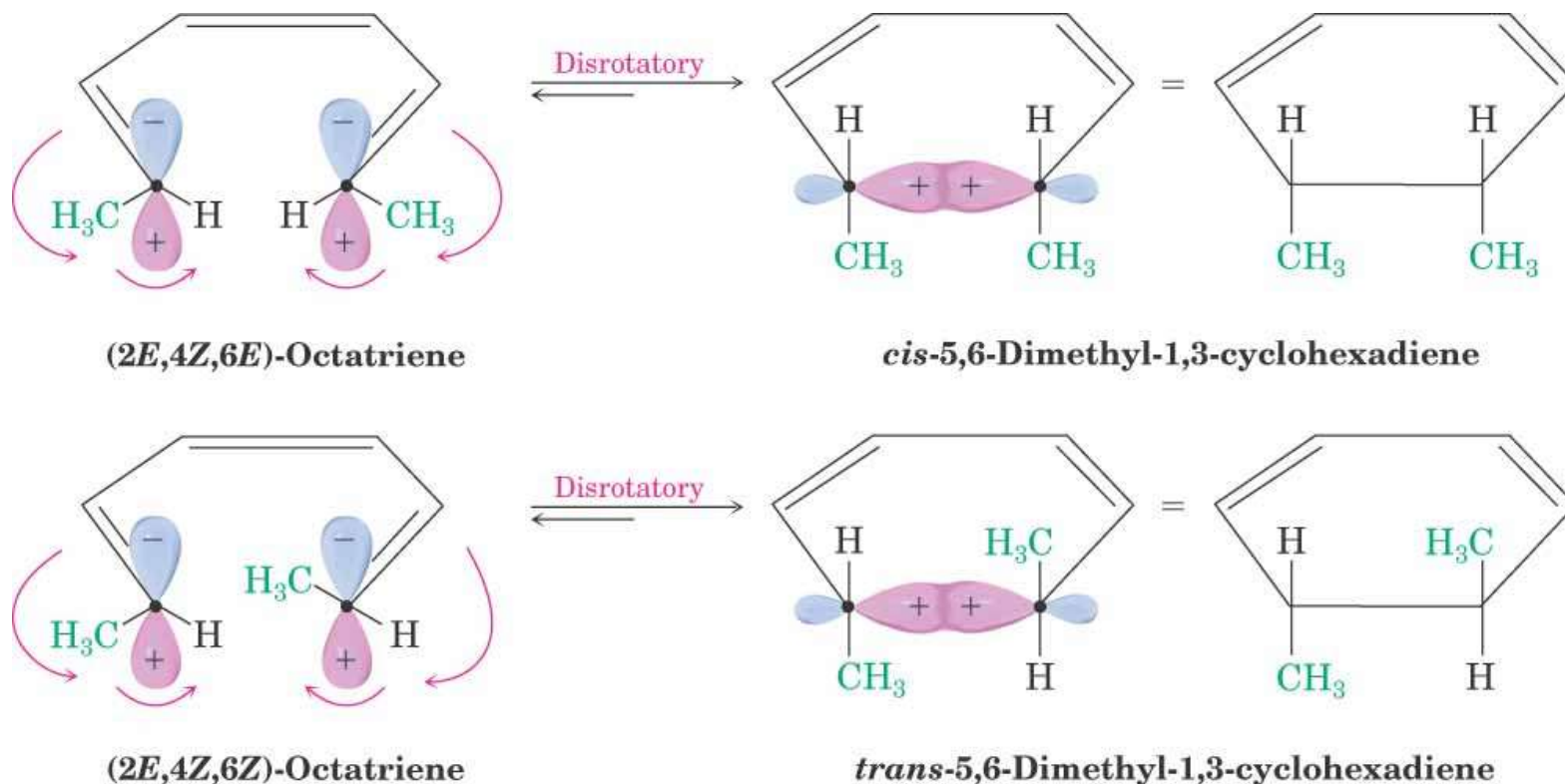


Stereochemistry of Thermal Electrocyclic Reactions

- **Determined by the symmetry of the polyene HOMO**
- **The ground-state electronic configuration is used to identify the HOMO**
- **(Photochemical reactions go through the excited-state electronic configuration)**

Ring Closure of Conjugated Trienes

- Involves lobes of like sign on the same side of the molecule and disrotatory ring closure

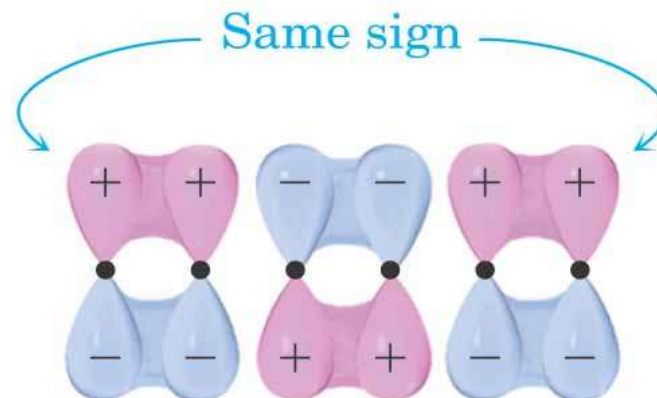


Contrast: Electrocyclic Opening to Diene

- **Conjugated dienes and conjugated trienes react with opposite stereochemistry**
- **Different symmetries of the diene and triene HOMOs**
- **Dienes open and close by a conrotatory path**
- **Trienes open and close by a disrotatory path**



Diene HOMO



Triene HOMO

Photochemical Electrocyclic Reactions

- **Irradiation of a polyene excites one electron from HOMO to LUMO**
- **This causes the old LUMO to become the new HOMO, with changed symmetry**
- **This changes the reaction stereochemistry (symmetries of thermal and photochemical electrocyclic reactions are always opposite)**

Selection Rules for Electrocyclic Reactions

Electron pairs (double bonds)	Thermal reaction	Photochemical reaction
Even number	Conrotatory	Disrotatory
Odd number	Disrotatory	Conrotatory

Thank You



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