B.Sc. Semester-VI
GroupA / DSE-4
Organic Synthesis

II. Pericyclic Reactions

3. Electrocyclic Reaction (FMO Method)

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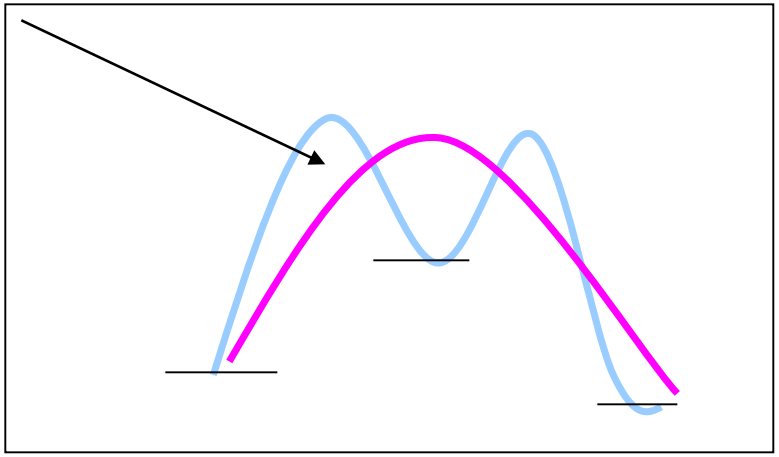
Pericyclic Reactions

- **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

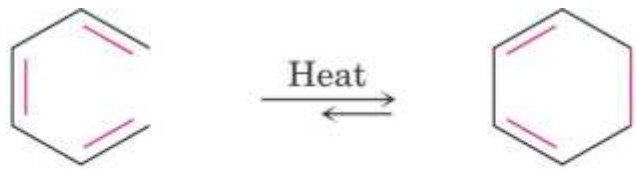
- **Three double bonds and six π MOs**
- **Only bonding orbitals, ψ_1, ψ_2, and ψ_3, are filled in the ground state**
- **On irradiation with ultraviolet light an electron is promoted from ψ_3 to the lowest-energy unfilled orbital (ψ_4*)**
- **This is the first (lowest energy) excited state**

Molecular Orbitals and Pericyclic Reactions

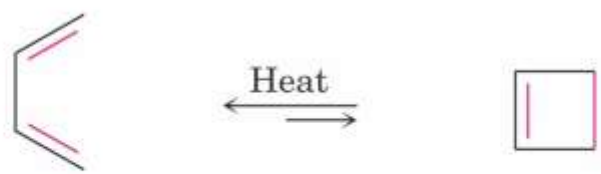
- **If the symmetries of both reactant and product orbitals match the reaction is said to be *symmetry allowed* under the Woodward-Hoffmann Rules (these relate the electronic configuration of reactants to the type of pericyclic reaction and its stereochemical imperatives)**
- **If the symmetries of reactant and product orbitals do not correlate, the reaction is *symmetry-disallowed* and there 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**

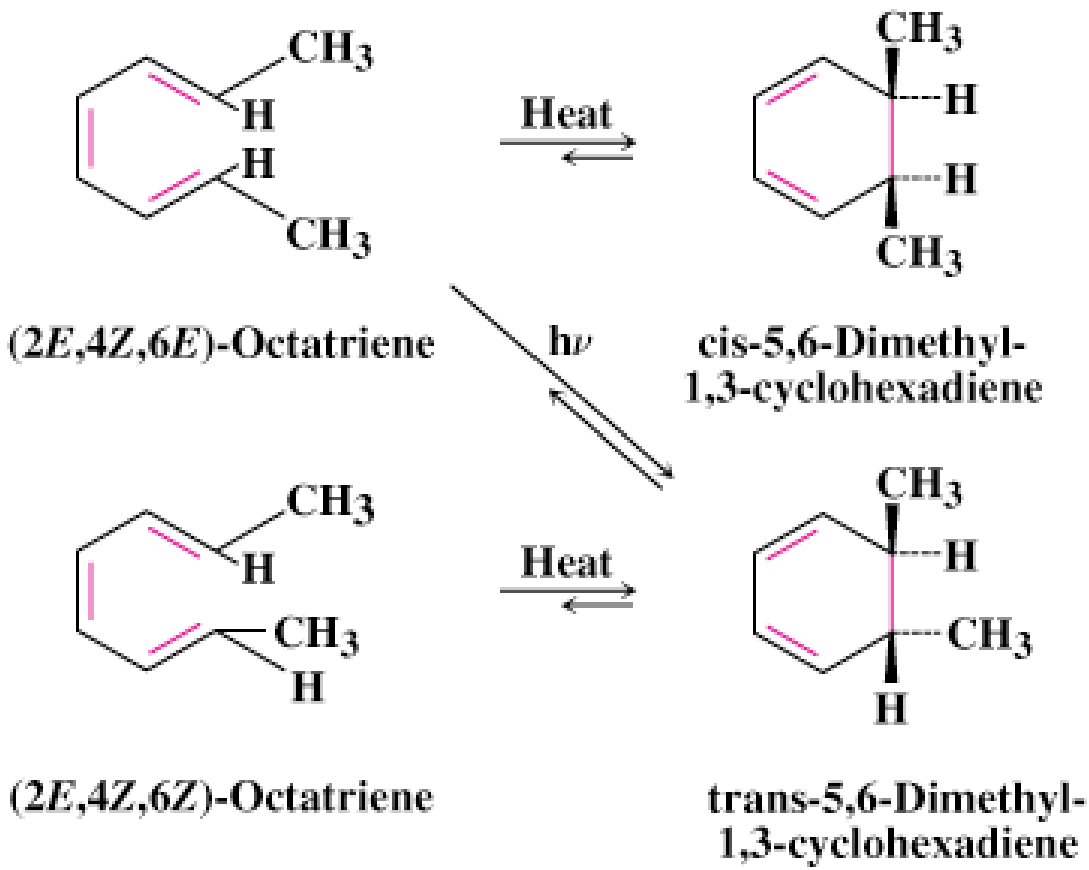


A conjugated triene **A cyclohexadiene**

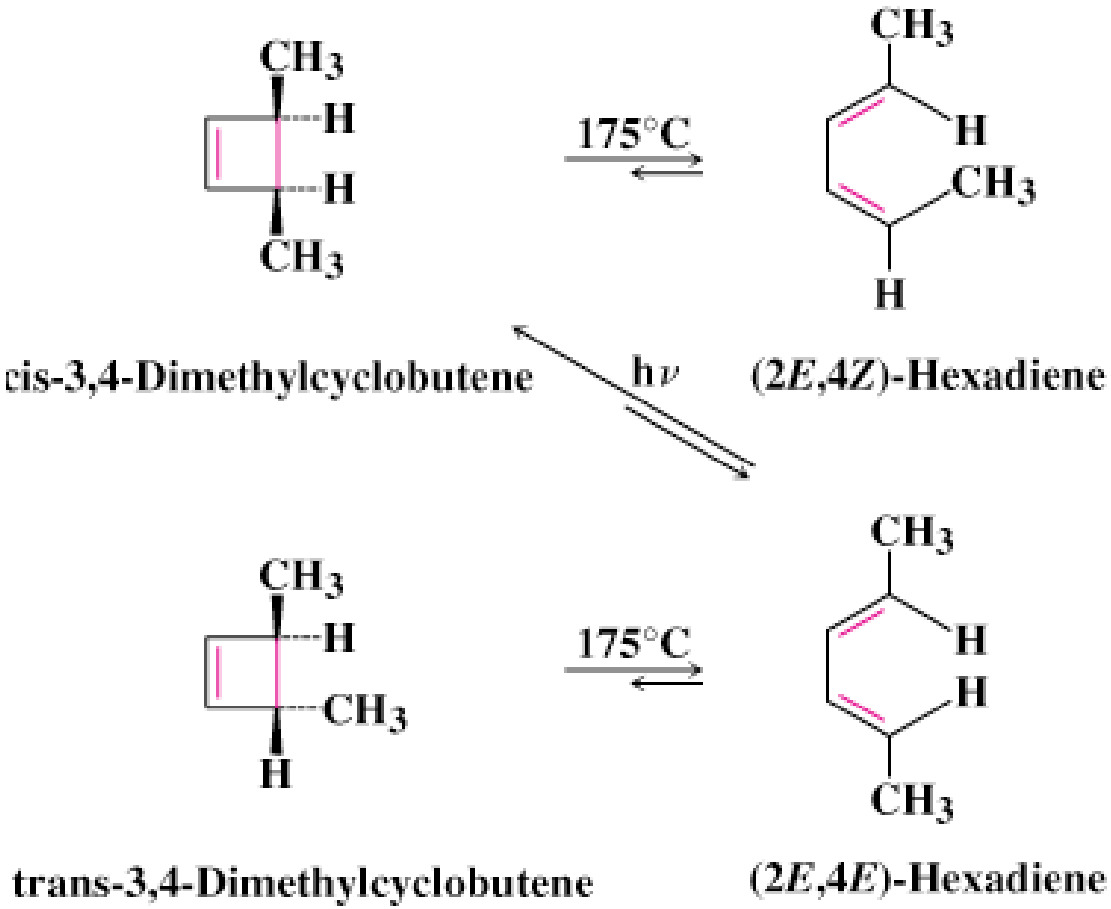


A conjugated diene **A cyclobutene**

Example: Electrocyclic Interconversions With Octatriene

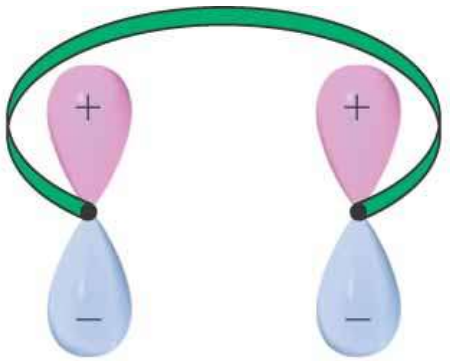


Example: Electrocyclic Interconversions with Dimethylcyclobutene



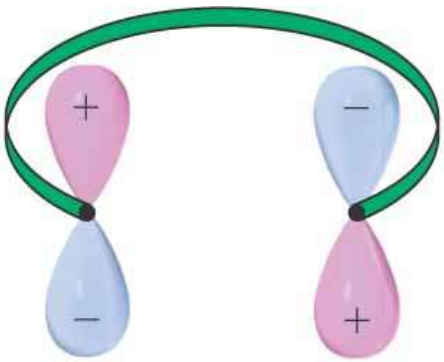
The Signs on the Outermost Lobes Must Match to Interact

- **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

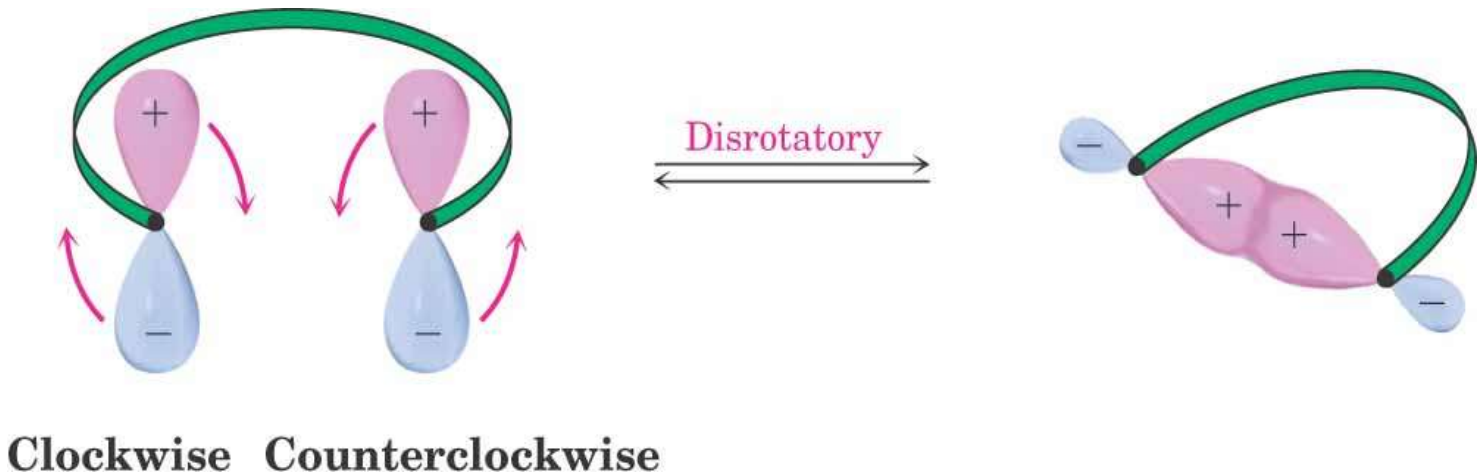
OR



Like lobes on opposite side

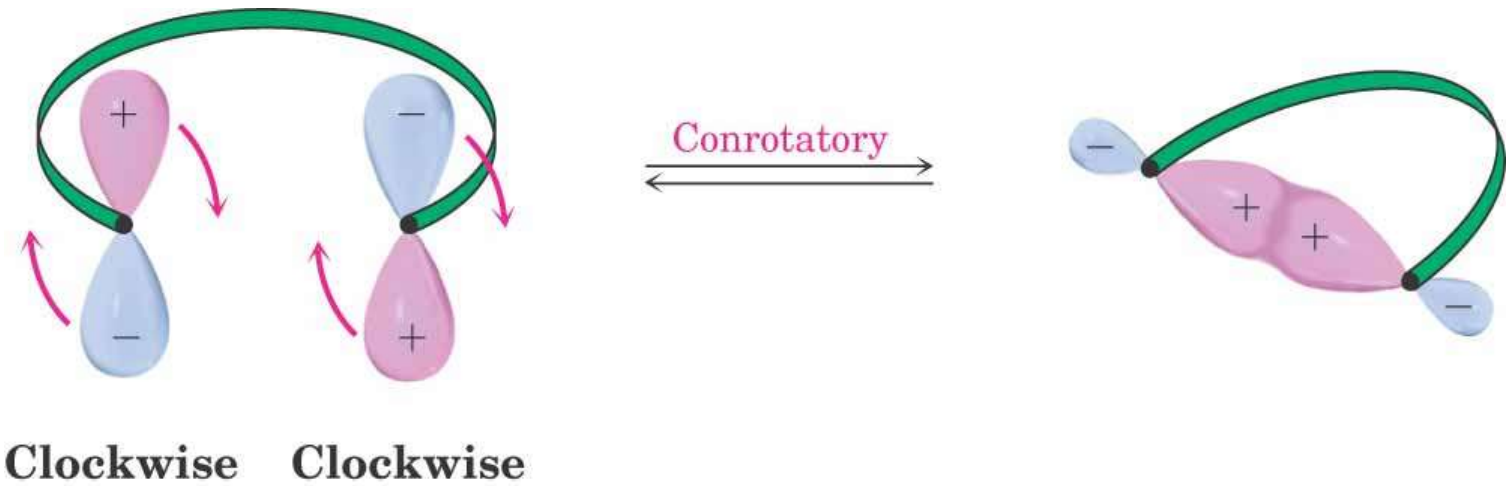
Disrotatory Orbital Rotation

- **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**



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)**

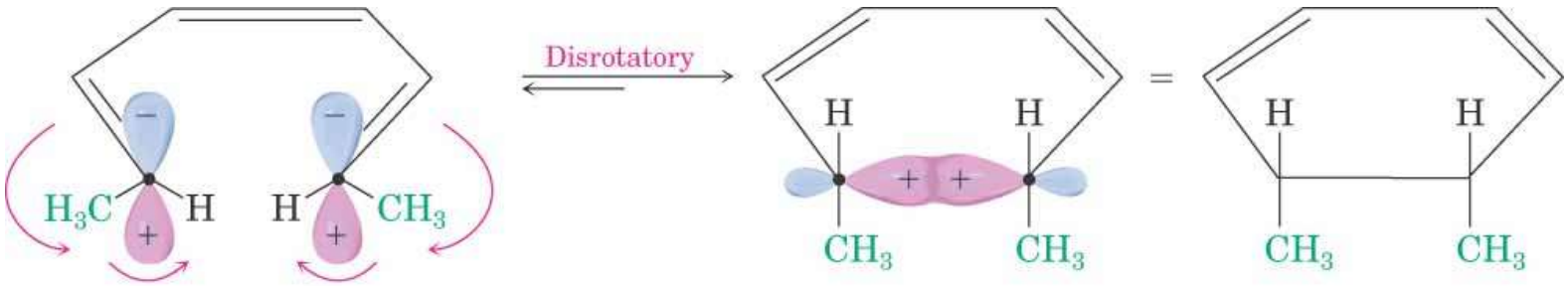


Stereochemistry of Thermal Electrocyclic Reactions

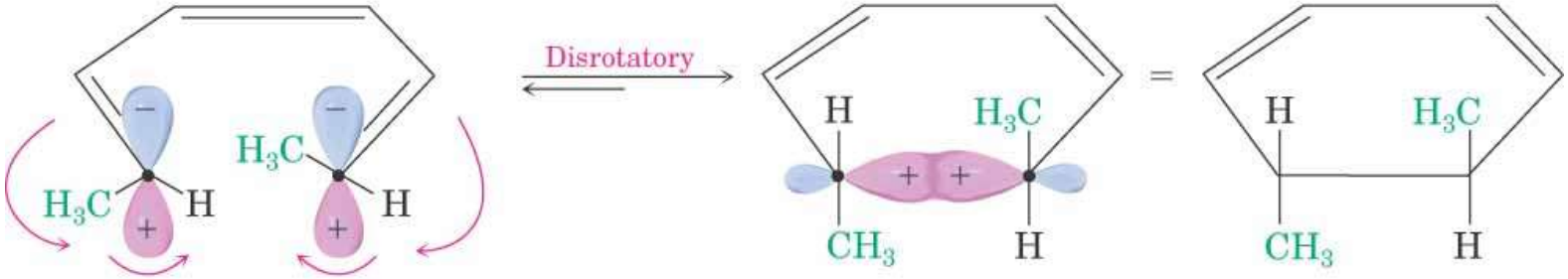
- **Determined by the symmetry of the polyene HOMO**
- **The ground-state electronic configuration is used to identify the HOMO**
- **(Photochemical reactions go through the excited-state electronic configuration)**

Ring Closure of Conjugated Trienes

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



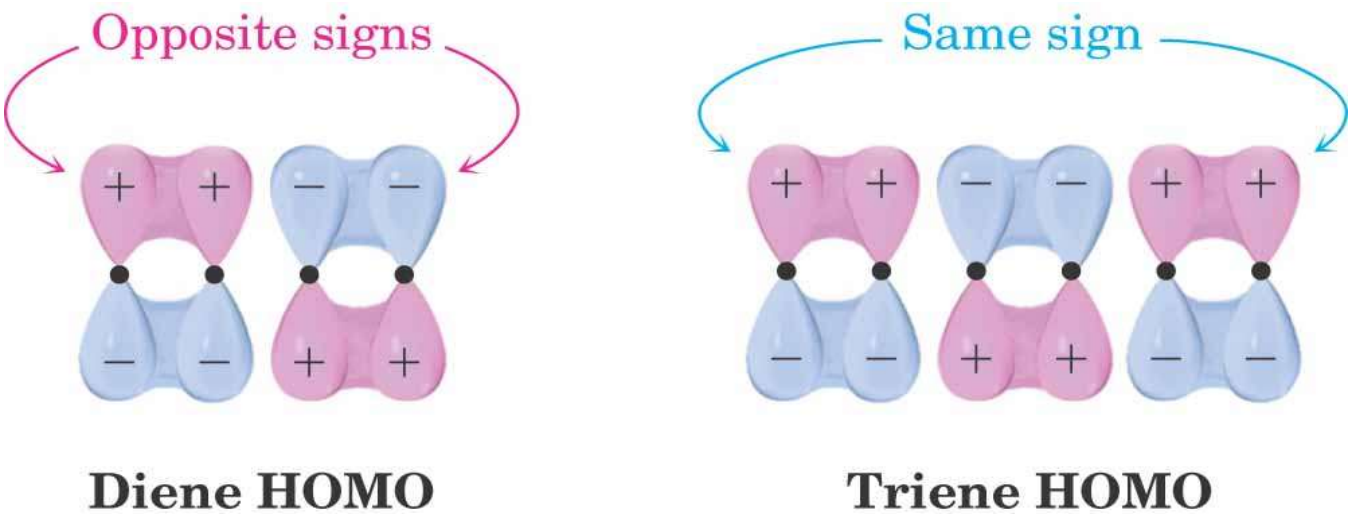
(2*E*,4*Z*,6*E*)-Octatriene **_cis_-5,6-Dimethyl-1,3-cyclohexadiene**



(2*E*,4*Z*,6*Z*)-Octatriene **_trans_-5,6-Dimethyl-1,3-cyclohexadiene**

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**



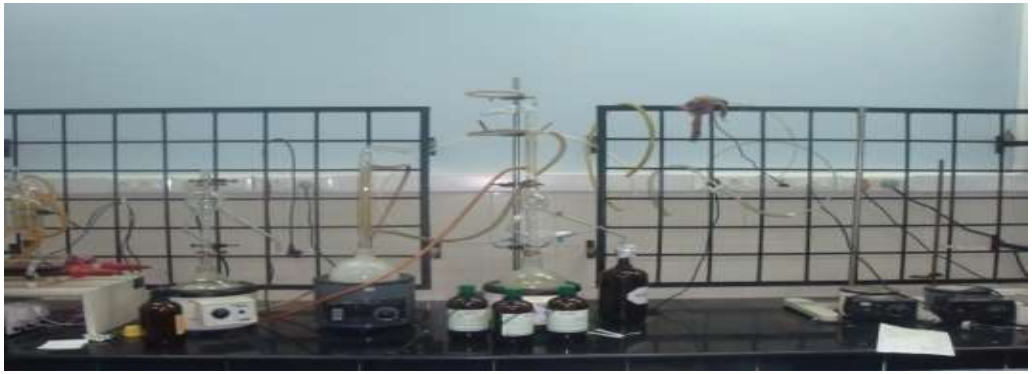
Photochemical Electrocyclic Reactions

- **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 electrocylic 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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