Recap - MOs of Larger Conjugated Polyenes

- The lowest energy orbital is always symmetric with respect to the principal mirror plane

- The energy of the MO increases as the no: of nodes increases

  Eg. ψ_1 - 0 nodes

  ψ_2 - 1 node

  ψ_n - n-1 nodes

  Remember to ignore the nodes of the AO

- **When you draw MOs place the nodes symmetrically**

Recap - MO and Reactions

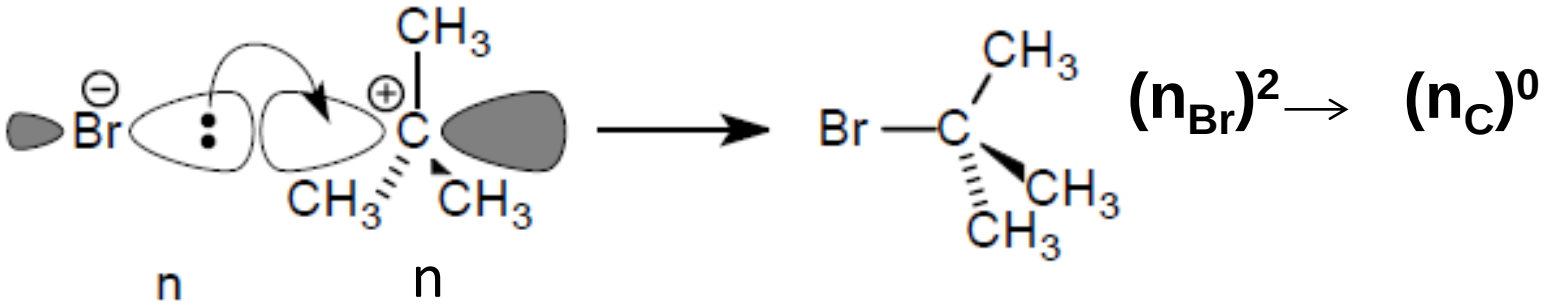
Electron donor – Occupied Oribtal i.e. HOMO
Electron acceptor – Unoccupied Oribtal i.e. LUMO

HOMO possibilities	**LUMO** possibilities
Filled/Occupied	Unfilled/Unoccupied
σ	**σ***
π	**π***
n (non-bonding)	**n (nonbonding)**

Explanation of Reactions Through Molecular Orbitals

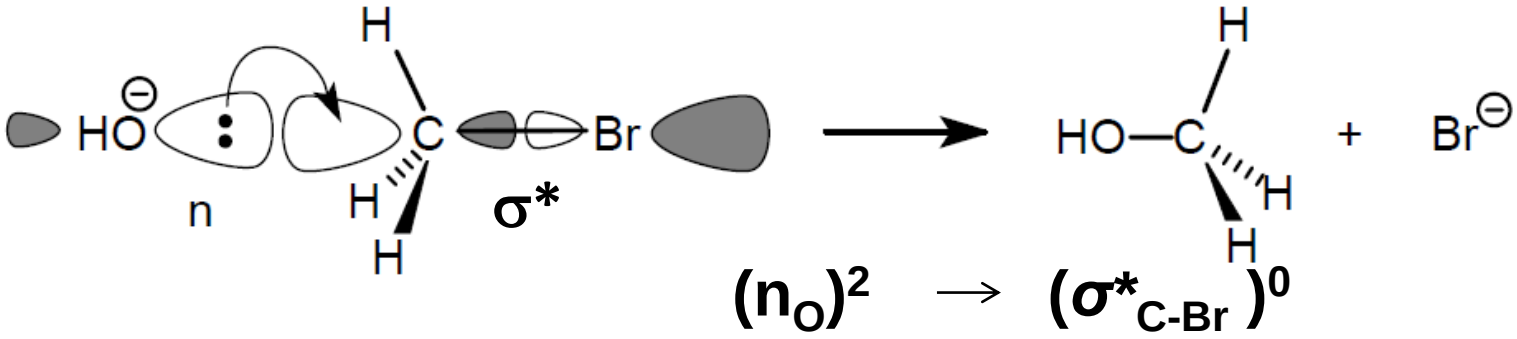
S_N1 Reaction – Attack from both sides of carbocation ok

$(CH_3)_3C^+ + :Br^- \rightarrow (CH_3)_3C–Br$



S_N2 Reaction – backside attack only possible

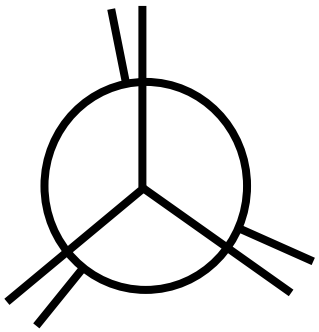
$HO^- + CH_3–Br \rightarrow HO–CH_3 + Br^-$



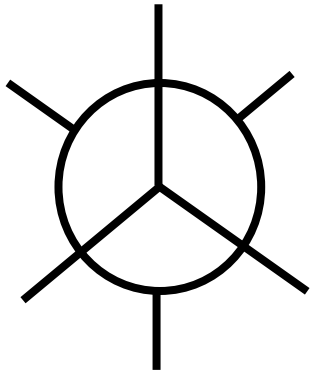
Rotational Barrier in Ethane

Barrier of 3 kcal mol^{-1} due to steric and electronic effects

Transition state is eclipsed

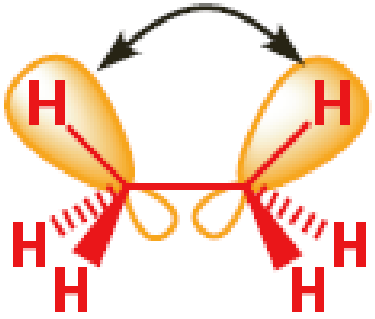


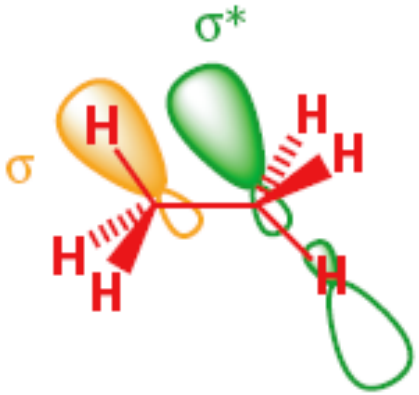
Most stable rotamer is staggered



eclipsed:

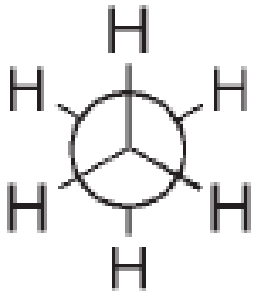
filled orbitals repel



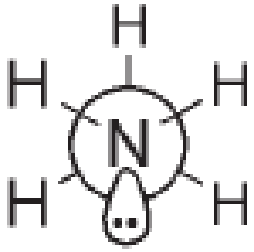


and empty C–H σ* antibonding orbital

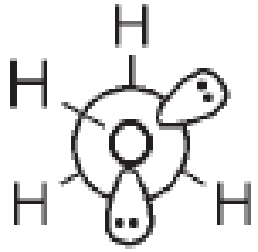
Lone Pairs Are Not Bad!



3 kcal



2 kcal



1 kcal

Or…….

Lone pairs or not that great for staggered conformation!!

Broad Classification: Organic Reactions

- **Polar Mechanism**

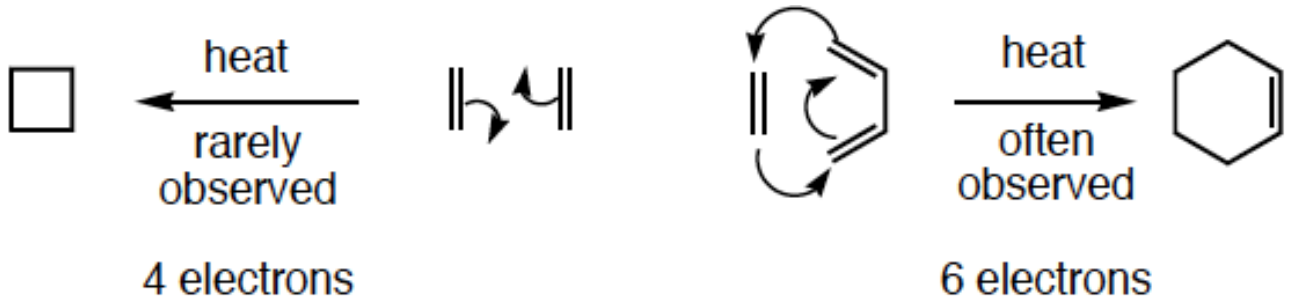
- **Radical Mechanism**

- **Concerted Reactions**
  All the bonding changes occur at the same time and in a single step – No intermediates involved !

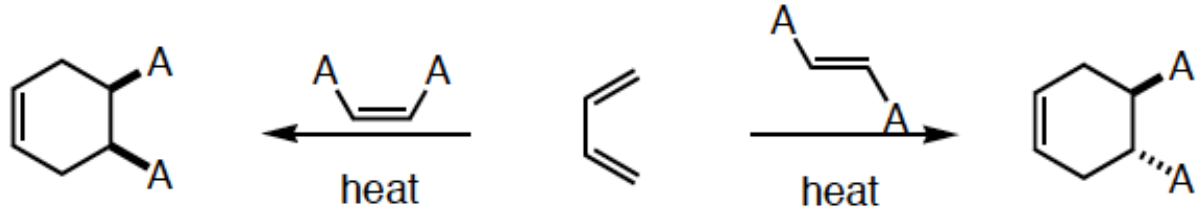
Pericyclic reactions – Concerted reactions that occur through a cyclic transition state

Pericyclic Reactions: Factors to Consider

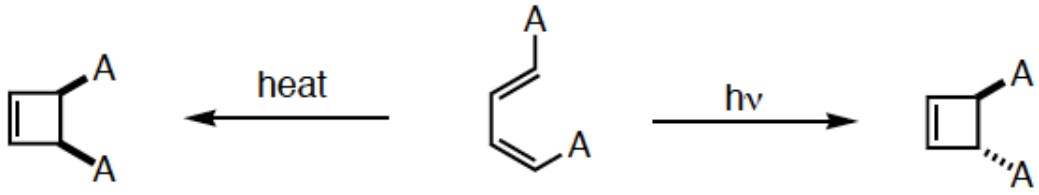
- Reactivity affected by number of electrons involved in reaction



- Reactions are stereospecific

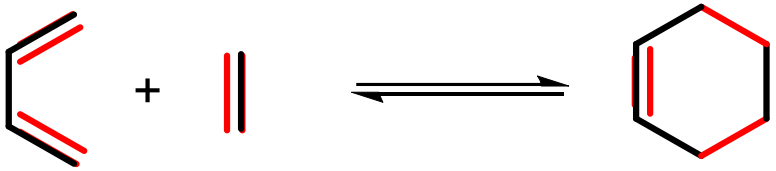


- Stereochemistry depends on reaction conditions

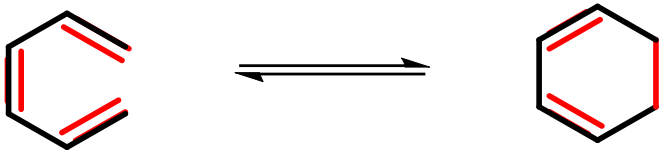


MOs play a very important role

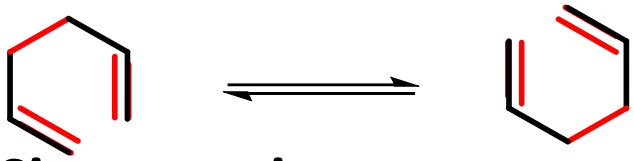
Classification of Pericyclic Reactions



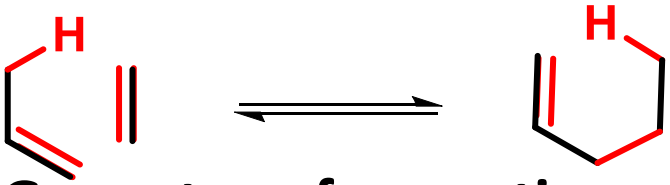
Cycloaddition reaction



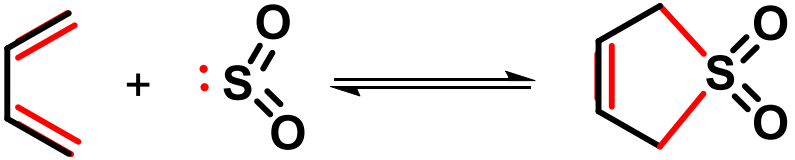
Electrocyclic reactions



Sigmatropic rearrangement



Group transfer reactions



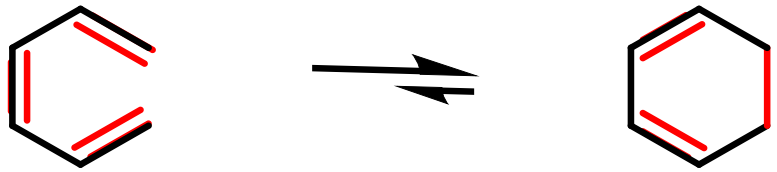
Cheletropic reactions

Reagents - Heat (Δ) or Light (hν)

Class 1- Electrocyclic Reactions

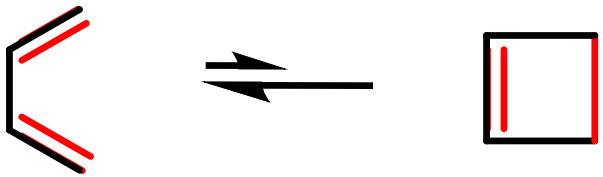
Cyclization of a **conjugated** polyene (ring closing)

- Outermost π bonds converted to σ bond and π bonds reorganized
- Classified based on the number of π electrons **highlighted in red**



Conjugated triene cyclohexadiene

6 e^- system



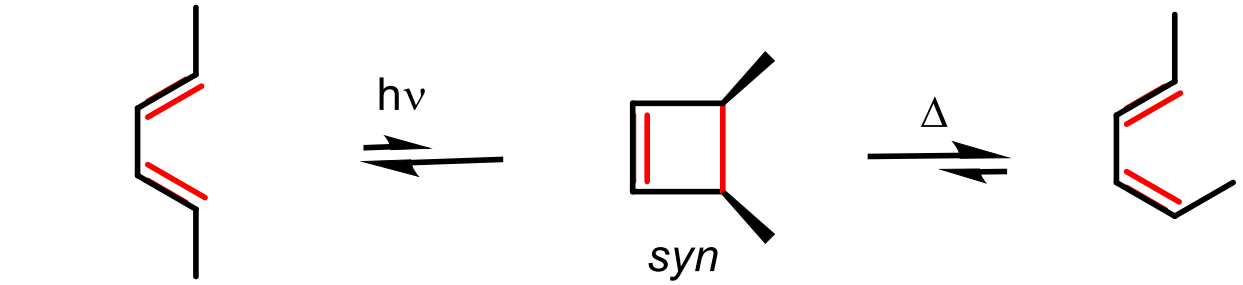
Conjugated diene cyclobutene

4 e^- system

Reverse process (ring opening)

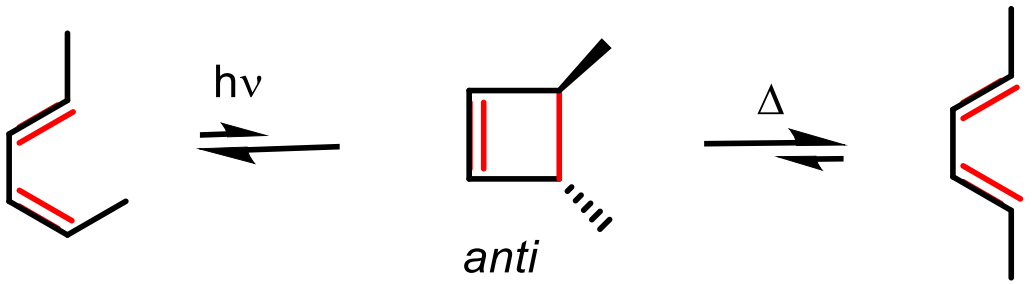
Striking Feature – Electrocyclic Reactions

Stereochemistry - Highly stereospecific



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

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



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

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

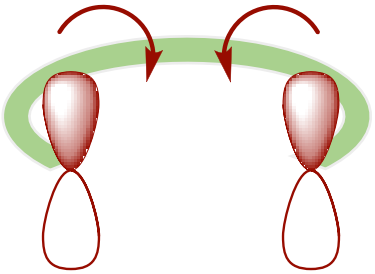
4n system

Pi bonds convert to a sigma (axial overlap)

How??

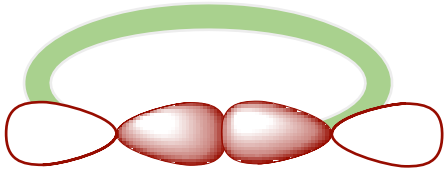
Orbital Interactions – Electrocyclic Reactions

Two possibilities

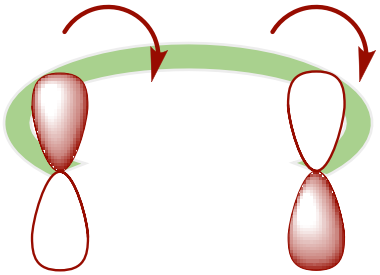


Outermost orbitals
Same symmetry

Dis rotatory



Bonding interaction
Symmetry allowed



Outermost orbitals
Opposite symmetry

Con rotatory

The lobes of the reactant MOs must of the correct sign (phase) for bonding to occur in the transition state leading to product

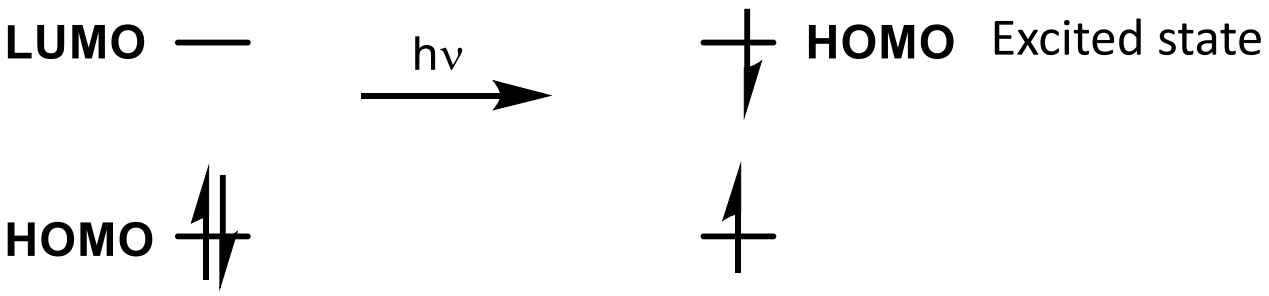
Understanding Stereospecificity

Frontier Molecular Orbitals (FMO) Theory

Stereochemistry of an electrocyclic reaction is determined by the symmetry of the polyene HOMO

Thermal Reactions - Ground state HOMO

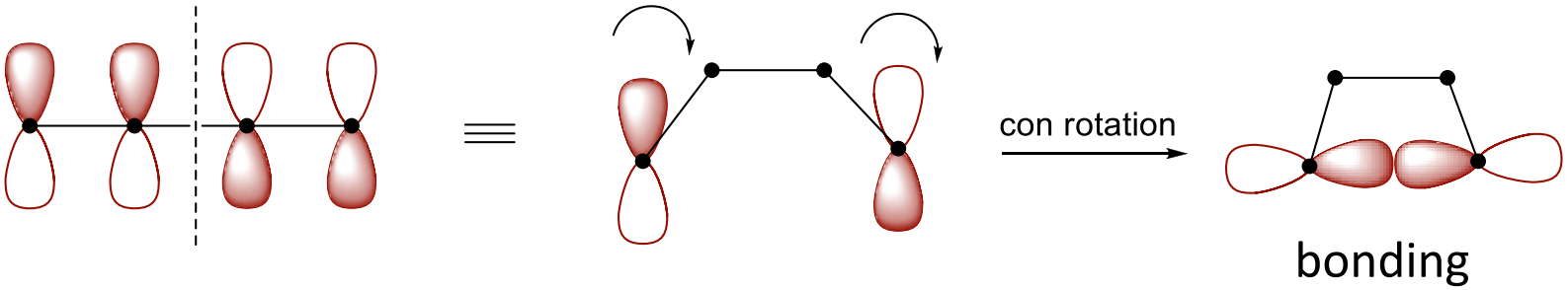
Photochemical Reactions – Excited state is the HOMO



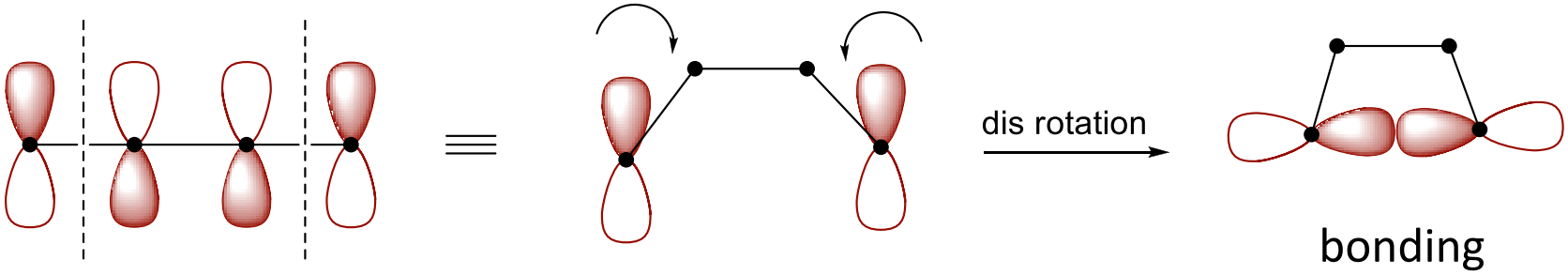
FMO Explanation – Butadiene Stereospecificity

Butadiene – 4 e^- system

Thermal reaction - HOMO is ψ_2

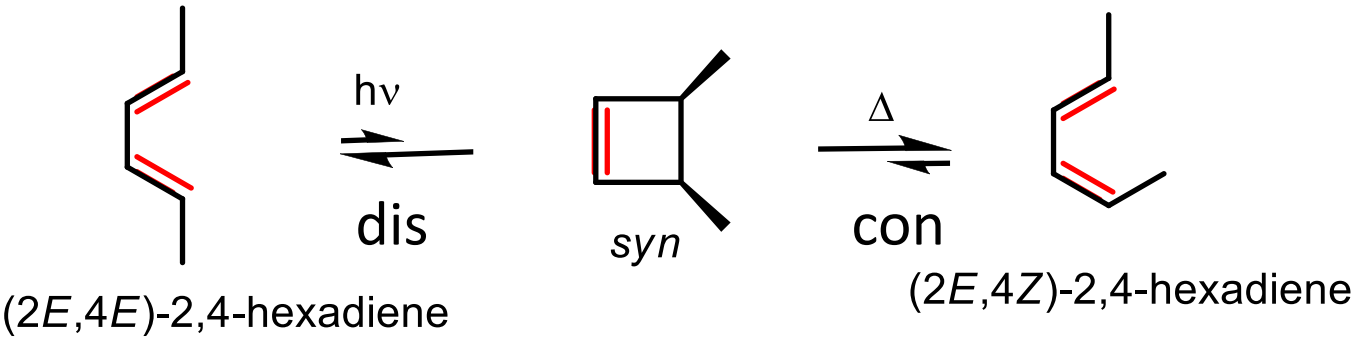


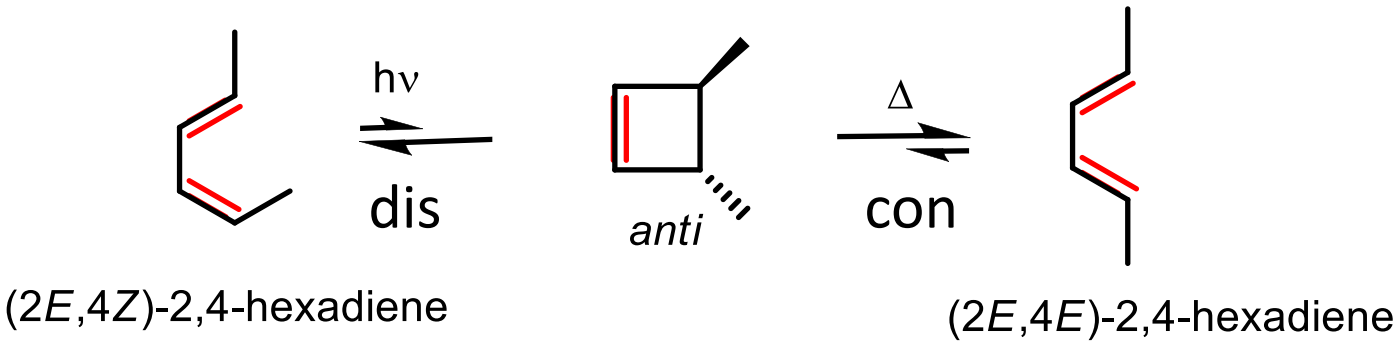
Photochemical reaction - HOMO is ψ_3



Is applicable to any 4n system

Revisiting Stereospecificity





4 e^- system

The groups attached to carbons undergoing dis/con will also rotate in that direction!!

Steps to Understand Stereospecificity

Any 4n system

Thermal conditions

- Draw **ground state** HOMO for butadiene
- Determine **mode of closure**

Photochemical conditions

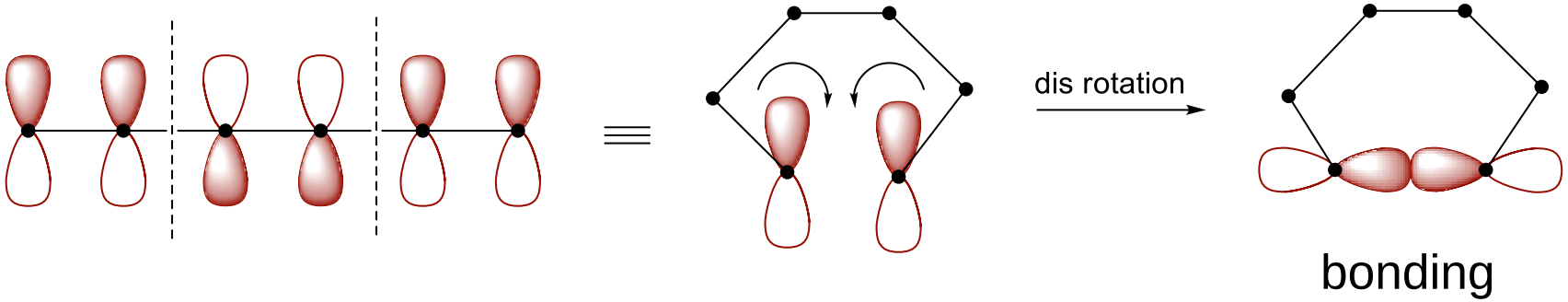
- Draw **excited state** HOMO for butadiene
- Determine **mode of closure**

Activity: FMO treatment for hexatriene

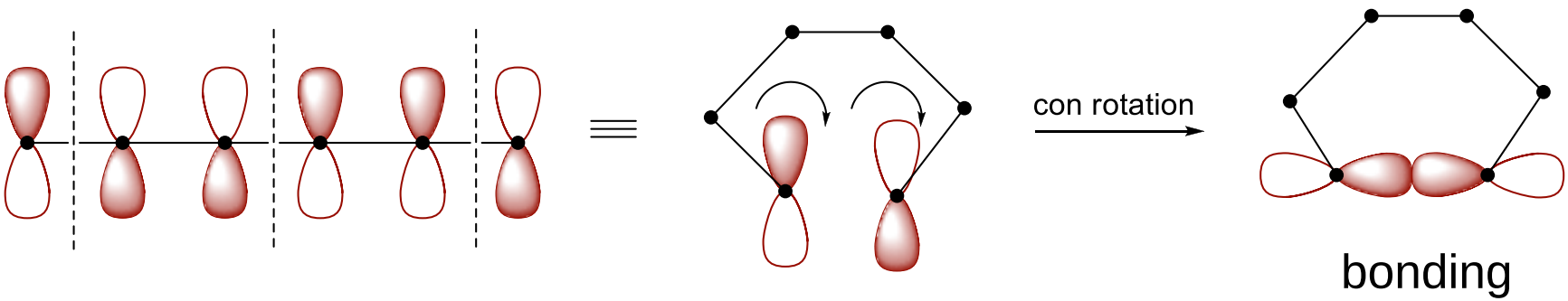
FMO Explanation – Hexatriene Systems

Hexatriene – 6 e^- system

Thermal reaction - HOMO is ψ_3



Photochemical reaction - HOMO is ψ_4



Is applicable to any 4n+2 system

Steps to Understand Stereospecificity

Any 4n + 2 system

Thermal conditions

- Draw **ground state** HOMO for hexatriene
  - Determine **mode of closure**

Photochemical conditions

- Draw **excited state** HOMO for hexatriene
  - Determine **mode of closure**

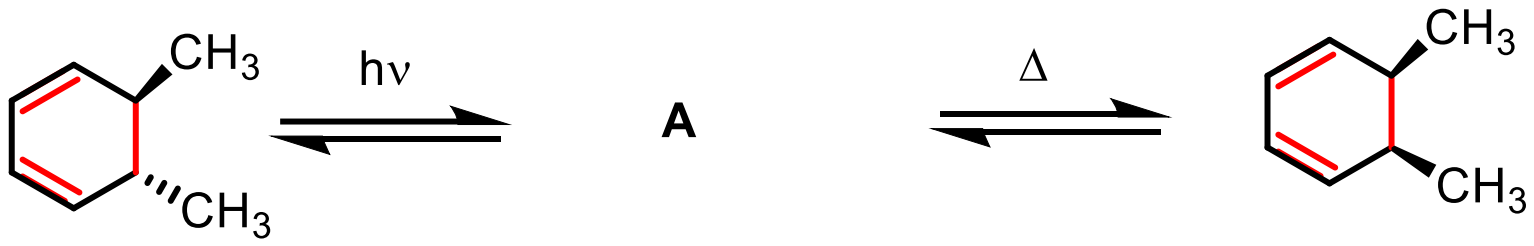
Woodward-Hoffman Rules

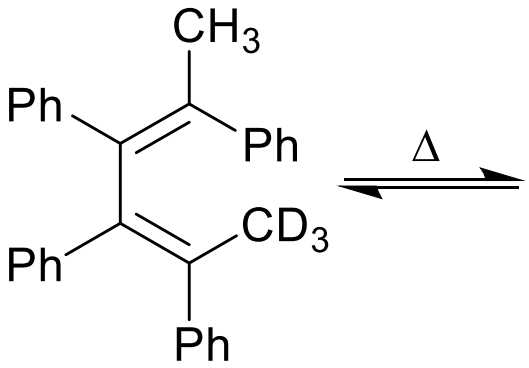
A pericyclic reaction can take place only if the symmetries of the reactant (**R**) MOs are the same as the symmetry of the product (**P**) MO

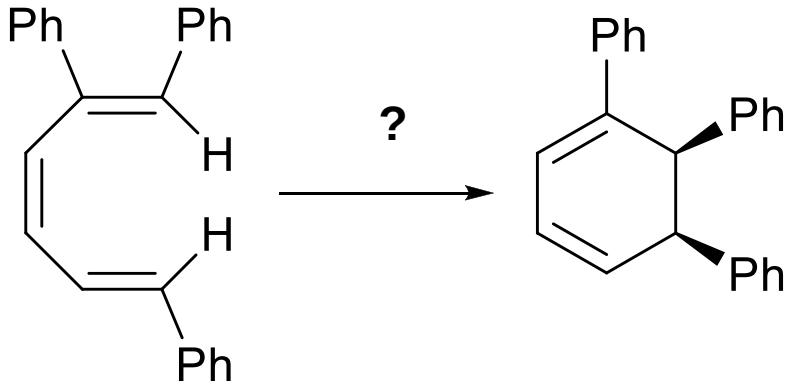
Based on electron count the same rules apply for the ring opening

System (no of electrons)	**Mode of rotation**	**Allowedness of the reaction**	
		Thermal	Photochemical
4n	con	allowed	forbidden
4n	dis	forbidden	allowed
4n+2	con	forbidden	allowed
4n+2	dis	allowed	forbidden

Activity

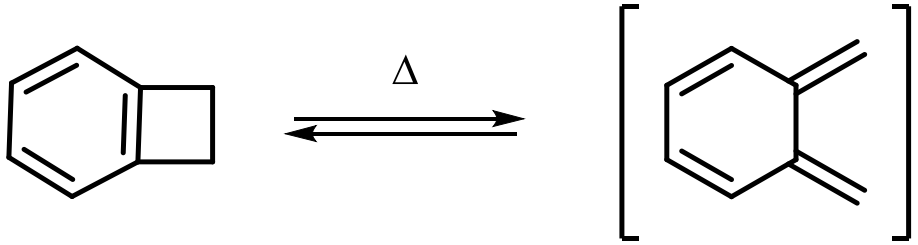




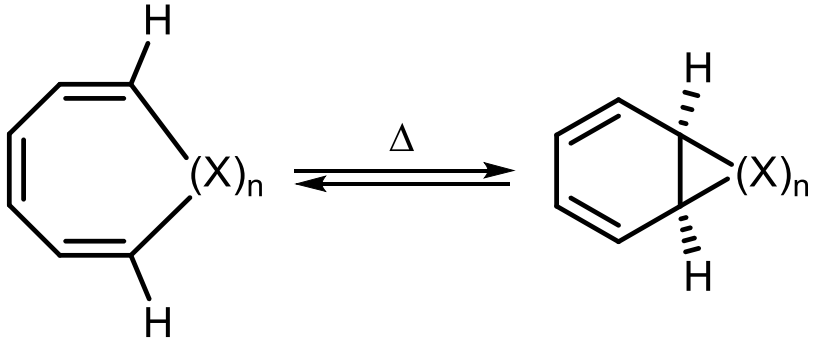


More Examples

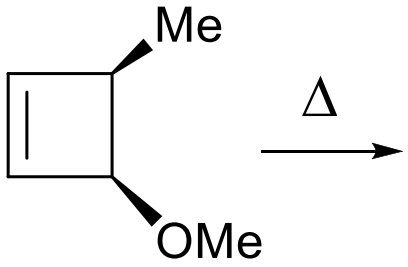
Thermal isomerization of benzocyclobutene to *ortho* quinodimethane

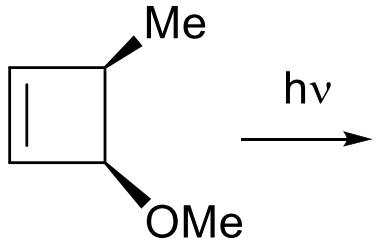


Thermal valence isomerization of cycloheptatriene-norcaradiene



Interesting examples





Selectivity in rotation – called as torquoselectivity

More Practice Problems