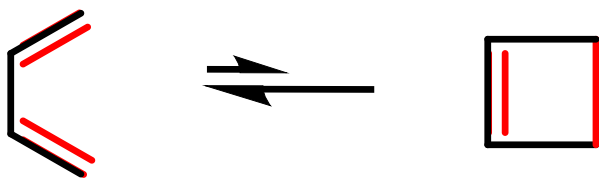


Recap – Electrocyclic reaction

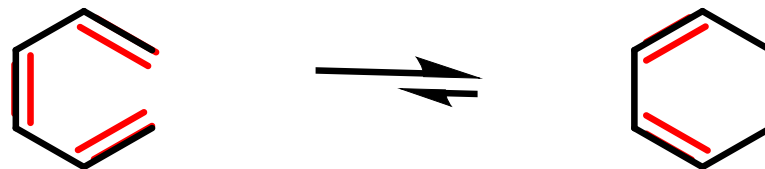
Cyclization of a **conjugated** polyene (**ring closing**)
Reverse process (**ring opening**)

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

4 e^- system



6 e^- system



Thermal conditions

- Draw **ground state** HOMO of **butadiene** (for $4n$ system) and **hexatriene** (for $4n+2$ system)
- Determine **mode of closure** (dis/con)

Photochemical conditions

- Draw **excited state** HOMO of **butadiene** (for $4n$ system) and **hexatriene** (for $4n+2$ system)
- Determine **mode of closure** (dis/con)

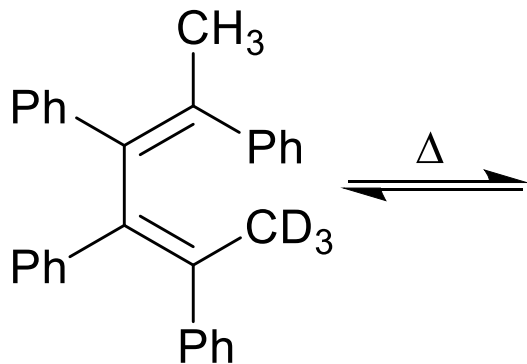
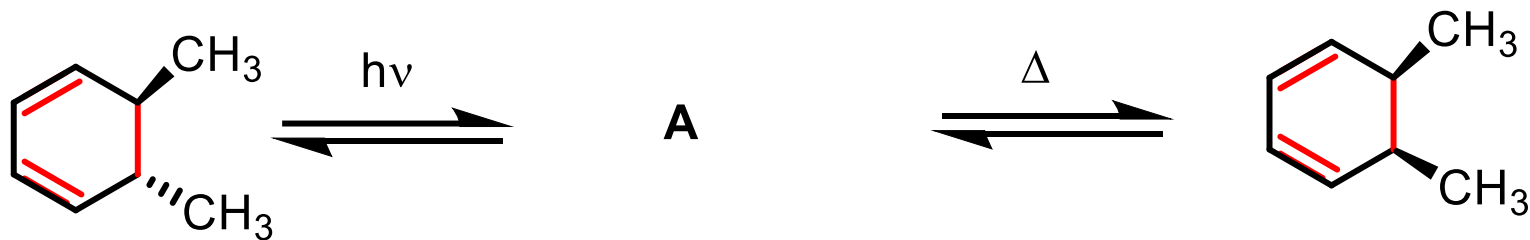
Recap – Electrocyclic Reactions

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

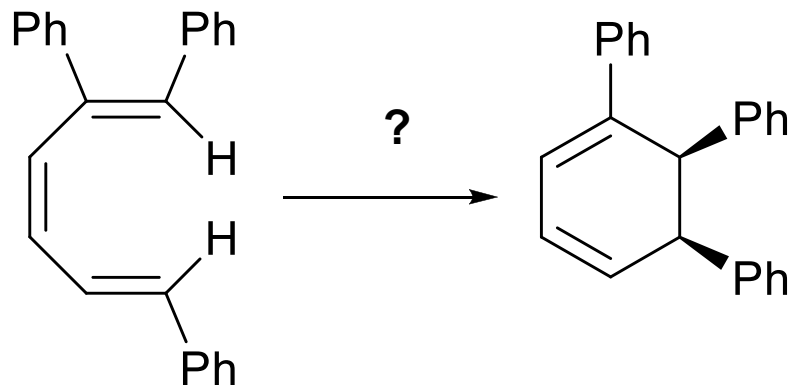
Based on electron count the same rules apply for the ring opening

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

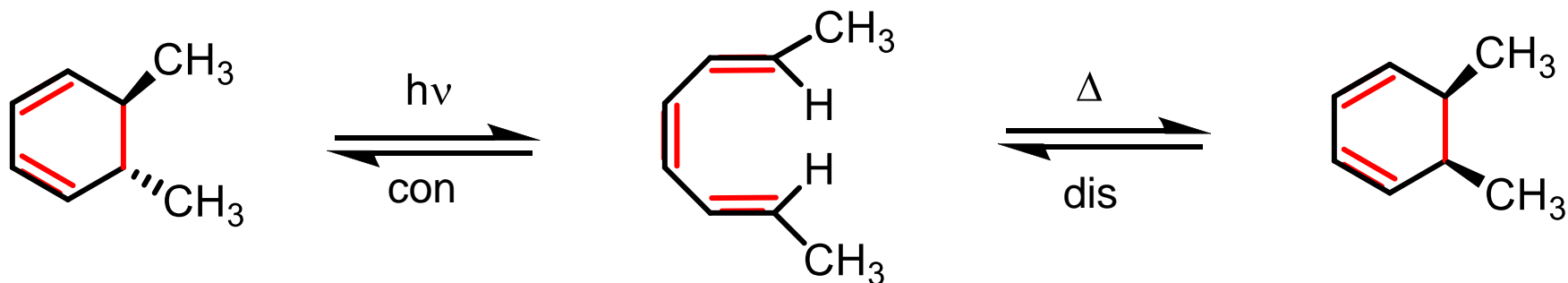
Activity



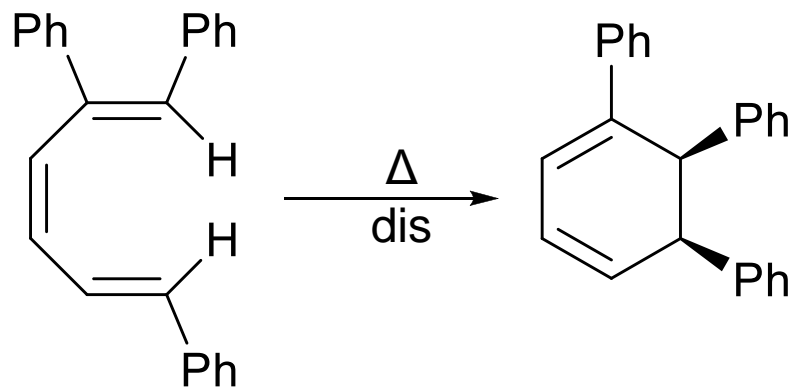
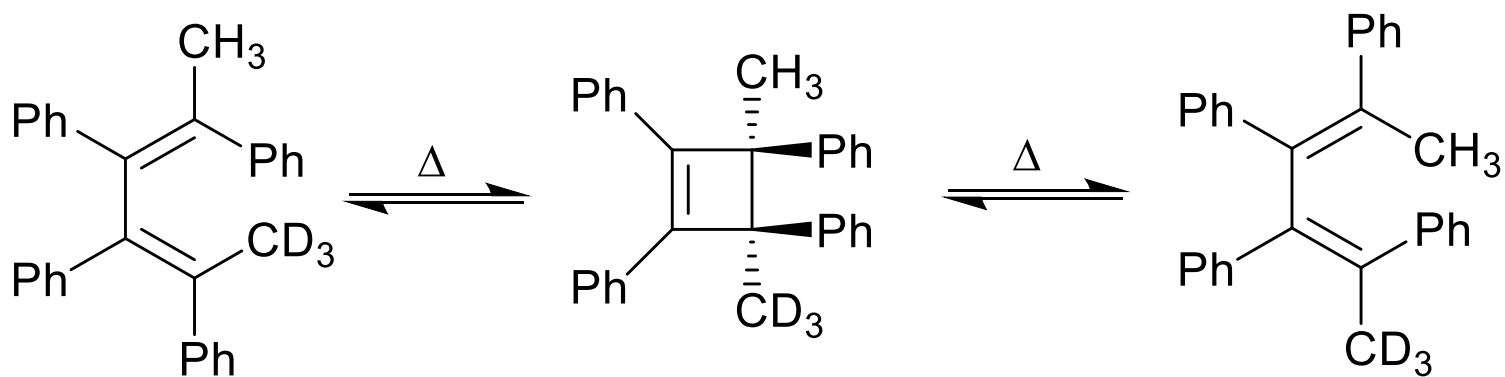
- Go to www.menti.com –
- Use code 3492 3318



Activity

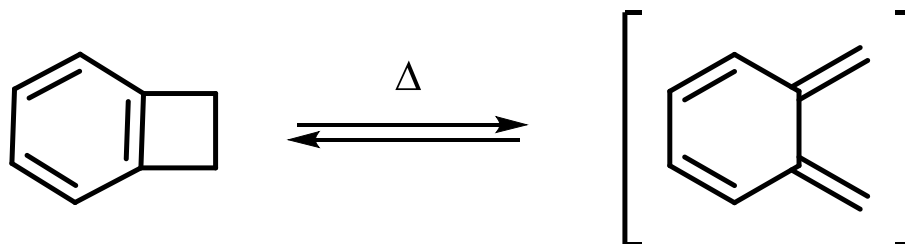


(2E,4Z,6E)-2,4,6-octatriene

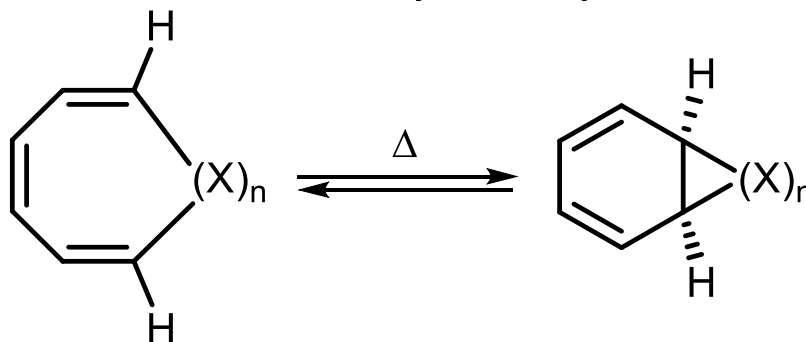


More Examples

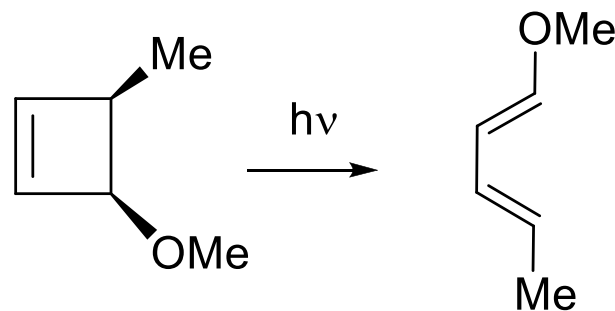
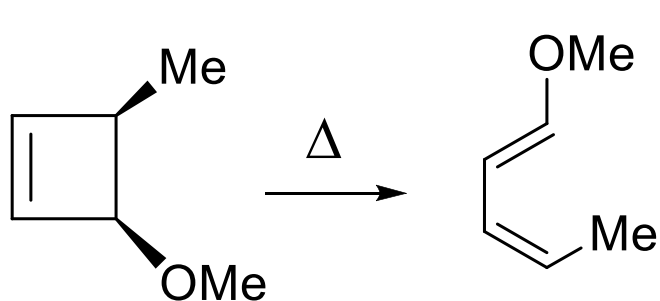
Thermal isomerization of benzocyclobutene to *ortho* quinodimethane



Thermal valence isomerization of cycloheptatriene-norcaradiene



Interesting examples

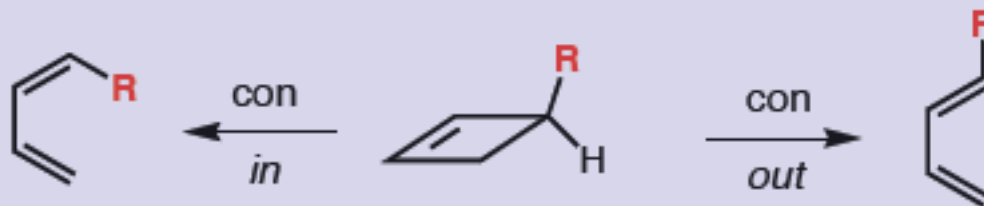


Selectivity in rotation – called as torquoselectivity

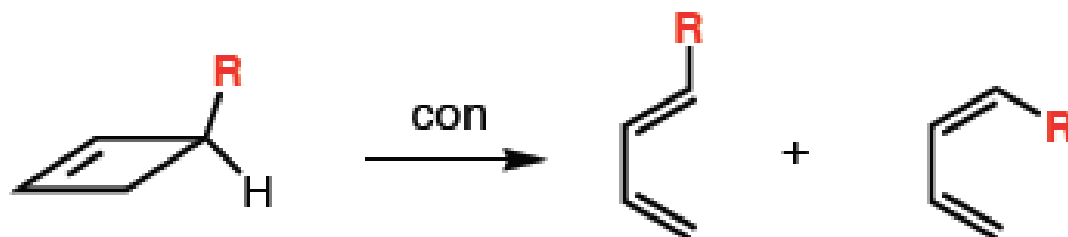
Electrocyclic Reaction: Torquoselectivity

Torquoselectivity is defined as the predisposition of a given R substituent for a given conrotatory motion

Houk et al. *Acc. Chem. Res.* **1996**, 29, 471



- Donor substituents prefer con–out mode
- p acceptor substituents prefer con–in mode

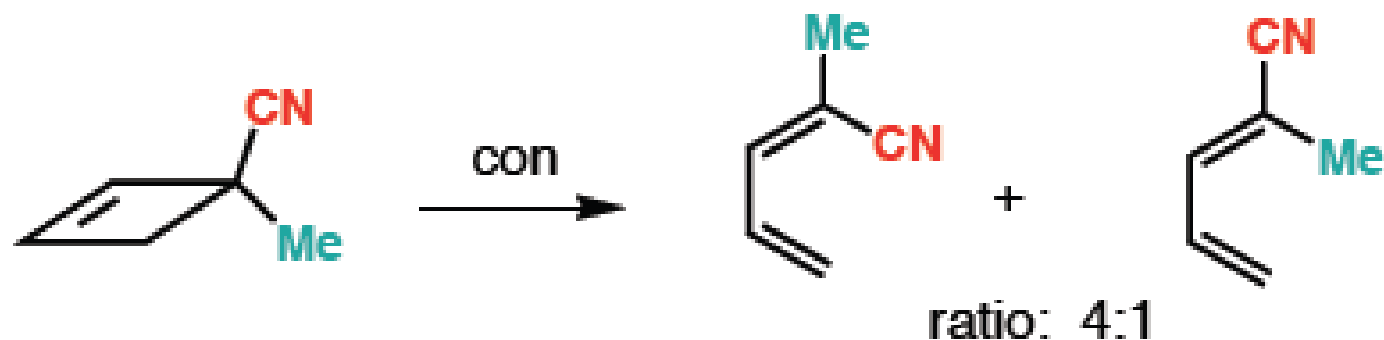
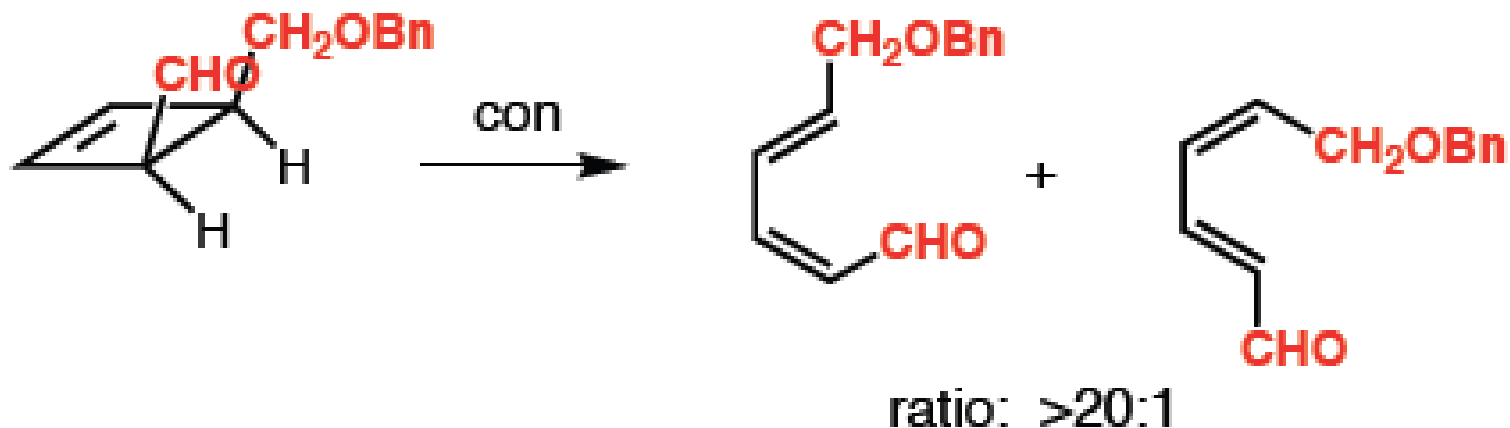


R = Me
R = CHO

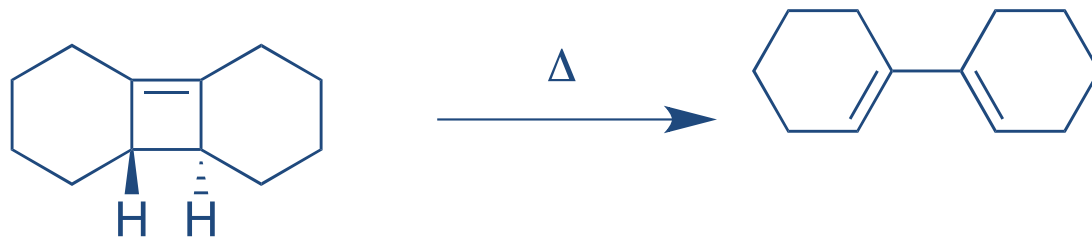
only
none

none
only

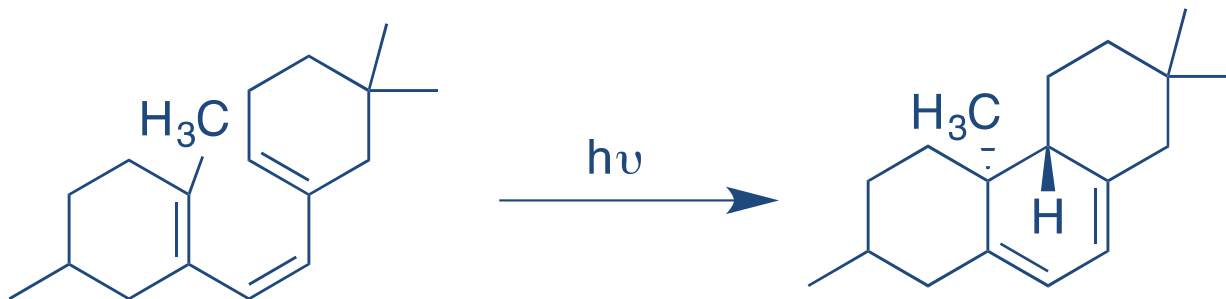
Electrocyclic Reaction: Torquoselectivity



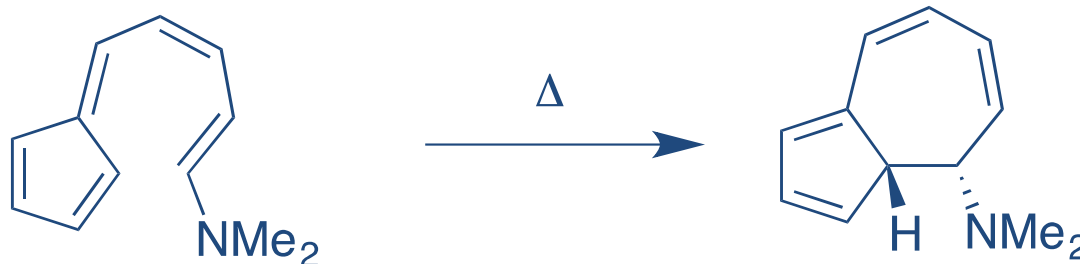
More Practice Problems



conrotatory

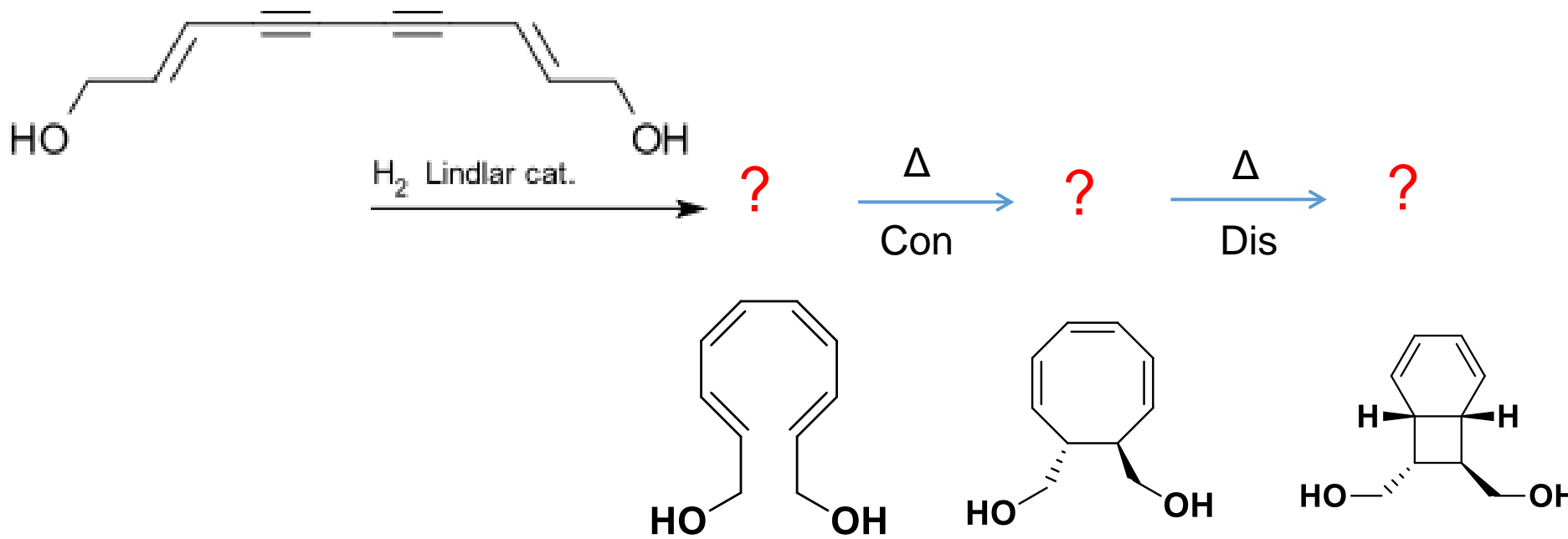
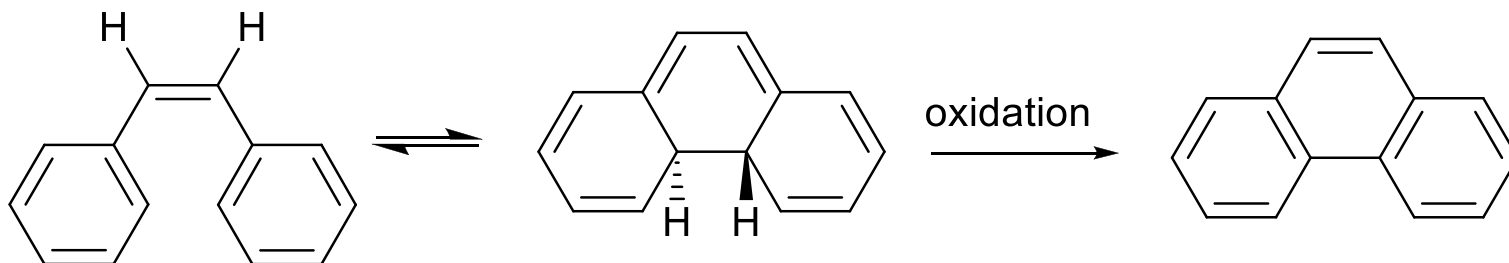


conrotatory

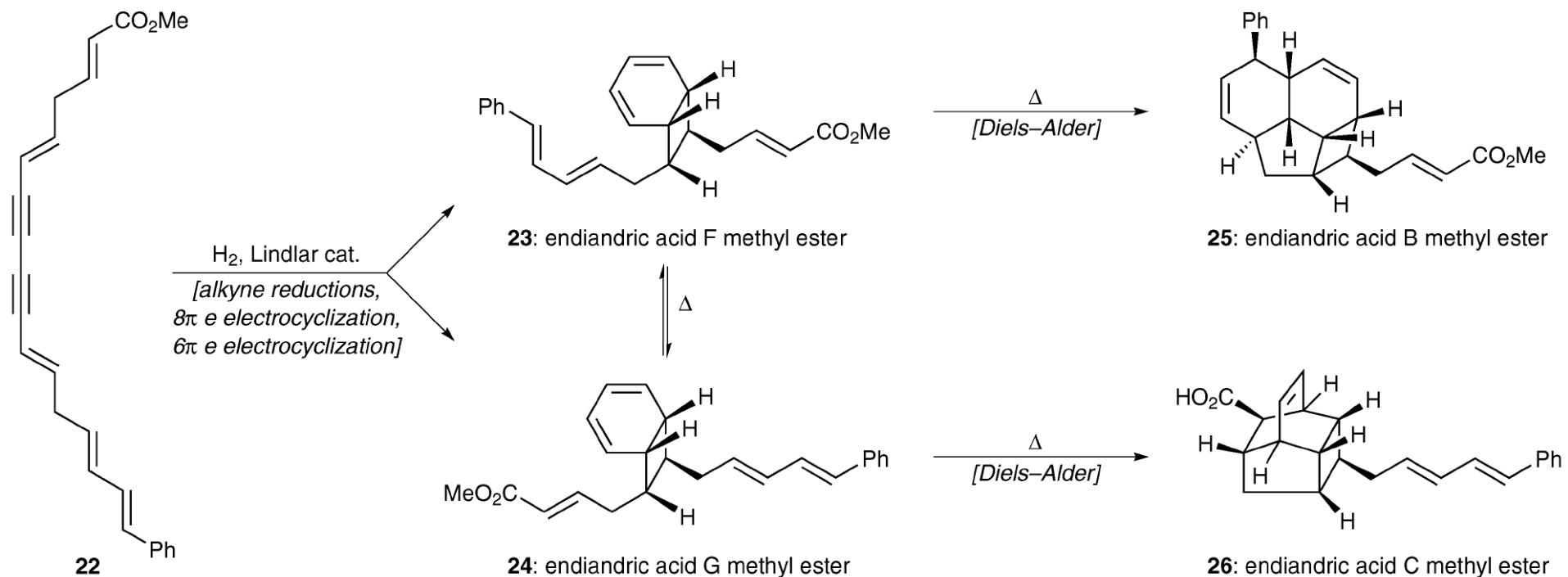


disrotatory

Synthetic Applications

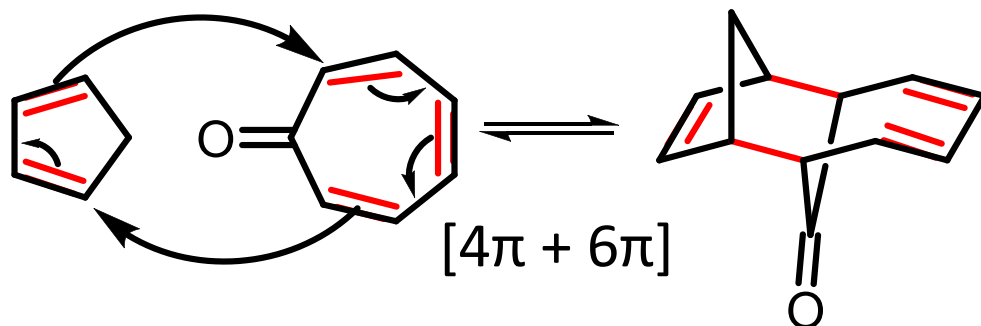
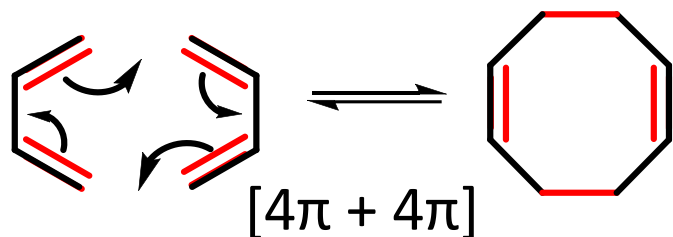
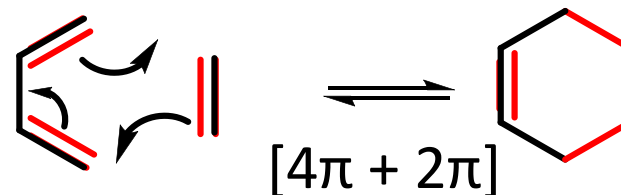
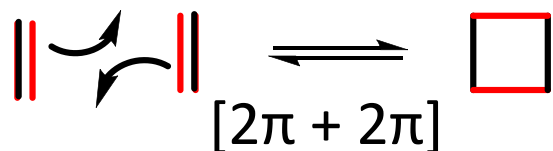


Synthesis of Endiandric acid



Cycloaddition Reactions

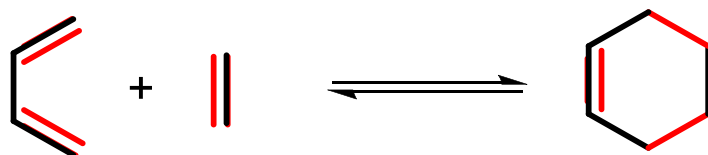
Involves the addition of two (or more) molecules to form a ring by transferring electrons from π bonds to form σ bonds



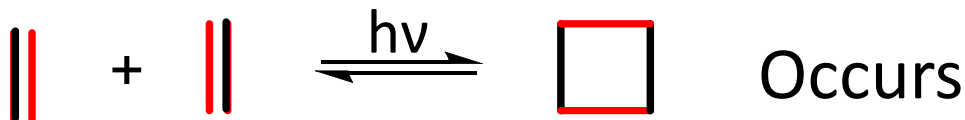
Classified by the number of π electrons interacting
(shown in red)

Ease of Reaction

Ease with which a cycloaddition takes place thermally depends on number of π electrons involved



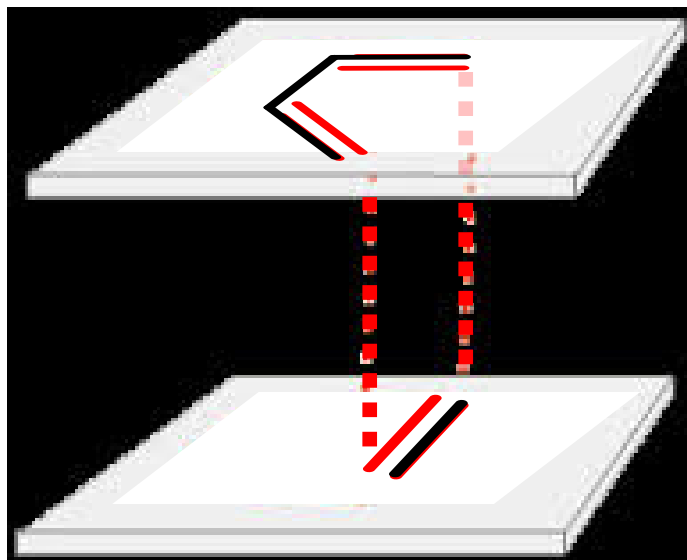
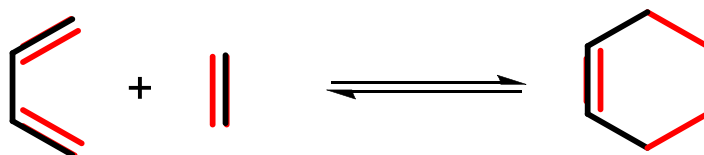
Diels-Alder a widely used reaction in organic synthesis



Why is this so ??

Interactions – Cycloaddition Reactions

Cycloadditions involve **facial** interactions and not **side by side** interactions



One face of 4π system

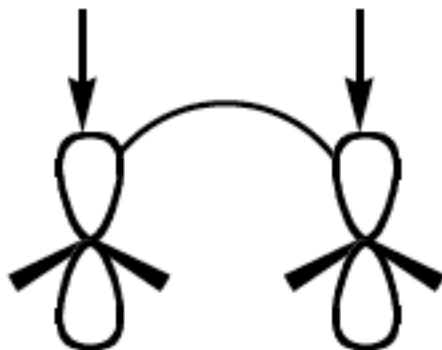
One face of 2π system

Modes of Facial Attack

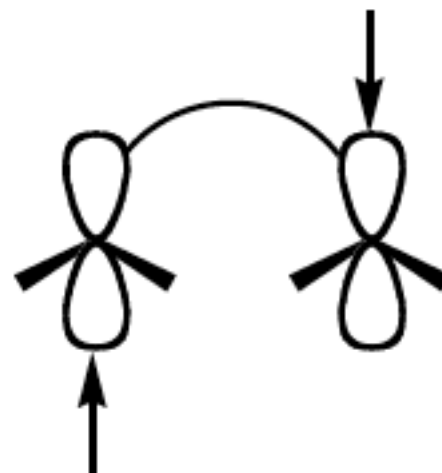
A pi system may be attacked by two distinct ways.

- If attack is from **the same face** of pi system, then the reaction is **suprafacial (s)** on the pi system.
- If attack is on **opposite faces** of pi system, then the reaction is **antarafacial (a)** on the pi system.

*Suprafacial
attack*



*Antarafacial
attack*



Remember the Symmetry Rules?

A successful cycloaddition reaction –

The terminal π lobes of the reactants must have the correct symmetry for bonding to occur

Frontier Molecular Orbital Theory

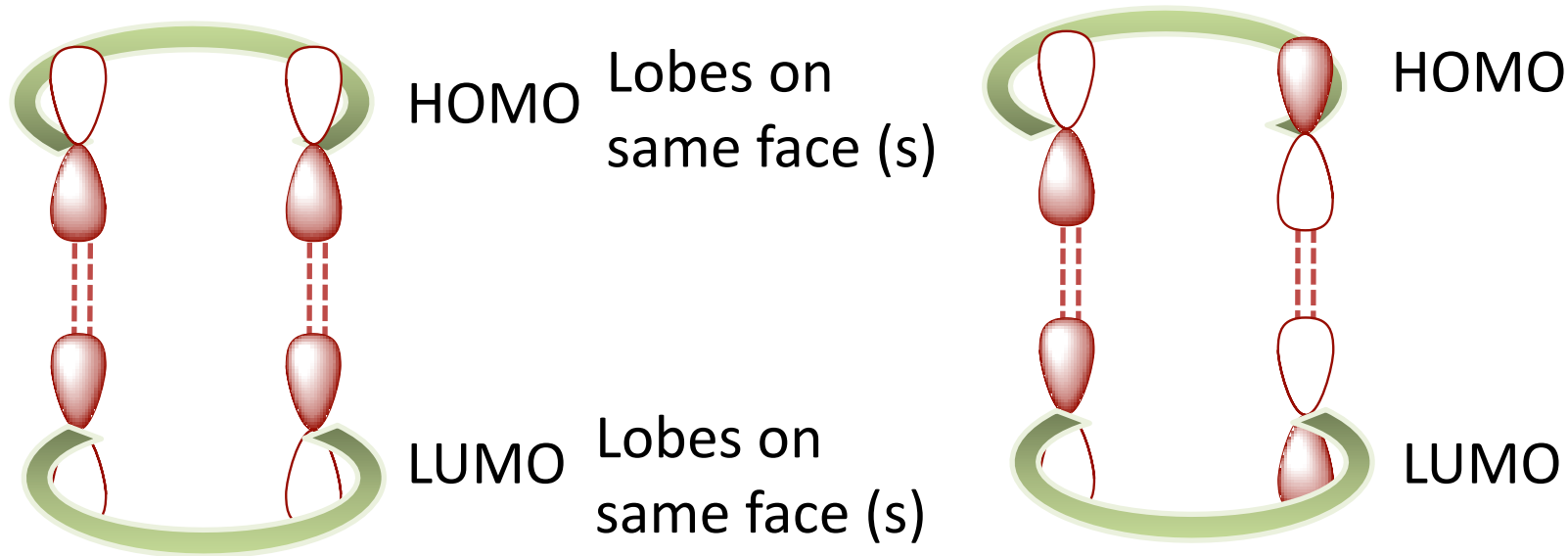
When two reactants undergo the cycloaddition reaction
HOMO of one reactant will interact with LUMO of the other.

Best interactions  Low HOMO-LUMO gap

Possibilities for Orbital Interactions

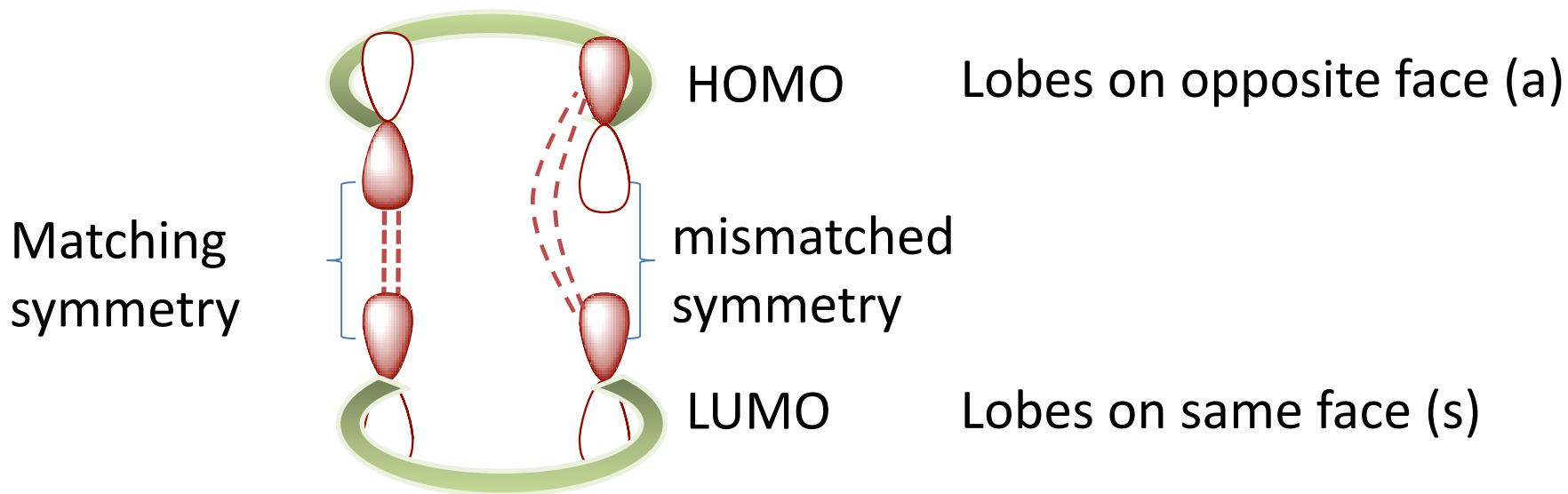
Remember - **Facial** interactions

Possibility One



Suprafacial – Suprafacial Interactions

Possibility 2 for Orbital Interactions

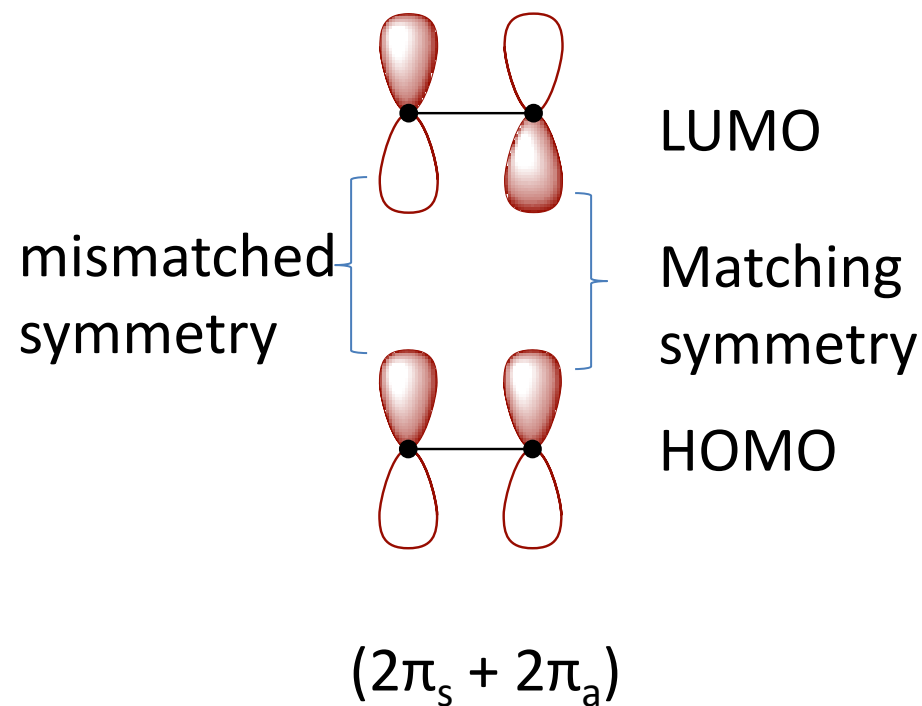


Suprafacial-Antarafacial interaction

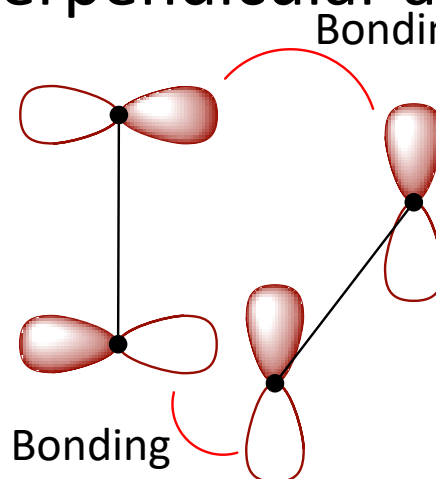
Symmetry allowed but geometrically difficult

FMO Explanation – $[2\pi + 2\pi]$

Thermal Conditions



Perpendicular approach

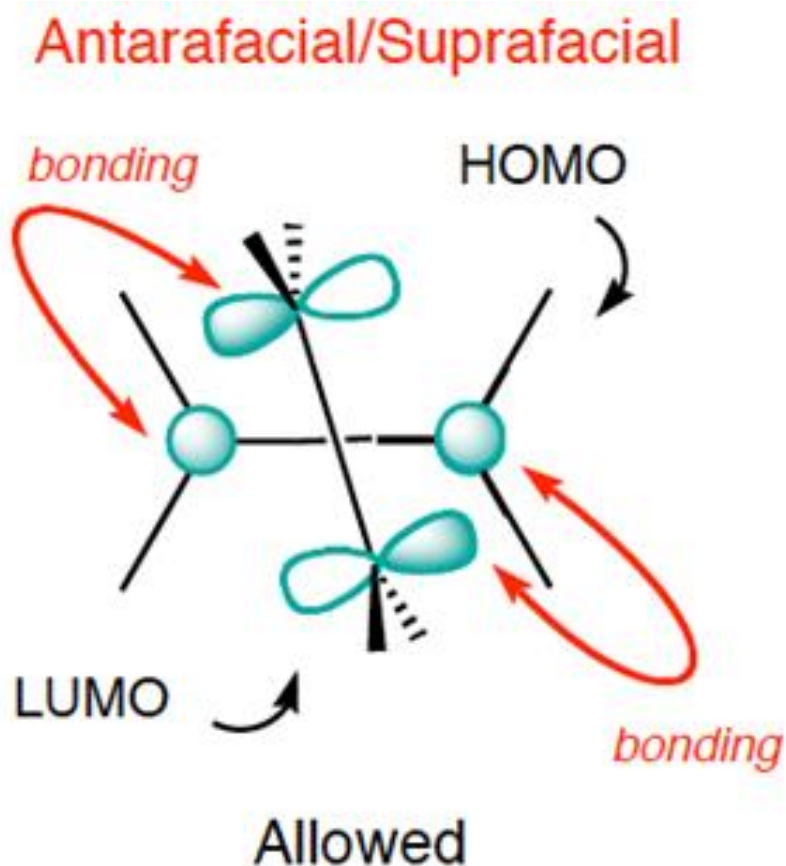


Geometric and steric constraints make this difficult

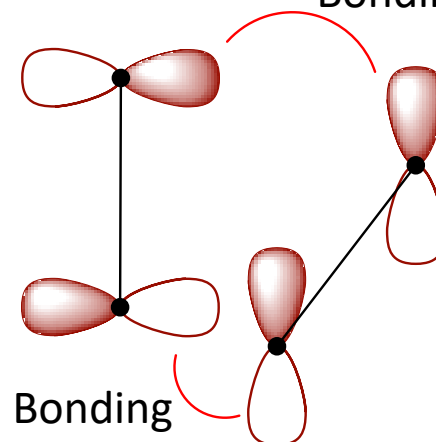
Difficult for thermal $[2\pi_s + 2\pi_a]$ cycloaddition to occur
What happens under photochemical conditions?

FMO Explanation – $[2\pi + 2\pi]$

Thermal Conditions



Perpendicular approach

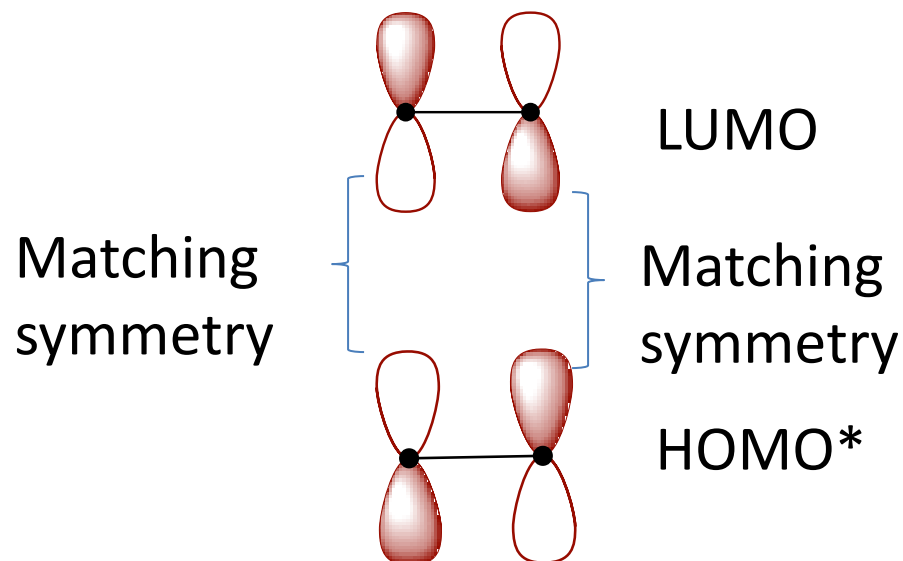


Geometric and steric constraints make this difficult

Difficult for thermal $[2\pi_s + 2\pi_a]$ cycloaddition to occur
What happens under photochemical conditions?

FMO Explanation – $[2\pi + 2\pi]$

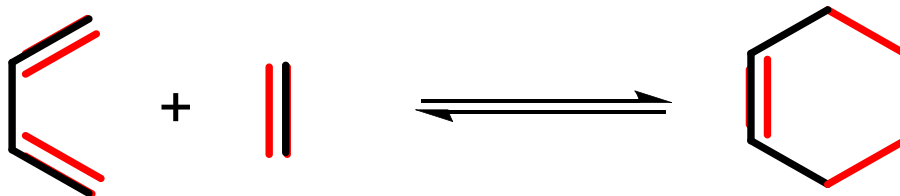
Photochemical Conditions



Suprafacial $[2\pi_s + 2\pi_s]$

Photochemical $[2\pi_s + 2\pi_s]$ cycloaddition easier to occur

$$[4\pi + 2\pi]$$



Diene
(2 double
bonds)

Dienophile
(likes diene)

For this course – Dienes – electron rich
Dienophile – electron deficient

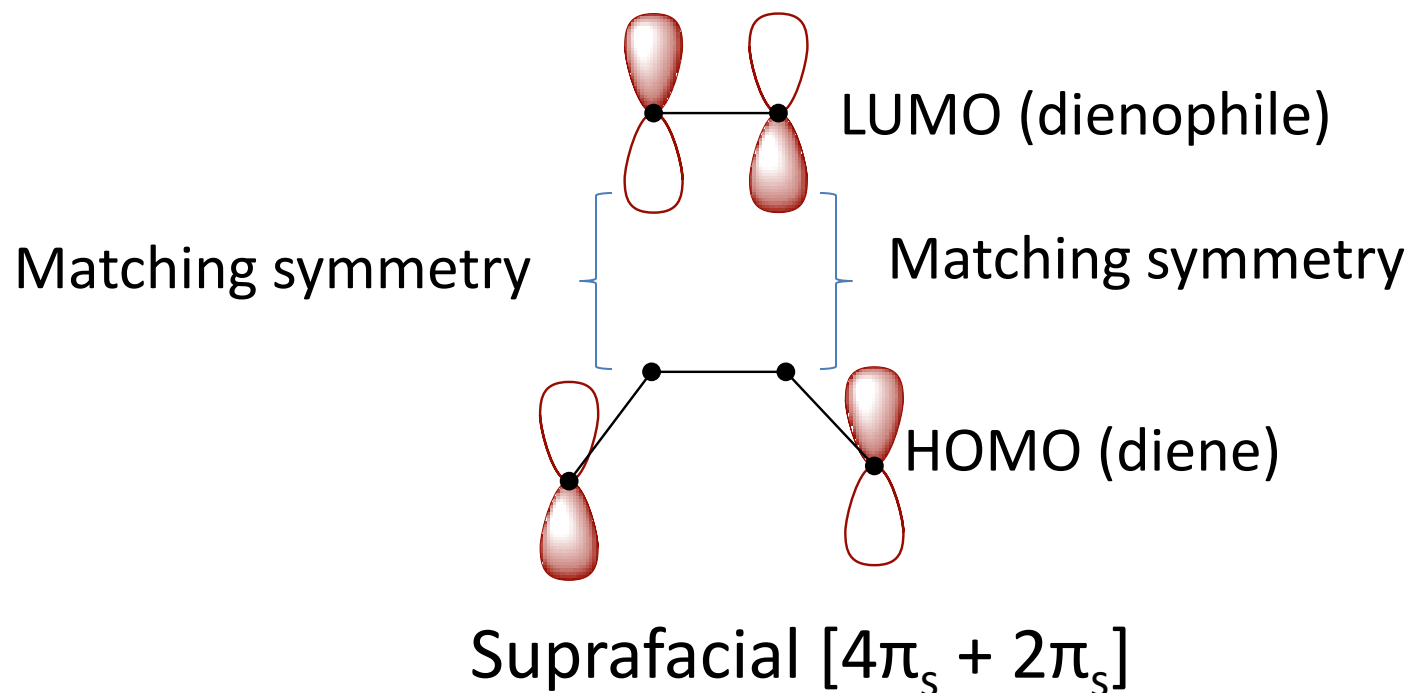
‘Normal’ electron demand Diel’s Alder Reactions

Typically: HOMO – e⁻ rich compd LUMO – e⁻ deficient compd

In this case diene – HOMO and dienophile - LUMO

FMO Explanation – $[4\pi + 2\pi]$

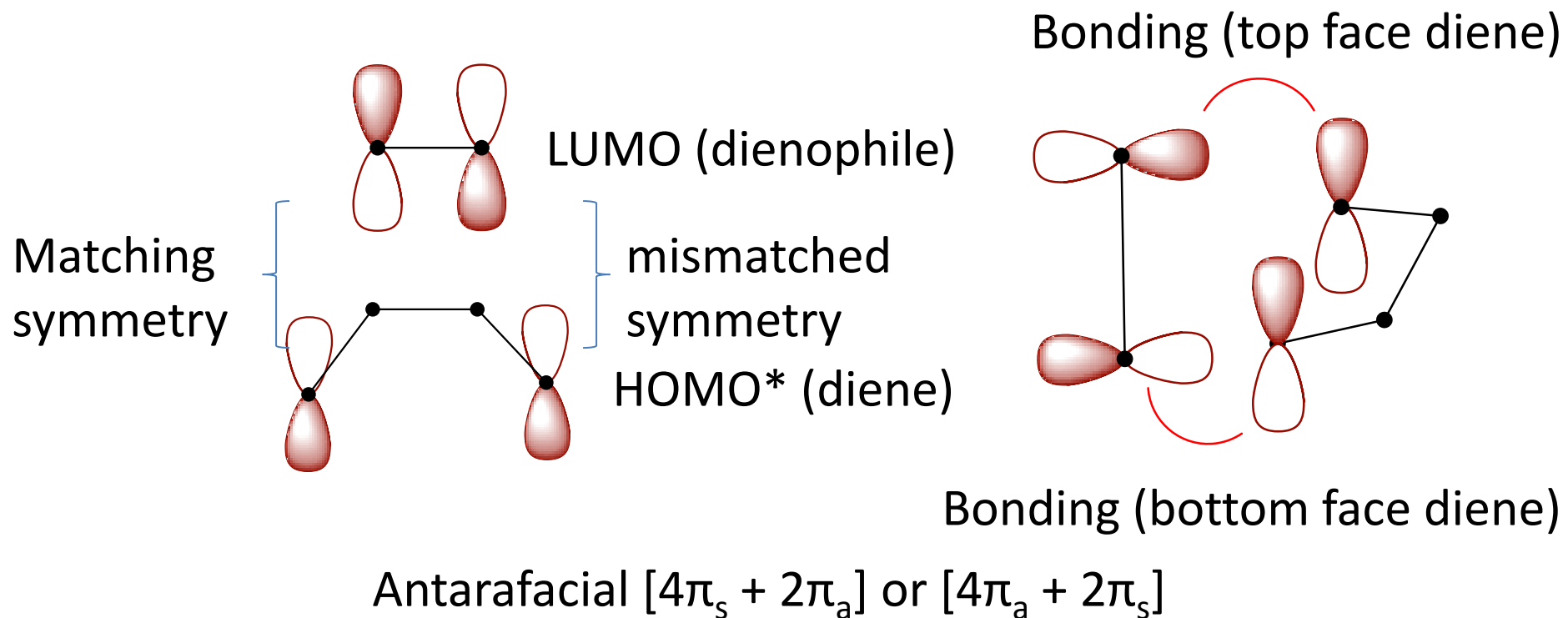
Thermal Conditions



Easy for thermal $4\pi_s + 2\pi_s$ cycloaddition to occur

FMO Explanation – $[4\pi + 2\pi]$

Photochemical Conditions



Photochemical $[4\pi + 2\pi]$ cycloaddition not easy to occur

Selection Rules for Cycloaddition

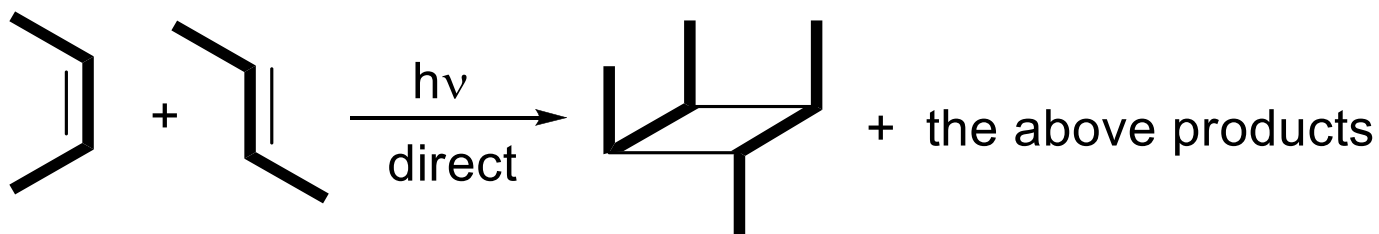
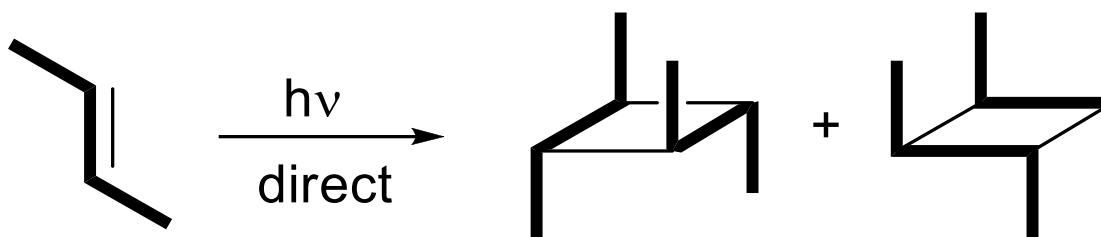
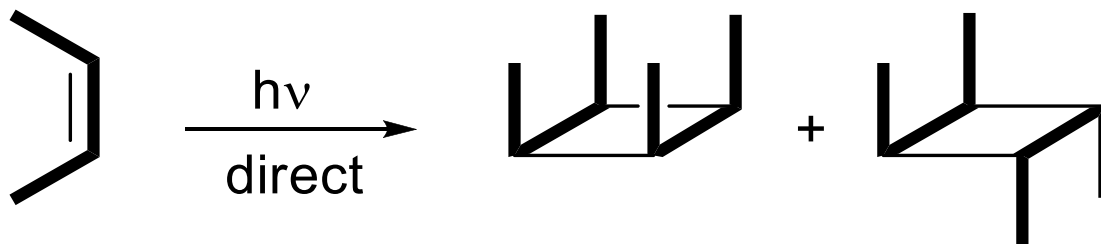
System (total no. of electrons)	Mode of addition	Allowedness of the reaction	
		Thermal	Photochemical
$4n$	s/s	forbidden	allowed
$4n$	s/a	allowed	forbidden
$4n+2$	s/s	allowed	forbidden
$4n+2$	s/a	forbidden	allowed

(n = natural number)

Since s/a mode is difficult to achieve mainly the s/s mode is observed

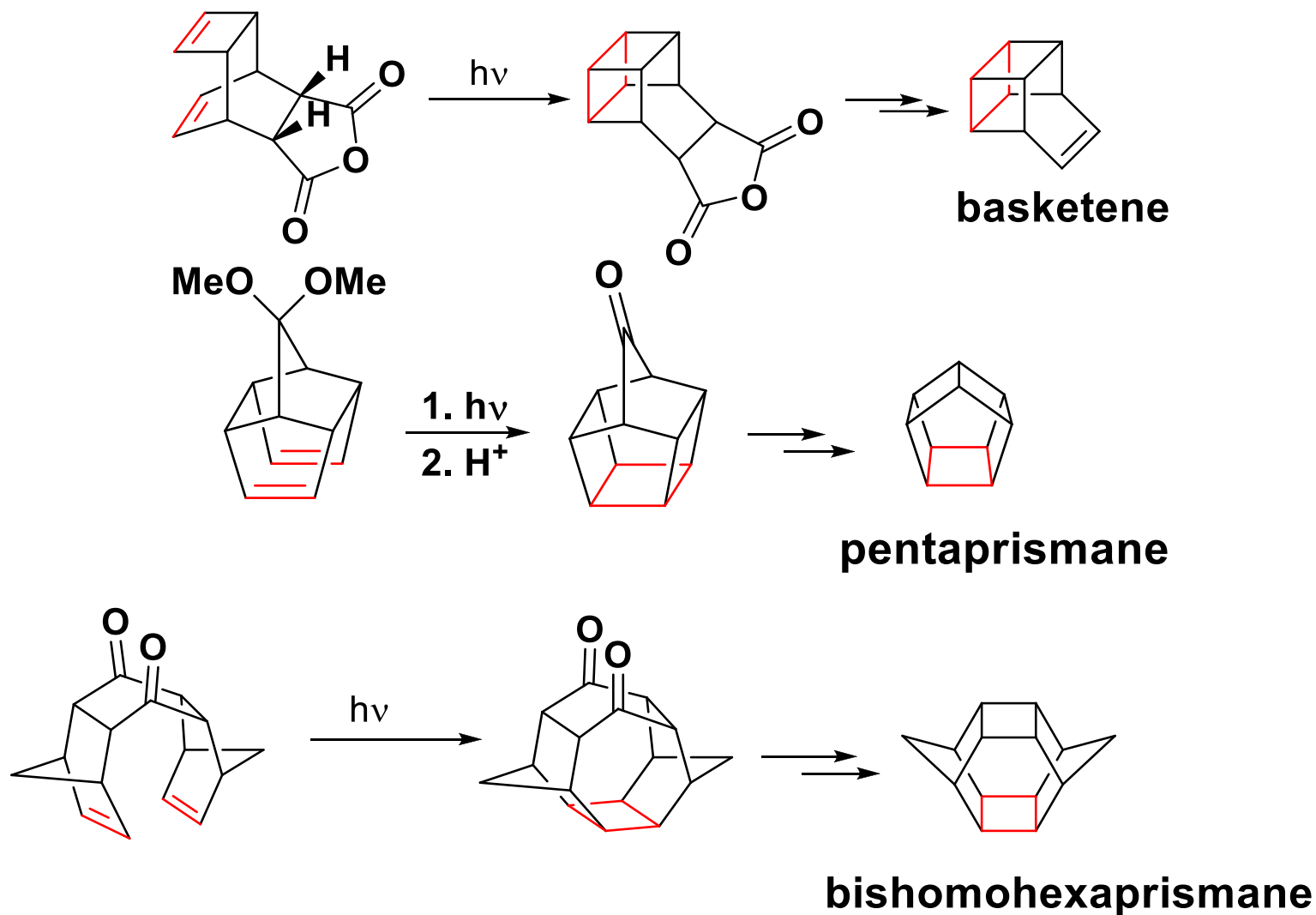
$[2\pi + 2\pi]$ Cycloaddition

$2\pi + 2\pi$ Cycloaddition



$2\pi + 2\pi$ Intramolecular Cycloaddition

Interesting Synthetic Applications



Provides access to strained caged compounds