



# **CHEM F111 : General Chemistry**

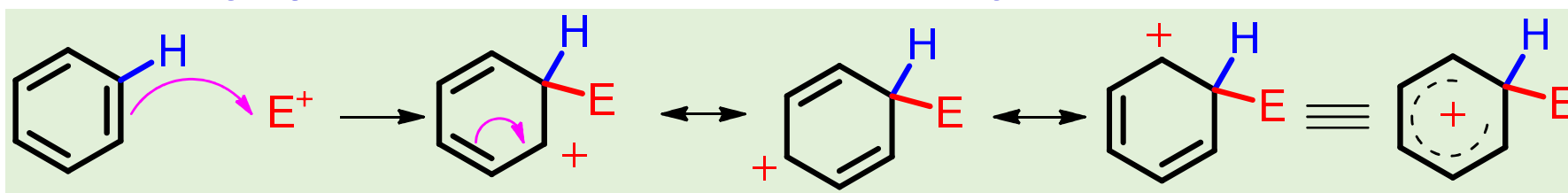
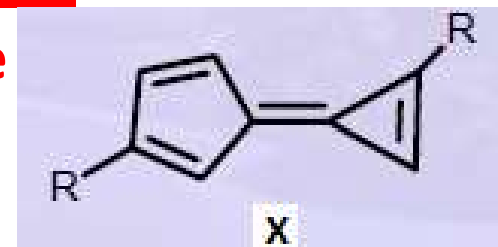
## **Semester II: AY 2017-18**

### **Lecture 37 (23-04-2018)**

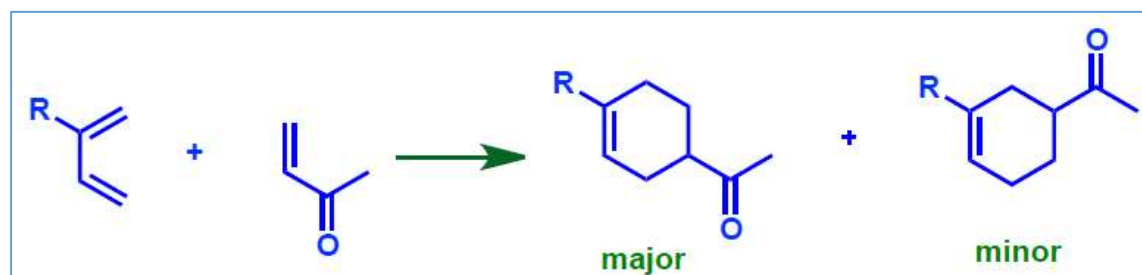
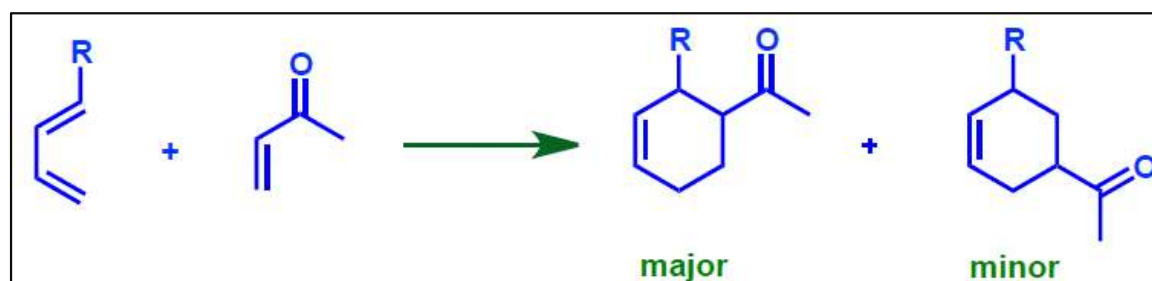
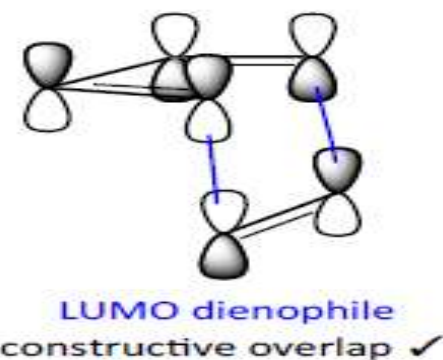
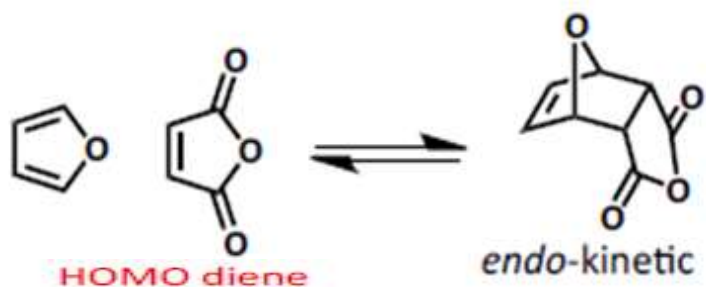
# Summary of Lecture 36



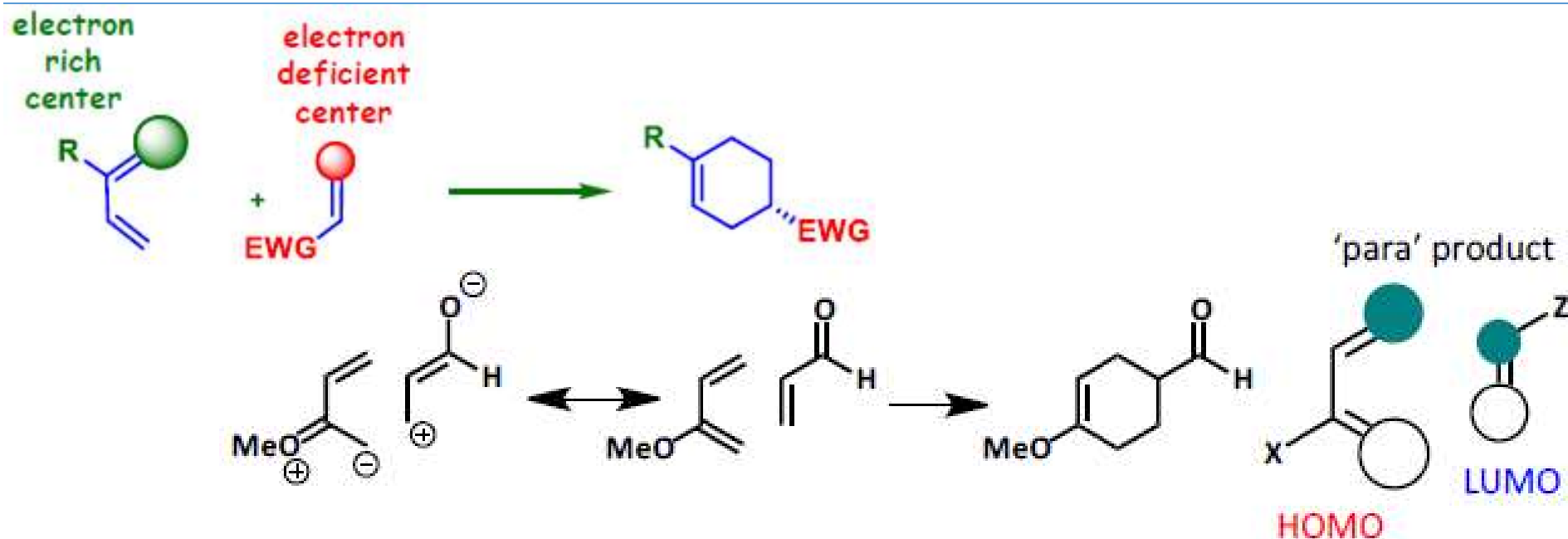
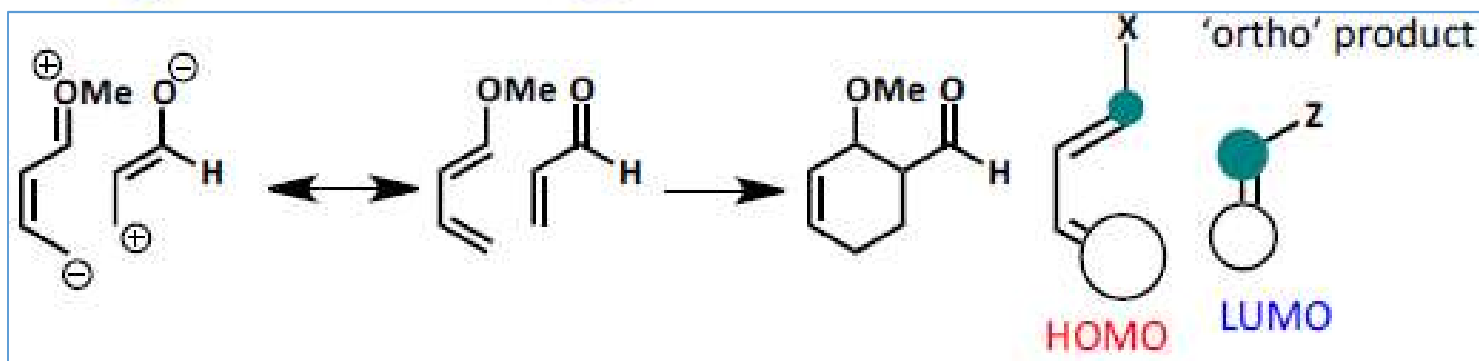
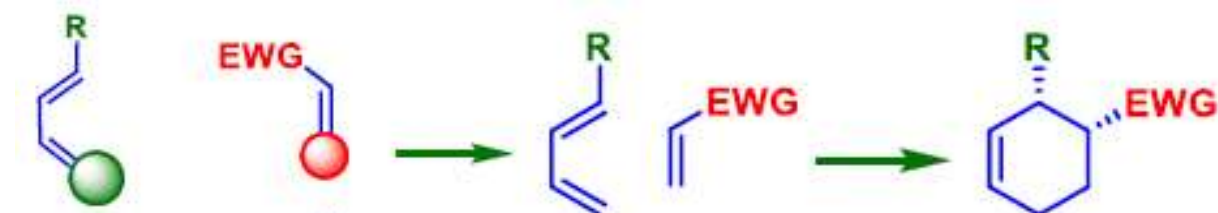
- ❑ Non-benzenoid Aromatics: **Annulenes and Azulene**
- ❑ *Chemical and Physical Properties of Conjugated Molecules*
- ❑ *Stability of benzene vs unsaturated compounds*



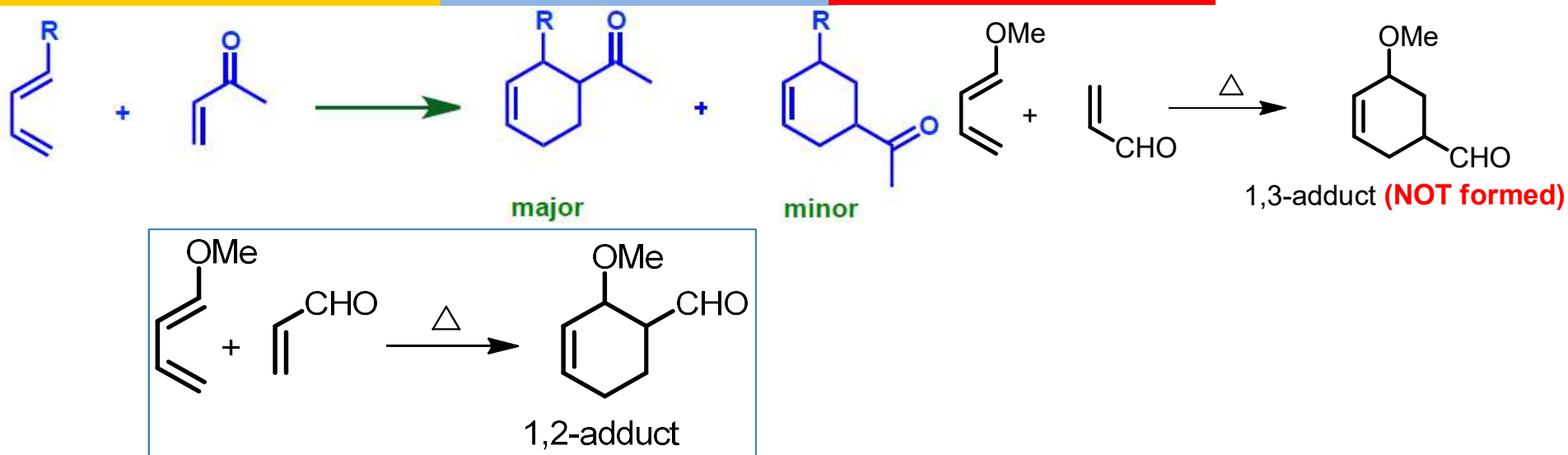
- ❑ *Pericyclic reactions (Diels-Alder and electrolytic cyclization)*



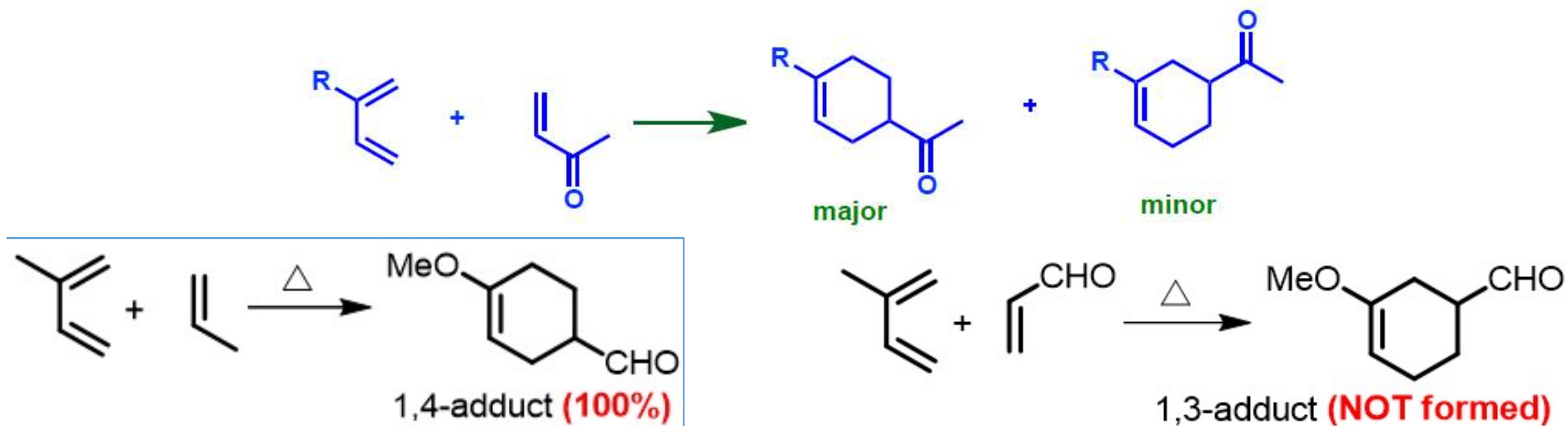
# [4+2] cycloaddition: Regioselectivity



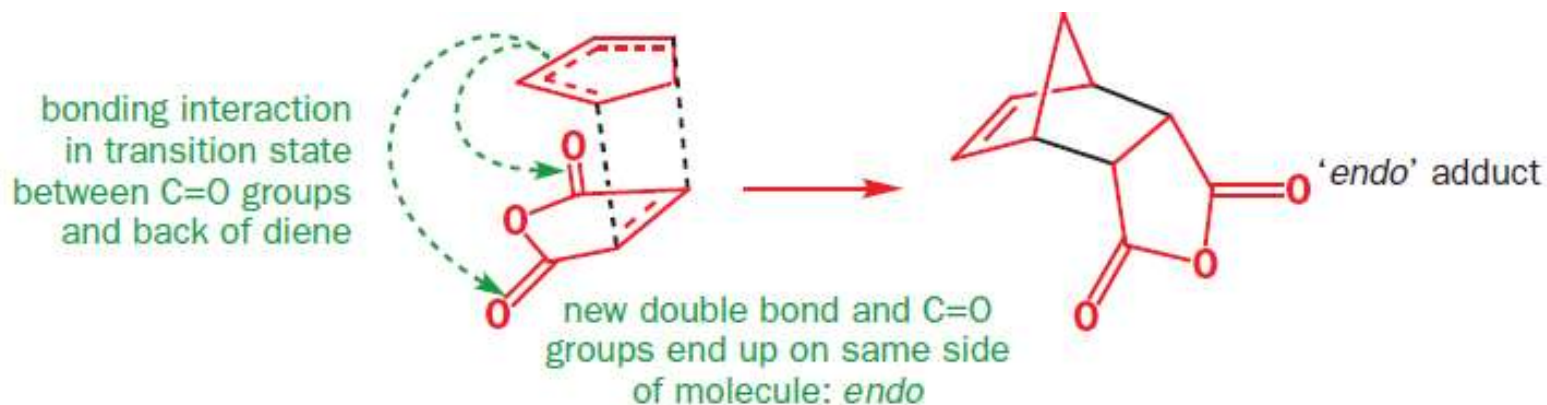
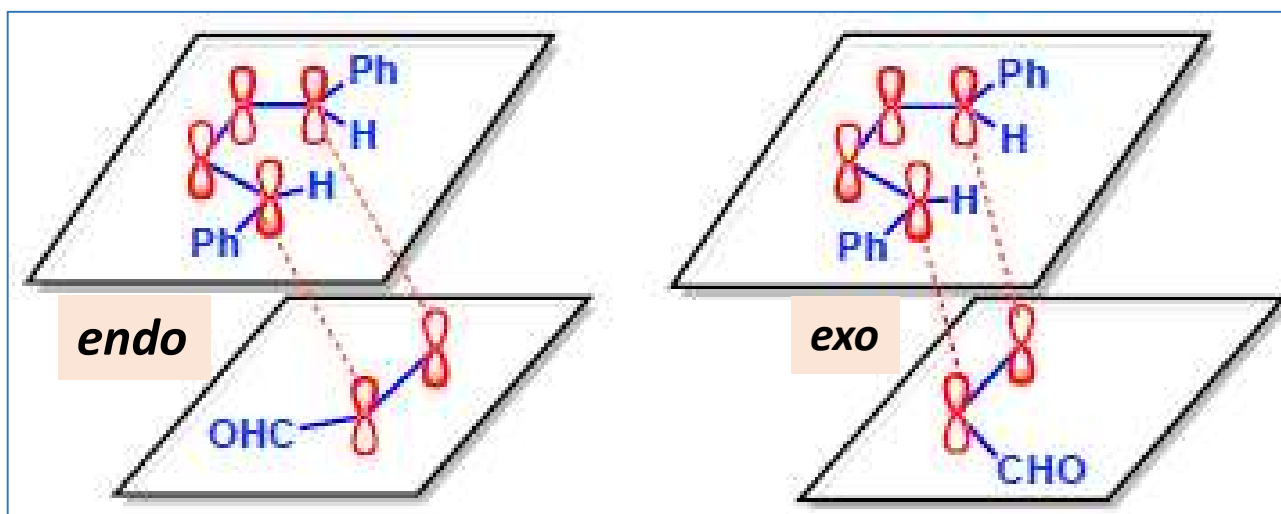
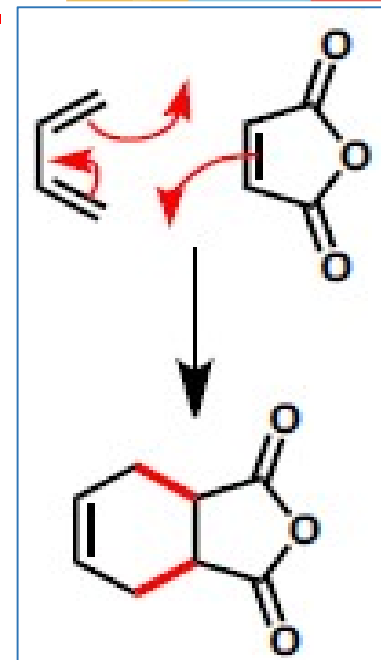
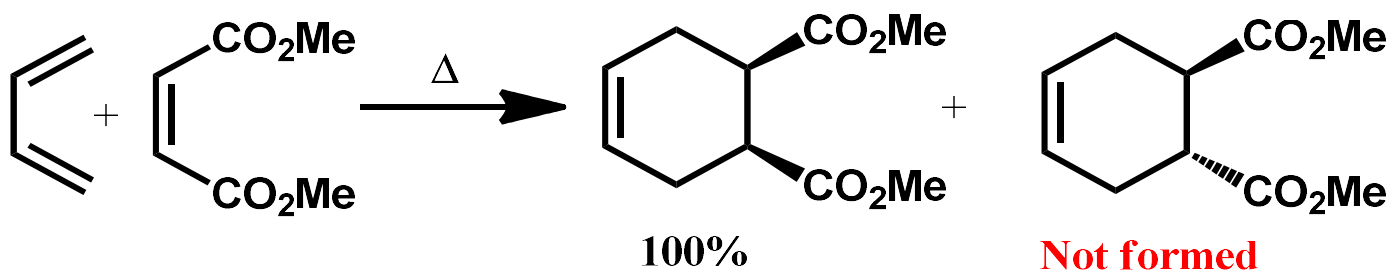
# [4+2] cycloaddition: Regioselectivity



❑ **Regioselective Reaction:** Dienes with electron-donating groups and dienophiles with electron-withdrawing groups react well together.

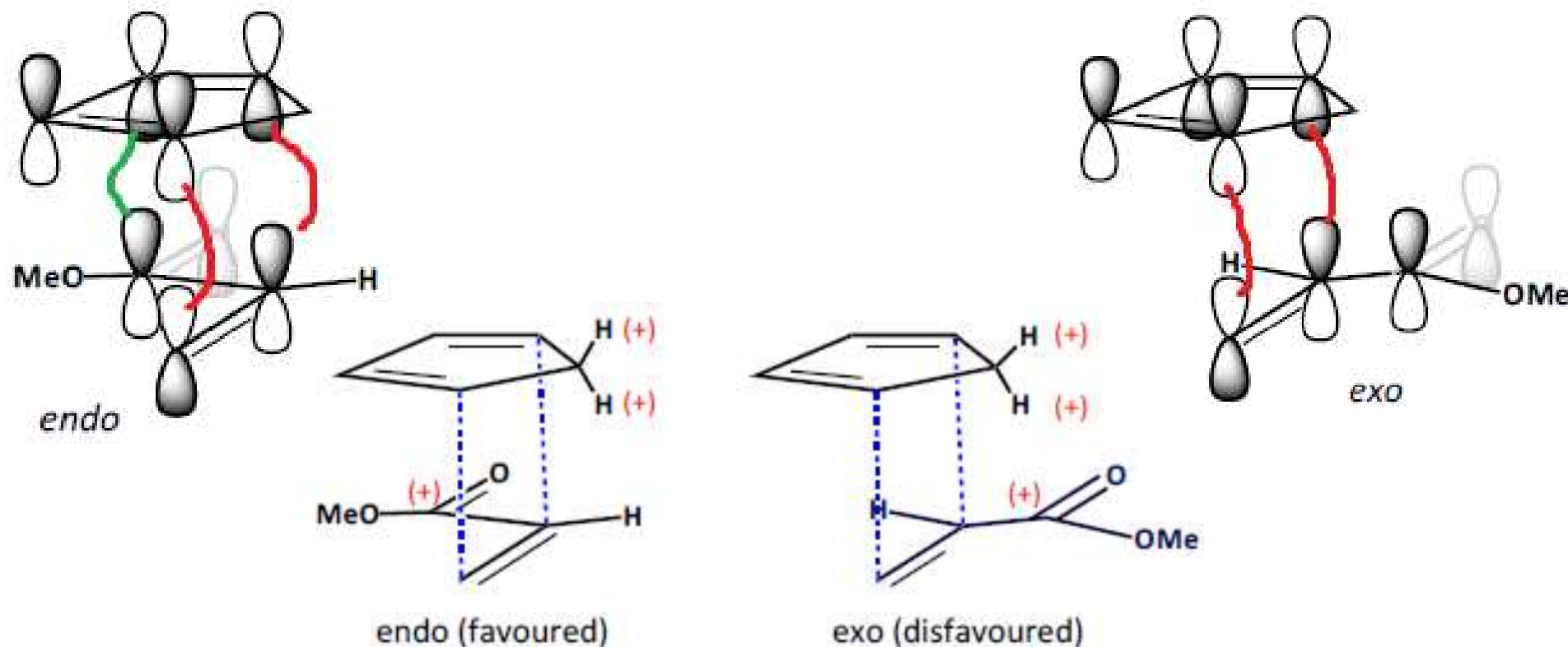


# Stereo-specificity of Diels-Alder Reaction





# [4+2] cycloaddition: stereoselectivity



## Cycloadditions

- Diels-Alder reaction the *endo* rule – *endo*-product is generally the major product with dienophiles containing  $\pi$ -conjugating substituents.

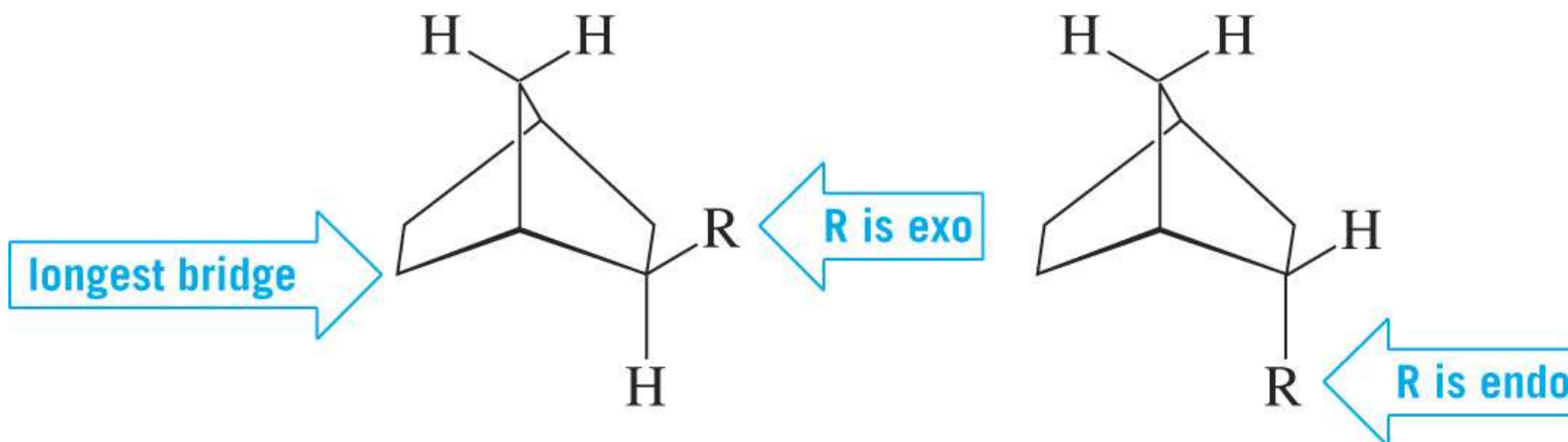


- Secondary orbital overlap is a simple explanation for the kinetic preference for the *endo*-adduct –

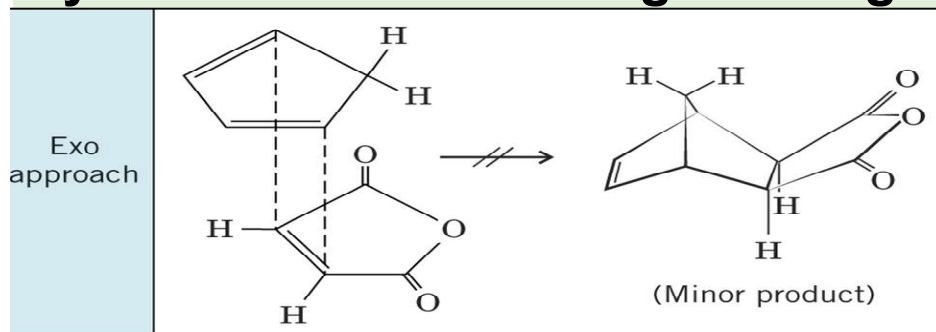
# Diels-Alder Reaction: Endo vs Exo products



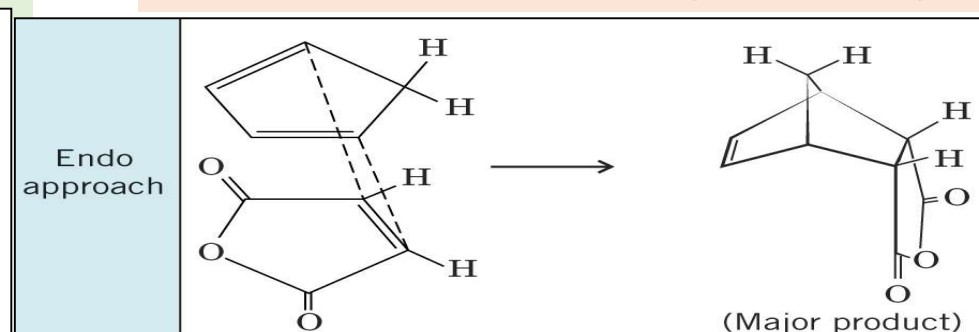
- The Diels-Alder reaction occurs primarily in an *endo*- rather than an *exo*-fashion when the reaction is kinetically controlled.



A group that is *exo* in a bicyclic ring system is *anti* to the longest bridge



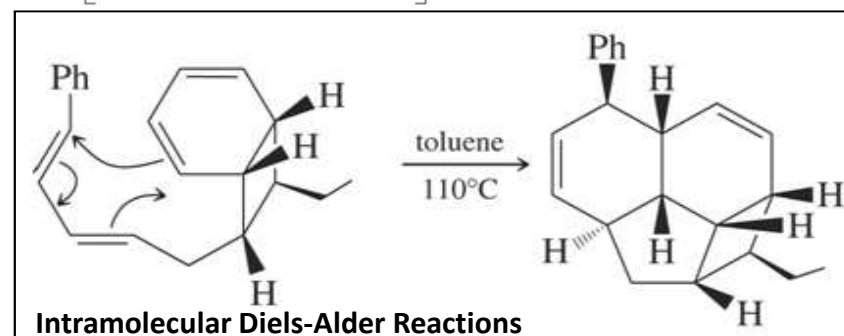
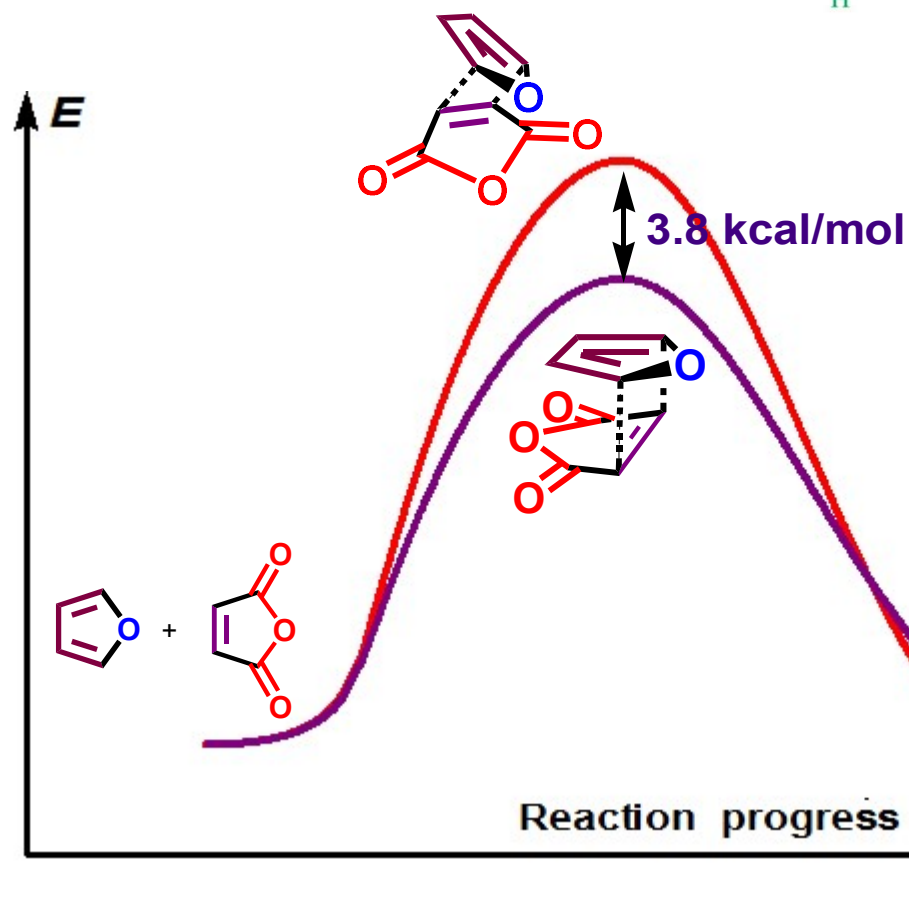
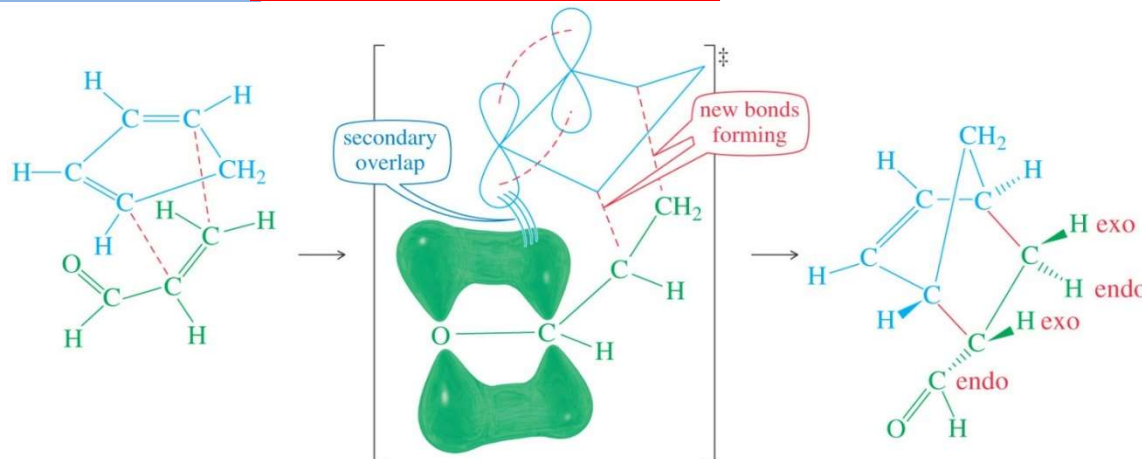
A group that is *endo* is on the same side as the longest bridge



# Diels-Alder Reaction: Endo vs Exo products



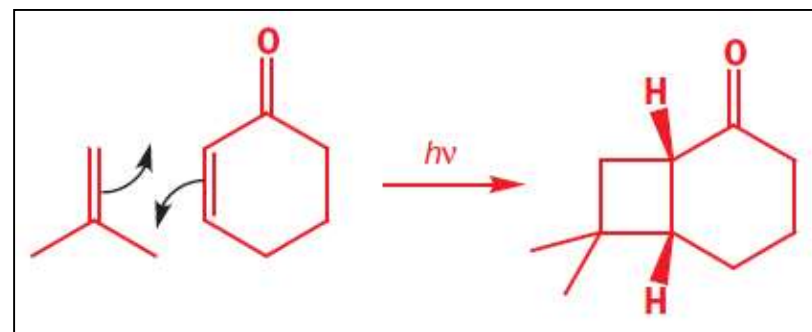
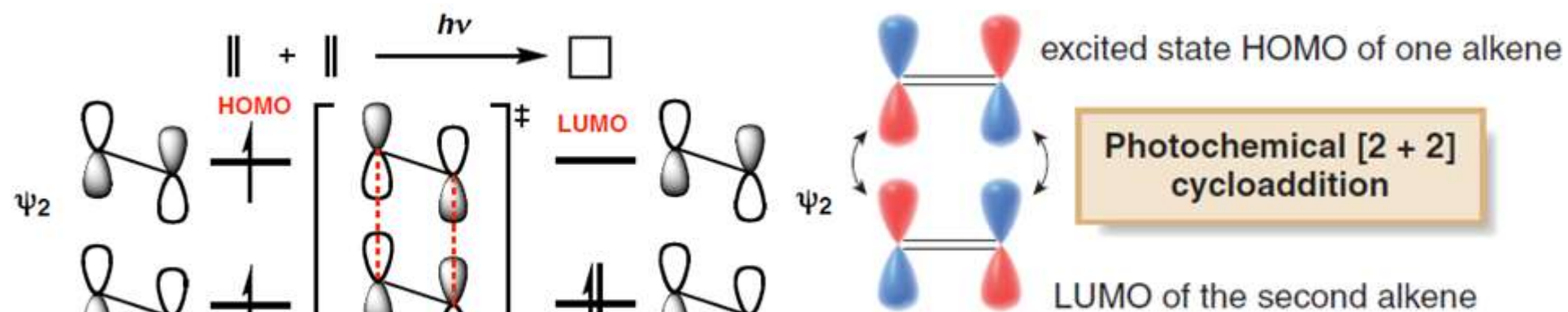
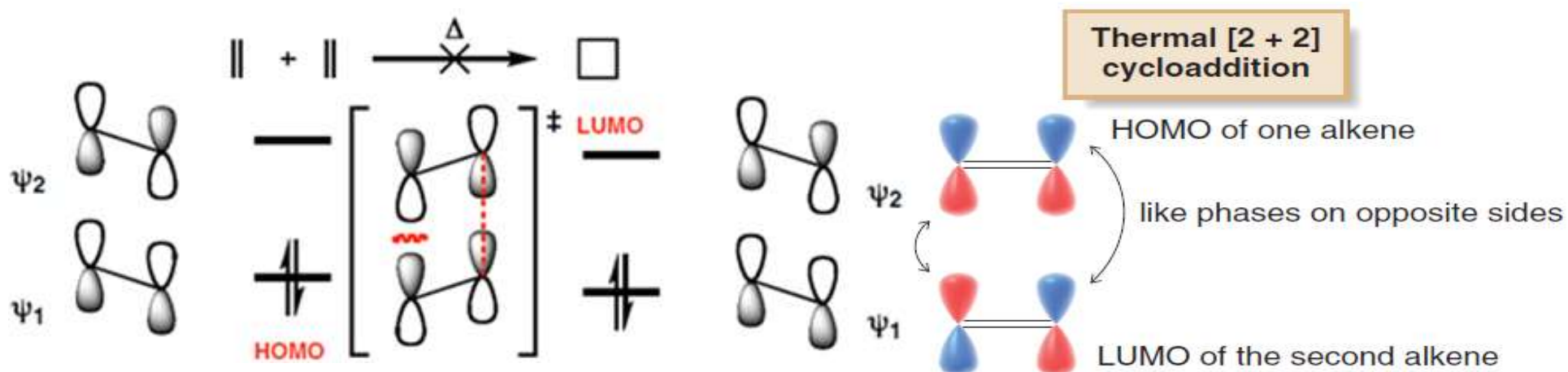
In endo product  $\pi$ -orbitals of the electron-withdrawing groups on the dienophile have a secondary overlap with the  $\pi$ -orbitals of C2 and C3 in the diene.



[4+2]-cycloaddition is feasible under thermal whereas [2+2]-cycloaddition is feasible under photochemical condition, Why?



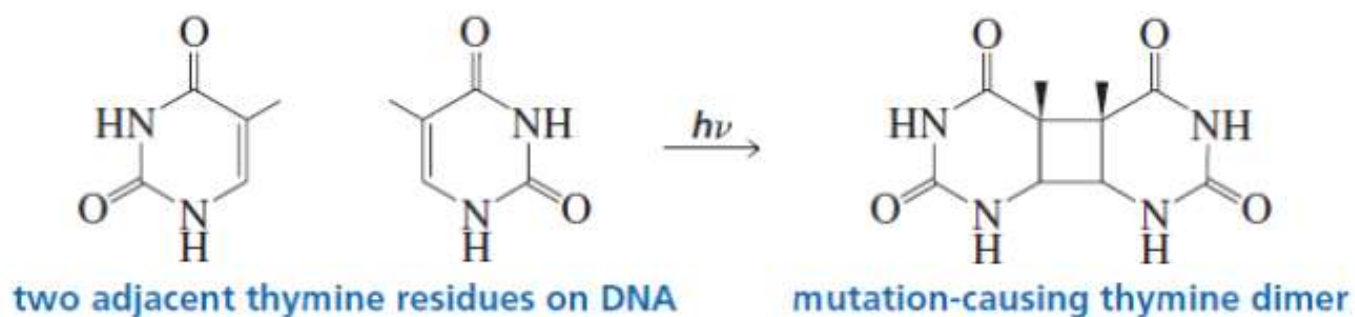
# [2+2] cycloaddition under photochemical conditions



## Electrocyclic Reaction under *photochemical condition*



Exposure to ultraviolet light causes skin cancer. This is one of the reasons why many scientists are concerned about the thinning ozone layer. The ozone layer absorbs ultraviolet radiation high in the atmosphere, protecting organisms on Earth's surface. One cause of skin cancer is the formation of *thymine dimers*. At any point in DNA where there are two adjacent thymine residues, a cycloaddition reaction can occur, resulting in the formation of a thymine dimer. Because cycloaddition reactions take place only under photochemical conditions, the reaction takes place only in the presence of ultraviolet light.

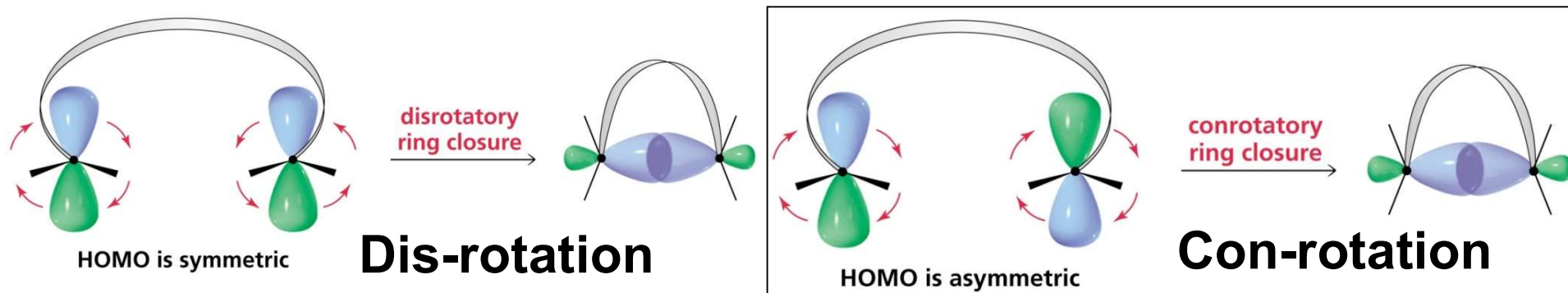


**Thymine dimers can cause cancer because they interfere with the structural integrity of DNA. Any modification of DNA structure can lead to mutations and possibly to cancer.**

# Electrolytic cyclization reaction



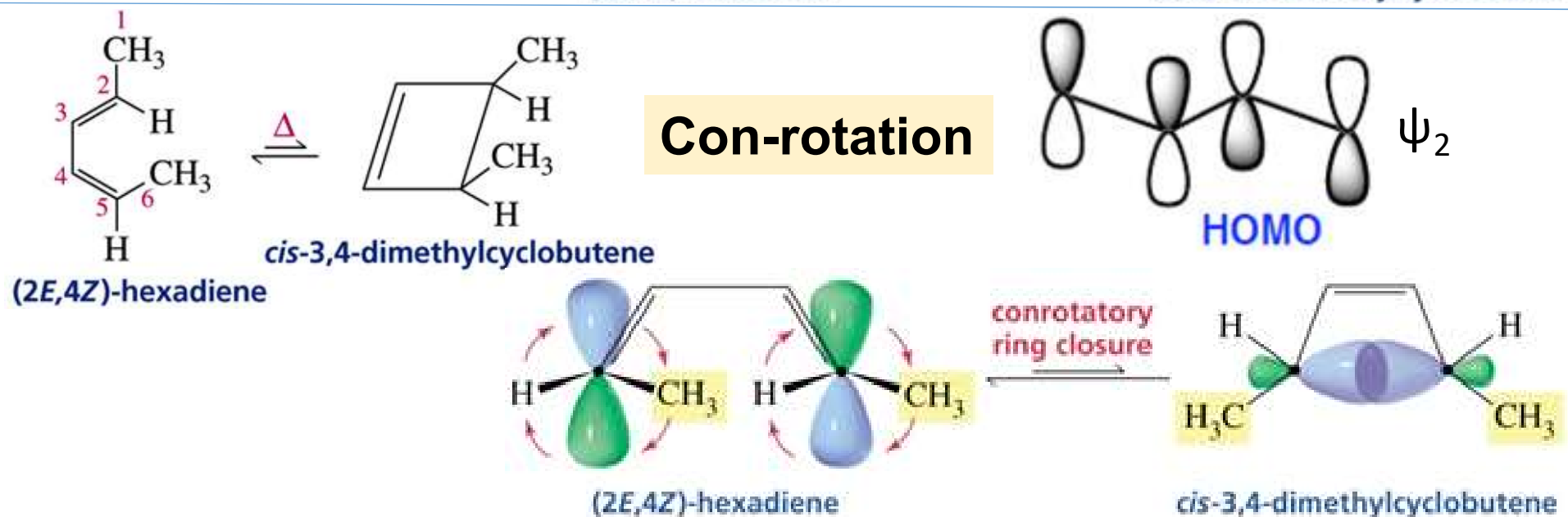
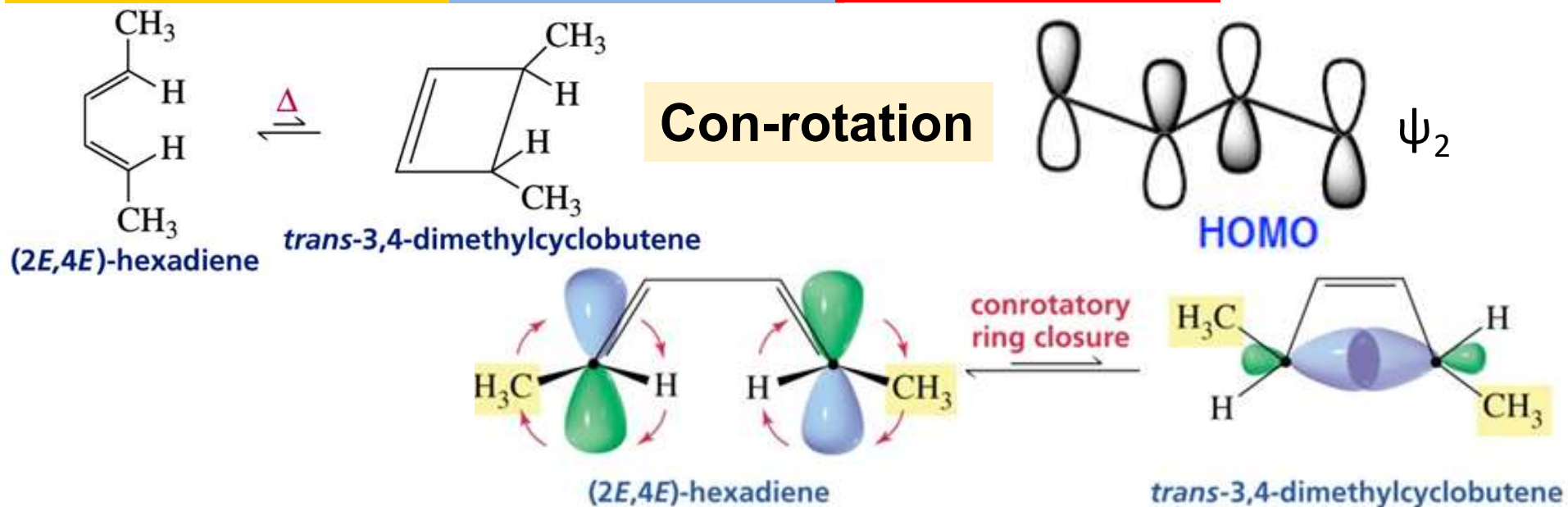
- ❑ To form the new  $\sigma$  bond in the electrocyclic reaction, the  $\pi$ -orbitals at the end of the conjugated system must overlap head-to-head.



- ❑ Only the symmetry of the HOMO is important in determining the course of the reaction.

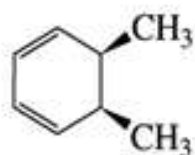
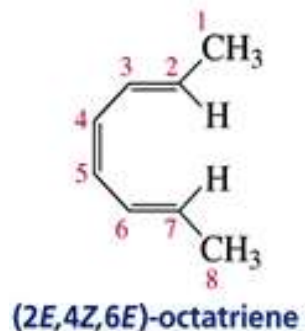
- A symmetry-allowed pathway is one in which in-phase orbitals overlap.
- If a reaction is symmetry-forbidden, it cannot take place by a concerted pathway.
- The symmetry of the HOMO of the compound undergoing ring closure controls the stereochemical outcome of an electrocyclic reaction.

# Electrolytic cyclization reaction



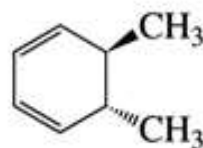
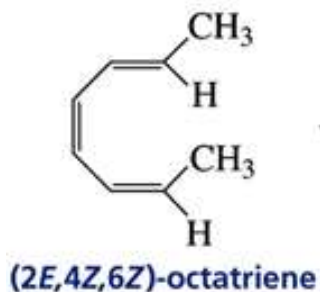
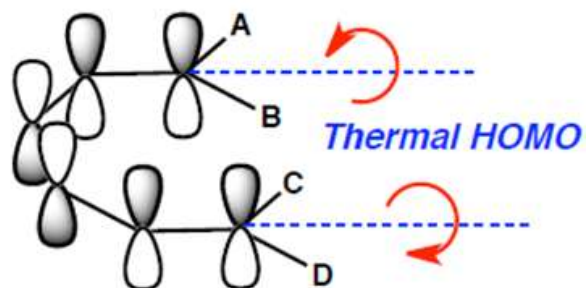
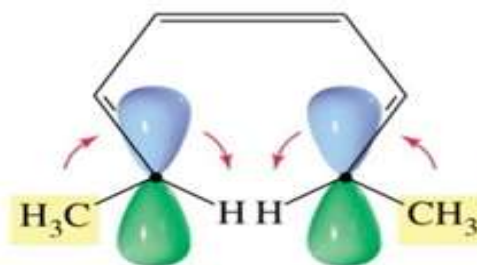


# Electrolytic cyclization reaction



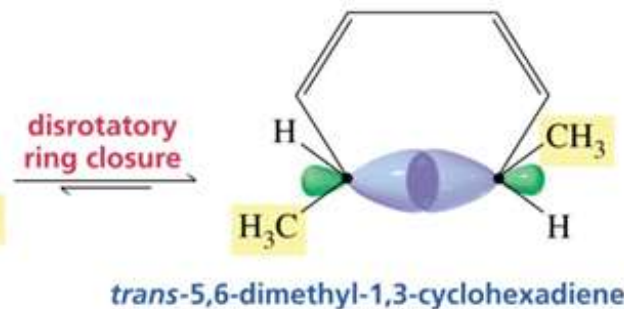
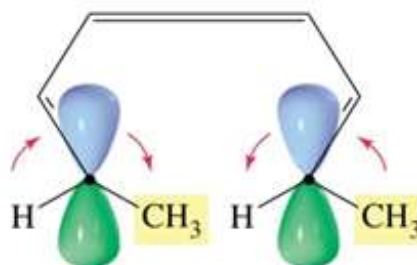
*cis*-5,6-dimethyl-1,3-cyclohexadiene

**Dis-rotation**



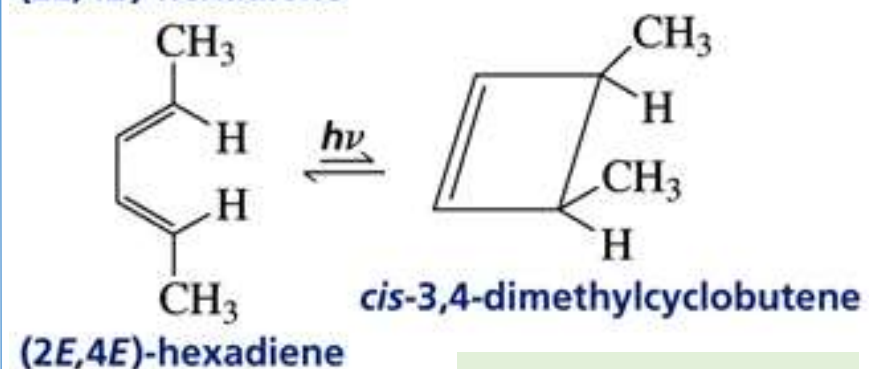
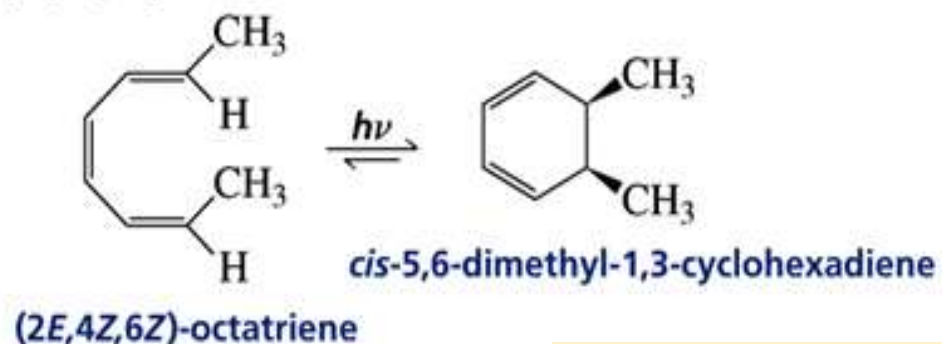
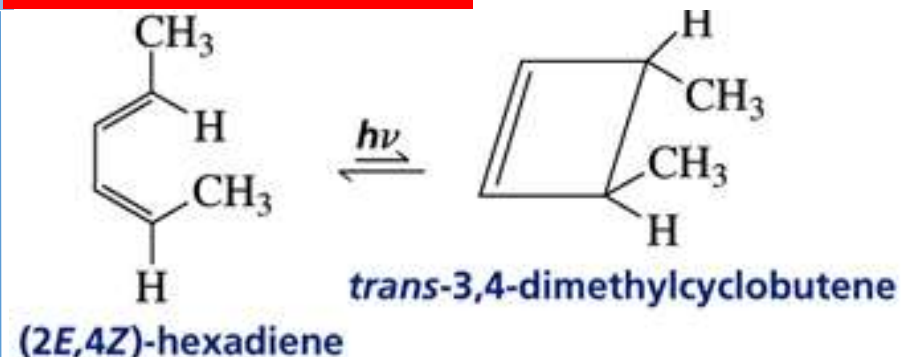
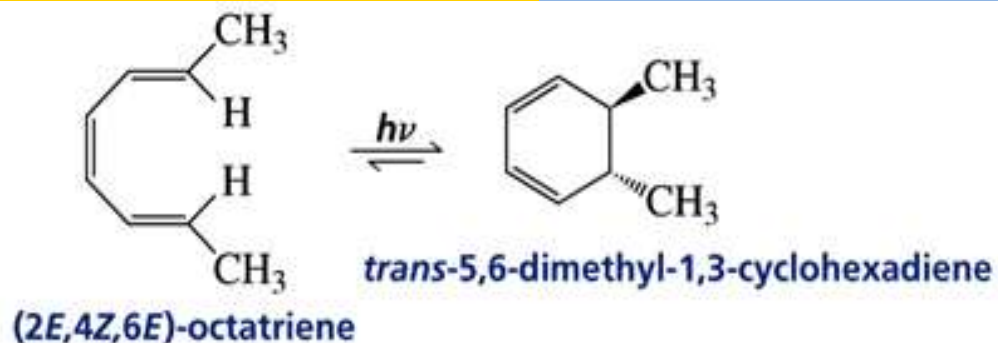
*trans*-5,6-dimethyl-1,3-cyclohexadiene

**Dis-rotation**





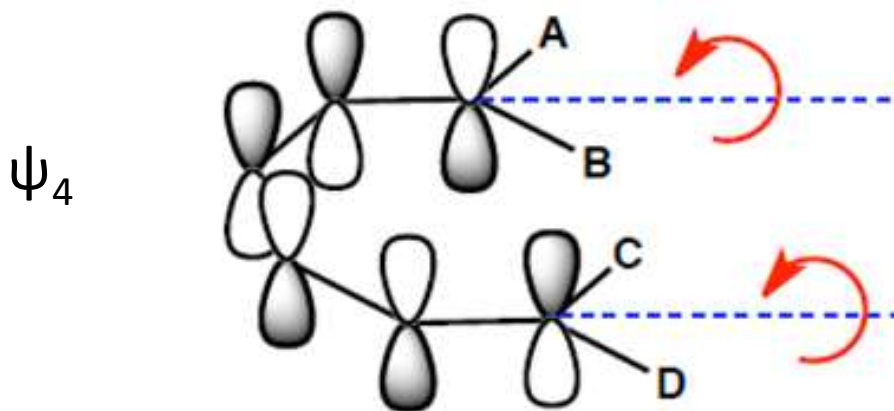
# Electrocyclic Reaction under *photochemical condition*



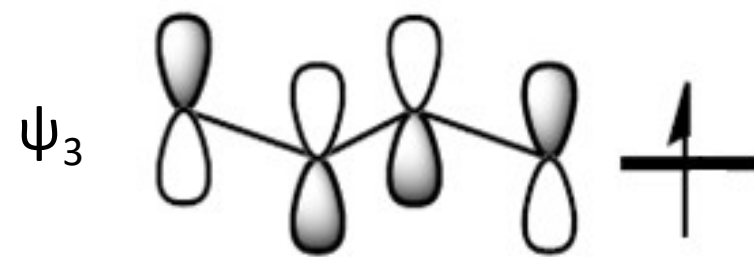
**Con-rotation**

**Dis-rotation**

*Photochemical HOMO*



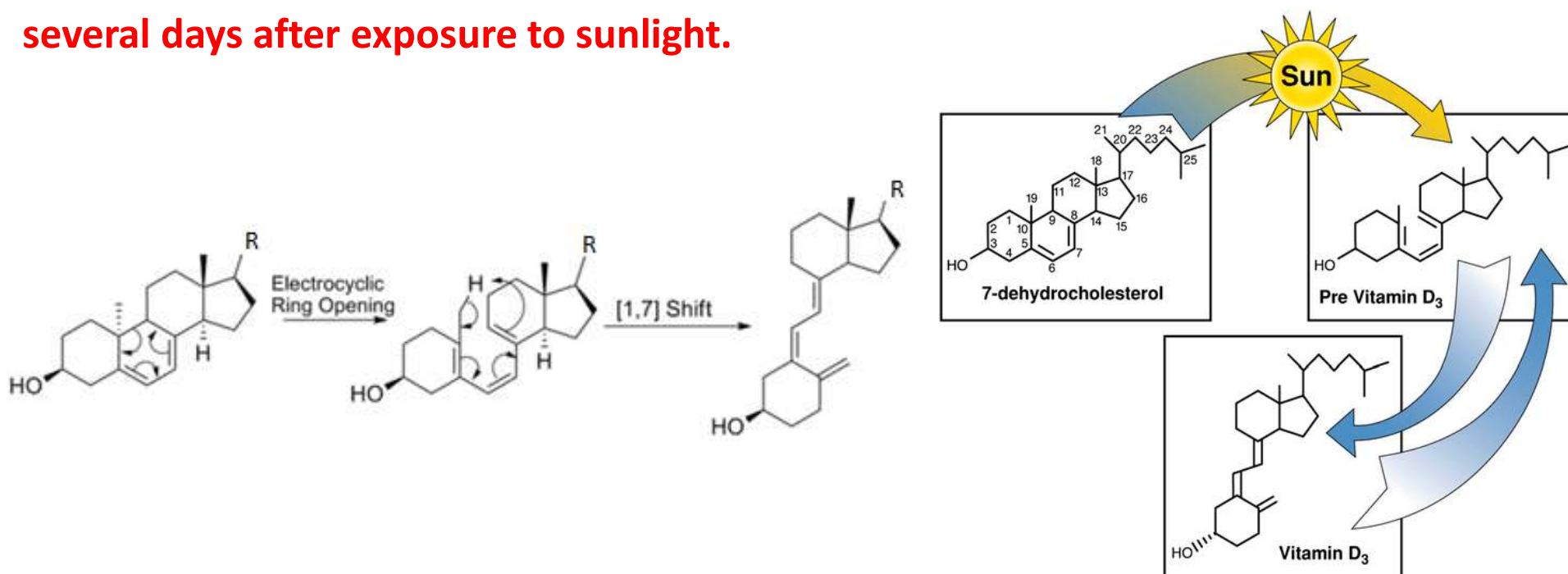
*Photochemical HOMO*



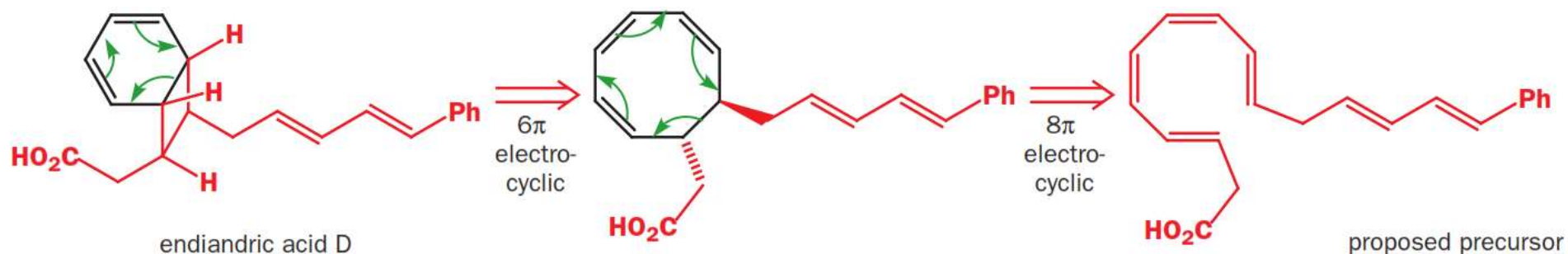
# Electrocyclic Reaction under *photochemical condition*



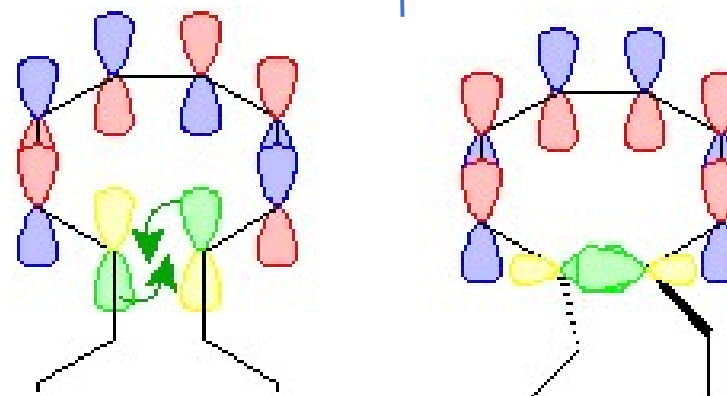
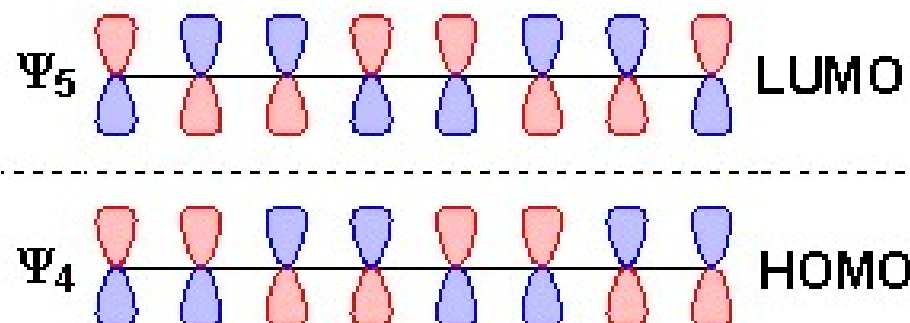
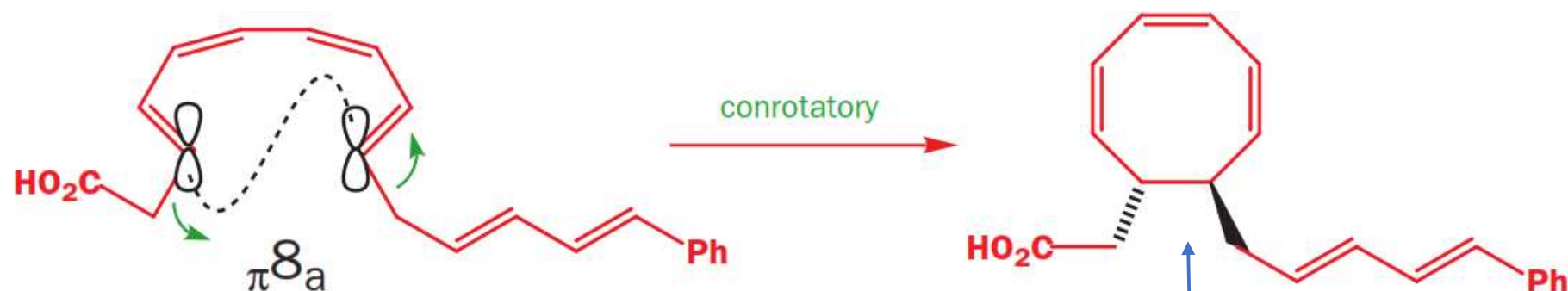
A Biological Reaction Involving an Electrocyclic Reaction **7-Dehydrocholesterol**, a steroid found in skin, is converted into vitamin by two pericyclic reactions. The first is an electrocyclic reaction that opens one of the sixmembered rings in the starting material to form provitamin D<sub>3</sub>. This reaction occurs under photochemical conditions. The provitamin D<sub>3</sub> then undergoes a [1,7] sigmatropic rearrangement to form vitamin. The sigmatropic rearrangement takes place under thermal conditions and is slower than the electrocyclic reaction, so vitamin D<sub>3</sub> continues to be synthesized for several days after exposure to sunlight.



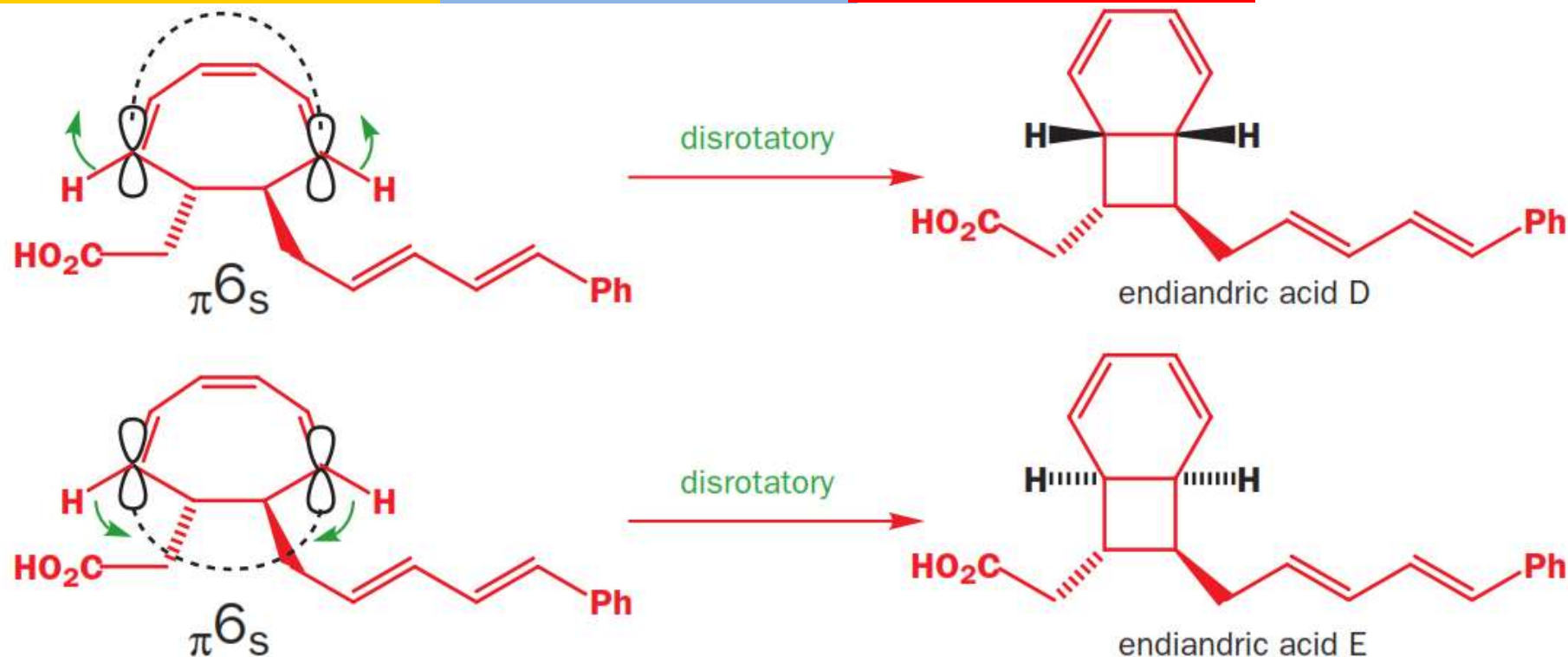
# Electrocyclic Reaction under *photochemical* condition



Antibiotic studies



# Electrocyclic Reaction under *photochemical condition*



## Summary of Electrocyclic Reaction

	Electron pairs (double bonds)	Thermal reaction	Photochemical reaction
(4n)	Even number	Conrotatory	Disrotatory
(4n+2)	Odd number	Disrotatory	Conrotatory