# **Pericyclic Reactions**

## Organic Reaction can be divided in to

- 1. Polar reaction
- 2. Radical reaction and
- 3. Pericyclic reaction.

a polar reaction

$$H: \stackrel{\circ}{\text{C}}: + \stackrel{\delta^+}{\text{C}}H_3 - \stackrel{\delta^-}{\text{Br}} \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$$

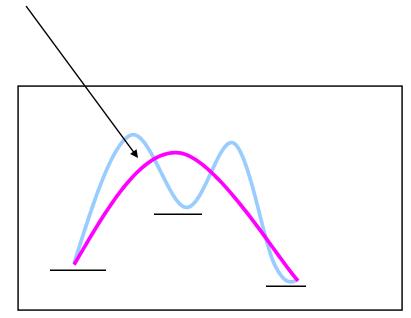
a radical reaction

$$CH_3\dot{C}H_2$$
 +  $Cl$   $\longrightarrow$   $CH_3CH_2Cl$  +  $\cdot Cl$ 

A **pericyclic reaction** occurs as a result of reorganizing the electrons in the reactant(s).

# Pericyclic Reactions – What Are?

- 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

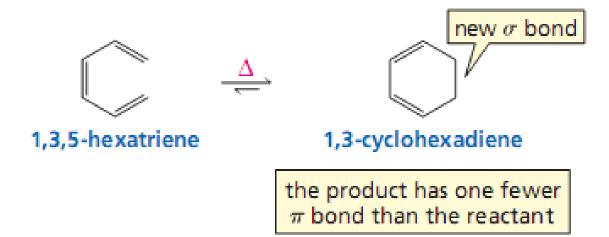


## **Types of Pericyclic Reactions:**

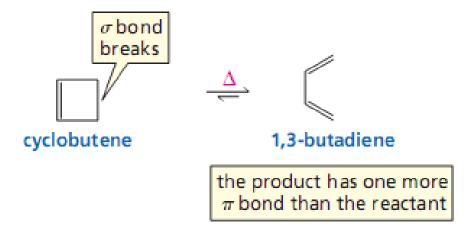
- Cycloaddition
- Electrocyclic Reactions
- Sigmatropic Rearrangements
- Group Transfer Reactions

An **electrocyclic reaction** is an intramolecular reaction in which a new  $\sigma$  (sigma) bond is formed between the ends of a conjugated  $\pi$  (pi) system. This reaction is easy to recognize—the product is a *cyclic* compound that has one more ring and one fewer  $\pi$  bond than the reactant.

### an electrocyclic reaction

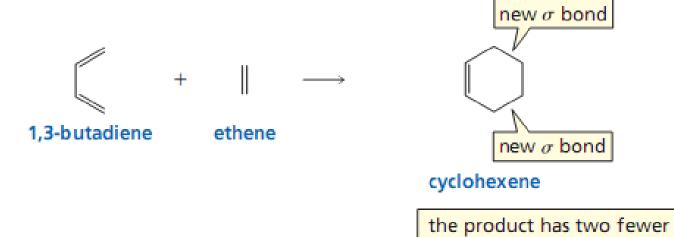


Electrocyclic reactions are reversible. In the reverse direction, an electrocyclic reaction is one in which a  $\sigma$  bond in a cyclic reactant breaks, forming a conjugated  $\pi$  system that has one  $more \ \pi$  bond than the cyclic reactant.



In a **cycloaddition reaction**, two different  $\pi$  bond–containing molecules react to form a cyclic compound. Each of the reactants loses a  $\pi$  bond, and the resulting cyclic product has two new  $\sigma$  bonds. The Diels–Alder reaction is a familiar example of a cycloaddition reaction (Section 8.8).

#### a cycloaddition reaction

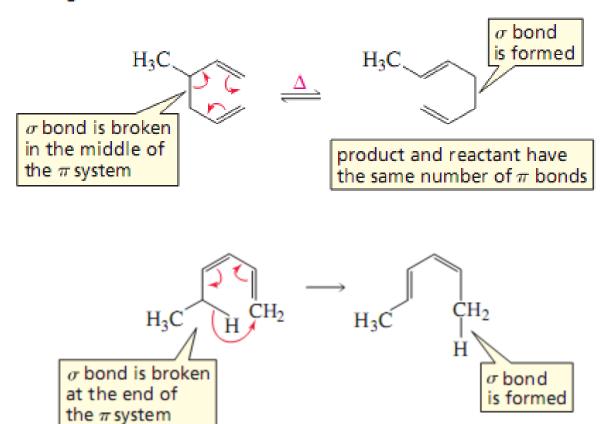


 $\pi$  bonds than the sum of the

 $\pi$  bonds in the reactants

In a **sigmatropic rearrangement**, a  $\sigma$  bond is broken in the reactant, a new  $\sigma$  bond is formed in the product, and the  $\pi$  bonds rearrange. The number of  $\pi$  bonds does not change (the reactant and the product have the same number of  $\pi$  bonds). The  $\sigma$  bond that is broken can be in the middle of the  $\pi$  system or at the end of the  $\pi$  system. The  $\pi$  system consists of the double-bonded carbons and the carbons immediately adjacent to them.

#### sigmatropic rearrangements



## **Characteristic of Pericyclic Reactions**

- They are all concerted reactions. This means that all the electron reorganization takes place in a single step. Therefore, there is one transition state and no intermediate.
- Because the reactions are concerted, they are highly stereoselective.
- The reactions are generally not affected by catalysts.

We will see that the configuration of the product formed in a pericyclic reaction depends on

- the configuration of the reactant
- the number of conjugated double bonds or pairs of electrons in the reacting system
- · whether the reaction is a thermal reaction or a photochemical reaction

A photochemical reaction takes place when a reactant absorbs light

A thermal reaction takes place without the absorption of light

## PROBLEM 1◆

Examine the following pericyclic reactions. For each reaction, indicate whether it is an electrocyclic reaction, a cycloaddition reaction, or a sigmatropic rearrangement.

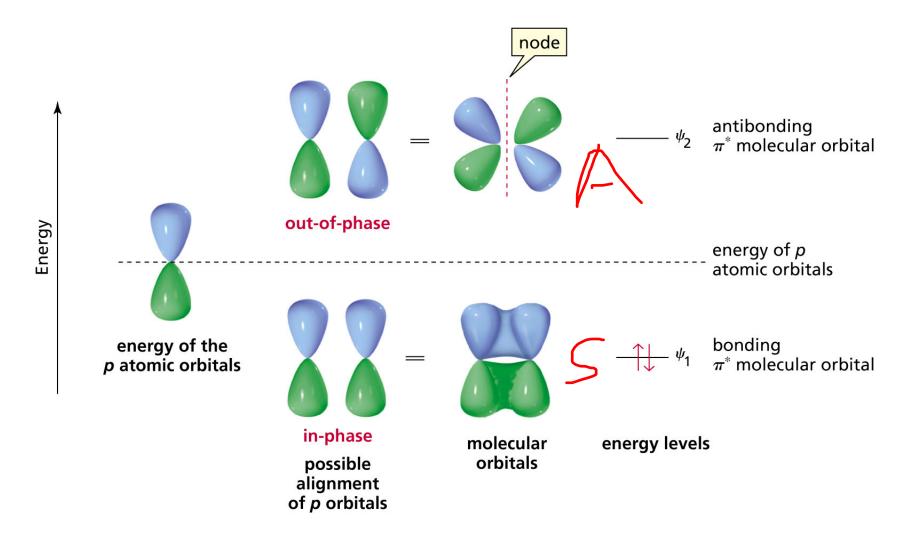
c. 
$$CH_2 + CHOCH_3 \rightarrow CH_3$$

d. 
$$CHCH_3$$
 +  $CHCH_3$  +  $CHCH_3$  CH<sub>2</sub> +  $CHCH_3$ 

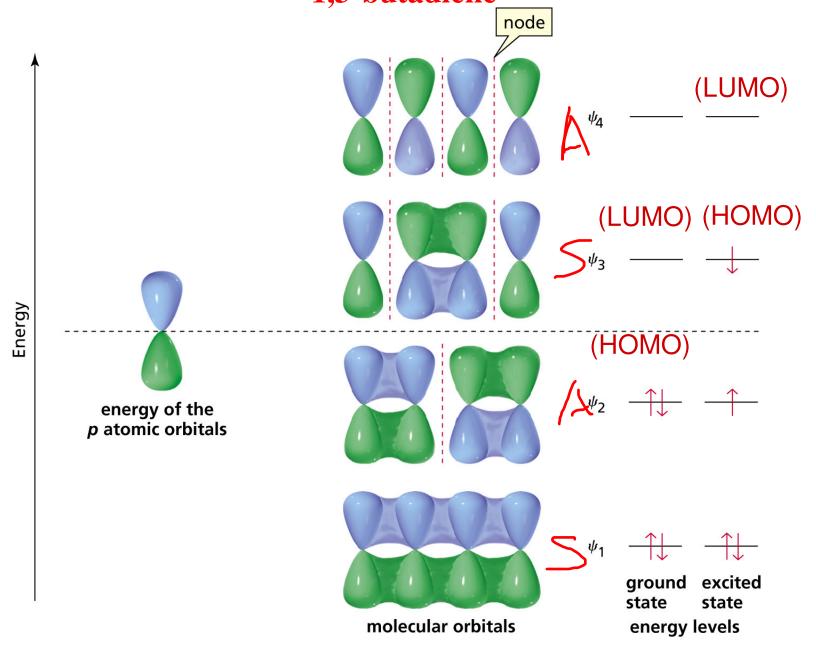
## **Molecular Orbitals and Orbital Symmetry**

A molecular orbital can be described by the linear combination of atomic orbital (LCAO). In a pi-molecular orbital, each electron that previously occupied a p atomic orbital surrounding an individual carbon nucleus surrounds the entire part of the molecule that is included in the interacting p-orbitals.

## A Molecular Orbital Description of Ethene



Four *p* atomic orbitals interact to give the four p MOs of 1,3-butadiene



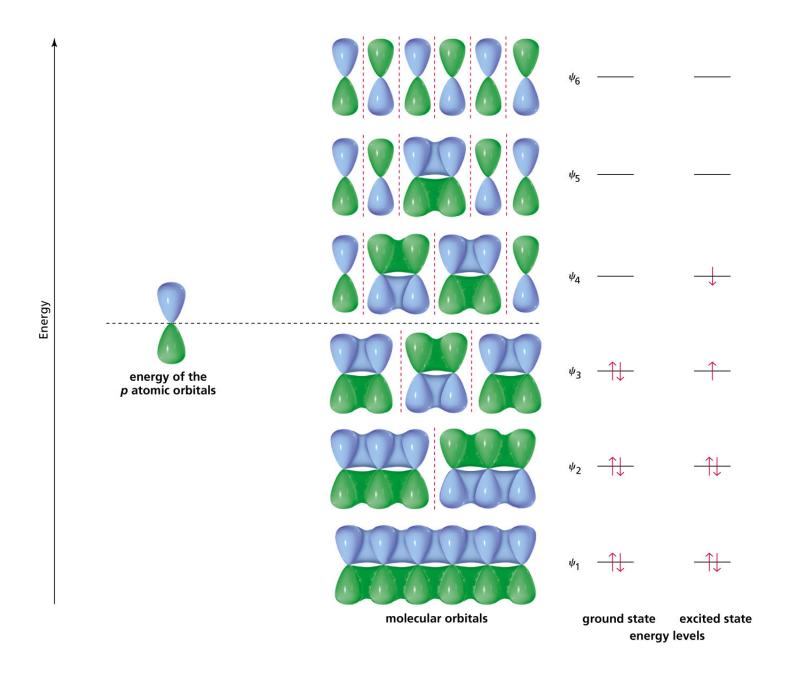
## From the MO diagram of 1,3-butadiene ...

 $\psi_1$  and  $\psi_3$  are symmetric MOs

 $\psi_2$  and  $\psi_4$  are asymmetric MOs

The ground state HOMO and the excited HOMO have opposite symmetry

## A Molecular Orbital Description of 1,3,5-hexatriene



- A MO is bonding if the number of bonding interactions is greater than the number of nodes
- A MO is antibonding if the number of bonding interactions is fewer than the number of nodes
- The normal electronic state of a molecule is known as its ground state
- The ground state electron can be promoted from its HOMO to its LUMO by absorption of light (excited state)
- In a thermal reaction the reactant is in its ground state; in a photochemical reaction, the reactant is in its 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

## PROBLEM 2◆

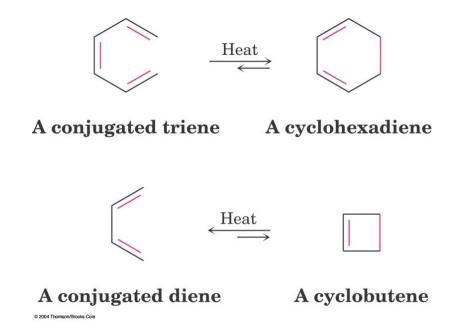
Answer the following questions for the  $\pi$  molecular orbitals of 1,3,5-hexatriene:

- a. Which are the bonding orbitals, and which are the antibonding orbitals?
- b. Which orbitals are the HOMO and the LUMO in the ground state?
- c. Which orbitals are the HOMO and the LUMO in the excited state?
- d. Which orbitals are symmetric, and which are asymmetric?
- e. What is the relationship between HOMO and LUMO and symmetric and asymmetric orbitals?

## PROBLEM 3◆

- a. How many  $\pi$  molecular orbitals does 1,3,5,7-octatetraene have?
- b. What is the designation of its HOMO ( $\psi_1, \psi_2$ , etc.)?
- c. How many nodes does its highest-energy  $\pi$  molecular orbital have between the nuclei?

## **Electrocyclic Reactions**



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

## **Thermal**

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

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



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

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

## **Photochemical**

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

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

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

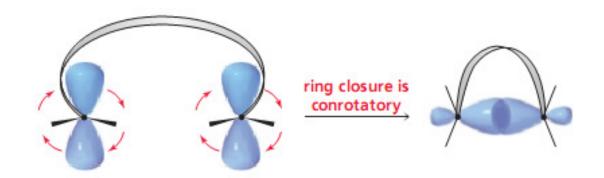
cis-5,6-dimethyl-1,3-cyclohexadiene

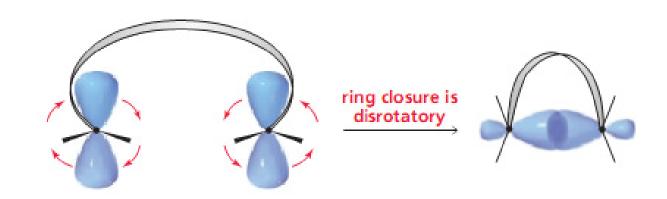
(2E,4Z)-hexadiene

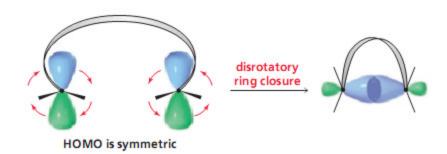
cis-3,4-dimethylcyclobutene

cis-3,4-dimethylcyclobutene

# **Explanation:**

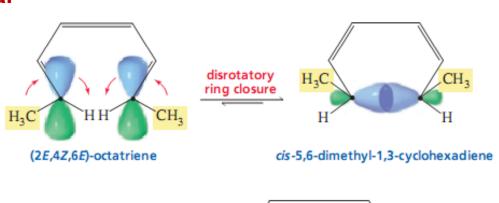


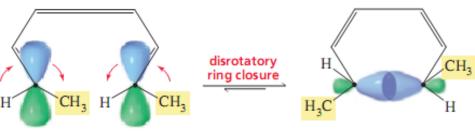




Notice that a **symmetry-allowed pathway** is one in which in-phase orbitals overlap; a **symmetry-forbidden pathway** is one in which out-of-phase orbitals would overlap. A symmetry-allowed reaction can take place under relatively mild conditions. If a reaction

#### **Thermal**

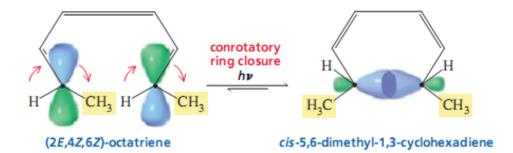




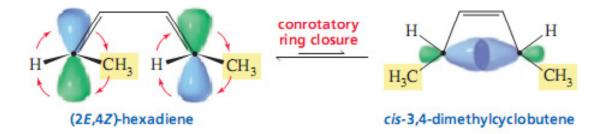
(2E,4Z,6Z)-octatriene

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

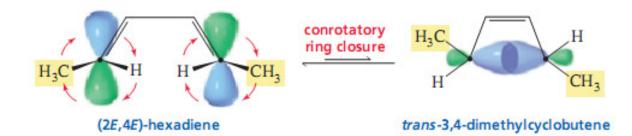
#### **Photochemical**



## **Butadiene System**



Similarly, conrotatory ring closure of (2E,4E)-hexadiene leads to the trans product.



the ground-state HOMO of a compound with an even number of conjugated double bonds is asymmetric, whereas the ground-state HOMO of a compound with an odd number of conjugated double bonds is symmetric.

### **Selection rule**

Table 29.1 Woodward-Hoffmann Rules for Electrocyclic Reactions			
Number of conjugated $\pi$ bonds	Reaction conditions	Allowed mode of ring closure	
Even number	Thermal	Conrotatory	
	Photochemical	Disrotatory	
Odd number	Thermal	Disrotatory	
	Photochemical	Conrotatory	

Table 29.2 Configuration of the Product of an Electrocyclic Reaction		
Substituents in the reactant	Mode of ring closure	Configuration of the product
Point in opposite directions	Disrotatory Conrotatory	cis trans
Point in the same direction	Disrotatory Conrotatory	trans cis

#### PROBLEM 7◆

Which of the following are correct? Correct any false statements.

- A conjugated diene with an even number of double bonds undergoes conrotatory ring closure under thermal conditions.
- A conjugated diene with an asymmetric HOMO undergoes conrotatory ring closure under thermal conditions.
- c. A conjugated diene with an odd number of double bonds has a symmetric HOMO.

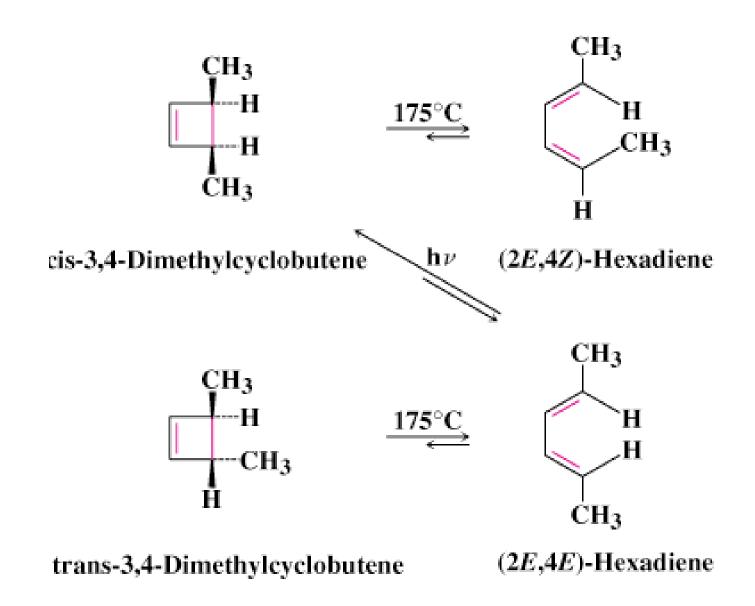
#### PROBLEM 8◆

- a. Identify the mode of ring closure for each of the following electrocyclic reactions.
- b. Are the indicated hydrogens cis or trans?

# Example: Electrocyclic Interconversions With Octatriene

CH<sub>3</sub>
Heat
$$CH_3$$
 $CH_3$ 
 $CH_$ 

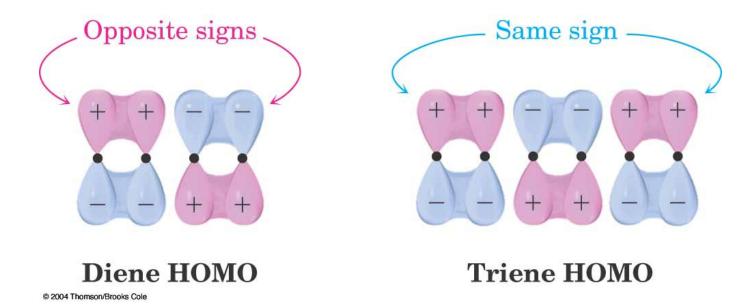
# Example: Electrocyclic Interconversions with Dimethylcyclobutene



28

# 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



## **Pericyclic Reactions in Biological Systems**

# A Biological Reaction Involving an Electrocyclic Reaction and a Sigmatropic Rearrangement

$$\begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$$

two adjacent thymine residues on DNA

mutation-causing thymine dimer

## **Cycloaddition Reactions**

In a cycloaddition reaction, two different  $\pi$  bond-containing molecules react to form a cyclic molecule by rearranging the  $\pi$  electrons and forming two new  $\sigma$  bonds. The Diels-Alder reaction is one of the best known examples of a cycloaddi-

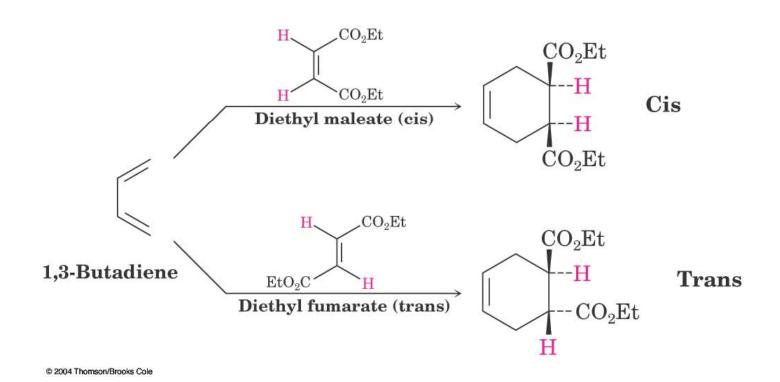
#### **Classification:**

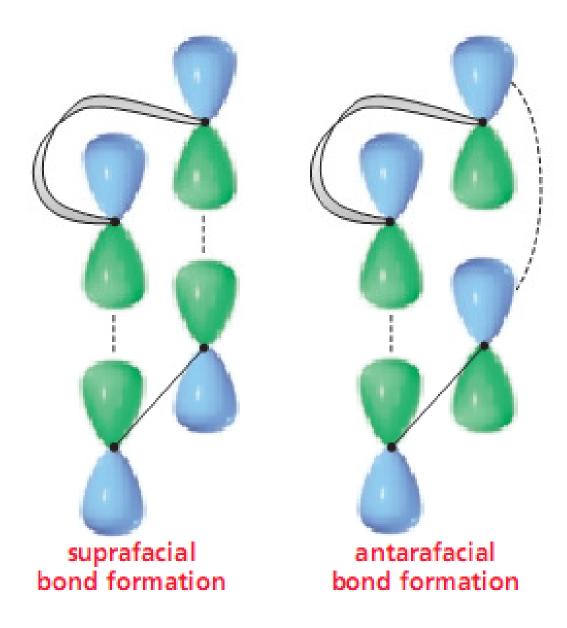
Depends on the number of  $\pi$  electrons that interact in the reaction (only interacting  $\pi$  electrons)

$$H_3C$$
 $H_3C$ 
 $H_3C$ 

CO<sub>2</sub>CH<sub>3</sub>

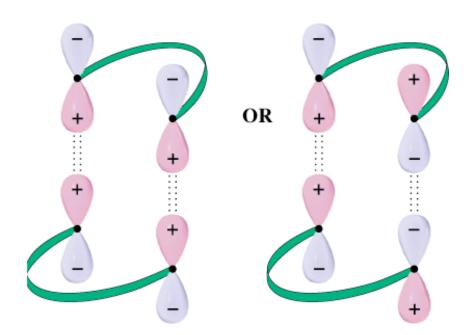
The Diels–Alder cycloaddition reaction is a pericyclic process that takes place between a diene (four  $\pi$  electrons) and a dienophile (two  $\pi$  electrons) to yield a cyclohexene product **Stereospecific with respect to substituents.** 





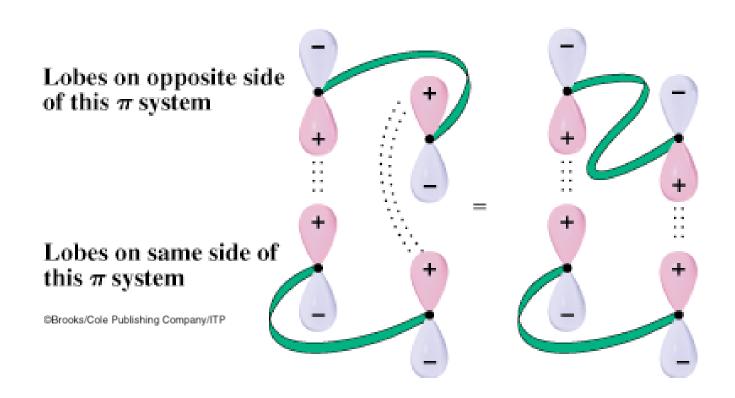
## **Rules for Cylcoadditions - Suprafacial Cycloadditions**

- The terminal  $\pi$  lobes of the two reactants must have the correct symmetry for bonding to occur
- Suprafacial cycloadditions take place when a bonding interaction occurs between lobes on the same face of one reactant and lobes on the same face of the other reactant



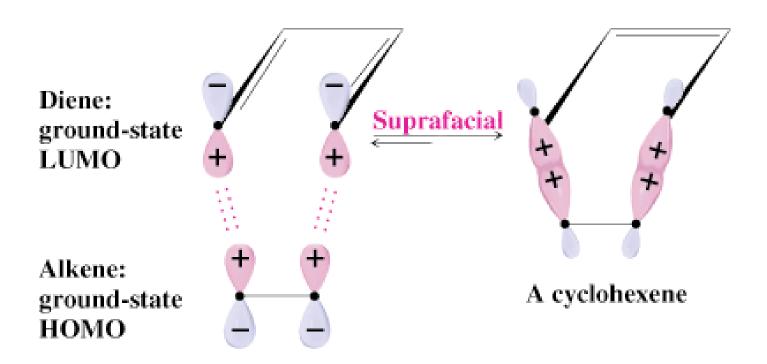
## Rules for Cylcoadditions - Antarafacial Cycloadditions

 These take place when a bonding interaction occurs between lobes on the same face of one reactant and lobes on opposite faces of the other reactant (not possible unless a large ring is formed)

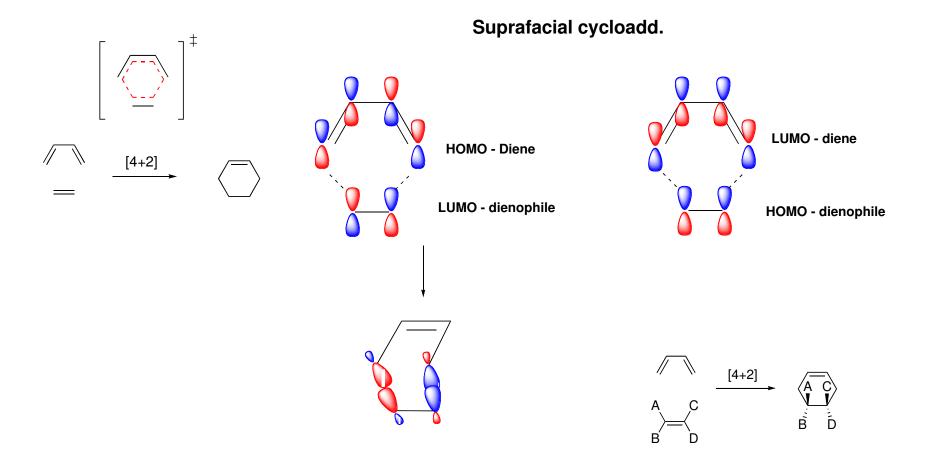


# Stereochemistry of Cycloadditions

- HOMO of one reactant combines with LUMO of other
- Possible in thermal [4 +2] cycloaddition

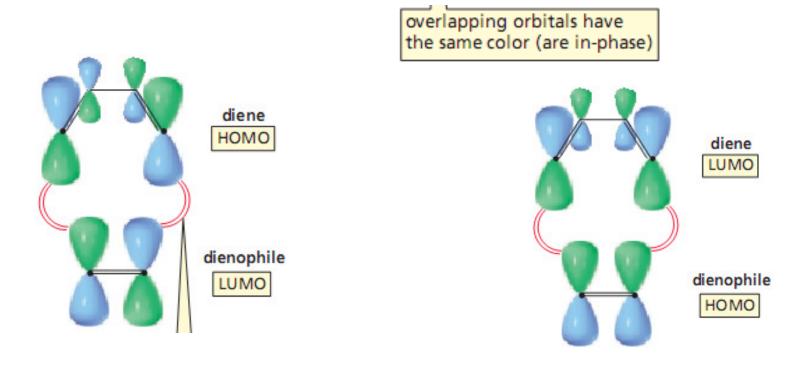


# **Cycloadditions (i.e. Diels Alder)**



Stereospesific react.

Frontier molecular orbital analysis of a [4 + 2] cycloaddition reaction. The HOMO of either of the reactants can be used with the LUMO of the other. Both situations require suprafacial overlap for bond formation.



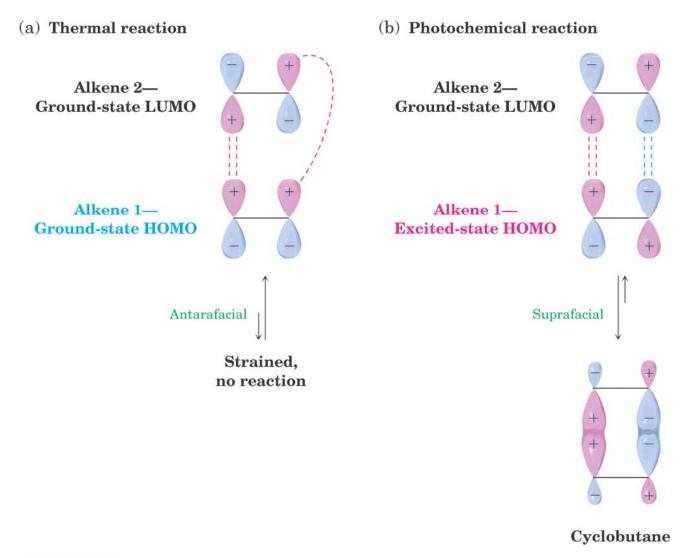
Does this reaction proceed under Photochemical condition???

# [2+2] Cylcoadditions

A [2 + 2] cycloaddition reaction does not occur under thermal conditions but does take place under photochemical conditions.

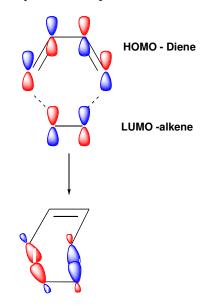
$$+$$
  $\stackrel{\Delta}{\longrightarrow}$  no reaction  $+$   $+$   $\stackrel{h\nu}{\longrightarrow}$ 

• Only the excited-state HOMO of one alkene and the LUMO can combine by a suprafacial pathway in the combination of two alkenes

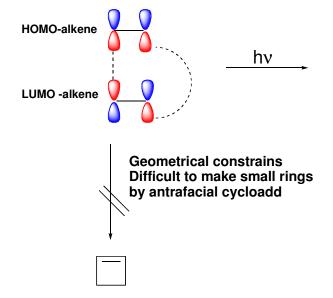


# [2+2] Cycloadditions

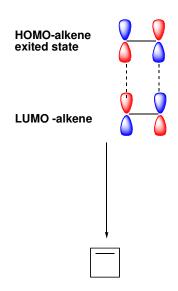
#### Suprafacial cycloadd.



#### Antarafacial cycloadd. (termal cond.)



#### Suprafacial cycloadd. (photochem. cond.)



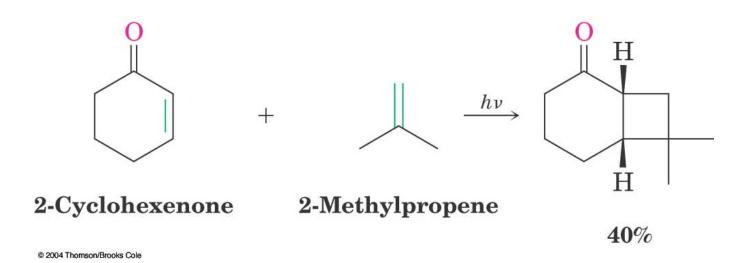
# Photochemical [2+2] Cycloaddition

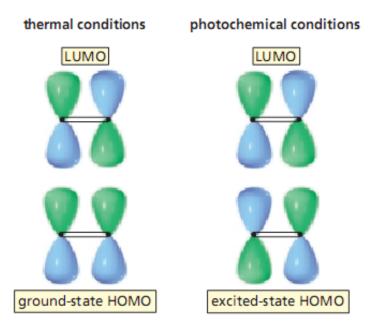
 Mechanism of most of theses reactions are not clear due to isomerisation.

3. 
$$\frac{0^{\circ} \text{ C}}{[4+2]}_{\text{H}_3\text{C}}$$
  $\frac{1}{[4+2]}_{\text{H}_3\text{C}}$   $\frac{1}{[6+4]}$  4.  $\frac{[6+4]}{[6+4]}$ 

# Formation of Four-Membered Rings

• Photochemical [2 + 2] cycloaddition reaction occurs smoothly





The frontier molecular orbitals in Figure 29.6 show why this is so. Under thermal conditions, suprafacial overlap is not symmetry-allowed (the overlapping orbitals are out-of-phase). Antarafacial overlap is symmetry-allowed but is not possible because of the small size of the ring. Under photochemical conditions, however, the reaction can take place because the symmetry of the excited-state HOMO is opposite that of the ground-state HOMO. Therefore, overlap of the excited-state HOMO of one alkene with the LUMO of the second alkene involves symmetry-allowed suprafacial bond formation.

Notice in the photochemical reaction that only one of the reactants is in an excited state. Because of the very short lifetimes of excited states, it is unlikely that two reactants in their excited states would find one another to interact. The selection rules for cycloaddition reactions are summarized in Table 29.3.

Table 29.3 Woodward-Hoffmann Rules for Cycloaddition Reactions		
Sum of the number of $\pi$ bonds in the reacting systems of both reagents	Reaction conditions	Allowed mode of ring closure
Even number	Thermal	Antarafacial <sup>a</sup>
	Photochemical	Suprafacial
Odd number	Thermal	Suprafacial
	Photochemical	Antarafacial <sup>a</sup>
<sup>a</sup> Although antarafacial ring closure is symmetry-allowed, it can occur only with large rings.		

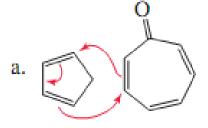
No. of electrons	Reactions in the ground state (termal)	Reactions in exited state (Photochem.)
4n	Antarafacial	Suprafacial
4n + 2	Suprafacial	Antarafacial

# PROBLEM 10 SOLVED

Compare the reaction of 2,4,6-cycloheptatrienone with cyclopentadiene to that with ethene. Why does 2,4,6-cycloheptatrienone use two  $\pi$  electrons in one reaction and four  $\pi$  electrons in the other?

a. 
$$\bigcirc$$
 +  $\bigcirc$  +  $\bigcirc$  +  $\bigcirc$  +  $\bigcirc$  +  $\bigcirc$  CH<sub>2</sub>=CH<sub>2</sub>  $\longrightarrow$   $\bigcirc$ 

**SOLUTION** Both reactions are [4 + 2] cycloaddition reactions. When 2,4,6-cycloheptatrienone reacts with cyclopentadiene, it uses two of its  $\pi$  electrons because cyclopentadiene is the four- $\pi$ -electron reactant. When 2,4,6-cycloheptatrienone reacts with ethene, it uses four of its  $\pi$  electrons because ethene is the two- $\pi$ -electron reactant.



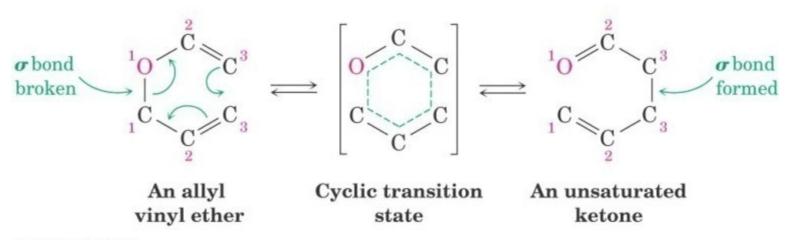
# Sigmatropic Rearrangements

$$\begin{array}{c} H_3C \\ H \\ \end{array} \\ \begin{array}{c} H \\ \end{array} \\ \begin{array}{c} G \\ \end{array} \\ \begin{array}{c} H \\ \end{array} \\ \begin{array}{c} G \\ \end{array} \\ \\ \begin{array}{c} G \\ \end{array} \\ \begin{array}{c} G \\ \\ \end{array} \\ \\ \begin{array}{c} G \\ \\ \end{array} \\ \begin{array}{c} G \\ \\ \\$$

- A  $\sigma$  -bonded substituent atom or group migrates across a  $\pi$  electron system from one position to another
- As bond is broken in the reactant, the  $\pi$  bonds move, and a new s bond is formed in the product

# A [1,5] rearrangement

# A [3,3] rearrangement



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# **Sigmatropic Rearrangements**

#### a [2,3] sigmatropic rearrangement

# **Rules for Numbering:**

- Mentally break the  $\sigma$ -bond in the reactant and give a number 1 to both the attached atoms.
- Identify the new  $\sigma$ -bond in the product.
- Count the number of atoms in each of the fragments that connect the broken  $\sigma$ -bond and the new  $\sigma$ -bond.
- The two numbers are put in a brackets with the smaller number stated first.

#### a [1,5] sigmatropic rearrangement

#### a [1,3] sigmatropic rearrangement

$$\begin{array}{c} CH_3 \\ CH_3C - CH = CH_2 \\ CH_3C - CH = CH_2 \\ CH_3 \end{array} \xrightarrow{\Delta} \begin{array}{c} CH_3 \\ CH_3C = CH - CH_2 \\ CH_3 \end{array} \xrightarrow{\text{new bond formed}}$$

#### a [3,3] sigmatropic rearrangement

$$\begin{array}{c|c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

#### a [2,3] sigmatropic rearrangement

bond broken 
$$R - N = N$$
 $R - N = N$ 
 $R - N = N$ 

# PROBLEM 12

- a. Name the kind of sigmatropic rearrangement that occurs in each of the following reactions.
- b. Using arrows, show the electron rearrangement that takes place in each of the reactions.

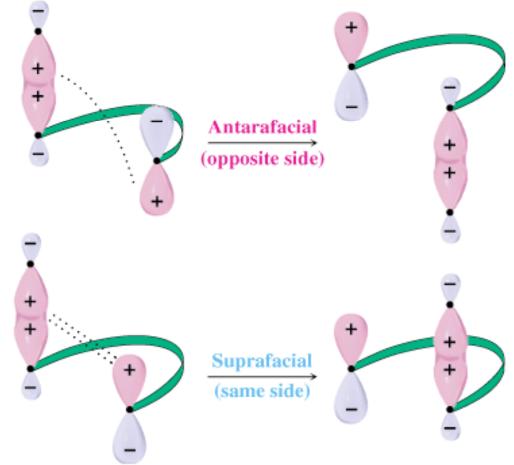
1. 
$$CH_3$$
  $CH_2$   $CH_2$   $CH_3$ 

2. 
$$CH_2$$
  $CH_3$   $CH_3$ 

4. 
$$CH_3$$
  $A CH_2$ 

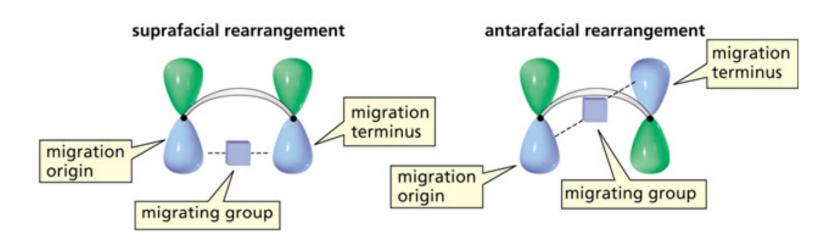
# Sigmatropic Stereospecificity: Suprafacial and Antarafacial

- Migration of a group across the same face of the  $\pi$  system is a *suprafacial* rearrangement
- Migration of a group from one face of the  $\pi$  system to the other face is called an *antarafacial* rearrangement



# The Supra / Antara Concept:

#### **Consider the Transition state of the reaction:**

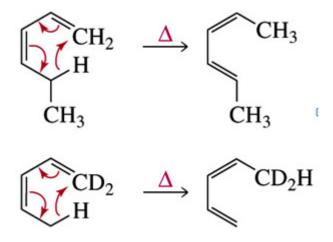


- •The group that migrate is bonded partially to the migration origin and to migration terminus
- •Sigmatropic rearrangements have cyclic transition states
- Rearrangement must be suprafacial if the transition state has six or fewer atoms in the ring

#### 1,3-hydrogen shifts

A [1,3] sigmatropic rearrangement involves a  $\pi$ -bond and a pair of  $\sigma$ -electron thus it involves **two pairs of electrons**.

# 1,5-hydrogen shifts



A [1,5] sigmatropic rearrangement involves two  $\pi$ -bonds and a pair of  $\sigma$ -electron thus it involves **three** pairs of electrons.

# 1,7-hydrogen shift

$$CH - C_4H_9 \longrightarrow CH_3$$

$$CH_2$$

$$CH_3$$

# a Cope rearrangement

$$\begin{array}{cccc}
C_6H_5 & & & \\
CH_3 & & & \\
\end{array}$$

$$C_6H_5$$

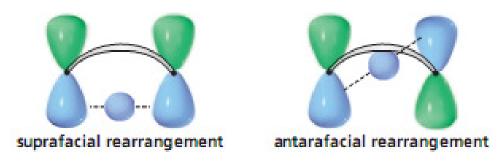
$$CH_3$$

# a Claisen rearrangement

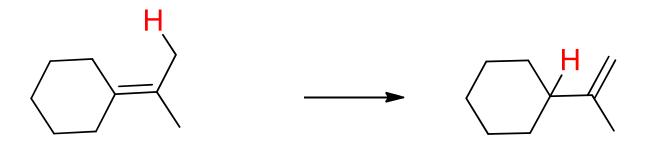
$$CH_3$$
 $\Delta$ 
 $CH_3$ 

# Migration of Hydrogen

#### migration of hydrogen



# 1,3-Sigmatropic rearrangement.



Two pairs of electrons are involved a,  $\sigma$ -pair and a  $\pi$ -pair, Thus a four membered transition state Equivalent to Butadiene system HOMO is Asymmetric Thus a antarafacial under a thermal condition is not possible.

1,3-Hydrogen shifts can take place if the reaction is carried out under photochemical conditions because the HOMO is symmetric under photochemical conditions, which means that hydrogen can migrate by a suprafacial pathway (Table 29.4).

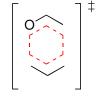
$$\bigcirc \longleftarrow \longleftarrow \longleftarrow \longleftarrow \longleftarrow \longleftarrow \longleftarrow$$

# **Sigmatropic Rearrangements**

# [3,3] Rearrangements; Claisen rearrang. etc.

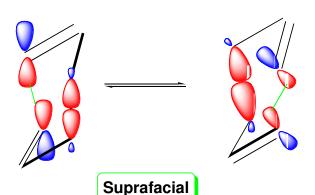
#### Claisen rearrangement

Allyl-vinyl ether or Allyl aryl ether

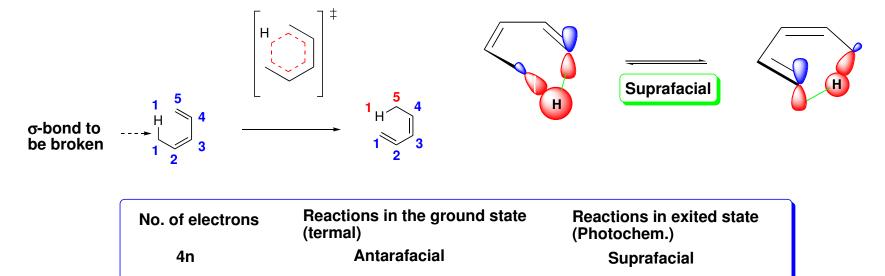


#### **Cope rearrangement**

#### **Oxy-Cope rearrangement**



# [1,5] Rearrangement (H-shift)

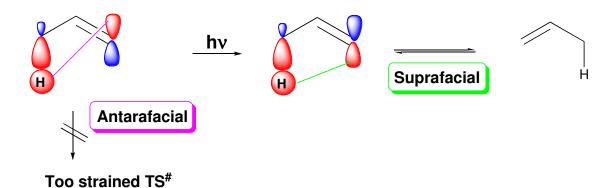


**Antarafacial** 

**Suprafacial** 

# [1,3] Rearrangement (H-shift)

4n + 2



# Some Examples of Sigmatropic Rearrangements

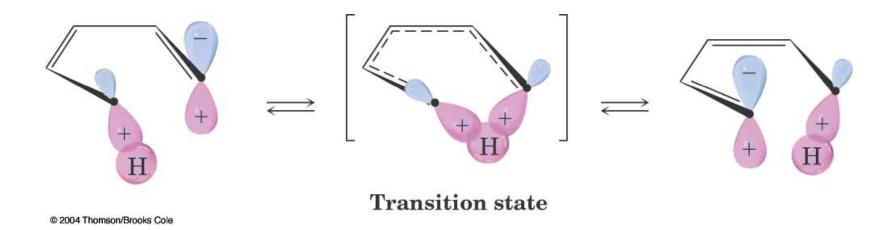
- A [1,5] sigmatropic rearrangement involves three electron pairs (two  $\pi$  bonds and one s bond)
- Orbital-symmetry rules predict a suprafacial reaction
- 5-methylcyclopentadiene rapidly rearranges at room temperature

# [1,5]Sigmatropic Rearrangement

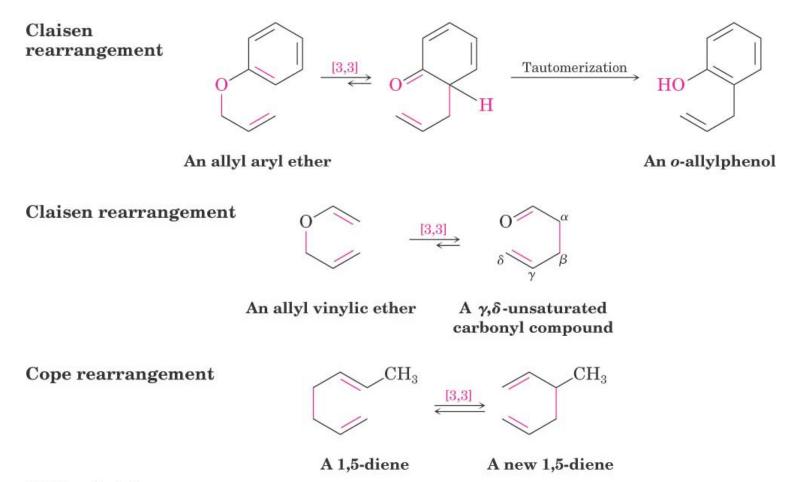
• Heating 5,5,5-trideuterio-(1,3Z)-pentadiene causes scrambling of deuterium between positions 1 and 5

$$\begin{array}{c|c} CD_3 & & \hline \\ CD_2 & & \hline \\ CH_2 & & & \\ \hline \\ CH_2 & & & \\ \hline \end{array}$$

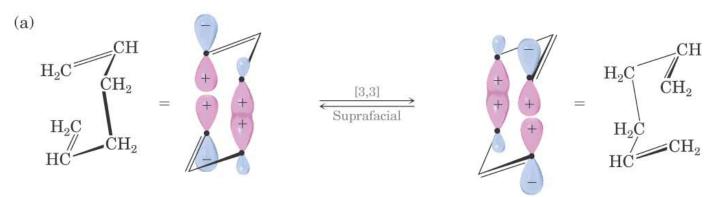
# Orbital Picture of a Suprafacial [1,5] H Shift



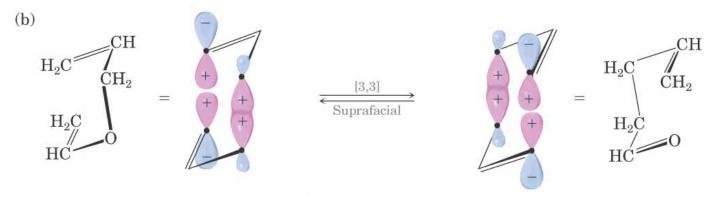
- Cope rearrangement of 1,5-hexadiene
- Claisen rearrangement of an allyl aryl ether



- Both involve reorganization of an odd number of electron pairs (two  $\pi$  bonds and one s bond)
- Both react by suprafacial pathways



Cope rearrangement of a 1,5-hexadiene



Claisen rearrangement of an allyl vinyl ether

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#### **Table 29.4 Woodward–Hoffmann Rules for Sigmatropic Rearrangements** Number of pairs of electrons Allowed mode Reaction conditions in the reacting system of ring closure Antarafacial<sup>a</sup> Even number Thermal Photochemical Suprafacial Odd number Thermal Suprafacial Photochemical. Antarafacial<sup>a</sup> <sup>a</sup> Although antarafacial ring closure is symmetry-allowed, it can occur only with large rings.

#### a Cope rearrangement

# $\begin{array}{c} C_6H_5 \\ CH_3 \end{array}$ $\begin{array}{c} C_6H_5 \\ CH_3 \end{array}$

#### a Claisen rearrangement

$$CH_3$$
  $\Delta$   $O$ 

#### PROBLEM 13◆

a. Give the product of the following reaction:

b. If the terminal  $sp^2$  carbon of the substituent bonded to the benzene ring is labeled with <sup>14</sup>C, where will the label be in the product?

[1,5] Sigmatropic migrations of hydrogen are well known. They involve three pairs of electrons, so they take place by a suprafacial pathway under thermal conditions.

#### 1,5-hydrogen shifts

$$\begin{array}{ccc} CH_2 & \stackrel{\Delta}{\longrightarrow} & CH_3 \\ CH_3 & & CH_3 \\ \end{array}$$

#### PROBLEM 15

Account for the difference in the products obtained under photochemical and thermal conditions.

$$CD_3 \xrightarrow{h_{\nu}} CD_2$$

$$CD_3 \xrightarrow{\Delta}^D CD_2$$

[1,7] Sigmatropic hydrogen migrations involve four pairs of electrons. They can take place under thermal conditions because the eight-membered-ring transition state allows the required antarafacial rearrangement.

#### 1,7-hydrogen shift

$$CH-C_4H_9$$
  $\longrightarrow$   $CH_3$ 

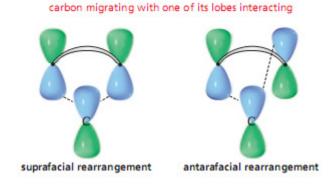
# PROBLEM 16 SOLVED

5-Methyl-1,3-cyclopentadiene rearranges to give a mixture of 5-methyl-1,3-cyclopentadiene, 1-methyl-1,3-cyclopentadiene, and 2-methyl-1,3-cyclopentadiene. Show how these products are formed.

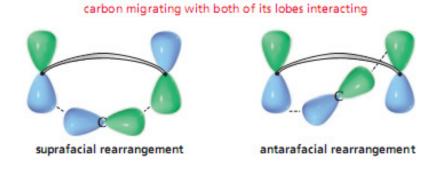
**SOLUTION** Notice that both equilibria involve [1,5] sigmatropic rearrangements. Although a hydride moves from one carbon to an adjacent carbon, the rearrangements are not called 1,2-shifts because this would not account for all the atoms involved in the rearranged  $\pi$  electron system.

# Migration of Carbon

Unlike hydrogen, which can migrate in only one way because of its spherical s orbital, carbon has two ways to migrate because it has a two-lobed p orbital. Carbon can simultaneously interact with the migration origin and the migration terminus using one of its lobes.



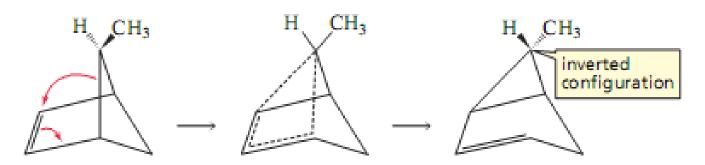
Carbon can also simultaneously interact with the migration source and the migration terminus using both lobes of its p orbital.



If the reaction requires a suprafacial rearrangement, carbon will migrate using one of its lobes if the HOMO is symmetric and will migrate using both of its lobes if the HOMO is asymmetric.

When carbon migrates with only one of its p lobes interacting with the migration source and migration terminus, the migrating group retains its configuration because bonding is always to the same lobe. When carbon migrates with both of its p lobes interacting, bonding in the reactant and bonding in the product involve different lobes. Therefore, migration occurs with inversion of configuration.

The following [1,3] sigmatropic rearrangement has a four-membered-ring transition state that requires a suprafacial pathway. The reacting system has two pairs of electrons, so its HOMO is asymmetric. Therefore, the migrating carbon interacts with the migration source and the migration terminus using both of its lobes, so it undergoes inversion of configuration.



# **PROBLEM 17**

[1,3] Sigmatropic migrations of hydrogen cannot occur under thermal conditions, but [1,3] sigmatropic migrations of carbon can occur under thermal conditions. Explain.

# PROBLEM 18◆

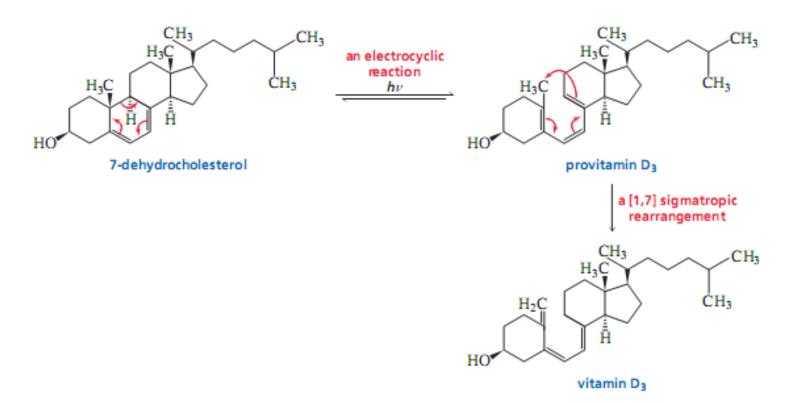
- a. Will thermal 1,3-migrations of carbon occur with retention or inversion of configuration?
- b. Will thermal 1,5-migrations of carbon occur with retention or inversion of configuration?

# **Pericyclic Reactions in Biological Systems**

two adjacent thymine residues on DNA

mutation-causing thymine dimer

# A Biological Reaction Involving an Electrocyclic Reaction and a Sigmatropic Rearrangement

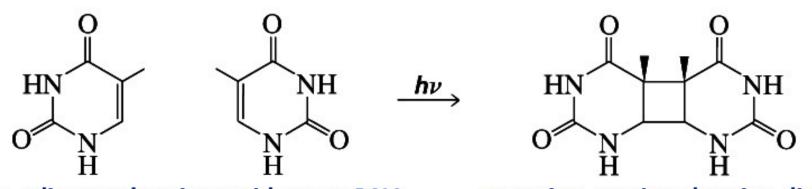


# 29.7 Summary of the Selection Rules for Pericyclic Reactions

The selection rules that determine the outcome of electrocyclic reactions, cycloaddition reactions, and sigmatropic rearrangements are summarized in Tables 29.1, 29.3, and 29.4, respectively. This is still a lot to remember. Fortunately, the selection rules for all pericyclic reactions can be summarized in one word: "TE-AC."

- If TE (Thermal/Even) describes the reaction, the outcome is given by AC (Antarafacial or Conrotatory).
- If one of the letters of TE is incorrect (it is not Thermal/Even but is Thermal/Odd or Photochemical/Even), the outcome is not given by AC (the outcome is Suprafacial or Disrotatory).
- If both of the letters of TE are incorrect (Photochemical/Odd), the outcome is given by AC (Antarafacial or Conrotatory)—"two negatives make a positive."

# Pericyclic Reactions in Biological Systems



two adjacent thymine residues on DNA

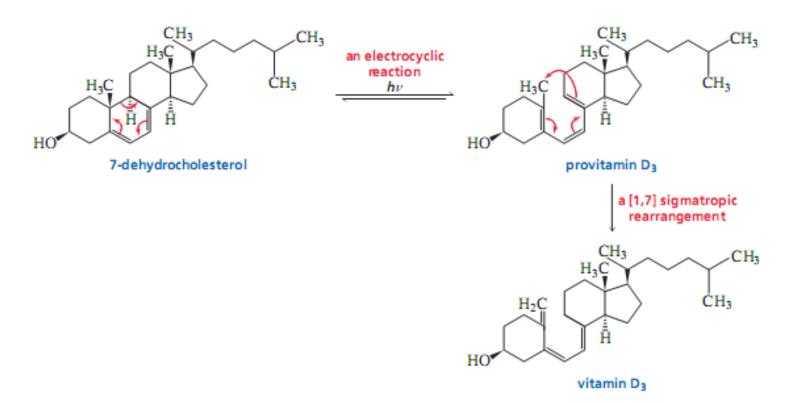
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# A Biological Reaction Involving an Electrocyclic Reaction and a Sigmatropic Rearrangement



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