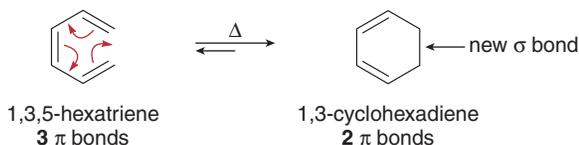# Pericyclic Reactions

Although most organic reactions take place by way of ionic or radical intermediates, a number of useful reactions occur in one-step processes that do *not* form reactive intermediates.

> • A pericyclic reaction is a concerted reaction that proceeds through a cyclic transition state.

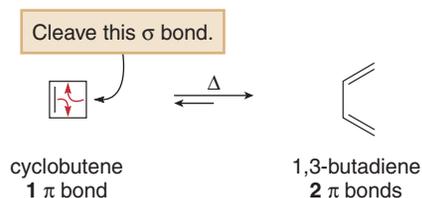Stereospecific reactions were first discussed in Chapter 10.

Pericyclic reactions require light or heat and are completely stereospecific; that is, a single stereoisomer of the reactant forms a single stereoisomer of the product. We will consider two categories of pericyclic reactions: **electrocyclic reactions** and **cycloadditions.**

An electrocyclic reaction is a reversible reaction that can involve ring closure or ring opening.
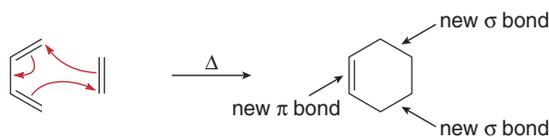
> • An electrocyclic ring closure is an intramolecular reaction that forms a cyclic product containing one more σ bond and one fewer π bond than the reactant.

1,3,5-hexatriene
3 π bonds

1,3-cyclohexadiene
2 π bonds

← new σ bond

> • An electrocyclic ring-opening reaction is a reaction in which a σ bond of a cyclic reactant is cleaved to form a conjugated product with one more π bond.

Cleave this σ bond.

cyclobutene
1 π bond

1,3-butadiene
2 π bonds

> • A cycloaddition is a reaction between two compounds with π bonds to form a cyclic product with two new σ bonds.


new σ bond

new π bond

new σ bond

The Diels–Alder reaction in Chapter 16 is one example of a cycloaddition.

Two features determine the course of the reactions: the number of π bonds involved and whether the reaction occurs in the presence of heat (thermal conditions) or light (photochemical

conditions). These reactions follow a set of rules based on orbitals and symmetry first proposed by R. B. Woodward and Roald Hoffmann in 1965, and derived from theory described by Kenichi Fukui in 1954.

To understand pericyclic reactions we must review and expand upon what we learned about the molecular orbitals of systems with π bonds in Chapter 17.

Problem C.1　Classify each reaction as an electrocyclic reaction or a cycloaddition. Label the σ bonds that are broken or formed in each reaction.

a.

b.

c.
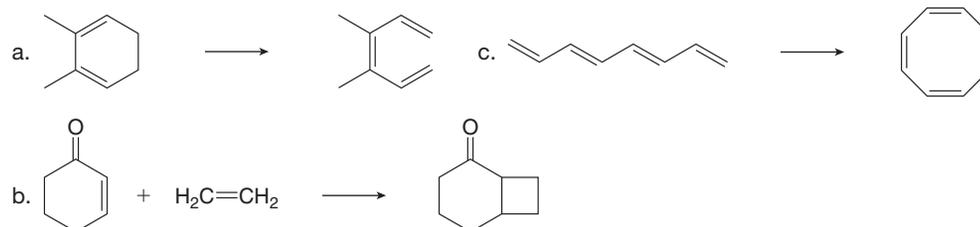
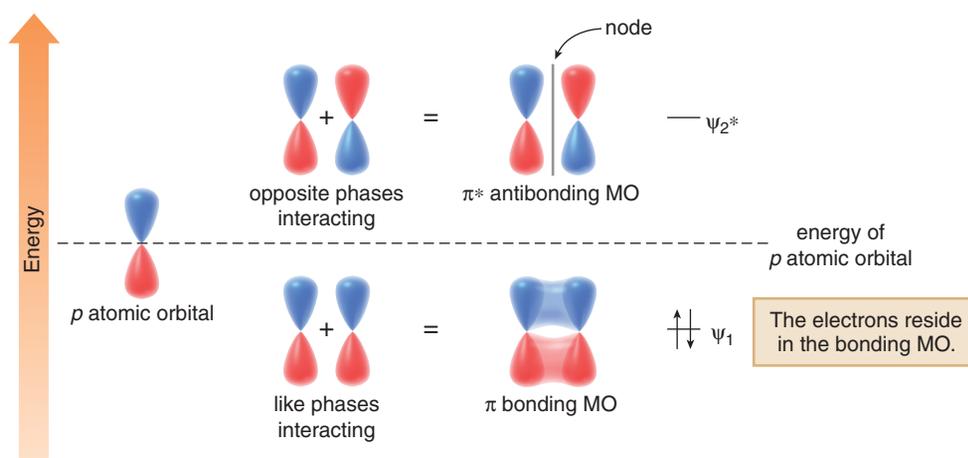## C.1　Background on Molecular Orbitals

In Section 17.9 we learned that molecular orbital (MO) theory describes bonds as the mathematical combination of atomic orbitals that forms a new set of orbitals called **molecular orbitals (MOs). The number of atomic orbitals used** *equals* **the number of molecular orbitals formed.**

Since pericyclic reactions involve π bonds, let's examine the molecular orbitals that result from p orbital overlap in ethylene, 1,3-butadiene, and 1,3,5-hexatriene, molecules that contain one, two, and three π bonds, respectively. Keep in mind that the two lobes of a p orbital are opposite in phase, with a node of electron density at the nucleus.
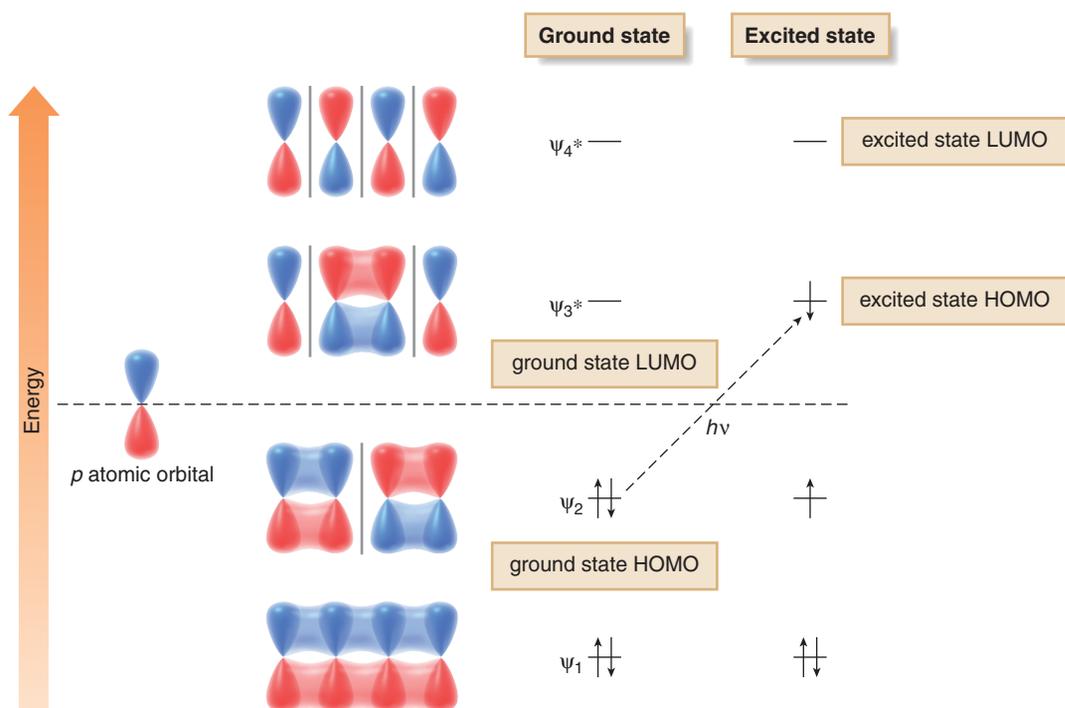
Ethylene

The π bond in ethylene (CH_2=CH_2) is formed by side-by-side overlap of two p orbitals on adjacent carbons. Two p orbitals can combine in two different ways. As shown in Figure C.1, when two p orbitals of similar phase overlap, a π bonding molecular orbital (designated as ψ_1) results. Two electrons occupy this lower-energy bonding molecular orbital. When two p orbitals of opposite phase combine, a π^* antibonding molecular orbital (designated as ψ_2^*) results. A destabilizing node occurs when two orbitals of opposite phase combine.

Figure C.1

The π and π^* molecular orbitals of ethylene

node

opposite phases interacting

$\pi*$ antibonding MO

ψ_2*

energy of p atomic orbital

p atomic orbital

like phases interacting

π bonding MO

ψ_1

The electrons reside in the bonding MO.

Figure C.2

The four π molecular orbitals of 1,3-butadiene

1,3-Butadiene

The two π bonds of 1,3-butadiene ($CH_2=CH-CH=CH_2$) are formed by overlap of four p orbitals on four adjacent carbons. As shown in Figure C.2, four p orbitals can combine in four different ways to form four molecular orbitals designated as $\psi_1-\psi_4$. Two are bonding molecular orbitals (ψ_1 and ψ_2), and two are antibonding molecular orbitals (ψ_3^* and ψ_4^*). The two bonding MOs are lower in energy than the p orbitals from which they are formed, whereas the two antibonding MOs are higher in energy than the p orbitals from which they are formed.

- In the ground-state electronic arrangement, the four π electrons occupy the two bonding molecular orbitals.

Also recall from Section 17.9:

- The highest energy orbital that contains electrons is called the highest occupied molecular orbital (HOMO). In the ground state of 1,3-butadiene, ψ_2 is the HOMO.
- The lowest energy orbital that contains no electrons is called the lowest unoccupied molecular orbital (LUMO). In the ground state of 1,3-butadiene, ψ_3^* is the LUMO.

The thermal reactions discussed in Section C.2 utilize reactants in their ground state electronic configuration.

When 1,3-butadiene absorbs light of appropriate energy, an electron is promoted from ψ_2 (the HOMO) to ψ_3^* (the LUMO) to form a higher energy electronic configuration, the **excited state.** In the excited state, the HOMO is now ψ_3^*. In the photochemical reactions in Section C.2, the reactant is in its excited state. As a result, the HOMO is ψ_3^* and the LUMO is ψ_4^* for 1,3-butadiene.

All conjugated dienes can be described by a set of molecular orbitals that are similar to those drawn in Figure C.2 for 1,3-butadiene.

Problem C.2   For each molecular orbital in Figure C.2, count the number of bonding interactions (interactions between adjacent orbitals of similar phase) and nodes. (a) How do these two values compare for a bonding molecular orbital? (b) How do these two values compare for an antibonding molecular orbital?

Figure C.3   The six π molecular orbitals of 1,3,5-hexatriene
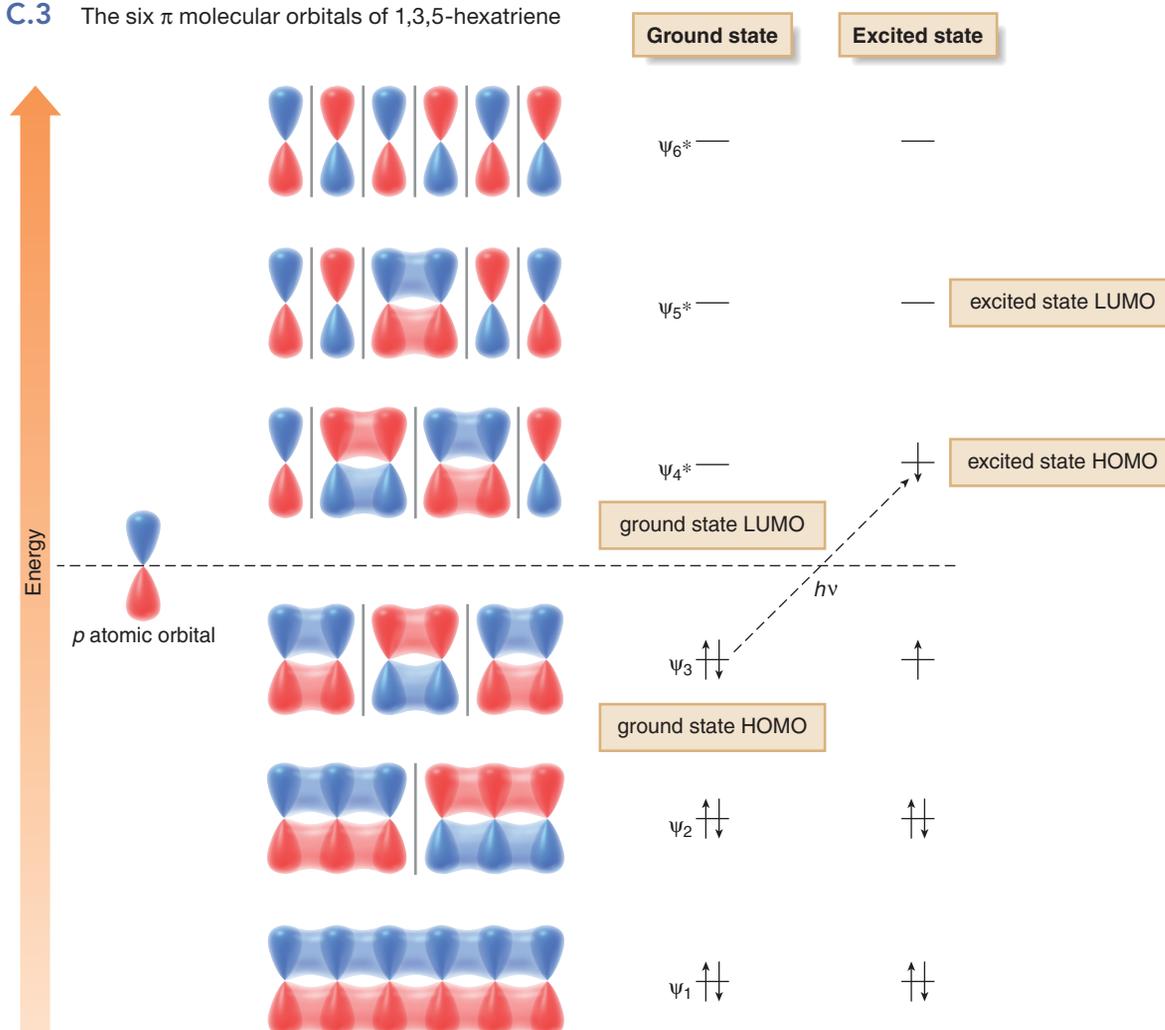
1,3,5-Hexatriene

The three π bonds of 1,3,5-hexatriene ($CH_2=CH-CH=CH-CH=CH_2$) are formed by overlap of six p orbitals on six adjacent carbons. As shown in Figure C.3, six p orbitals can combine in six different ways to form six molecular orbitals designated as $\psi_1-\psi_6$. Three are bonding molecular orbitals ($\psi_1-\psi_3$), and three are antibonding molecular orbitals ($\psi_4^*-\psi_6^*$).

In the ground state electronic configuration, the six π electrons occupy the three bonding MOs, ψ_3 is the HOMO, and ψ_4^* is the LUMO. In the excited state, which results from electron promotion from ψ_3 to ψ_4^*, ψ_4^* is the HOMO and ψ_5^* is the LUMO.

Problem C.3   (a) Using Figure C.2 as a guide, draw the molecular orbitals for 2,4-hexadiene. (b) Label the HOMO and the LUMO in the ground state. (c) Label the HOMO and the LUMO in the excited state.

Problem C.4   (a) How many π molecular orbitals are present in 1,3,5,7,9-decapentaene ($CH_2=CH-CH=CH-CH=CH-CH=CH-CH=CH_2$)? (b) How many are bonding MOs and how many are antibonding MOs? (c) How many nodes are present in ψ_1? (d) How many nodes are present in ψ_{10}^*?
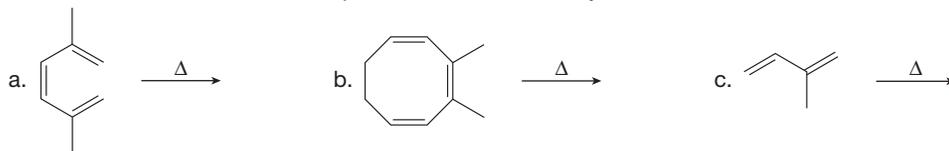
C.2 Electrocyclic Reactions

An electrocyclic reaction is a reversible reaction that involves ring closure of a conjugated polyene to a cycloalkene, or ring opening of a cycloalkene to a conjugated polyene. For example, ring closure of 1,3,5-hexatriene forms 1,3-cyclohexadiene, a product with one more σ bond and one fewer π bond than the reactant. Ring opening of cyclobutene forms 1,3-butadiene, a product with one fewer σ bond and one more π bond than the reactant.

1,3,5-hexatriene   1,3-cyclohexadiene

cyclobutene   1,3-butadiene
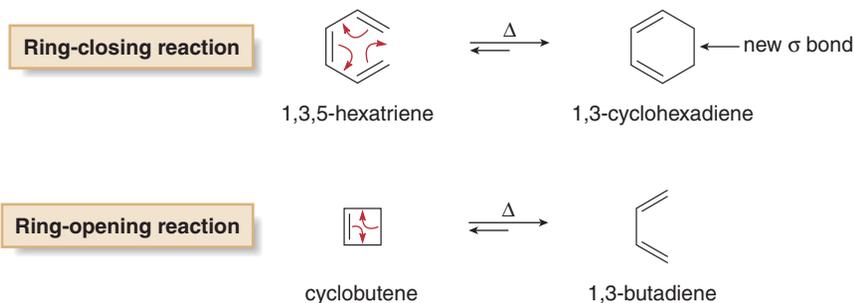
To draw the product in each reaction, use curved arrows and begin at a π bond. Move the π electrons to an adjacent carbon–carbon bond and continue in a cyclic fashion. In a ring-forming reaction, this process forms a new σ bond that now joins the ends of the conjugated polyene. In a ring-opening reaction, this process breaks a σ bond to form a conjugated polyene with one more π bond.
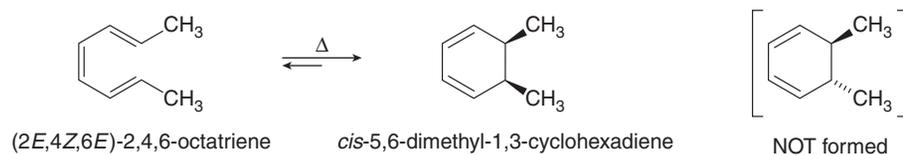
Whether the reactant or product predominates at equilibrium depends on the ring size of the cyclic compound. Generally, a six-membered ring is favored over an acyclic triene at equilibrium. In contrast, an acyclic diene is favored over a strained four-membered ring.

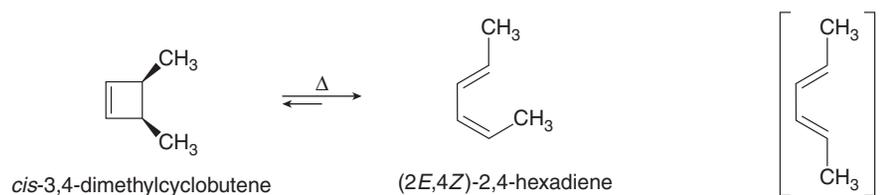**Problem C.5** Use curved arrows and draw the product of each electrocyclic reaction.

a.   b.   c.

Stereochemistry and Orbital Symmetry

Electrocyclic reactions are completely stereospecific. For example, ring closure of (2E,4Z,6E)-2,4,6-octatriene yields a single product with cis methyl groups on the ring. Ring opening of *cis*-3,4-dimethylcyclobutene forms a single conjugated diene with one Z alkene and one E alkene.

(2E,4Z,6E)-2,4,6-octatriene   *cis*-5,6-dimethyl-1,3-cyclohexadiene   NOT formed

cis product only

cis-3,4-dimethylcyclobutene   (2E,4Z)-2,4-hexadiene   NOT formed

(2E,4Z) diene only

Moreover, the stereochemistry of the product of an electrocyclic reaction depends on whether the reaction is carried out under thermal or photochemical reaction conditions—that is, with heat or light, respectively. Cyclization of (2*E*,4*E*)-2,4-hexadiene with heat forms a cyclobutene with trans methyl groups, whereas cyclization with light forms a cyclobutene with cis methyl groups.

Electrocyclic ring closure generally forms either an achiral meso compound or a mixture of chiral enantiomers. When enantiomers form, only one enantiomer is drawn in these reactions.

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

trans product only

cis product only
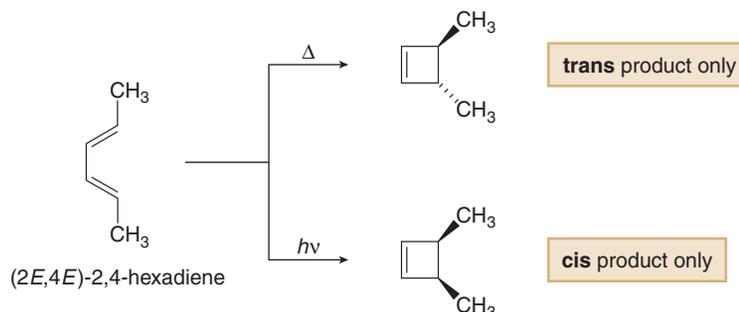
To understand these results, we must focus on the HOMO of the acyclic conjugated polyene that is either the reactant or product in an electrocyclic reaction. In particular, we must examine the *p* orbitals on the terminal carbons of the HOMO, and determine whether like phases of the orbitals are on the same side or on opposite sides of the molecule.


like phases on the same side

like phases on opposite sides

- An electrocyclic reaction occurs only when like phases of orbitals can overlap to form a bond. Such a reaction is *symmetry allowed.*
- An electrocyclic reaction cannot occur between orbitals of opposite phase. Such a reaction is *symmetry forbidden.*

To form a bond, the *p* orbitals on the terminal carbons must rotate so that like phases can interact to form the new σ bond. Two modes of rotation are possible.

- When like phases of the *p* orbitals are on the same side of the molecule, the two orbitals must rotate in opposite directions—one clockwise and one counterclockwise. Rotation in opposite directions is said to be *disrotatory.*

counterclockwise   clockwise   new σ bond
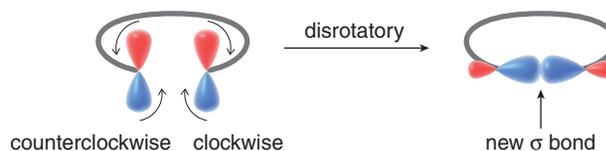
- When like phases of the *p* orbitals are on opposite sides of the molecule, the two orbitals must rotate in the same direction—both clockwise or both counterclockwise. Rotation in the same direction is said to be *conrotatory.*

clockwise   clockwise   new σ bond
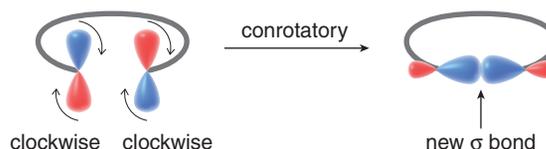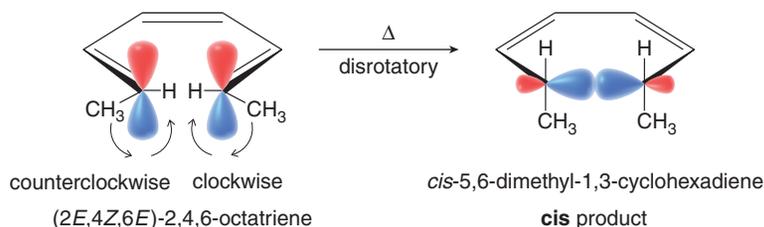
Thermal Electrocyclic Reactions

To explain the stereochemistry observed in electrocyclic reactions, we must examine the symmetry of the molecular orbital that contains the most loosely held π electrons. In a thermal reac-

tion, we consider the **HOMO of the ground state electronic configuration.** Rotation occurs in a disrotatory or conrotatory fashion so that like phases of the *p* orbitals on the terminal carbons of this molecular orbital combine.

- **The number of double bonds in the conjugated polyene determines whether rotation is conrotatory or disrotatory.**

Two examples illustrate different outcomes.

Thermal electrocyclic ring closure of (2*E*,4*Z*,6*E*)-2,4,6-octatriene yields a single product with cis methyl groups on the ring.

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

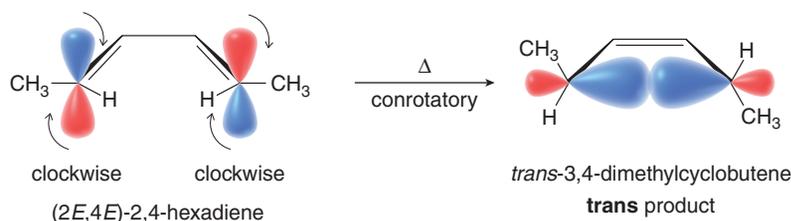(2*E*,4*Z*,6*E*)-2,4,6-octatriene   **cis** product

Cyclization occurs in a disrotatory fashion because the HOMO of a conjugated triene has like phases of the outermost *p* orbitals on the *same* side of the molecule (Figure C.3). A disrotatory ring closure is symmetry allowed because like phases of the *p* orbitals overlap to form the new σ bond of the ring. In the disrotatory ring closure, both methyl groups are pushed *down* (or *up*), making them *cis* in the product.

This is a specific example of the general process observed for conjugated polyenes with an *odd* number of π bonds. The HOMO of a conjugated polyene with an odd number of π bonds has like phases of the outermost *p* orbitals on the *same* side of the molecule. As a result:

- **Thermal electrocyclic reactions occur in a *disrotatory* fashion for a conjugated polyene with an *odd* number of π bonds.**

In contrast, thermal electrocyclic ring closure of (2*E*,4*E*)-2,4-hexadiene forms a cyclobutene with trans methyl groups.

The conrotatory ring closure of (2*E*,4*E*)-2,4-hexadiene is drawn with two clockwise rotations. The conrotatory ring closure could also be drawn with two counterclockwise rotations, leading to the enantiomer of the trans product drawn. Both enantiomers are formed in equal amounts.

clockwise   clockwise   *trans*-3,4-dimethylcyclobutene

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

Cyclization occurs in a conrotatory fashion because the HOMO of a conjugated diene has like phases of the outermost *p* orbitals on *opposite* sides of the molecule (Figure C.2). A conrotatory ring closure is symmetry allowed because like phases of the *p* orbitals overlap to form the new σ bond of the ring. In the conrotatory ring closure, one methyl group is pushed *down* and one methyl group is pushed *up,* making them *trans* in the product.
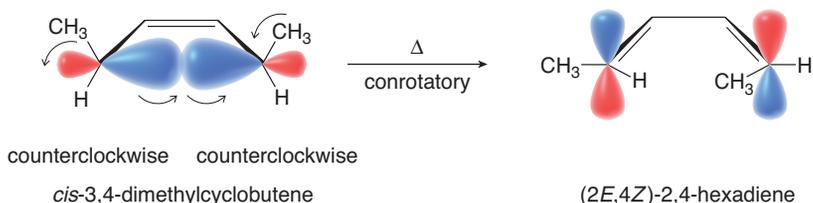
This is a specific example of the general process observed for conjugated polyenes with an *even* number of π bonds. The HOMO of a conjugated polyene with an even number of π bonds has like phases of the outermost *p* orbitals on *opposite* sides of the molecule. As a result:

- **Thermal electrocyclic reactions occur in a *conrotatory* fashion for a conjugated polyene with an *even* number of π bonds.**

Since electrocyclic reactions are reversible, **electrocyclic ring-opening reactions follow the same rules** as electrocyclic ring closures. Thus, thermal ring opening of *cis*-3,4-dimethylcyclobutene—
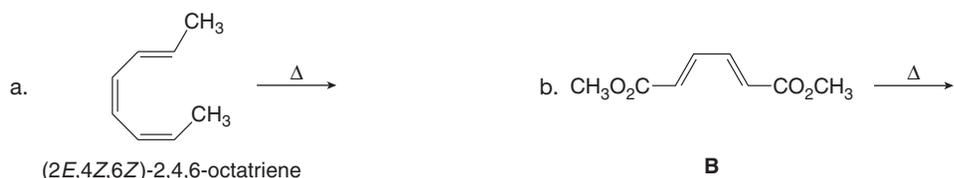
which ring opens to a diene with an *even* number of π bonds—occurs in a conrotatory fashion to form (2E,4Z)-2,4-hexadiene as the only product.

counterclockwise   counterclockwise

cis-3,4-dimethylcyclobutene   (2E,4Z)-2,4-hexadiene

Sample Problem C.1   Draw the product of each thermal electrocyclic ring closure.

a.

(2E,4Z,6Z)-2,4,6-octatriene
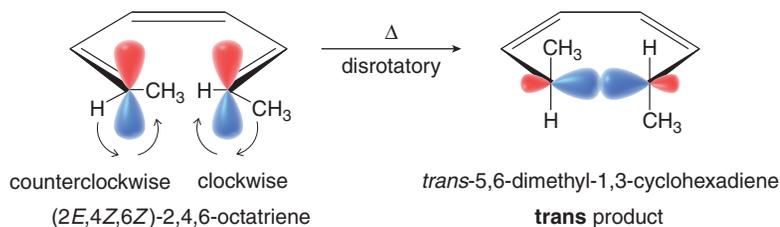
b. CH_3O_2C ⟶ $-CO_2CH_3$ $\xrightarrow{\Delta}$

B

Solution

Count the number of π bonds in the conjugated polyene to determine the mode of ring closure in a thermal electrocyclic reaction.

- A conjugated polyene with an **odd** number of π bonds undergoes **disrotatory** cyclization.
- A conjugated polyene with an **even** number of π bonds undergoes **conrotatory** cyclization.

a. (2E,4Z,6Z)-2,4,6-Octatriene contains three π bonds. The HOMO of a conjugated polyene with an odd number of π bonds has like phases of the outermost *p* orbitals on the *same* side of the molecule, and this results in disrotatory cyclization.

counterclockwise   clockwise   *trans*-5,6-dimethyl-1,3-cyclohexadiene
(2E,4Z,6Z)-2,4,6-octatriene   **trans** product

b. Diene **B** contains two π bonds. The HOMO of a conjugated polyene with an even number of π bonds has like phases of the outermost *p* orbitals on *opposite* sides of the molecule, and this results in conrotatory cyclization.

clockwise   clockwise

**B**   **trans** product

---
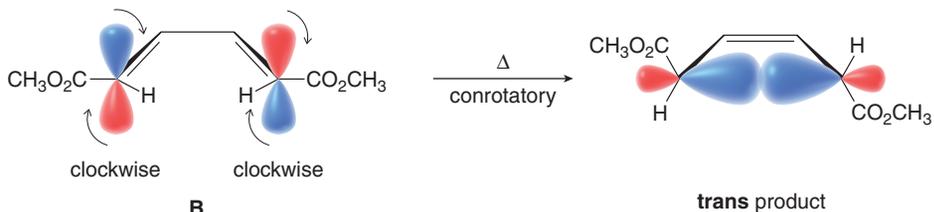
Problem C.6   What product is formed when each compound undergoes thermal electrocyclic ring opening or ring closure? Label each process as conrotatory or disrotatory and clearly indicate the stereochemistry around tetrahedral stereogenic centers and double bonds.

a.   b.   c.   d.

Problem C.7   What cyclic product is formed when each decatetraene undergoes thermal electrocyclic ring closure?

a.   b.
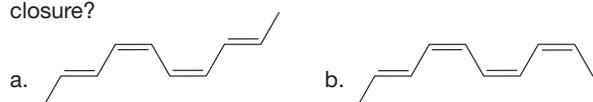
Photochemical Electrocyclic Reactions

Photochemical electrocyclic reactions follow similar principles as those detailed in thermal reactions with one important difference. **In photochemical reactions, we must consider the orbitals of the HOMO of the excited state to determine the course of the reaction.** The excited state HOMO has the *opposite* orientation of the outermost *p* orbitals compared to the HOMO of the ground state. As a result, **the method of ring closure of a photochemical electrocyclic reaction is *opposite* to that of a thermal electrocyclic reaction for the same number of π bonds.**

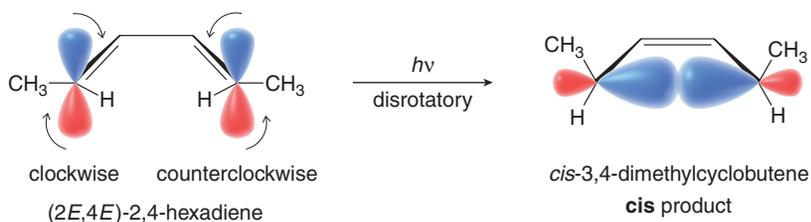Photochemical electrocyclic ring closure of (2E,4Z,6E)-2,4,6-octatriene yields a cyclic product with trans methyl groups on the ring.
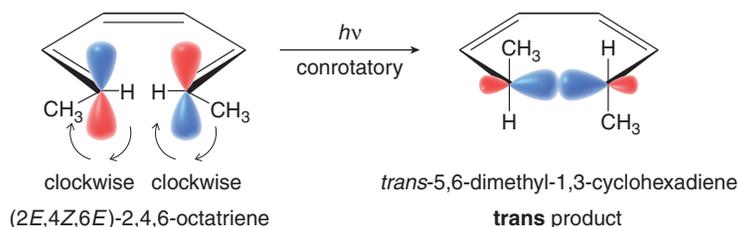
Cyclization occurs in a conrotatory fashion because the excited state HOMO of a conjugated triene has like phases of the outermost *p* orbitals on the *opposite* sides of the molecule (Figure C.3). In the conrotatory ring closure, one methyl group is pushed *down* and one methyl group is pushed *up,* making them *trans* in the product. This is a specific example of the general process observed for conjugated polyenes with an *odd* number of π bonds.

> • Photochemical electrocyclic reactions occur in a *conrotatory* fashion for a conjugated polyene with an *odd* number of π bonds.

Photochemical electrocyclic ring closure of (2E,4E)-2,4-hexadiene forms a cyclobutene with cis methyl groups.

Cyclization occurs in a disrotatory fashion because the excited state HOMO of a conjugated diene has like phases of the outermost *p* orbitals on the *same* side of the molecule (Figure C.2). In the disrotatory ring closure, both methyl groups are pushed *down* (or *up*), making them *cis* in the product. This is a specific example of the general process observed for conjugated polyenes with an *even* number of π bonds.

> • Photochemical electrocyclic reactions occur in a *disrotatory* fashion for a conjugated polyene with an *even* number of π bonds.

Problem C.8 What product is formed when each compound in Problem C.6 undergoes photochemical electrocyclic ring opening or ring closure? Label each process as conrotatory or disrotatory and clearly indicate the stereochemistry around tetrahedral stereogenic centers and double bonds.

Problem C.9 What cyclic product is formed when each decatetraene in Problem C.7 undergoes photochemical electrocyclic ring closure?

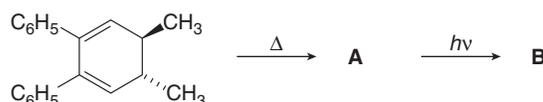## Summary of Electrocyclic Reactions

Table C.1 summarizes the rules, often called the **Woodward–Hoffmann rules,** for electrocyclic reactions under thermal or photochemical reaction conditions. The number of π bonds refers to the acyclic conjugated polyene that is either the reactant or product of an electrocyclic reaction.

Table C.1 Woodward–Hoffmann rules for electrocyclic reactions

| Number of π bonds	Thermal reaction	Photochemical reaction
Even	Conrotatory	Disrotatory
Odd	Disrotatory	Conrotatory

Sample Problem C.2   Identify **A** and **B** in the following reaction sequence. Label each process as conrotatory or disrotatory.

Solution
Ring opening of a cyclohexadiene forms a hexatriene with **three** π bonds. A conjugated polyene with an odd number of π bonds undergoes a thermal electrocyclic reaction in a disrotatory fashion (Table C.1). The resulting hexatriene (**A**) then undergoes a photochemical electrocyclic reaction in a conrotatory fashion to form a cyclohexadiene with cis methyl groups (**B**).
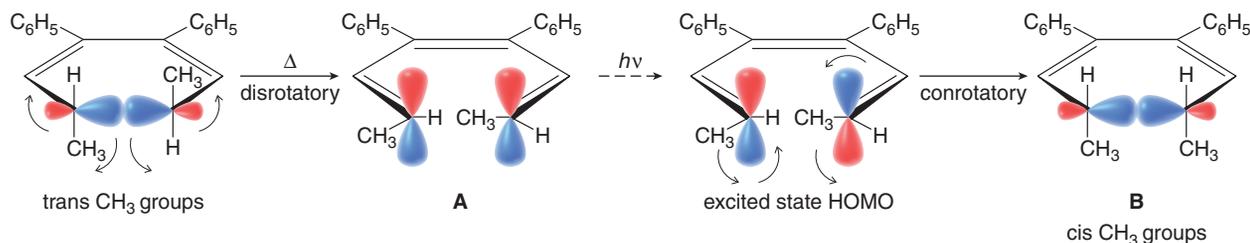
Problem C.10   Draw the product formed when each triene undergoes electrocyclic reaction under [1] thermal conditions; [2] photochemical conditions.

a.

b.

Problem C.11   What product would be formed by the disrotatory cyclization of the given triene? Would this reaction occur under photochemical or thermal conditions?

Problem C.12   Consider the following electrocyclic ring closure. Does the product form by a conrotatory or disrotatory process? Would this reaction occur under photochemical or thermal conditions?
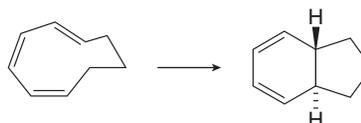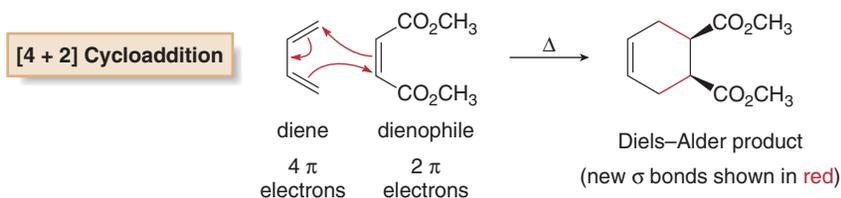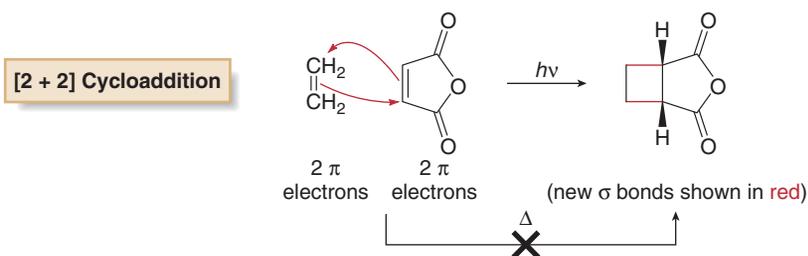
C.3 Cycloaddition Reactions

A cycloaddition is a reaction between two compounds with π bonds to form a cyclic product with two new σ bonds. Like electrocyclic reactions, cycloadditions are concerted, stereospecific reactions, and the course of the reaction is determined by the symmetry of the molecular orbitals of the reactants.

Cycloadditions can be initiated by heat (thermal conditions) or light (photochemical conditions). Cycloadditions are identified by the number of π electrons in the two reactants.

The Diels–Alder reaction is a thermal [4 + 2] cycloaddition that occurs between a diene with four π electrons and an alkene (dienophile) with two π electrons (Sections 16.12–16.14).

[4 + 2] Cycloaddition

diene — 4 π electrons

dienophile — 2 π electrons

Diels–Alder product (new σ bonds shown in red)

A photochemical [2 + 2] cycloaddition occurs between two alkenes, each with two π electrons, to form a cyclobutane. Thermal [2 + 2] cycloadditions do *not* take place.
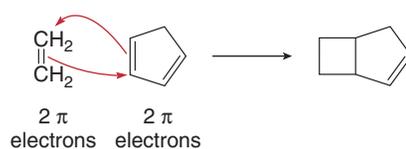

[2 + 2] Cycloaddition

2 π electrons   2 π electrons

(new σ bonds shown in red)

Sample Problem C.3   What type of cycloaddition is shown in each equation?
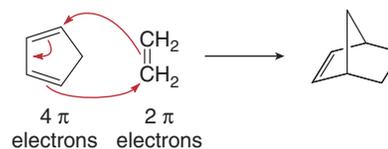

a.   ⬠ + $CH_2=CH_2$ ⟶

b.   ⬠ + $CH_2=CH_2$ ⟶
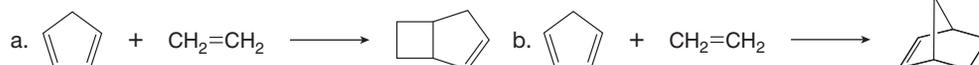
Solution

Count the number of π electrons *involved in each reactant* to classify the cycloaddition.

a. [2 + 2] Cycloaddition

CH_2
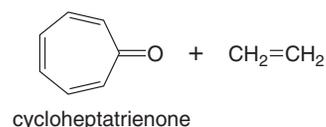‖
CH_2

2 π electrons   2 π electrons

b. [4 + 2] Cycloaddition

CH_2
‖
CH_2

4 π electrons   2 π electrons

---

Problem C.13   Consider cycloheptatrienone and ethylene, and draw a possible product formed from each type of cycloaddition: (a) [2 + 2]; (b) [4 + 2]; (c) [6 + 2].


=O   + $CH_2=CH_2$

cycloheptatrienone

Orbital Symmetry and Cycloadditions

To understand cycloaddition reactions, we examine the *p* orbitals of the terminal carbons of both reactants. Bonding can take place only when like phases of both sets of *p* orbitals can combine. Two modes of reaction are possible.

> • A suprafacial cycloaddition occurs when like phases of the *p* orbitals of both reactants are on the same side of the π system, so that two bonding interactions result.

Suprafacial bond formation

or
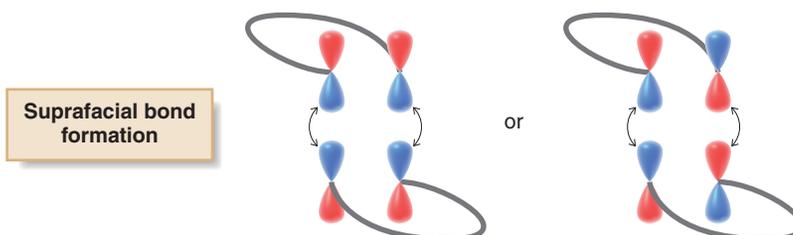
> • An antarafacial cycloaddition occurs when one π system must twist to align like phases of the *p* orbitals of the terminal carbons of the reactants.

Antarafacial bond formation

like phases on opposite sides

180° twist
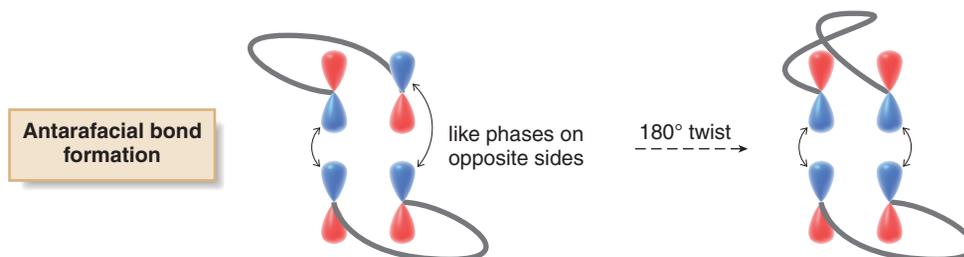
Because of the geometrical constraints of small rings, **cycloadditions that form four- or six-membered rings must take place by suprafacial pathways.**

Since cycloaddition involves the donation of electron density from one reactant to another, one reactant donates its most loosely held electrons—those occupying its HOMO—to a vacant orbital that can accept electrons—the LUMO—of the second reactant. The HOMO of either reactant can be used for analysis.

> • In a cycloaddition we examine the bonding interactions of the HOMO of one component with the LUMO of the second component.

[4 + 2] Cycloadditions

To examine the course of a [4 + 2] cycloaddition, let's arbitrarily choose the HOMO of the diene and the LUMO of the alkene, and look at the symmetry of the *p* orbitals on the terminal carbons of both components. Since two bonding interactions result from overlap of the like phases of both sets of *p* orbitals, **a [4 + 2] cycloaddition occurs readily by suprafacial reaction under thermal conditions.**
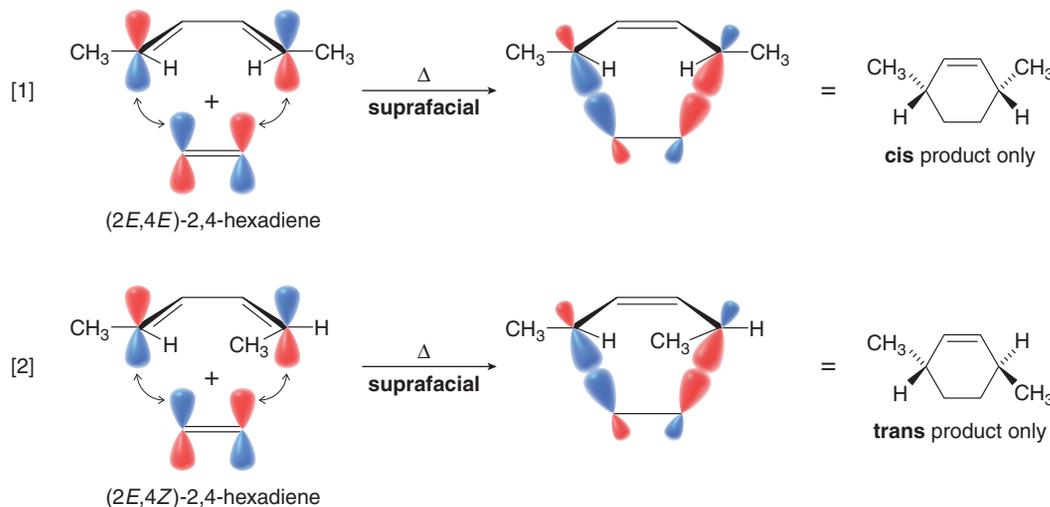
HOMO of the diene

Thermal [4 + 2] cycloaddition

Δ
suprafacial

two new σ bonds

LUMO of the alkene
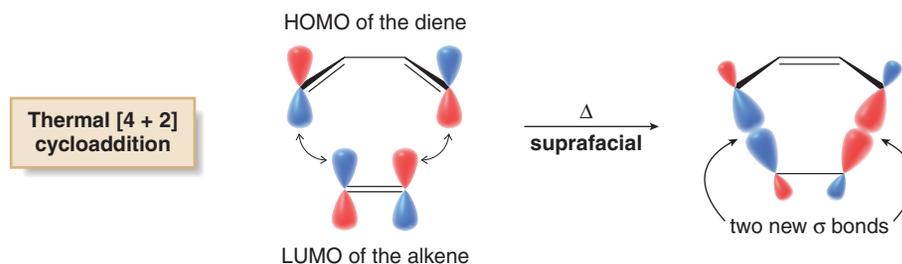
This is a specific example of a general cycloaddition involving an odd number of π bonds (three π bonds total, two from the diene and one from the alkene).

> • Thermal cycloadditions involving an *odd* number of π bonds proceed by a *suprafacial* pathway.

In Section 16.13, we learned that the stereochemistry of the dienophile is retained in the Diels–Alder product.

Because a Diels–Alder reaction follows a concerted, suprafacial pathway, the **stereochemistry of the diene is retained in the Diels–Alder product.** As a result, reaction of (2E,4E)-2,4-hexadiene with ethylene forms a cyclohexene with cis substituents (Reaction [1]), whereas reaction of (2E,4Z)-2,4-hexadiene with ethylene forms a cyclohexene with trans substituents (Reaction [2]).

[1]

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

cis product only

[2]

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

trans product only

Problem C.14   Show that a thermal suprafacial addition is symmetry allowed in a [4 + 2] cycloaddition by using the HOMO of the alkene and the LUMO of the diene.

Problem C.15   Draw the product (including stereochemistry) formed from each pair of reactants in a thermal [4 + 2] cycloaddition reaction.

a. [structure] + $CH_2=CH_2$ b. [structure] + [structure with CN groups]
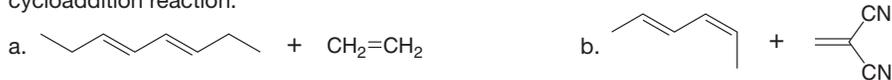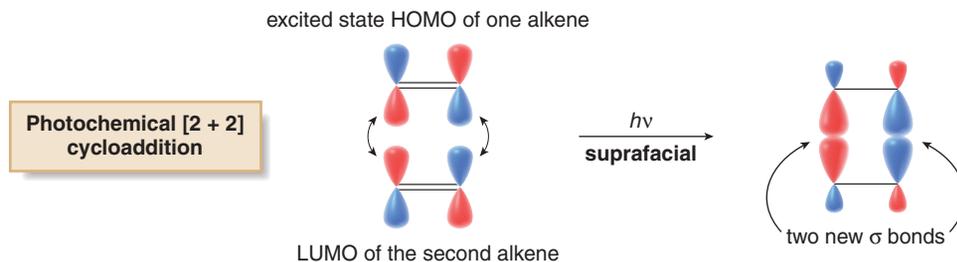
[2 + 2] Cycloadditions

In contrast to a [4 + 2] cycloaddition, a [2 + 2] cycloaddition does *not* occur under thermal conditions, but *does* take place photochemically. This result is explained by examining the symmetry of the HOMO and LUMO of the alkene reactants.

In a thermal [2 + 2] cycloaddition, like phases of the *p* orbitals on only one set of terminal carbons can overlap. For like phases to overlap on the other terminal carbon, the molecule must twist to allow for an antarafacial pathway. This process cannot occur to form small rings.

HOMO of one alkene

Thermal [2 + 2] cycloaddition

like phases on opposite sides

LUMO of the second alkene
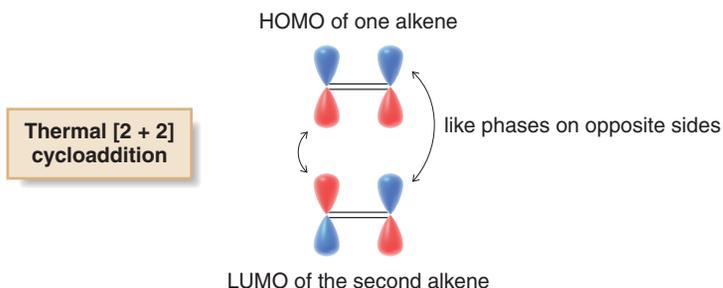
In a photochemical [2 + 2] cycloaddition, light energy promotes an electron from the ground state HOMO to form the excited state HOMO (designated as ψ_2^* in Figure C.1). Interaction of

this excited state HOMO with the LUMO of the second alkene then allows for overlap of the like phases of both sets of *p* orbitals. Two bonding interactions result and the reaction occurs by a suprafacial pathway.

excited state HOMO of one alkene

Photochemical [2 + 2] cycloaddition

$h\nu$

suprafacial

two new σ bonds

LUMO of the second alkene

This is a specific example of a general cycloaddition involving an even number of π bonds (two π bonds total, one from each alkene).

- **Photochemical cycloadditions involving an *even* number of π bonds proceed by a *suprafacial* pathway.**

Problem C.16   Draw the product formed in each cycloaddition.

a. C_6H_5 ⌢⌣ C_6H_5 + $\xrightarrow{h\nu}$

b.   + $CH_2{=}CH_2$ $\xrightarrow{h\nu}$
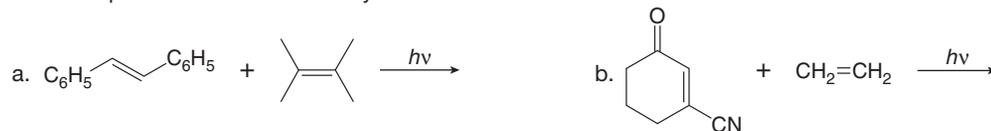
Summary of Cycloaddition Reactions

Table C.2 summarizes the Woodward–Hoffmann rules that govern cycloaddition reactions. The number of π bonds refers to the total number of π bonds from both components of the cycloaddition. For a given number of π bonds, the mode of cycloaddition is always *opposite* in thermal and photochemical reactions.

Table C.2 Woodward–Hoffmann rules for cycloaddition reactions

Number of π bonds	Thermal reaction	Photochemical reaction
Even	Antarafacial	Suprafacial
Odd	Suprafacial	Antarafacial

Problem C.17   Using the Woodward–Hoffmann rules, predict the stereochemistry for each cycloaddition: (a) a [6 + 4] photochemical reaction; (b) an [8 + 2] thermal reaction.

Problem C.18   Using orbital symmetry, explain why a Diels–Alder reaction does not take place under photochemical reaction conditions.

C.4 Summary of Rules for Pericyclic Reactions

Table C.3 summarizes the rules that govern pericyclic reactions, and in truth, this table holds a great deal of information. To keep track of this information, it may be helpful to **learn one row in the table only,** and then note the result when one or more conditions change. For example,

- A *thermal* reaction involving an *even* number of π bonds undergoes a *conrotatory* electrocyclic reaction or an *antarafacial* cycloaddition.

- If *one* of the reaction conditions changes—either from thermal to photochemical or from an even to an odd number of π bonds—the stereochemistry of the reaction changes to disrotatory or suprafacial.

- If *both* reaction conditions change—that is, a photochemical reaction with an odd number of electrons—the stereochemistry does *not* change. A conrotatory electrocyclic reaction or an antarafacial cycloaddition occurs.

**Table C.3** Summary of the stereochemical rules for pericyclic reactions

Reaction conditions	Number of π bonds	Electrocyclic reactions	Cycloadditions
Thermal	Even	Conrotatory	Antarafacial
	Odd	Disrotatory	Suprafacial
Photochemical	Even	Disrotatory	Suprafacial
	Odd	Conrotatory	Antarafacial

Problem C.19 Using the Woodward–Hoffmann rules in Table C.3, predict the stereochemistry of each reaction.
a. a [6 + 4] thermal cycloaddition
b. photochemical electrocyclic ring closure of 1,3,5,7,9-decapentaene
c. a [4 + 4] photochemical cycloaddition
d. photochemical ring opening of 1,3,5-cyclooctatriene

Problem C.20 Draw the product of each Diels–Alder reaction and indicate the stereochemistry at all stereogenic centers.
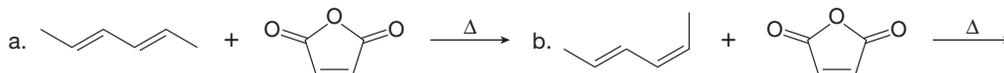

Problem C.21 Draw the product (including stereochemistry) formed in each pericyclic reaction.
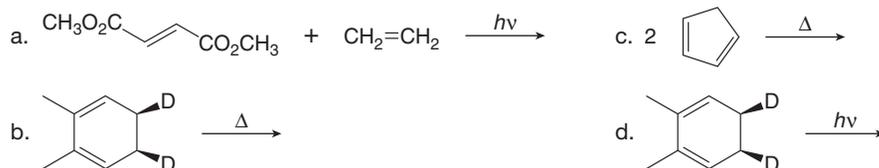
Problem C.22 Draw the product formed when diene **M** undergoes disrotatory cyclization. Indicate the stereochemistry at new sp^3 hybridized carbons. Will the reaction occur under thermal or photochemical conditions?


M
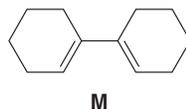
Problem C.23   (a) What product is formed when triene **N** undergoes thermal electrocyclic ring closure? (b) What product is formed when triene **N** undergoes photochemical ring closure? (c) Label each process as conrotatory or disrotatory.

N
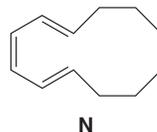
Problem C.24   What type of cycloaddition occurs in Reaction [1]? Draw the product of a similar process in Reaction [2]. Would you predict that these reactions occur under thermal or photochemical conditions?

Problem C.25   What cycloaddition products are formed in each reaction? Indicate the stereochemistry of each product.

a. 2 $\xrightarrow{h\nu}$

b. 2 $\xrightarrow{h\nu}$
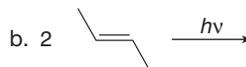
Problem C.26   The bicyclic alkene **P** can be prepared by thermal electrocyclic ring closure from cyclodecadiene **Q** or by photochemical electrocyclic ring closure from cyclodecadiene **R**. Draw the structures of **Q** and **R**, and indicate the stereochemistry of the process by which each reaction occurs.

P