

1.6 An Introduction to Molecular Orbital Theory

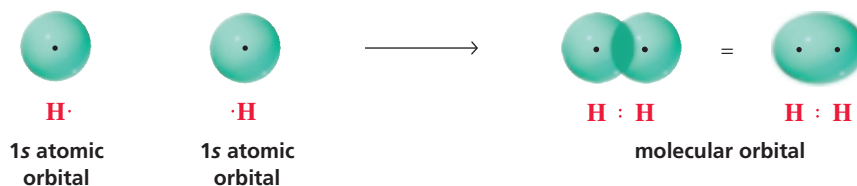


Movie:
H₂ bond formation

How do atoms form covalent bonds in order to form molecules? The Lewis model, which describes how atoms attain a complete octet by sharing electrons, tells us only part of the story. A drawback of the model is that it treats electrons like particles and does not take into account their wavelike properties.

Molecular orbital (MO) theory combines the tendency of atoms to fill their octets by sharing electrons (the Lewis model) with their wavelike properties—assigning electrons to a volume of space called an orbital. According to MO theory, covalent bonds result from the combination of atomic orbitals to form **molecular orbitals**—orbitals that belong to the whole molecule rather than to a single atom. Like an atomic orbital that describes the volume of space around the nucleus of an atom where an electron is likely to be found, a molecular orbital describes the volume of space around a molecule where an electron is likely to be found. Like atomic orbitals, molecular orbitals have specific sizes, shapes, and energies.

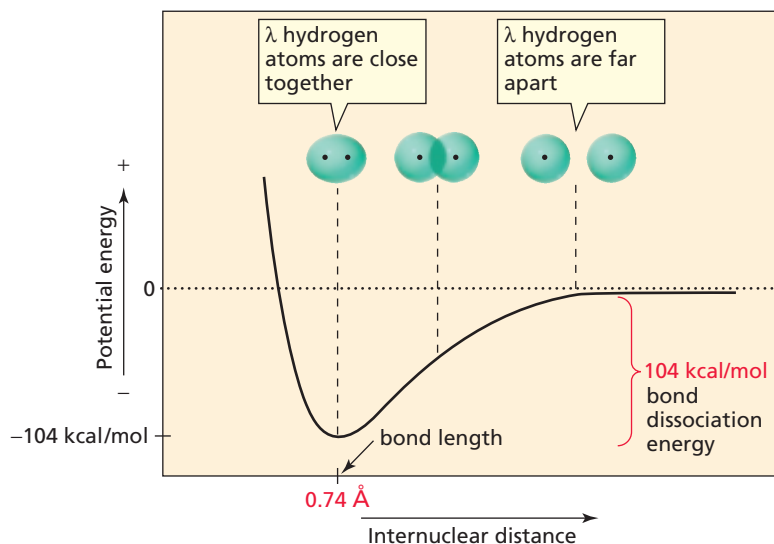
Let's look first at the bonding in a hydrogen molecule (H₂). As the 1s atomic orbital of one hydrogen atom approaches the 1s atomic orbital of a second hydrogen atom, they begin to overlap. As the atomic orbitals move closer together, the amount of overlap increases until the orbitals combine to form a molecular orbital. The covalent bond that is formed when the two s atomic orbitals overlap is called a **sigma (σ) bond**. A σ bond is cylindrically symmetrical—the electrons in the bond are symmetrically distributed about an imaginary line connecting the centers of the two atoms joined by the bond. (The term σ comes from the fact that cylindrically symmetrical molecular orbitals possess σ symmetry.)



During bond formation, energy is released as the two orbitals start to overlap, because the electron in each atom not only is attracted to its own nucleus but also is attracted to the positively charged nucleus of the other atom (Figure 1.2). Thus, the attraction of the negatively charged electrons for the positively charged nuclei is what holds the atoms together. The more the orbitals overlap, the more the energy decreases

Figure 1.2 ▶

The change in energy that occurs as two 1s atomic orbitals approach each other. The internuclear distance at minimum energy is the length of the H—H covalent bond.

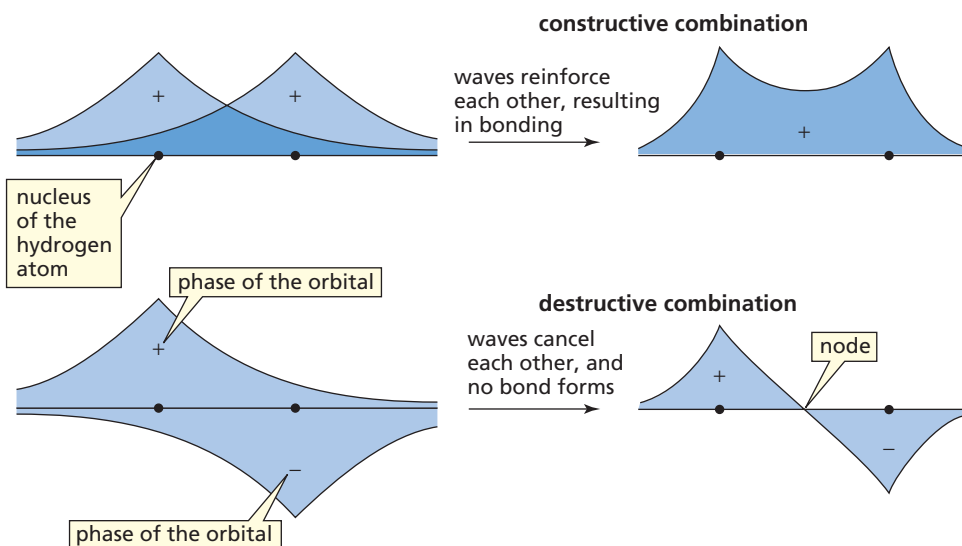


until the atoms approach each other so closely that their positively charged nuclei start to repel each other. This repulsion causes a large increase in energy. We see that maximum stability (i.e., minimum energy) is achieved when the nuclei are a certain distance apart. This distance is the **bond length** of the new covalent bond. The length of the H—H bond is 0.74 Å.

As Figure 1.2 shows, energy is released when a covalent bond forms. When the H—H bond forms, 104 kcal/mol (or 435 kJ/mol)* of energy is released. Breaking the bond requires precisely the same amount of energy. Thus, the **bond strength**—also called the **bond dissociation energy**—is the energy required to break a bond, or the energy released when a bond is formed. Every covalent bond has a characteristic bond length and bond strength.

Orbitals are conserved—the number of molecular orbitals formed must equal the number of atomic orbitals combined. In describing the formation of an H—H bond, however, we combined two atomic orbitals, but discussed only one molecular orbital. Where is the other molecular orbital? It is there, but it contains no electrons.

Atomic orbitals can combine in two different ways: constructively and destructively. They can combine in a constructive, additive manner, just as two light waves or sound waves may reinforce each other (Figure 1.3). This is called a **σ (sigma) bonding molecular orbital**. Atomic orbitals can also combine in a destructive way, canceling each other. The cancellation is similar to the darkness that occurs when two light waves cancel each other or to the silence that occurs when two sound waves cancel each other (Figure 1.3). This destructive type of interaction is called a **σ^* antibonding molecular orbital**. An antibonding orbital is indicated by an asterisk (*).



Maximum stability corresponds to minimum energy.

◀ **Figure 1.3**

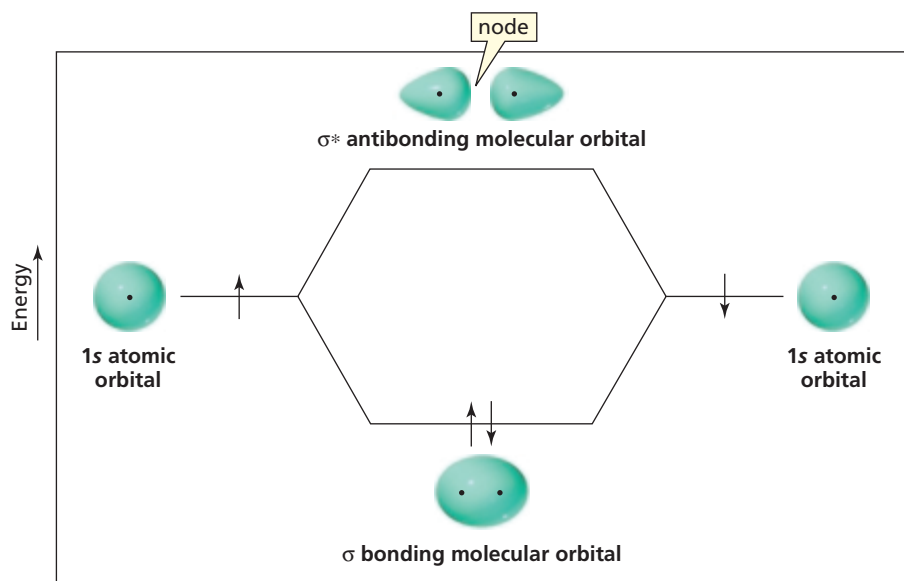
The wave functions of two hydrogen atoms can interact to reinforce, or enhance, each other (top) or can interact to cancel each other (bottom). Note that waves that interact constructively are in-phase, whereas waves that interact destructively are out-of-phase.

The σ bonding molecular orbital and σ^* antibonding molecular orbital are shown in the molecular orbital diagram in Figure 1.4. In an MO diagram, the energies are represented as horizontal lines; the bottom line is the lowest energy level, the top line the highest energy level. We see that any electrons in the bonding orbital will most likely be found between the nuclei. This increased electron density between the nuclei is what binds the atoms together. Because there is a node between the nuclei in the antibonding molecular orbital, any electrons that are in that orbital are more likely to be found anywhere except between the nuclei, so the nuclei are more exposed to one another and will be forced apart by electrostatic repulsion. Thus, electrons that occupy this orbital detract from, rather than aid, the formation of a bond between the atoms.

*1 kcal = 4.184 kJ. Joules are the Système International (SI) units for energy, although many chemists use calories. We will use both in this book.

Figure 1.4 ▶

Atomic orbitals of $\text{H}\cdot$ and molecular orbitals of H_2 . Before covalent bond formation, each electron is in an atomic orbital. After covalent bond formation, both electrons are in the bonding molecular orbital. The antibonding molecular orbital is empty.



When two atomic orbitals overlap, two molecular orbitals are formed—one lower in energy and one higher in energy than the atomic orbitals.

The MO diagram shows that the bonding molecular orbital is more stable—is lower in energy—than the individual atomic orbitals. This is because the more nuclei an electron “feels,” the more stable it is. The antibonding molecular orbital, with less electron density between the nuclei, is less stable—is of higher energy—than the atomic orbitals.

After the MO diagram is constructed, the electrons are assigned to the molecular orbitals. The aufbau principle and the Pauli exclusion principle, which apply to electrons in atomic orbitals, also apply to electrons in molecular orbitals: Electrons always occupy available orbitals with the lowest energy, and no more than two electrons can occupy a molecular orbital. Thus, the two electrons of the $\text{H}-\text{H}$ bond occupy the lower energy bonding molecular orbital (Figure 1.4), where they are attracted to both positively charged nuclei. It is this electrostatic attraction that gives a covalent bond its strength. Therefore, the greater the overlap of the atomic orbitals, the stronger is the covalent bond. The strongest covalent bonds are formed by electrons that occupy the molecular orbitals with the lowest energy.

The MO diagram in Figure 1.4 allows us to predict that H_2^+ would not be as stable as H_2 because H_2^+ has only one electron in the bonding orbital. We can also predict that He_2 does not exist: Because each He atom would bring two electrons, He_2 would have four electrons—two filling the lower energy bonding molecular orbital and the remaining two filling the higher energy antibonding molecular orbital. The two electrons in the antibonding molecular orbital would cancel the advantage to bonding gained by the two electrons in the bonding molecular orbital.

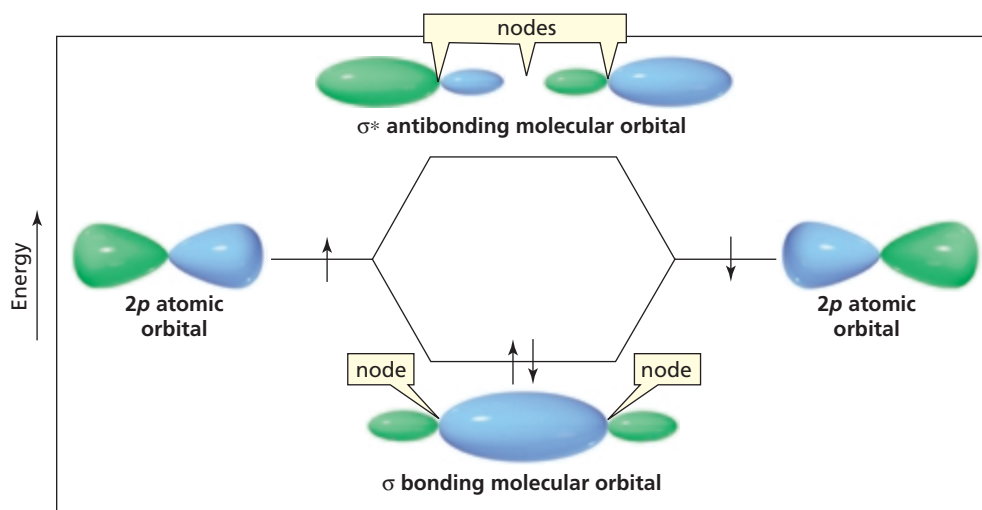
In-phase overlap forms a bonding MO; out-of-phase overlap forms an antibonding MO.

PROBLEM 13 ♦

Predict whether or not He_2^+ exists.

Two p atomic orbitals can overlap either end-on or side-to-side. Let’s first look at end-on overlap. End-on overlap forms a σ bond. If the overlapping lobes of the p orbitals are in-phase (a blue lobe of one p orbital overlaps a blue lobe of the other p orbital), a σ bonding molecular orbital is formed (Figure 1.5). The electron density of the σ bonding molecular orbital is concentrated between the nuclei, which causes the back lobes (the nonoverlapping lobes) of the molecular orbital to be quite small. The σ bonding molecular orbital has two nodes—a nodal plane passing through each of the nuclei.

If the overlapping lobes of the p orbitals are out-of-phase (a blue lobe of one p orbital overlaps a green lobe of the other p orbital), a σ^* antibonding molecular orbital is



◀ **Figure 1.5**

End-on overlap of two p orbitals to form a σ bonding molecular orbital and a σ^* antibonding molecular orbital.

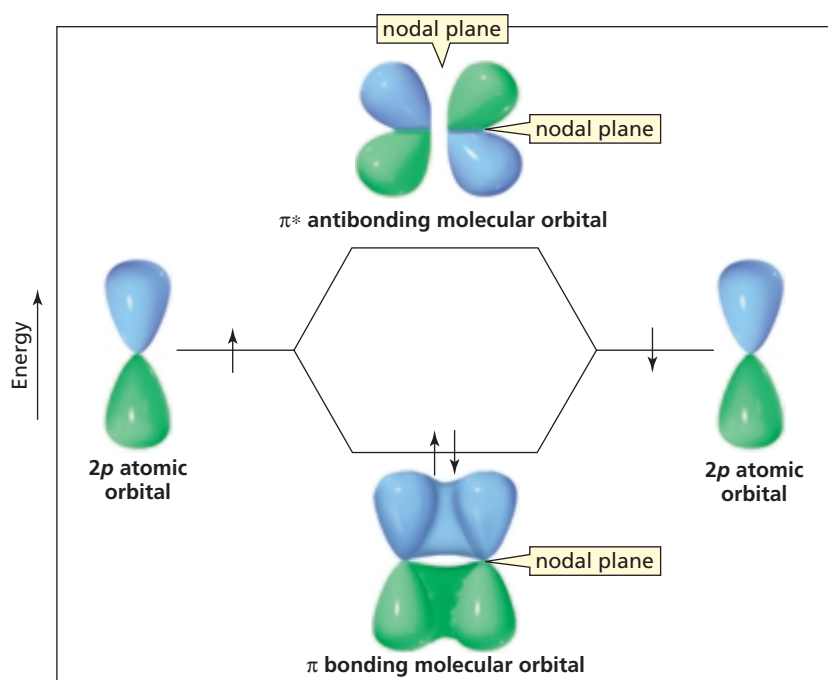
formed. The σ^* antibonding molecular orbital has *three* nodes. (Notice that after each node, the phase of the molecular orbital changes.)

Unlike the σ bond formed as a result of end-on overlap, side-to-side overlap of two p atomic orbitals forms a **pi (π) bond** (Figure 1.6). Side-to-side overlap of two in-phase p atomic orbitals forms a π bonding molecular orbital, whereas side-to-side overlap of two out-of-phase p orbitals forms a π^* antibonding molecular orbital. The π bonding molecular orbital has one node—a nodal plane that passes through both nuclei. The π^* antibonding molecular orbital has two nodal planes. Notice that σ bonds are cylindrically symmetrical, but π bonds are not.

The extent of overlap is greater when p orbitals overlap end-on than when they overlap side-to-side. This means that a σ bond formed by the end-on overlap of p orbitals is stronger than a π bond formed by the side-to-side overlap of p orbitals. It also means that a σ bonding molecular orbital is more stable than a π bonding molecular orbital because the stronger the bond, the more stable it is. Figure 1.7 shows a molecular orbital diagram of two identical atoms using their three degenerate atomic orbitals to form three bonds—one σ bond and two π bonds.

Side-to-side overlap of two p atomic orbitals forms a π bond. All other covalent bonds in organic molecules are σ bonds.

A σ bond is stronger than a π bond.

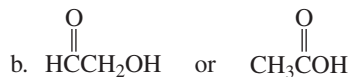


◀ **Figure 1.6**

Side-to-side overlap of two parallel p orbitals to form a π bonding molecular orbital and a π^* antibonding molecular orbital.

PROBLEM 11 ♦

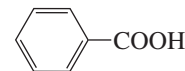
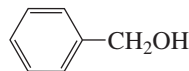
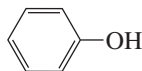
Which is a stronger acid?

**PROBLEM 12** ♦

Which is a stronger base?

**PROBLEM 13** ♦

Rank the following compounds in order of decreasing acid strength:

**7.11 A Molecular Orbital Description of Stability**

We have used contributing resonance structures to show why compounds are stabilized by electron delocalization. Why compounds are stabilized by electron delocalization can also be explained by molecular orbital (MO) theory.

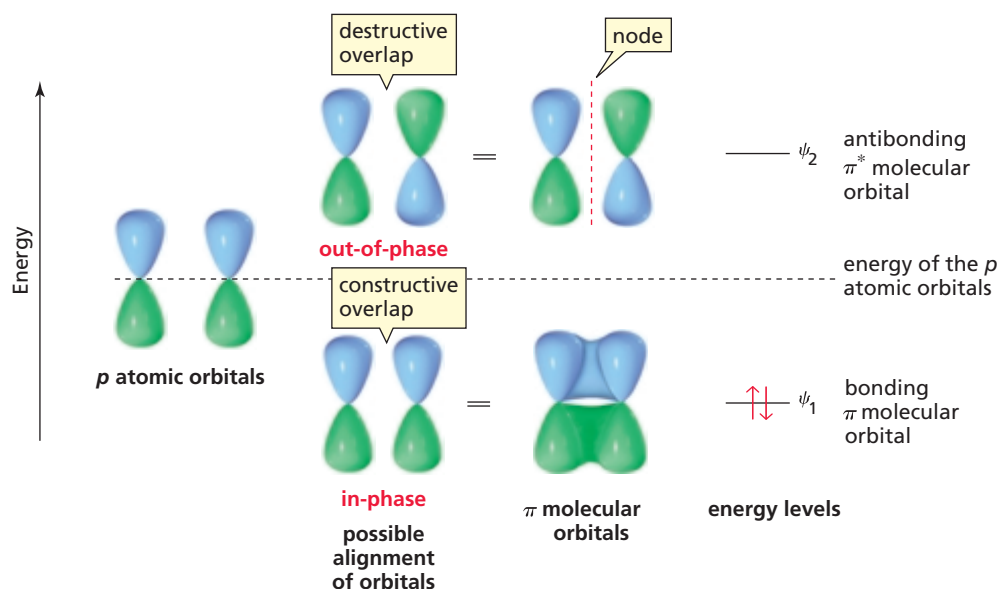
In Section 1.5, we saw that the two lobes of a p orbital have opposite phases. We also saw that when two in-phase p orbitals overlap, a covalent bond is formed, and when two out-of-phase p orbitals overlap, they cancel each other and produce a node between the two nuclei (Section 1.6). A *node* is a region where there is zero probability of finding an electron.

Let's review how the π molecular orbitals of ethene are constructed. An MO description of ethene is shown in Figure 7.8. The two p orbitals can be either in-phase or out-of-phase. (The different phases are indicated by different colors.) Notice that the number of orbitals is conserved—the number of molecular orbitals equals the number of atomic orbitals that produced them. Thus, the two atomic p orbitals of ethene overlap to produce two molecular orbitals. Side-to-side overlap of in-phase p orbitals (lobes of the same color) produces a **bonding molecular orbital** designated ψ_1 (the Greek letter psi). The bonding molecular orbital is lower in energy than the p atomic orbitals, and it encompasses both carbons. In other words, each electron in the bonding molecular orbital spreads over both carbon atoms.

Side-to-side overlap of out-of-phase p orbitals produces an **antibonding molecular orbital**, ψ_2 , which is higher in energy than the p atomic orbitals. The antibonding molecular orbital has a node between the lobes of opposite phases. The bonding MO arises from *constructive overlap* of the atomic orbitals, whereas the antibonding MO arises from *destructive overlap*. In other words, the overlap of in-phase orbitals holds atoms together—it is a bonding interaction—whereas the overlap of out-of-phase orbitals pulls atoms apart—it is an antibonding interaction.

The π electrons are placed in molecular orbitals according to the same rules that govern the placement of electrons in atomic orbitals (Section 1.2): the aufbau principle (orbitals are filled in order of increasing energy), the Pauli exclusion principle (each

Take a few minutes to review
Section 1.6.



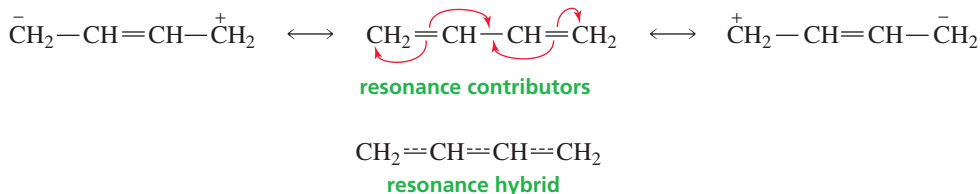
▲ **Figure 7.8**

The distribution of electrons in ethene. Overlapping of in-phase p orbitals produces a bonding molecular orbital that is lower in energy than the p atomic orbitals. Overlapping of out-of-phase p orbitals produces an antibonding molecular orbital that is higher in energy than the p atomic orbitals.

orbital can hold two electrons of opposite spin), and Hund's rule (an electron will occupy an empty degenerate orbital before it will pair up with an electron that is already present in an orbital).

1,3-Butadiene and 1,4-Pentadiene

The π electrons in 1,3-butadiene are delocalized over four sp^2 carbons. In other words, there are four carbons in the π system. A molecular orbital description of 1,3-butadiene is shown in Figure 7.9.

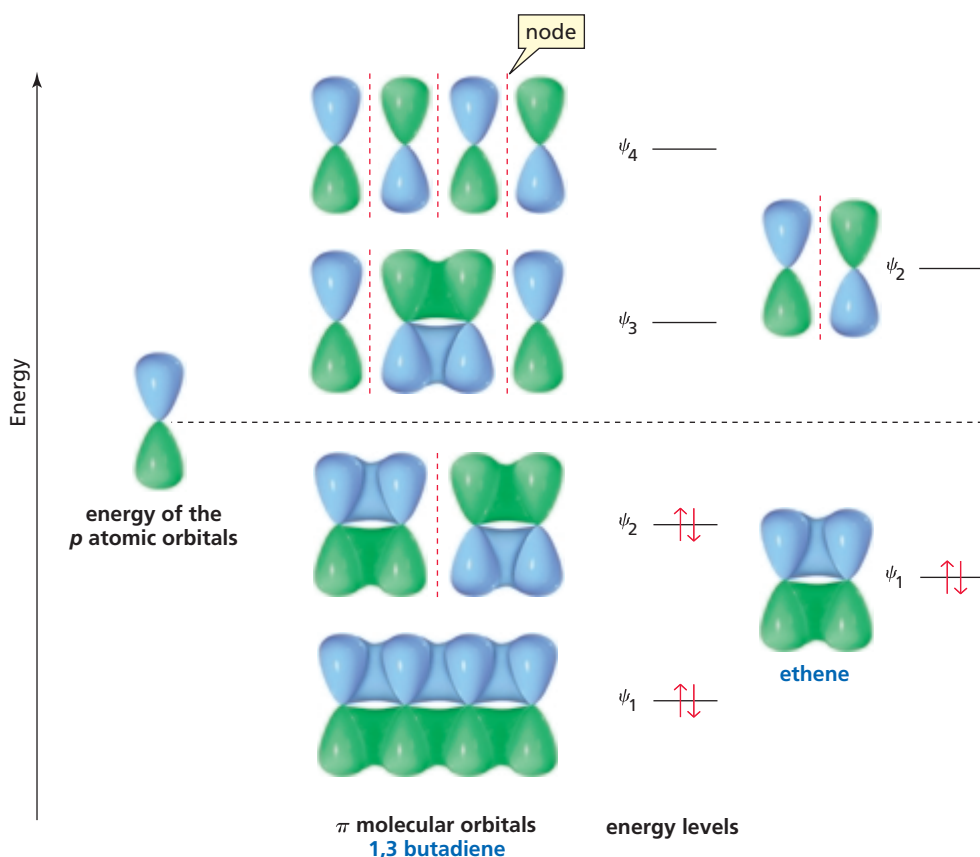


Each of the four carbons contributes one p atomic orbital, and the four p atomic orbitals combine to produce four π molecular orbitals: ψ_1 , ψ_2 , ψ_3 , and ψ_4 . Thus, a molecular orbital results from the **linear combination of atomic orbitals (LCAO)**. Half of the MOs are bonding (π) MOs (ψ_1 and ψ_2), and the other half are antibonding (π^*) MOs (ψ_3 and ψ_4), and they are given the designations ψ_1 , ψ_2 , ψ_3 , and ψ_4 , in order of increasing energy. The energies of the bonding and antibonding MOs are symmetrically distributed above and below the energy of the p atomic orbitals.

Notice that as the MOs increase in energy, the number of nodes increases and the number of bonding interactions decreases. The lowest-energy MO (ψ_1) has only the node that bisects the p orbitals—it has no nodes between the nuclei because all the blue lobes overlap on one face of the molecule and all the green lobes overlap on the other face; ψ_1 has three bonding interactions; ψ_2 has one node between the nuclei and two bonding interactions (for a net of one bonding interaction); ψ_3 has two nodes between the nuclei and one bonding interaction (for a net of one antibonding interaction); and ψ_4 has three nodes between the nuclei—three antibonding interactions—and no bonding interactions. The four π electrons of 1,3-butadiene reside in ψ_1 and ψ_2 .

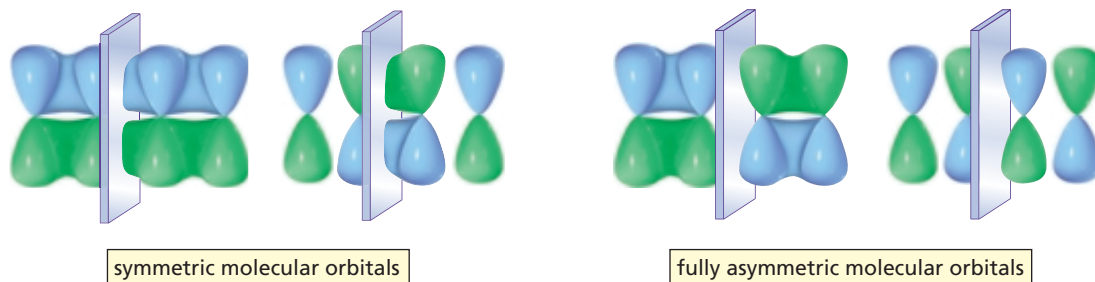
Figure 7.9 ▶

Four p atomic orbitals overlap to produce four molecular orbitals in 1,3-butadiene, and two p atomic orbitals overlap to produce two molecular orbitals in ethene. In both compounds, the bonding MOs are filled and the antibonding MOs are empty.



1,3-Butadiene's lowest-energy MO (ψ_1) is particularly stable because it has three bonding interactions and its two electrons are delocalized over all four nuclei—they encompass all the carbons in the π system. The MO next in energy (ψ_2) is also a bonding MO because it has one more bonding interaction than antibonding interaction; it is not as strongly bonding or as low in energy as ψ_1 . These two bonding MOs show that the greatest π electron density in a compound with two double bonds joined by one single bond is between C-1 and C-2 and between C-3 and C-4, but there is some π electron density between C-2 and C-3—just as the resonance contributors show. They also show why 1,3-butadiene is most stable in a planar conformation: If 1,3-butadiene weren't planar, there would be little or no overlap between C-2 and C-3. Overall, ψ_3 is an antibonding MO: It has one more antibonding interaction than bonding interaction, but it is not as strongly antibonding as ψ_4 , which has no bonding interactions and three antibonding interactions.

Both ψ_1 and ψ_3 are **symmetric molecular orbitals**; they have a plane of symmetry, so one half is the mirror image of the other half. Both ψ_2 and ψ_4 are **fully asymmetric**; they do not have a plane of symmetry, but would have one if one half of the MO were turned upside down. Notice that as the MOs increase in energy, they alternate from being symmetric to asymmetric.



The energies of the MOs of 1,3-butadiene and ethene are compared in Figure 7.9. Notice that the average energy of the electrons in 1,3-butadiene is lower than the electrons in ethene. This lower energy is the resonance energy. In other words, 1,3-butadiene is stabilized by electron delocalization (resonance).

PROBLEM 14 ♦

What is the total number of nodes in the ψ_3 and ψ_4 molecular orbitals of 1,3-butadiene?

The highest-energy molecular orbital of 1,3-butadiene that contains electrons is ψ_2 . Therefore, ψ_2 is called the **highest occupied molecular orbital (HOMO)**. The lowest-energy molecular orbital of 1,3-butadiene that does not contain electrons is ψ_3 ; ψ_3 is called the **lowest unoccupied molecular orbital (LUMO)**.

The molecular orbital description of 1,3-butadiene shown in Figure 7.9 represents the electronic configuration of the molecule in its ground state. If the molecule absorbs light of an appropriate wavelength, the light will promote an electron from its HOMO to its LUMO (from ψ_2 to ψ_3). The molecule then is in an excited state (Section 1.2). The excitation of an electron from the HOMO to the LUMO is the basis of ultraviolet and visible spectroscopy (Section 8.9).

HOMO = the highest occupied molecular orbital.

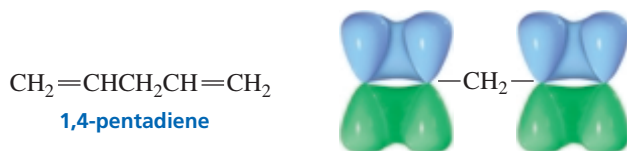
LUMO = the lowest unoccupied molecular orbital.

PROBLEM 15 ♦

Answer the following questions for the π molecular orbitals of 1,3-butadiene:

- Which are the bonding MOs and which are the antibonding MOs?
- Which MOs are symmetric and which are asymmetric?
- Which MO is the HOMO and which is the LUMO in the ground state?
- Which MO is the HOMO and which is the LUMO in the excited state?
- What is the relationship between the HOMO and the LUMO and symmetric and asymmetric orbitals?

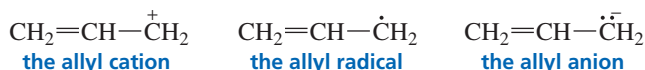
Now let's look at the π molecular orbitals of 1,4-pentadiene.



1,4-Pentadiene, like 1,3-butadiene, has four π electrons. However, unlike the delocalized π electrons in 1,3-butadiene, the π electrons in 1,4-pentadiene are completely separate from one another. In other words, the electrons are localized. The molecular orbitals of 1,4-pentadiene have the same energy as those of ethene—a compound with one pair of localized π electrons. Thus, molecular orbital theory and contributing resonance structures are two different ways to show that the π electrons in 1,3-butadiene are delocalized and that electron delocalization stabilizes a molecule.

The Allyl Cation, the Allyl Radical, and the Allyl Anion

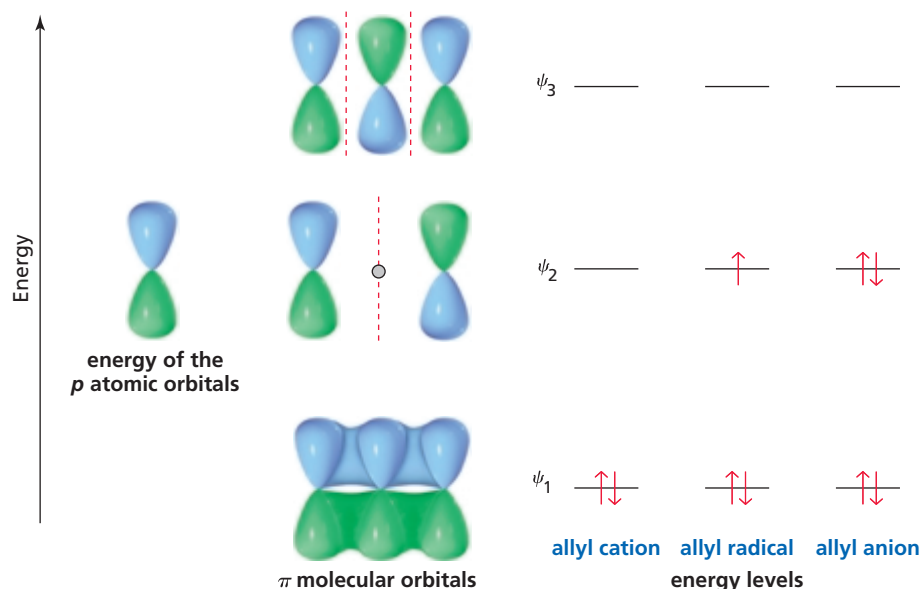
Let's now look at the molecular orbitals of the allyl cation, the allyl radical, and the allyl anion.



The three p atomic orbitals of the allyl group combine to produce three π molecular orbitals: ψ_1 , ψ_2 , and ψ_3 (Figure 7.10). The bonding MO (ψ_1) encompasses all the

Figure 7.10 ▶

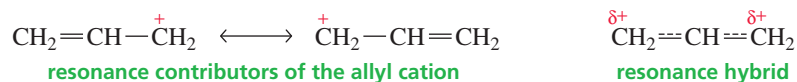
The distribution of electrons in the molecular orbitals of the allyl cation, the allyl radical, and the allyl anion. Three p atomic orbitals overlap to produce three π molecular orbitals.



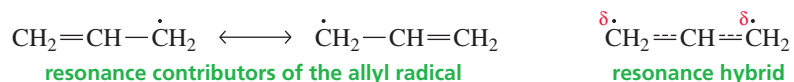
carbons in the π system. In an acyclic π system, the number of bonding MOs always equals the number of antibonding MOs. Therefore, when there is an odd number of MOs, one of them must be a **nonbonding molecular orbital**. In an allyl system, ψ_2 is a nonbonding MO. We have seen that as the energy of the MO increases, the number of nodes increases. Consequently, the ψ_2 MO must have a node—in addition to the one that ψ_1 has that bisects the p orbitals. The only symmetrical position for a node in ψ_2 is for it to pass through the middle carbon. (You also know that it needs to pass through the middle carbon because that is the only way ψ_2 can be fully asymmetric, which it must be, since ψ_1 and ψ_3 are symmetric.)

You can see from Figure 7.10 why ψ_2 is called a nonbonding molecular orbital: There is no overlap between the p orbital on the middle carbon and the p orbital on either of the end carbons. Notice that a nonbonding MO has the same energy as the isolated p atomic orbitals. The third molecular orbital (ψ_3) is an antibonding MO.

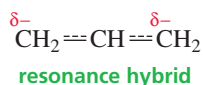
The two π electrons of the allyl cation are in the bonding MO, which means that they are spread over all three carbons. Consequently, the two carbon–carbon bonds in the allyl cation are identical, with each having some double-bond character. The positive charge is shared equally by the end carbon atoms, which is another way of showing that the stability of the allyl cation is due to electron delocalization.



The allyl radical has two electrons in the bonding π molecular orbital, so these electrons are spread over all three carbon atoms. The third electron is in the nonbonding MO. The molecular orbital diagram shows that the third electron is shared equally by the end carbons, with none of the electron density on the middle carbon. This is in agreement with what the resonance contributors show: Only the end carbons have radical character.

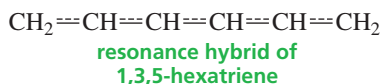
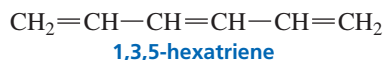


Finally, the allyl anion has two electrons in the nonbonding MO. These two electrons are shared equally by the end carbon atoms. This again agrees with what the resonance contributors show.

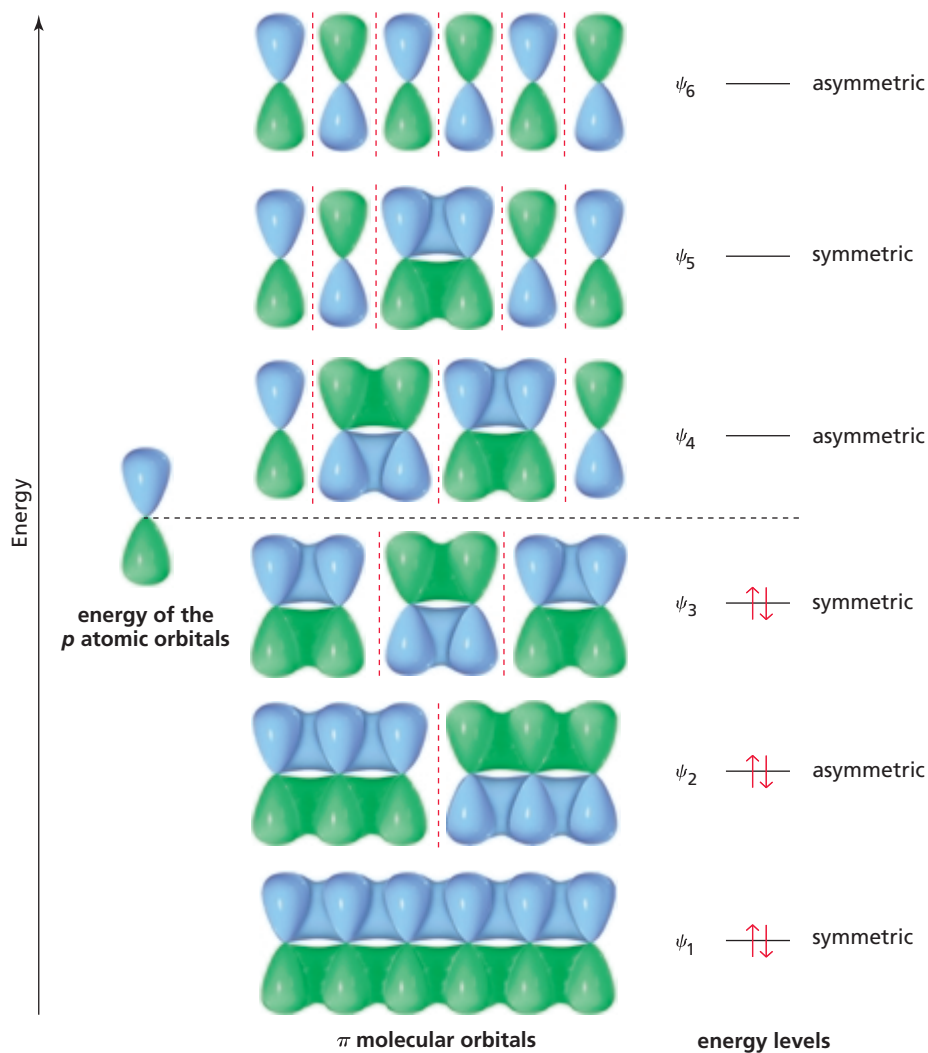


1,3,5-Hexatriene and Benzene

1,3,5-Hexatriene, with six carbon atoms, has six p atomic orbitals.



The six p atomic orbitals combine to produce six π molecular orbitals: ψ_1 , ψ_2 , ψ_3 , ψ_4 , ψ_5 , and ψ_6 (Figure 7.11). Half of the MOs (ψ_1 , ψ_2 , and ψ_3) are bonding MOs, and the other half (ψ_4 , ψ_5 , and ψ_6) are antibonding. 1,3,5-Hexatriene's six π electrons occupy the three bonding MOs (ψ_1 , ψ_2 , and ψ_3), and two of the electrons (those in ψ_1) are delocalized over all six carbons. Thus, molecular orbital theory and resonance contributors are two different ways of showing that the π electrons in 1,3,5-hexatriene are delocalized. Notice in the figure that as the MOs increase in energy, the number of nodes increases, the number of bonding interactions decreases, and the MOs alternate from being symmetric to being asymmetric.



◀ **Figure 7.11**

Six p atomic orbitals overlap to produce the six π molecular orbitals of 1,3,5-hexatriene. The six electrons occupy the three bonding molecular orbitals ψ_1 , ψ_2 , and ψ_3 .

PROBLEM 16 ♦

Answer the following questions for the π molecular orbitals of 1,3,5-hexatriene:

- Which are the bonding MOs and which are the antibonding MOs?
- Which MOs are symmetric and which are asymmetric?
- Which MO is the HOMO and which is the LUMO in the ground state?
- Which MO is the HOMO and which is the LUMO in the excited state?
- What is the relationship between the HOMO and the LUMO and symmetric and asymmetric orbitals.

Like 1,3,5-hexatriene, benzene has a six-carbon π system. The six-carbon π system in benzene, however, is cyclic. The six p atomic orbitals combine to produce six π molecular orbitals (Figure 7.12). Three of the MOs are bonding (ψ_1 , ψ_2 , and ψ_3) and three are antibonding (ψ_4 , ψ_5 , and ψ_6). Benzene's six π electrons occupy the three lowest-energy MOs (the bonding MOs). The two electrons in ψ_1 are delocalized over the six carbon atoms. The method used to determine the relative energies of the MOs of compounds with cyclic π systems is described in Section 15.6.

Figure 7.12 ▶

Benzene has six π molecular orbitals, three bonding (ψ_1 , ψ_2 , ψ_3) and three antibonding (ψ_4 , ψ_5 , ψ_6). The six π electrons occupy the three bonding molecular orbitals.

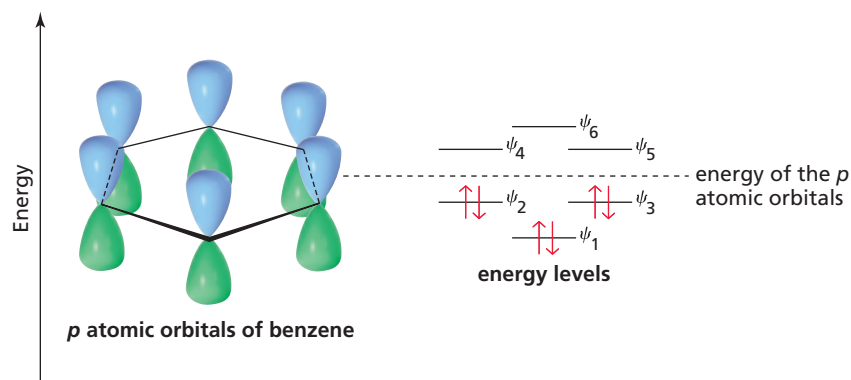


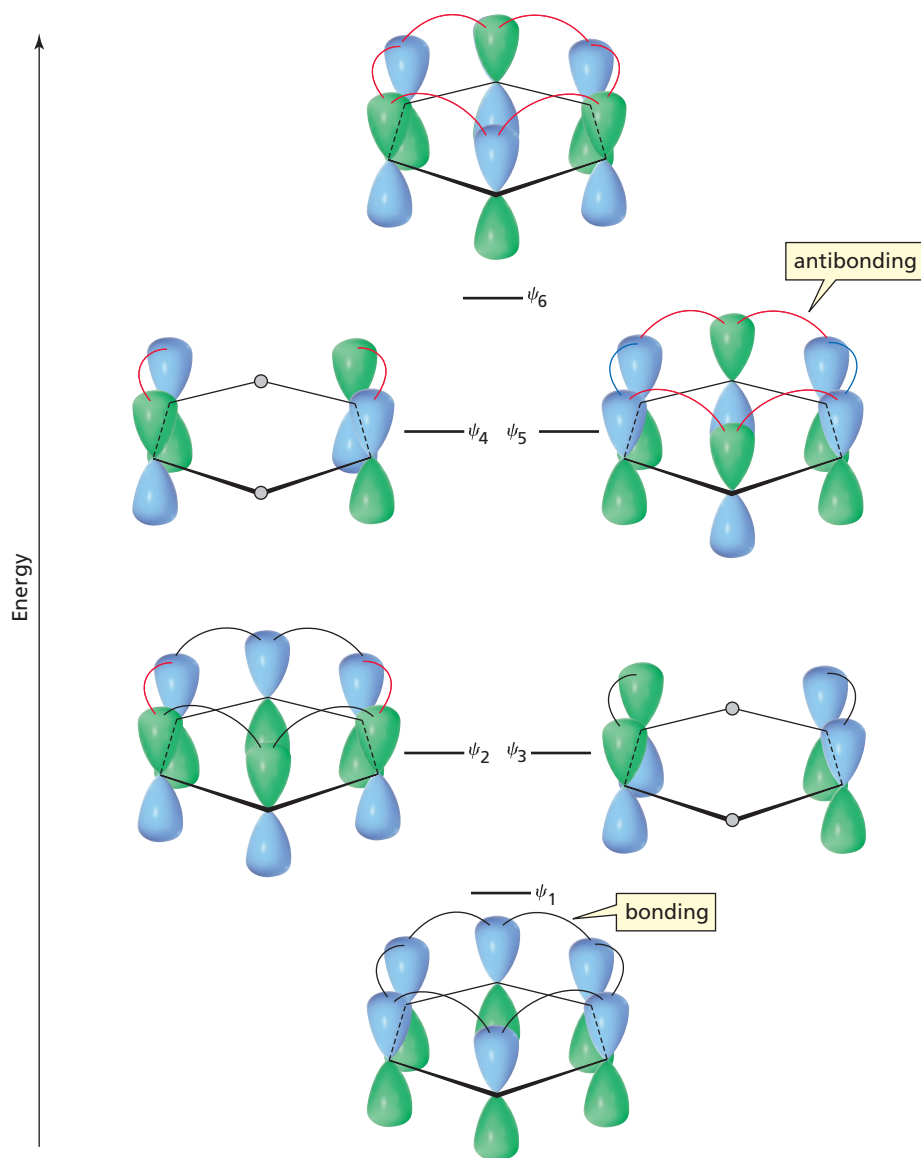
Figure 7.13 shows that there are *six* bonding interactions in the lowest-energy MO (ψ_1) of benzene—one more than in the lowest-energy MO of 1,3,5-hexatriene (Figure 7.12). In other words, putting the three double bonds into a ring is accompanied by an increase in stabilization. Each of the other two bonding MOs of benzene (ψ_2 and ψ_3) has a node in addition to the node that bisects the p orbitals. These two orbitals are degenerate: ψ_2 has four bonding interactions and two antibonding interactions, for a net of two bonding interactions, and ψ_3 also has two bonding interactions. Thus, ψ_2 and ψ_3 are bonding MOs, but they are not as strongly bonding as ψ_1 .

The energy levels of the MOs of ethene, 1,3-butadiene, 1,3,5-hexatriene, and benzene are compared in Figure 7.14. You can see that benzene is a particularly stable molecule—more stable than 1,3,5-hexatriene and much more stable than a molecule with one or more isolated double bonds. Compounds such as benzene that are unusually stable because of large delocalization energies are called **aromatic compounds**. The structural features that cause a compound to be aromatic are discussed in Section 15.1.

PROBLEM 17 ♦

How many bonding interactions are there in the ψ_1 and ψ_2 molecular orbitals of the following compounds?

- 1,3-butadiene
- 1,3,5,7-octatetraene

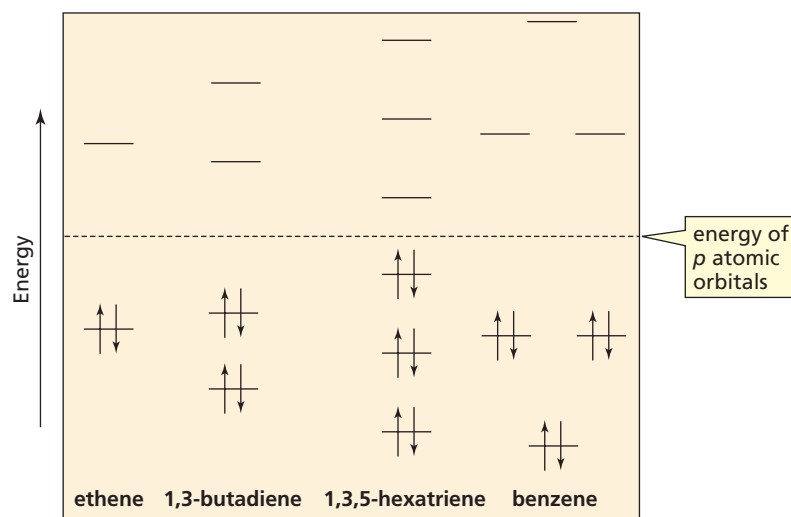


◀ **Figure 7.13**

As the energy of the π molecular orbitals increases, the number of nodes increases and the net number of bonding interactions decreases.



Tutorial:
Common terms



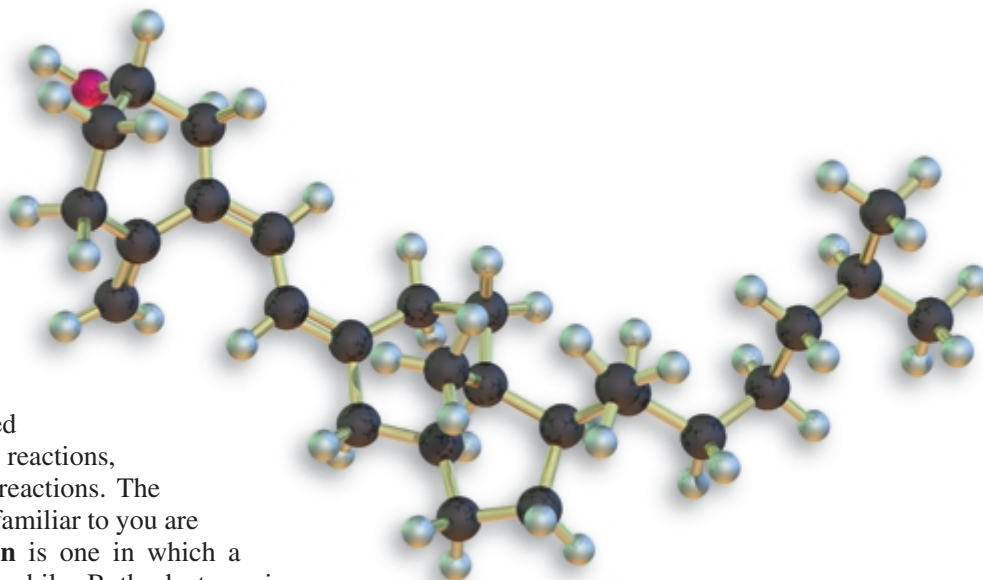
◀ **Figure 7.14**

A comparison of the energy levels of the π molecular orbitals of ethene, 1,3-butadiene, 1,3,5-hexatriene, and benzene.

29

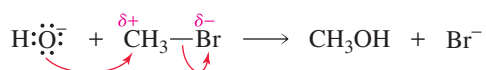
Pericyclic Reactions

Reactions of organic compounds can be divided into three classes—polar reactions, radical reactions, and pericyclic reactions. The most common and the ones most familiar to you are polar reactions. A **polar reaction** is one in which a nucleophile reacts with an electrophile. Both electrons in the new bond come from the nucleophile.



Vitamin D

a polar reaction



A **radical reaction** is one in which a new bond is formed using one electron from each of the reactants.

a radical reaction

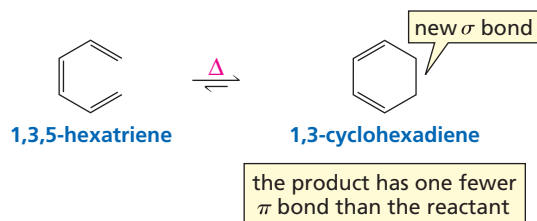


A **pericyclic reaction** occurs as a result of reorganizing the electrons in the reactant(s). In this chapter we will look at the three most common types of pericyclic reactions—electrocyclic reactions, cycloaddition reactions, and sigmatropic rearrangements.

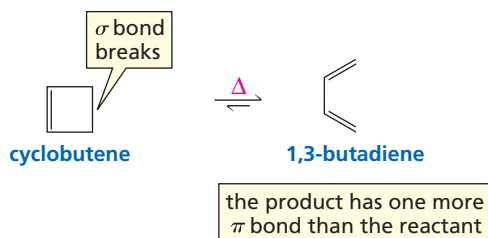
29.1 Three Kinds of Pericyclic Reactions

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

an electrocyclic reaction

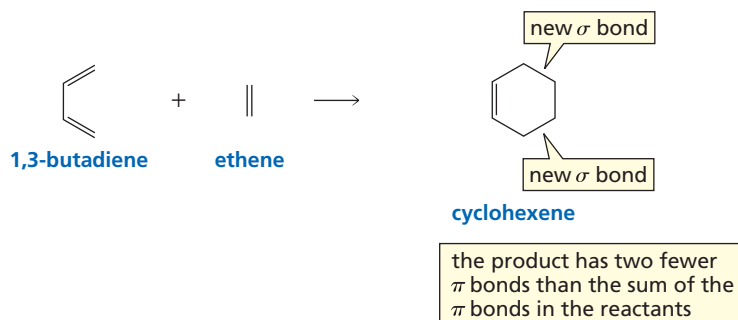


Electrocyclic reactions are reversible. In the reverse direction, an electrocyclic reaction is one in which a σ bond in a cyclic reactant breaks, forming a conjugated π system that has one *more* π bond than the cyclic reactant.



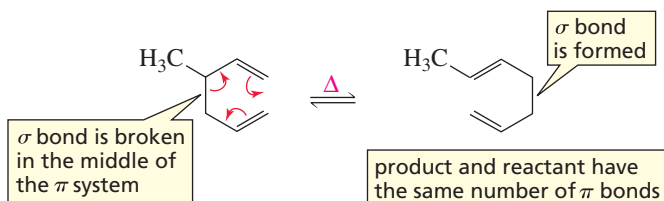
In a **cycloaddition reaction**, two different π bond-containing molecules react to form a cyclic compound. Each of the reactants loses a π bond, and the resulting cyclic product has two new σ bonds. The Diels–Alder reaction is a familiar example of a cycloaddition reaction (Section 8.8).

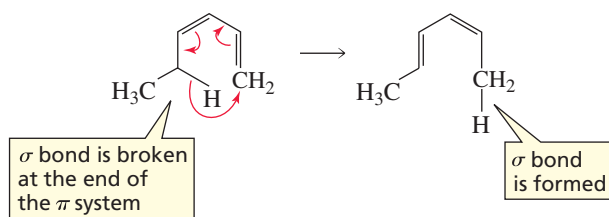
a cycloaddition reaction



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

sigmatropic rearrangements





Notice that electrocyclic reactions and sigmatropic rearrangements occur within a single π system—they are *intramolecular* reactions. In contrast, cycloaddition reactions involve the interaction of two different π systems—they are usually *intermolecular* reactions. The three kinds of pericyclic reactions share the following common features:

- 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** is one that takes place when a reactant absorbs light. A **thermal reaction** takes place *without* the absorption of light. Despite its name, a thermal reaction does not necessarily require more heat than what is available at room temperature. Some thermal reactions do require additional heat in order to take place at a reasonable rate, but others readily occur at, or even below, room temperature.

For many years, pericyclic reactions puzzled chemists. Why did some pericyclic reactions take place only under thermal conditions, whereas others took place only under photochemical conditions, and yet others were successfully carried out under both thermal and photochemical conditions? Another puzzling aspect of pericyclic reactions was the configurations of the products that were formed. After many pericyclic reactions had been investigated, it became apparent that if a pericyclic reaction could take place under both thermal and photochemical conditions, the configuration of the product formed under one set of conditions was different from the configuration of the product formed under the other set of conditions. For example, if the *cis* isomer was obtained under thermal conditions, the *trans* isomer was obtained under photochemical conditions and vice versa.

It took two very talented chemists, each bringing his own expertise to the problem, to explain the puzzling behavior of pericyclic reactions. In 1965, R. B. Woodward, an experimentalist, and Roald Hoffmann, a theorist, developed the **conservation of orbital symmetry theory** to explain the relationship among the structure and configuration of the reactant, the conditions (thermal and/or photochemical) under which the reaction takes place, and the configuration of the product. Because the behavior of pericyclic reactions is so precise, it is not surprising that everything about their behavior can be explained by one simple theory. The difficult part was having the insight to arrive at the theory.

The conservation of orbital symmetry theory states that *in-phase orbitals overlap during the course of a pericyclic reaction*. The conservation of orbital symmetry theory was based on the **frontier orbital theory** put forth by Kenichi Fukui in 1954. Although Fukui's theory was more than 10 years old, it had been overlooked because of its mathematical complexity and Fukui's failure to apply it to stereoselective reactions.

Roald Hoffmann and Kenichi Fukui shared the 1981 Nobel Prize in chemistry for the conservation of orbital symmetry theory and the frontier orbital theory. **R. B. Woodward** did not receive a share in the prize because he died two years before it was awarded, and Alfred Nobel's will stipulates that the prize cannot be awarded posthumously. Woodward, however, had received the 1965 Nobel Prize in chemistry for his work in organic synthesis.



Robert B. Woodward (1917–1979)

was born in Boston and first became acquainted with chemistry in his home laboratory. He entered MIT at the age of 16 and received a Ph.D. the same year that those who entered MIT with him received their B.A.'s. He went to Harvard as a postdoctoral fellow and remained there for his entire career. Cholesterol, cortisone, strychnine, reserpine (the first tranquilizing drug), chlorophyll, tetracycline, and vitamin B₁₂ are just some of the complicated organic molecules Woodward synthesized. He received the Nobel Prize in chemistry in 1965.



Roald Hoffmann was born in Poland in 1937 and came to the United States when he was 12. He received a B.S. from Columbia and a Ph.D. from Harvard. When the conservation of orbital symmetry theory was proposed, he and Woodward were both on the faculty at Harvard. Hoffmann is presently a professor of chemistry at Cornell.

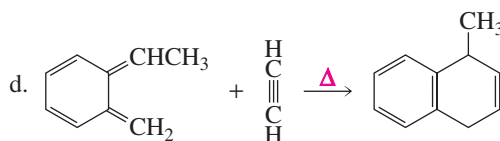
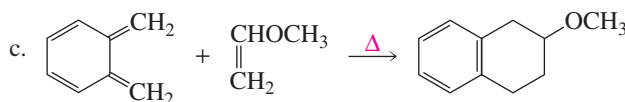
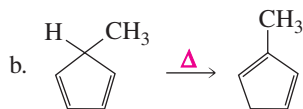
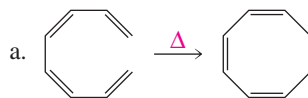
Kenichi Fukui (1918–1998) was born in Japan. He was a professor at Kyoto University until 1982 when he became president of the Kyoto Institute of Technology. He was the first Japanese to receive the Nobel Prize in chemistry.

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According to the conservation of orbital symmetry theory, whether a compound will undergo a pericyclic reaction under particular conditions *and* what product will be formed both depend on molecular orbital symmetry. To understand pericyclic reactions, therefore, we must now review molecular orbital theory. We will then be able to understand how the symmetry of a molecular orbital controls both the conditions under which a pericyclic reaction takes place and the configuration of the product that is formed.

PROBLEM 1 ♦

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

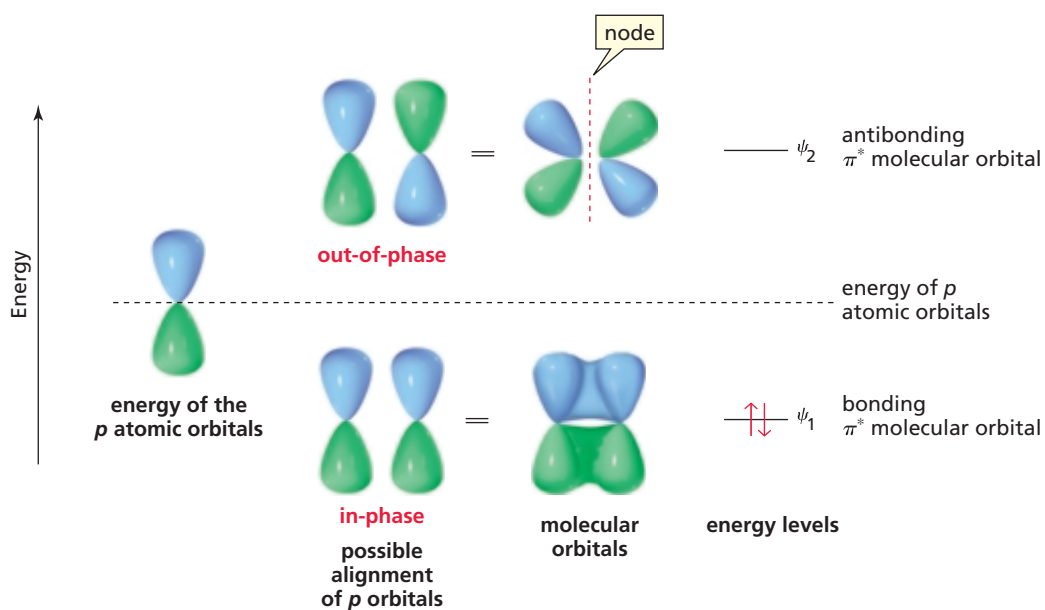


29.2 Molecular Orbitals and Orbital Symmetry

The overlap of p atomic orbitals to form π molecular orbitals can be described mathematically using quantum mechanics. The result of the mathematical treatment can be described simply in nonmathematical terms by **molecular orbital (MO) theory**. You were introduced to molecular orbital theory in Sections 1.6 and 7.11. Take a few minutes to review the following key points raised in these sections.

- The two lobes of a p orbital have opposite phases. When two in-phase atomic orbitals interact, a covalent bond is formed. When two out-of-phase atomic orbitals interact, a node is created between the two nuclei.
- Electrons fill molecular orbitals according to the same rules—the aufbau principle, the Pauli exclusion principle, Hund's rule—that govern how they fill atomic orbitals: An electron goes into the available molecular orbital with the lowest energy, and only two electrons can occupy a particular molecular orbital (Section 1.2).
- Because the π -bonding portion of a molecule is perpendicular to the framework of the σ bonds, the π bonds can be treated independently. Each carbon atom that forms a π bond has a p orbital, and the p orbitals of the carbon atoms combine to produce a π molecular orbital. Thus, a molecular orbital can be described by the **linear combination of atomic orbitals (LCAO)**. In a π molecular orbital, each electron that previously occupied a p atomic orbital surrounding an individual carbon nucleus now surrounds the entire part of the molecule that is included in the interacting p orbitals.

A molecular orbital description of ethene is shown in Figure 29.1. (To show the different phases of the two lobes of a p orbital, one phase is represented by a blue lobe and the other phase by a green lobe.)¹ Because ethene has one π bond, it has two p atomic orbitals that combine to produce two π molecular orbitals. The in-phase interaction of the two p atomic orbitals gives a **bonding π molecular orbital**, designated by ψ_1 (ψ is the Greek letter psi). The bonding molecular orbital is of lower energy than the isolated p atomic orbitals. The two p atomic orbitals of ethene can also interact out-of-phase. Interaction of out-of-phase orbitals gives an **antibonding π^* molecular orbital**, ψ_2 , which is of higher energy than the p atomic orbitals. The bonding molecular orbital results from additive interaction of the atomic orbitals, whereas the antibonding molecular orbital results from subtractive interaction. In other words, the interaction of in-phase orbitals holds atoms together, while the interaction of out-of-phase orbitals pushes atoms apart. Because electrons reside in the available molecular orbitals with the lowest energy and two electrons can occupy a molecular orbital, the two π electrons of ethene reside in the bonding π molecular orbital. This molecular orbital picture describes all molecules with one carbon–carbon double bond.



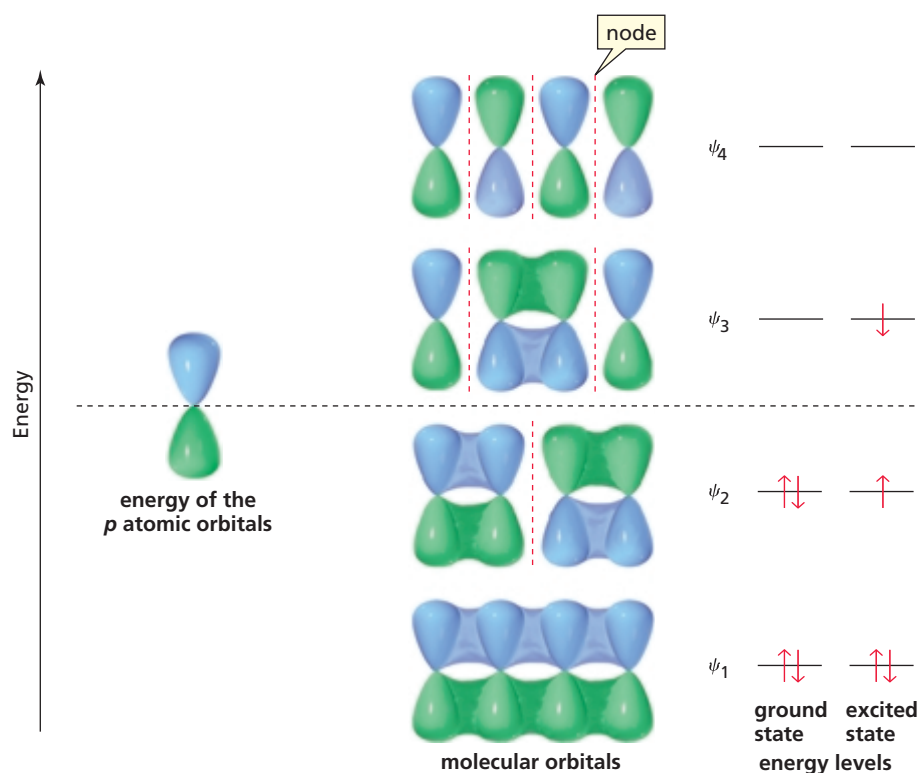
▲ **Figure 29.1**

Interaction of in-phase p atomic orbitals gives a bonding π molecular orbital that is lower in energy than the p atomic orbitals. Interaction of out-of-phase π atomic orbitals gives an antibonding π^* molecular orbital that is higher in energy than the p atomic orbitals.

1,3-Butadiene has two conjugated π bonds, so it has four p atomic orbitals (Figure 29.2). Four atomic orbitals can combine linearly in four different ways. Consequently, there are four π molecular orbitals: ψ_1 , ψ_2 , ψ_3 , and ψ_4 . Notice that orbitals are conserved: Four atomic orbitals combine to produce four molecular orbitals. Half are bonding molecular orbitals (ψ_1 and ψ_2) and the other half are antibonding molecular orbitals (ψ_3 and ψ_4). Because the four π electrons will reside in the available molecular orbitals with the lowest energy, two electrons are in ψ_1 and two are in ψ_2 . Remember that although the molecular orbitals have different energies, they are all valid and they all coexist. This molecular orbital picture describes all molecules with two conjugated carbon–carbon double bonds.

Orbitals are conserved—two atomic orbitals combine to produce two molecular orbitals, four atomic orbitals combine to produce four molecular orbitals, six atomic orbitals combine to produce six molecular orbitals, etc.

¹Because the different phases of the p orbital result from the different mathematical signs (+ and -) of the wave function of the electron, some chemists represent the different phases by a (+) and a (-).



▲ **Figure 29.2**

Four p atomic orbitals interact to give the four π molecular orbitals of 1,3-butadiene.



Tutorial:
 π Molecular orbitals

If you examine the interacting orbitals in Figure 29.2, you will see that in-phase orbitals interact to give a bonding interaction and out-of-phase orbitals interact to create a node. Recall that a node is a place in which there is zero probability of finding an electron (Section 1.5). You will also see that as the energy of the molecular orbital increases, the number of bonding interactions decreases and the number of nodes *between* the nuclei increases. For example, ψ_1 has three bonding interactions and zero nodes between the nuclei, ψ_2 has two bonding interactions and one node between the nuclei, ψ_3 has one bonding interaction and two nodes between the nuclei, and ψ_4 has zero bonding interactions and three nodes between the nuclei. Notice that a molecular orbital is bonding if the number of bonding interactions is greater than the number of nodes between the nuclei, and a molecular orbital is antibonding if the number of bonding interactions is fewer than the number of nodes between the nuclei.

The normal electronic configuration of a molecule is known as its **ground state**. In the ground state of 1,3-butadiene, the *highest occupied molecular orbital (HOMO)* is ψ_2 , and the *lowest unoccupied molecular orbital (LUMO)* is ψ_3 . If a molecule absorbs light of an appropriate wavelength, the light will promote an electron from its ground-state HOMO to its LUMO (from ψ_2 to ψ_3). The molecule is then in an **excited state**. In the excited state, the HOMO is ψ_3 and the LUMO is ψ_4 . In a thermal reaction the reactant is in its ground state; in a photochemical reaction the reactant is in an excited state.

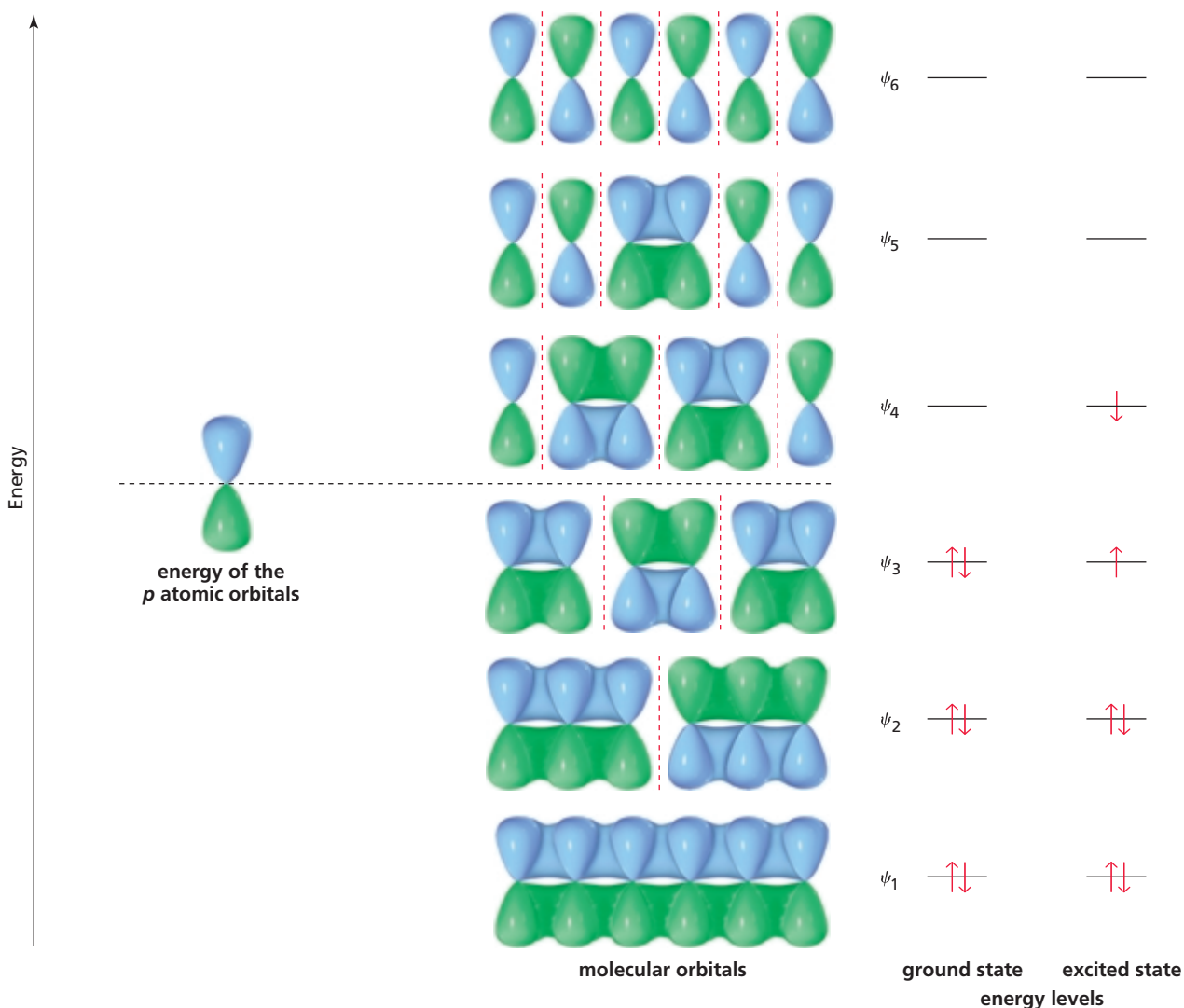
Some molecular orbitals are *symmetric* and some are *asymmetric* (also called *dissymmetric*), and they are easy to distinguish. If the p orbitals at the ends of the molecular orbital are in-phase (both have blue lobes on the top and green lobes on the bottom), the molecular orbital is symmetric. If the two end p orbitals are out-of-phase, the molecular orbital is asymmetric. In Figure 29.2, ψ_1 and ψ_3 are **symmetric molecular orbitals** and ψ_2 and ψ_4 are **asymmetric molecular orbitals**. Notice that as the molecular orbitals increase in energy, they alternate in being symmetric and

asymmetric. Therefore, *the ground-state HOMO and the excited-state HOMO always have opposite symmetries*—one is symmetric and the other is asymmetric. A molecular orbital description of 1,3,5-hexatriene, a compound with three conjugated double bonds, is shown in Figure 29.3. As a review, examine the figure and note

The ground-state HOMO and the excited-state HOMO have opposite symmetries.

- the distribution of electrons in the ground and excited states
- that the number of bonding interactions decreases and the number of nodes increases as the molecular orbitals increase in energy
- that the molecular orbitals alternate from symmetric to asymmetric as the molecular orbitals increase in energy

Although the chemistry of a compound is determined by all its molecular orbitals, we can learn a great deal about the chemistry of a compound by looking at only the **highest occupied molecular orbital (HOMO)** and the **lowest unoccupied molecular orbital (LUMO)**. These two molecular orbitals are known as the **frontier orbitals**. We will now see that simply by evaluating *one* of the frontier molecular orbitals of the reactant(s) in a pericyclic reaction, we can predict the conditions under which the reaction will occur (thermal or photochemical, or both) and the products that will be formed.



▲ Figure 29.3

Six p atomic orbitals interact to give the six π molecular orbitals of 1,3,5-hexatriene.

PROBLEM 2 ♦

Answer the following questions for the π molecular orbitals of 1,3,5-hexatriene:

- Which are the bonding orbitals, and which are the antibonding orbitals?
- Which orbitals are the HOMO and the LUMO in the ground state?
- Which orbitals are the HOMO and the LUMO in the excited state?
- Which orbitals are symmetric, and which are asymmetric?
- What is the relationship between HOMO and LUMO and symmetric and asymmetric orbitals?

PROBLEM 3 ♦

- How many π molecular orbitals does 1,3,5,7-octatetraene have?
- What is the designation of its HOMO (ψ_1 , ψ_2 , etc.)?
- How many nodes does its highest-energy π molecular orbital have between the nuclei?

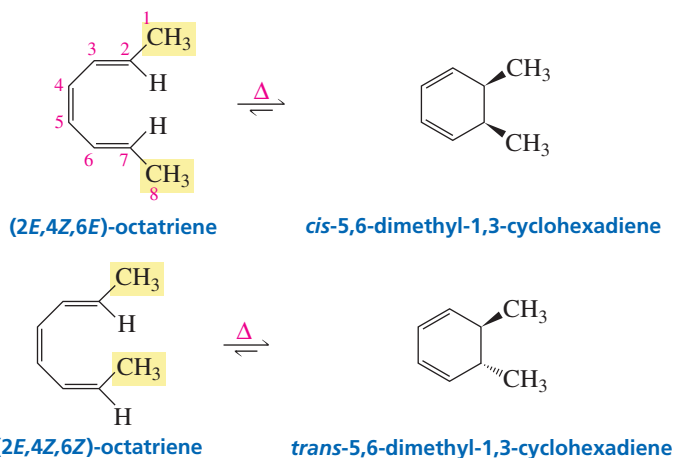
PROBLEM 4

Give a molecular orbital description for each of the following:

- | | |
|-------------------|-------------------------|
| a. 1,3-pentadiene | c. 1,3,5-heptatriene |
| b. 1,4-pentadiene | d. 1,3,5,8-nonatetraene |

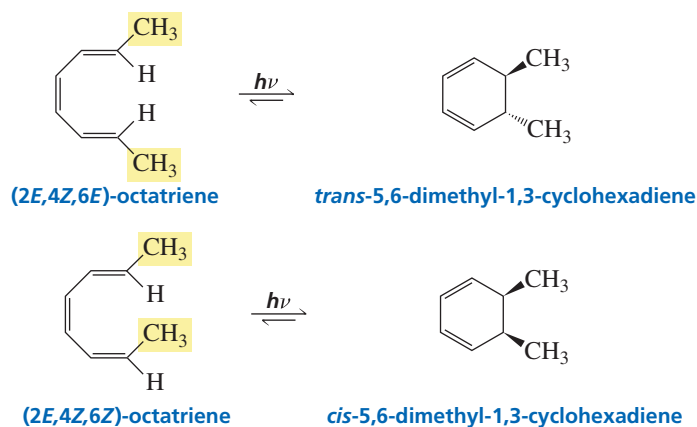
29.3 Electrocyclic Reactions

An *electrocyclic reaction* is an intramolecular reaction in which the rearrangement of π electrons leads to a cyclic product that has one fewer π bond than the reactant. An electrocyclic reaction is completely stereoselective—it preferentially forms one stereoisomer. For example, when $(2E,4Z,6E)$ -octatriene undergoes an electrocyclic reaction under thermal conditions, only the *cis* product is formed; when $(2E,4Z,6Z)$ -octatriene undergoes an electrocyclic reaction under thermal conditions, only the *trans* product is formed. Recall that *E* means the high-priority groups are on opposite sides of the double bond, and *Z* means the high-priority groups are on the same side of the double bond (Section 3.5).

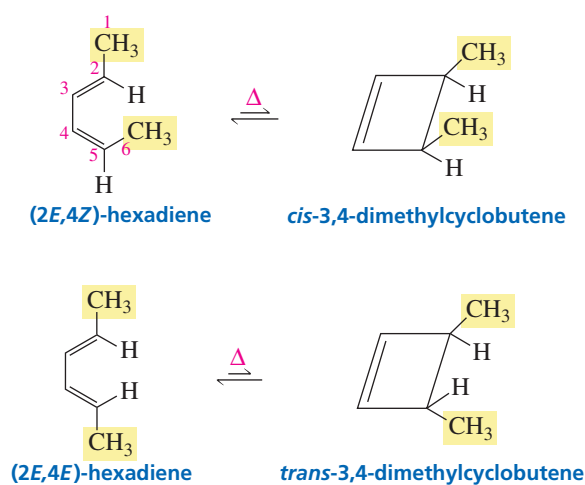


However, when the reactions are carried out under photochemical conditions, the products have opposite configurations: The compound that forms the *cis* isomer under

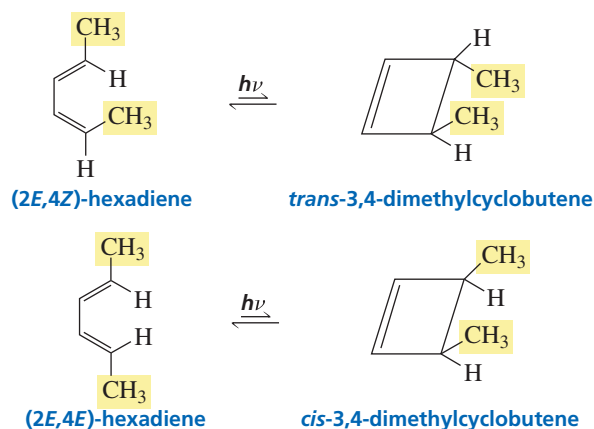
thermal conditions forms the trans isomer under photochemical conditions, and the compound that forms the trans isomer under thermal conditions forms the cis isomer under photochemical conditions.



Under thermal conditions, $(2E,4Z)$ -hexadiene cyclizes to *cis*-3,4-dimethylcyclobutene, and $(2E,4E)$ -hexadiene cyclizes to *trans*-3,4-dimethylcyclobutene.



As we saw with the octatrienes, the configuration of the product changes if the reactions are carried out under photochemical conditions: The trans isomer is obtained from $(2E,4Z)$ -hexadiene instead of the cis isomer; the cis isomer is obtained from $(2E,4E)$ -hexadiene instead of the trans isomer.



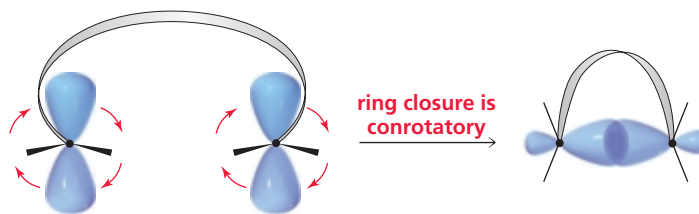


Tutorial:
Electrocyclic reactions

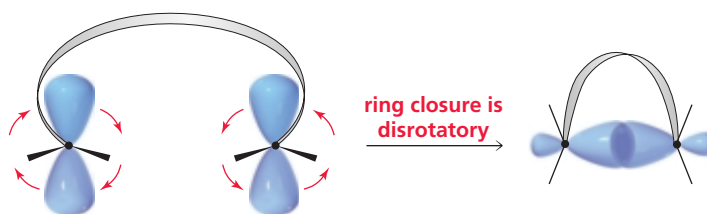
Electrocyclic reactions are reversible. The cyclic compound is favored for electrocyclic reactions that form six-membered rings, whereas the open-chain compound is favored for electrocyclic reactions that form four-membered rings because of the angle strain and torsional strain associated with four-membered rings (Section 2.11).

Now we will use what we have learned about molecular orbitals to explain the configuration of the products of the previous reactions. We will then be able to predict the configuration of the product of any other electrocyclic reaction.

The product of an electrocyclic reaction results from the formation of a new σ bond. For this bond to form, the p orbitals at the ends of the conjugated system must rotate so they overlap head-to-head (and rehybridize to sp^3). Rotation can occur in two ways. If both orbitals rotate in the same direction (both clockwise or both counterclockwise), ring closure is **conrotatory**.

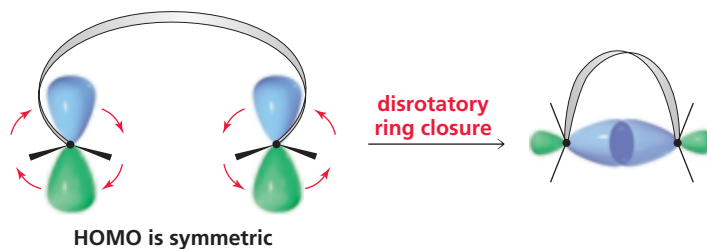


If the orbitals rotate in opposite directions (one clockwise, the other counterclockwise), ring closure is **disrotatory**.



The mode of ring closure depends on the symmetry of the HOMO of the compound undergoing ring closure. Only the symmetry of the HOMO is important in determining the course of the reaction because this is where the highest energy electrons are. These are the most loosely held electrons and therefore the ones most easily moved during a reaction.

To form the new σ bond, the orbitals must rotate so that in-phase p orbitals overlap, because in-phase overlap is a bonding interaction. Out-of-phase overlap would be an antibonding interaction. If the HOMO is symmetric (the end orbitals are identical), rotation will have to be disrotatory to achieve in-phase overlap. In other words, disrotatory ring closure is symmetry-allowed, whereas conrotatory ring closure is symmetry-forbidden.



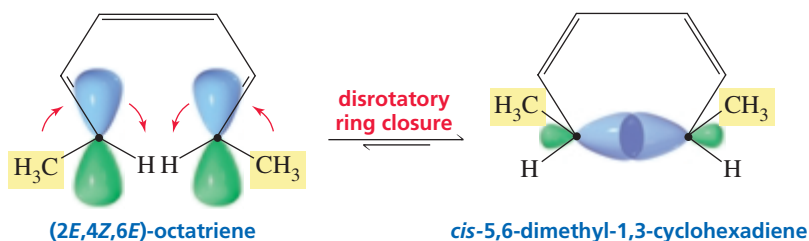
If the HOMO is asymmetric, rotation has to be conrotatory in order to achieve in-phase overlap. In other words, conrotatory ring closure is symmetry-allowed, whereas disrotatory ring closure is symmetry-forbidden.



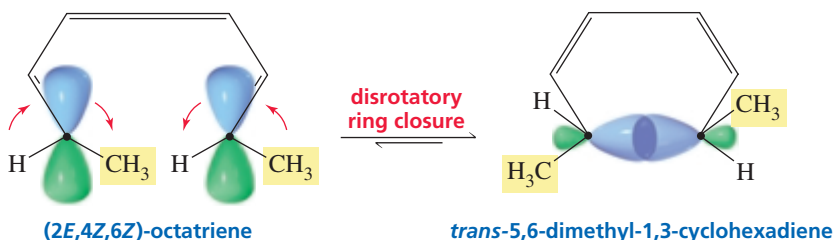
Notice that a **symmetry-allowed pathway** is one in which in-phase orbitals overlap; a **symmetry-forbidden pathway** is one in which out-of-phase orbitals would overlap. A symmetry-allowed reaction can take place under relatively mild conditions. If a reaction is symmetry-forbidden, it cannot take place by a concerted pathway. If a symmetry-forbidden reaction takes place at all, it must do so by a nonconcerted mechanism.

Now we are ready to learn why the electrocyclic reactions discussed at the beginning of this section form the indicated products, and why the configuration of the product changes if the reaction is carried out under photochemical conditions.

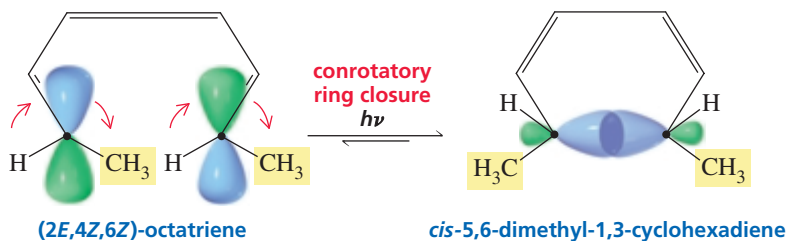
The ground-state HOMO (ψ_3) of a compound with three conjugated π bonds, such as $(2E,4Z,6E)$ -octatriene, is symmetric (Figure 29.3). This means that ring closure under *thermal conditions* is disrotatory. In disrotatory ring closure of $(2E,4Z,6E)$ -octatriene, the methyl groups are both pushed up (or down), which results in formation of the *cis* product.



In disrotatory ring closure of $(2E,4Z,6Z)$ -octatriene, one methyl group is pushed up and the other is pushed down, which results in formation of the *trans* product.



If the reaction takes place under *photochemical conditions*, we must consider the excited-state HOMO rather than the ground-state HOMO. The excited-state HOMO (ψ_4) of a compound with three π bonds is asymmetric (Figure 29.3). Therefore, under photochemical conditions, $(2E,4Z,6Z)$ -octatriene undergoes conrotatory ring closure, so both methyl groups are pushed down (or up) and the *cis* product is formed.

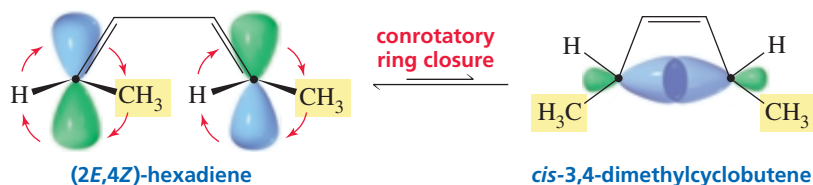


A symmetry-allowed pathway requires in-phase orbital overlap.

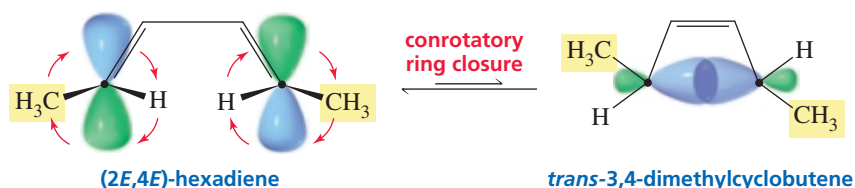
The symmetry of the HOMO of the compound undergoing ring closure controls the stereochemical outcome of an electrocyclic reaction.

We have just seen why the configuration of the product formed under photochemical conditions is the opposite of the configuration of the product formed under thermal conditions: The ground-state HOMO is symmetric—so disrotatory ring closure occurs, whereas the excited-state HOMO is asymmetric—so conrotatory ring closure occurs. Thus, the stereochemical outcome of an electrocyclic reaction depends on the symmetry of the HOMO of the compound undergoing ring closure.

Now let's see why ring closure of (2*E*,4*Z*)-hexadiene forms *cis*-3,4-dimethylcyclobutene. The compound undergoing ring closure has two conjugated π bonds. The ground-state HOMO of a compound with two conjugated π bonds is asymmetric (Figure 29.2), so ring closure is conrotatory. Conrotatory ring closure of (2*E*,4*Z*)-hexadiene leads to the *cis* product.



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



If the reaction is carried out under photochemical conditions, however, the excited-state HOMO of a compound with two conjugated π bonds is symmetric. (Recall that the ground-state HOMO and the excited-state HOMO have opposite symmetries.) So (2*E*,4*Z*)-hexadiene will undergo disrotatory ring closure, resulting in the *trans* product, whereas (2*E*,4*E*)-hexadiene will undergo disrotatory ring closure and form the *cis* product.

We have seen that the ground-state HOMO of a compound with two conjugated double bonds is asymmetric, whereas the ground-state HOMO of a compound with three conjugated double bonds is symmetric. If we examine molecular orbital diagrams for compounds with four, five, six, and more conjugated double bonds, we can conclude that *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.* Therefore, from the number of conjugated double bonds in a compound, we can immediately tell whether ring closure will be conrotatory (an even number of conjugated double bonds) or disrotatory (an odd number of conjugated double bonds) under thermal conditions. However, if the reaction takes place under photochemical conditions, everything is reversed since the ground-state and excited-state HOMOs have opposite symmetries; if the ground-state HOMO is symmetric, the excited-state HOMO is asymmetric and vice versa.

We have seen that the stereochemistry of an electrocyclic reaction depends on the mode of ring closure, and the mode of ring closure depends on the number of conjugated π bonds in the reactant *and* on whether the reaction is carried out under thermal or photochemical conditions. What we have learned about electrocyclic reactions can be summarized by the **selection rules** listed in Table 29.1. These are also known as the **Woodward–Hoffmann rules** for electrocyclic reactions.

The rules in Table 29.1 are for determining whether a given electrocyclic reaction is “allowed by orbital symmetry.” There are also selection rules to determine whether cycloaddition reactions (Table 29.3) and sigmatropic rearrangements (Table 29.4) are

The ground-state HOMO of a compound with an even number of conjugated double bonds is asymmetric.

The ground-state HOMO of a compound with an odd number of conjugated double bonds is symmetric.

Table 29.1 Woodward–Hoffmann Rules for Electrocyclic Reactions

Number of conjugated π bonds	Reaction conditions	Allowed mode of ring closure
Even number	Thermal	Conrotatory
	Photochemical	Disrotatory
Odd number	Thermal	Disrotatory
	Photochemical	Conrotatory

“allowed by orbital symmetry.” It can be rather burdensome to memorize these rules (and worrisome if they are forgotten during an exam), but all the rules can be summarized by the mnemonic “TE-AC.” How to use “TE-AC” is explained in Section 29.7.

PROBLEM 5

- For conjugated systems with two, three, four, five, six, and seven conjugated π bonds, construct quick molecular orbitals (just draw the p orbitals at the ends of the conjugated system as they are drawn on p. 000) to show whether the HOMO is symmetric or asymmetric). X-Ref
- Using these drawings, convince yourself that the Woodward–Hoffmann rules in Table 29.1 are valid.
- Using these drawings, convince yourself that the “TE-AC” shortcut method for learning the information in Table 29.1 is valid (see Section 29.7).

PROBLEM 6

- Under thermal conditions, will ring closure of (2*E*,4*Z*,6*Z*,8*E*)-decatetraene be conrotatory or disrotatory?
- Will the product have the cis or the trans configuration?
- Under photochemical conditions, will ring closure be conrotatory or disrotatory?
- Will the product have the cis or the trans configuration?

The series of reactions in Figure 29.4 illustrates just how easy it is to determine the mode of ring closure and therefore the product of an electrocyclic reaction. The reactant of the first reaction has three conjugated double bonds and is undergoing ring closure under thermal conditions. Ring closure, therefore, is disrotatory (Table 29.1). Disrotatory ring closure of this reactant causes the hydrogens to be cis in the ring-closed product. To determine the relative positions of the hydrogens, draw them in the reactant and then draw arrows showing disrotatory ring closure (Figure 29.4a).

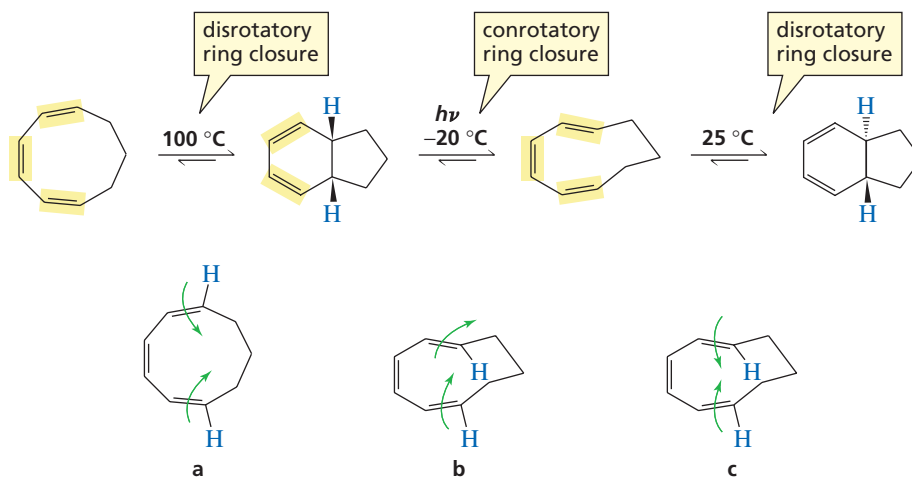


Figure 29.4
Determining the stereochemistry of the product of an electrocyclic reaction.

The second step is a ring-opening electrocyclic reaction that takes place under photochemical conditions. Because of the principle of microscopic reversibility (Section 15.12), the orbital symmetry rules used for a ring-closure reaction also apply to the reverse ring-opening reaction. The compound undergoing reversible ring closure has three conjugated double bonds. Because the reaction occurs under photochemical conditions, ring opening (and ring closure) is conrotatory. (Notice that the number of conjugated double bonds used to determine the mode of ring opening/closure in reversible electrocyclic reactions is the number in the compound undergoing ring closure.) If conrotatory rotation is to result in a product with cis hydrogens, the hydrogens in the compound undergoing ring closure must point in the same direction (Figure 29.4b).

The third step is a thermal ring closure of a compound with three conjugated double bonds, so ring closure is disrotatory. Drawing the hydrogens and the arrows (Figure 29.4c) allows you to determine the relative positions of the hydrogens in the ring-closed product.

Notice that in all these electrocyclic reactions, if the bonds to the substituents in the reactant point in *opposite directions* (as in Figure 29.4a), the substituents will be *cis* in the product if ring closure is disrotatory and *trans* if ring closure is conrotatory. On the other hand, if they point in the *same direction* (as in Figure 29.4b or 29.4c), they will be *trans* in the product if ring closure is disrotatory and *cis* if ring closure is conrotatory (Table 29.2).

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	cis
	Conrotatory	trans
Point in the same direction	Disrotatory	trans
	Conrotatory	cis

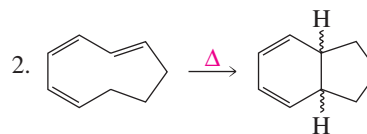
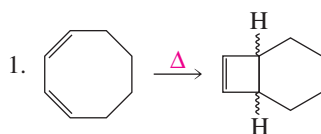
PROBLEM 7♦

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.
- A conjugated diene with an odd number of double bonds has a symmetric HOMO.

PROBLEM 8♦

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

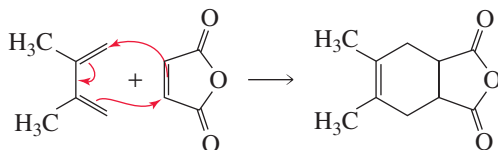


29.4 Cycloaddition Reactions

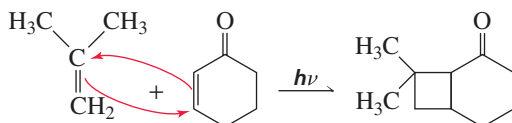
In a *cycloaddition reaction*, two different π bond-containing molecules react to form a cyclic molecule by rearranging the π electrons and forming two new σ bonds. The Diels–Alder reaction is one of the best known examples of a cycloaddition reaction (Section 8.8). Cycloaddition reactions are classified according to the

number of π electrons that interact in the reaction. The Diels–Alder reaction is a [4 + 2] cycloaddition reaction because one reactant has four interacting π electrons and the other reactant has two interacting π electrons. Only the π electrons participating in electron rearrangement are counted.

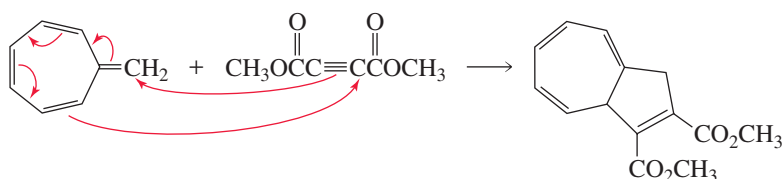
[4 + 2] cycloaddition (a Diels–Alder reaction)



[2 + 2] cycloaddition

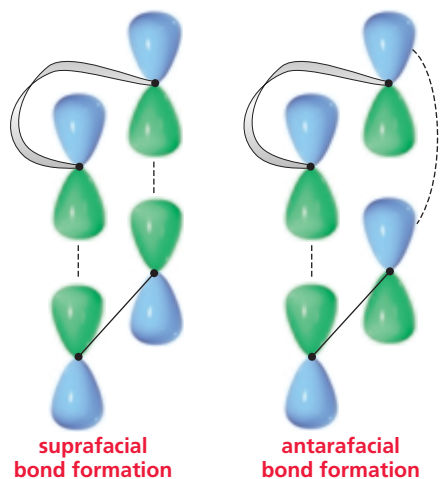


[8 + 2] cycloaddition



In a cycloaddition reaction, the orbitals of one molecule must overlap with the orbitals of the second molecule. Therefore, the frontier molecular orbitals of both reactants must be evaluated to determine the outcome of the reaction. Because the new σ bonds in the product are formed by donation of electron density from one reactant to the other reactant, we must consider the HOMO of one of the molecules and the LUMO of the other because only an empty orbital can accept electrons. It does not matter which reacting molecule's HOMO is used. It is required only that we use the HOMO of one and the LUMO of the other.

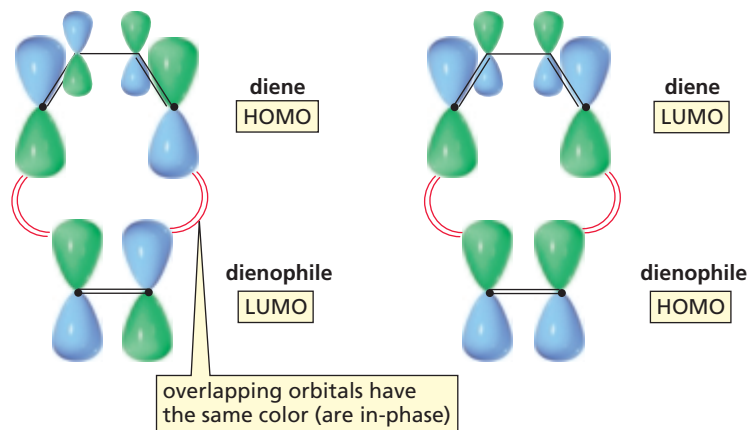
There are two modes of orbital overlap for the simultaneous formation of two σ bonds—*suprafacial* and *antarafacial*. Bond formation is **suprafacial** if both σ bonds form on the same side of the π system. Bond formation is **antarafacial** if the two σ bonds form on opposite sides of the π system. Suprafacial bond formation is similar to syn addition, whereas antarafacial bond formation resembles anti addition (Section 5.19).



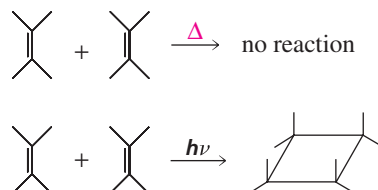
A cycloaddition reaction that forms a four-, five-, or six-membered ring must involve suprafacial bond formation. The geometric constraints of these small rings make the antarafacial approach highly unlikely even if it is symmetry-allowed. (Remember that symmetry-allowed means the overlapping orbitals are in-phase.) Antarafacial bond formation is more likely in cycloaddition reactions that form larger rings.

Frontier orbital analysis of a [4 + 2] cycloaddition reaction shows that overlap of in-phase orbitals to form the two new σ bonds requires suprafacial orbital overlap (Figure 29.5). This is true whether we use the LUMO of the dienophile (a system with one π bond; Figure 29.1) and the HOMO of the diene (a system with two conjugated π bonds; Figure 29.2) or the HOMO of the dienophile and the LUMO of the diene. Now we can understand why Diels–Alder reactions occur with relative ease (Section 8.8).

Figure 29.5 ▶ 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.



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



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.


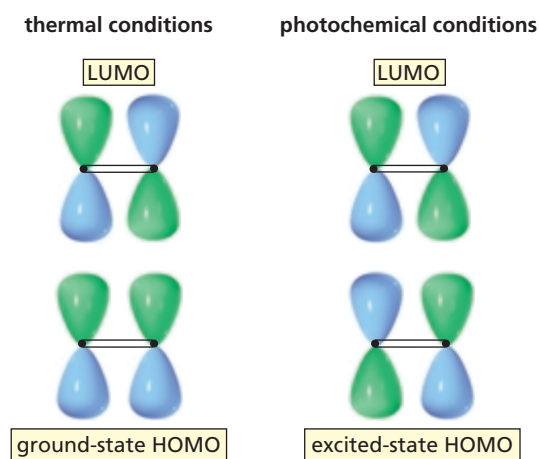
 Tutorial:
Cycloaddition reactions

Figure 29.6 ▶ Frontier molecular orbital analysis of a [2 + 2] cycloaddition reaction under thermal and photochemical conditions.



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 π bonds in the reacting systems of both reagents	Reaction conditions	Allowed mode of ring closure
Even number	Thermal	Antarafacial ^a
	Photochemical	Suprafacial
Odd number	Thermal	Suprafacial
	Photochemical	Antarafacial ^a

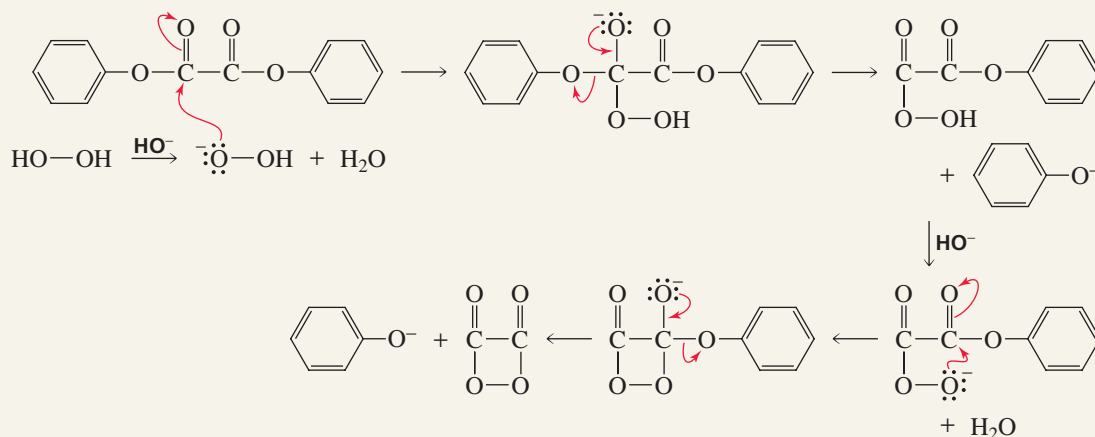
^a Although antarafacial ring closure is symmetry-allowed, it can occur only with large rings.



COLD LIGHT

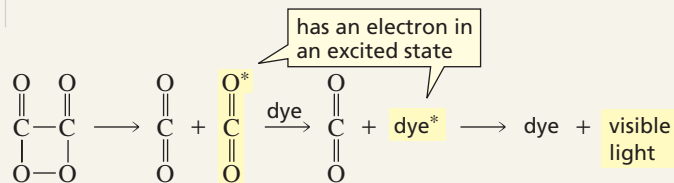
A reverse [2 + 2] cycloaddition reaction is responsible for the cold light given off by light sticks. A light stick contains a thin glass vial that holds a mixture of sodium hydroxide and hydrogen peroxide suspended in a

solution of diphenyloxalate and a dye. When the vial breaks, two nucleophilic acyl substitution reactions occur that form a compound with an unstable four-membered ring. Recall that phenoxide ion is a relatively good leaving group (Section 17.10).



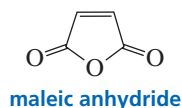
Suprafacial overlap to form a four-membered ring can take place only under photochemical conditions, so one of the reactants must be in an excited state. Therefore, one of the two carbon dioxide molecules formed when the four-membered ring breaks is in an excited state (indicated by an asterisk). When the electron in the excited state drops down to the ground state, a photon of ultraviolet light is released—which is *not* visible to the human eye. However, in the presence of a dye, the excited carbon dioxide molecule can transfer some of its energy to the dye molecule, which causes an electron in the dye to be promoted to an excited state. When the electron of the dye

drops down to the ground state, a photon of visible light is released—which *is* visible to the human eye. In Section 29.6 you will see that a similar reaction is responsible for the light given off by fireflies.



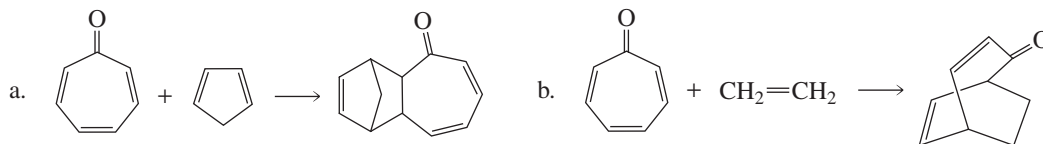
PROBLEM 9

Explain why maleic anhydride reacts rapidly with 1,3-butadiene but does not react at all with ethene under thermal conditions.



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 π electrons in one reaction and four π electrons in the other?



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

**PROBLEM 11**

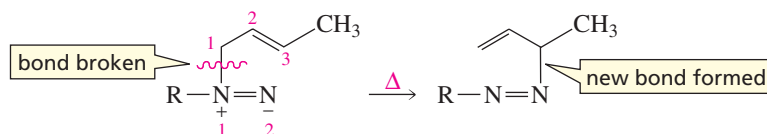
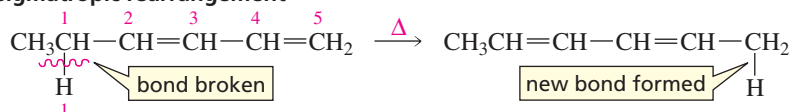
Will a concerted reaction take place between 1,3-butadiene and 2-cyclohexenone in the presence of ultraviolet light?

29.5 Sigmatropic Rearrangements

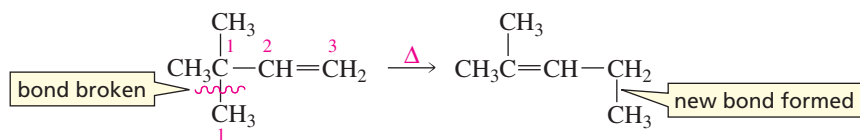
The last class of concerted pericyclic reactions that we will consider is the group of reactions known as *sigmatropic rearrangements*. In a **sigmatropic rearrangement**, a σ bond in the reactant is broken, a new σ bond is formed, and the π electrons rearrange. The σ bond that breaks is a bond to an allylic carbon. It can be a σ bond between a carbon and a hydrogen, between a carbon and another carbon, or between a carbon and an oxygen, nitrogen, or sulfur. “Sigmatropic” comes from the Greek word *tropos*, which means “change,” so sigmatropic means “sigma-change.”

AU: OK as changed?

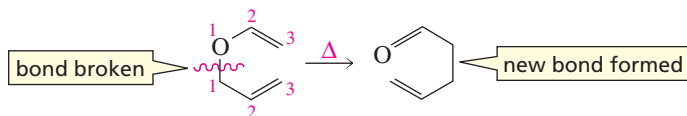
The numbering system used to describe a sigmatropic rearrangement differs from any numbering system you have seen previously. First, mentally break the σ bond in the reactant and give a **number 1** label to the atoms that were attached by the bond. Then look at the new σ bond in the product. Count the number of atoms in each of the fragments that connect the broken σ bond and the new σ bond. The two numbers are put in brackets with the smaller number stated first. For example, in the following [2,3] sigmatropic rearrangement, two atoms (N, N) connect the old and new σ bonds in one fragment and three atoms (C, C, C) connect the old and new σ bonds in the other fragment.

a [2,3] sigmatropic rearrangement**a [1,5] sigmatropic rearrangement**

a [1,3] sigmatropic rearrangement

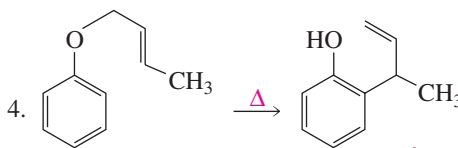
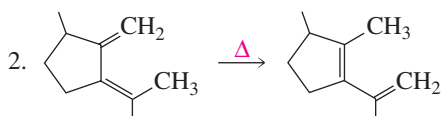
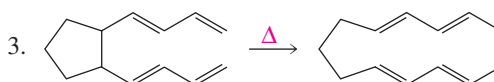
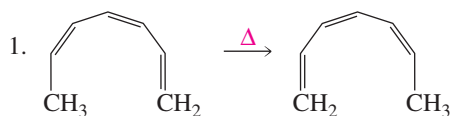


a [3,3] sigmatropic rearrangement

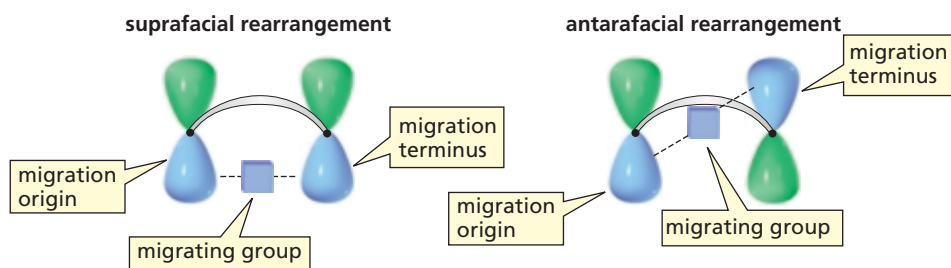


PROBLEM 12

- 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.



In the transition state of a sigmatropic rearrangement, the group that migrates is partially bonded to the migration origin and partially bonded to the migration terminus. There are two possible modes for rearrangement. If the migrating group remains on the same face of the π system, the rearrangement is **suprafacial**. If the migrating group moves to the opposite face of the π system, the rearrangement is **antarafacial**.



Sigmatropic rearrangements have cyclic transition states. If the transition state has six or fewer atoms in the ring, rearrangement must be suprafacial because of the geometric constraints of small rings.

A [1,3] sigmatropic rearrangement involves a π bond and a pair of σ electrons, or we can say that it involves two pairs of electrons. A [1,5] sigmatropic rearrangement involves two π bonds and a pair of σ electrons (three pairs of electrons), and a [1,7] sigmatropic rearrangement involves four pairs of electrons. The symmetry rules for sigmatropic rearrangements are nearly the same as those for cycloaddition reactions—the only difference is that we count the number of pairs of electrons rather than the number of π bonds? (Compare Tables 29.3 and 29.4.) Recall that 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.

Table 29.4 Woodward–Hoffmann Rules for Sigmatropic Rearrangements

Number of pairs of electrons in the reacting system	Reaction conditions	Allowed mode of ring closure
Even number	Thermal	Antarafacial ^a
	Photochemical	Suprafacial
Odd number	Thermal	Suprafacial
	Photochemical	Antarafacial ^a

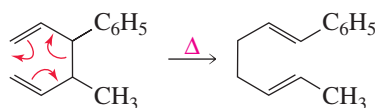
^a Although antarafacial ring closure is symmetry-allowed, it can occur only with large rings.



Tutorial:
Sigmatropic rearrangements

A **Cope² rearrangement** is a [3,3] sigmatropic rearrangement of a 1,5-diene. A **Claisen³ rearrangement** is a [3,3] sigmatropic rearrangement of an allyl vinyl ether. Both rearrangements form six-membered-ring transition states. The reactions, therefore, must be able to take place by a suprafacial pathway. Whether or not a suprafacial pathway is symmetry-allowed depends on the number of pairs of electrons involved in the rearrangement (Table 29.4). Because [3,3] sigmatropic rearrangements involve three pairs of electrons, they occur by a suprafacial pathway under thermal conditions. Therefore, both Cope and Claisen rearrangements readily take place under thermal conditions.

a Cope rearrangement

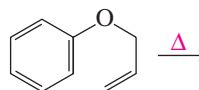


a Claisen rearrangement



PROBLEM 13♦

- a. Give the product of the following reaction:

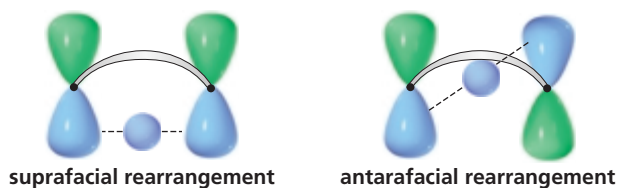


- b. If the terminal sp^2 carbon of the substituent bonded to the benzene ring is labeled with ^{14}C , where will the label be in the product?

Migration of Hydrogen

When a hydrogen migrates in a sigmatropic rearrangement, the s orbital of hydrogen is partially bonded to both the migration origin and the migration terminus in the transition state. Therefore, a [1,3] sigmatropic migration of hydrogen involves a four-membered-ring transition state. Because two pairs of electrons are involved, the HOMO is asymmetric. The selection rules, therefore, require an antarafacial rearrangement for a 1,3-hydrogen shift under thermal conditions (Table 29.4). Consequently, 1,3-hydrogen shifts do not occur under thermal conditions because the four-membered-ring transition state does not allow the required antarafacial rearrangement.

migration of hydrogen

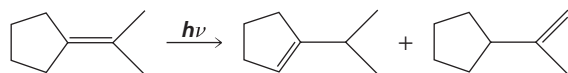


²Cope also discovered the Cope elimination (p. 000).

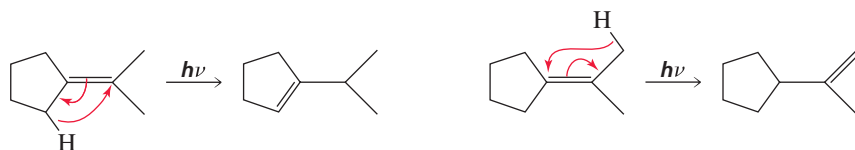
³Claisen also discovered the Claisen condensation (p. 000).

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).

1,3-hydrogen shifts

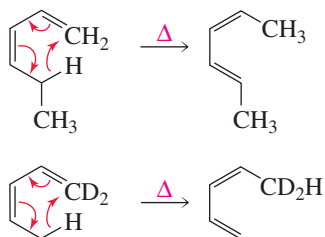


Two products are obtained in the previous reaction because two different allylic hydrogens can undergo a 1,3-hydrogen shift.



[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

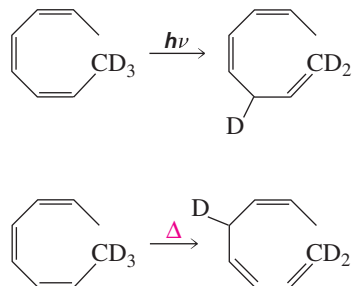


PROBLEM 14

Why was a deuterated compound used in the preceding example?

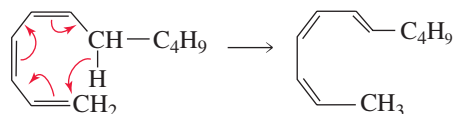
PROBLEM 15

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



[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.

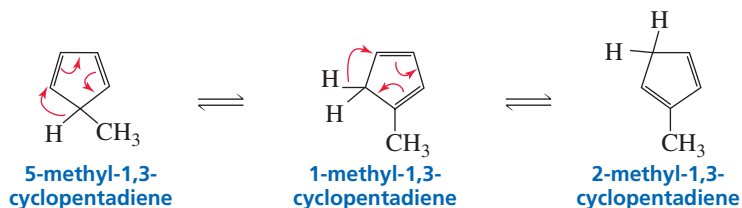
1,7-hydrogen shift



PROBLEM 16 SOLVED

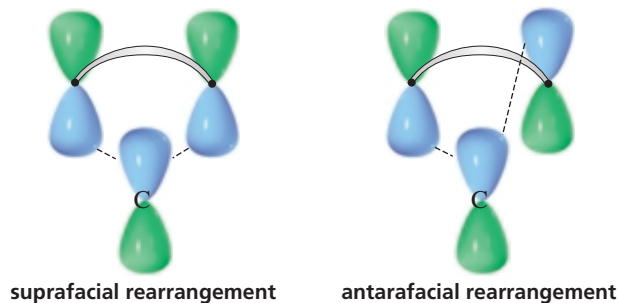
5-Methyl-1,3-cyclopentadiene rearranges to give a mixture of 5-methyl-1,3-cyclopentadiene, 1-methyl-1,3-cyclopentadiene, and 2-methyl-1,3-cyclopentadiene. Show how these products are formed.

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 π electron system.

**Migration of Carbon**

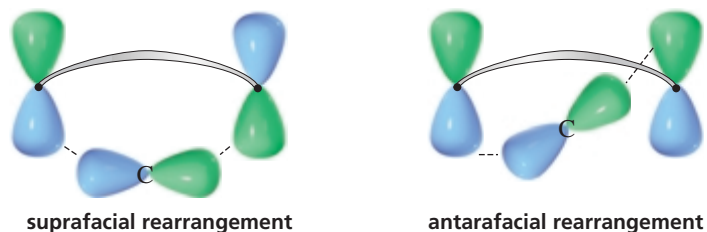
Unlike hydrogen, which can migrate in only one way because of its spherical s orbital, carbon has two ways to migrate because it has a two-lobed p orbital. Carbon can simultaneously interact with the migration origin and the migration terminus using one of its lobes.

carbon migrating with one of its lobes interacting



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

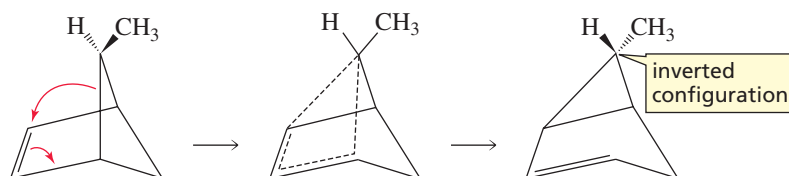
carbon migrating with both of its lobes interacting



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.

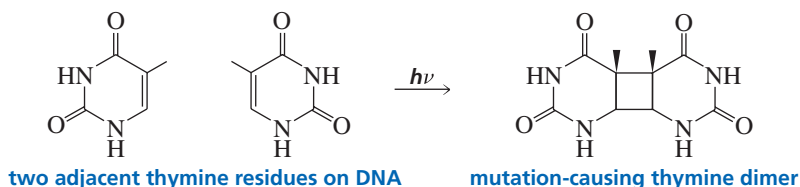
PROBLEM 18♦

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

29.6 Pericyclic Reactions in Biological Systems

Biological Cycloaddition Reactions

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 (Section 9.9). One cause of skin cancer is the formation of *thymine dimers*. At any point in DNA where there are two adjacent thymine residues (Section 27.1), a [2 + 2] cycloaddition reaction can occur, resulting in the formation of a thymine dimer. Because [2 + 2] cycloaddition reactions take place only under photochemical conditions, the reaction takes place only in the presence of ultraviolet light.



3-D Molecules:
Thymine dimer;
DNA photolyase

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.

Fortunately, there are enzymes that repair damaged DNA. When a repair enzyme recognizes a thymine dimer, it reverses the [2 + 2] cycloaddition reaction to regenerate the original T–T sequence. Repair enzymes, however, are not perfect, and some damage always remains uncorrected. People who do not have the repair enzyme (called DNA photolyase) that removes thymine dimers rarely live beyond the age of 20. Fortunately, this genetic defect is rare.

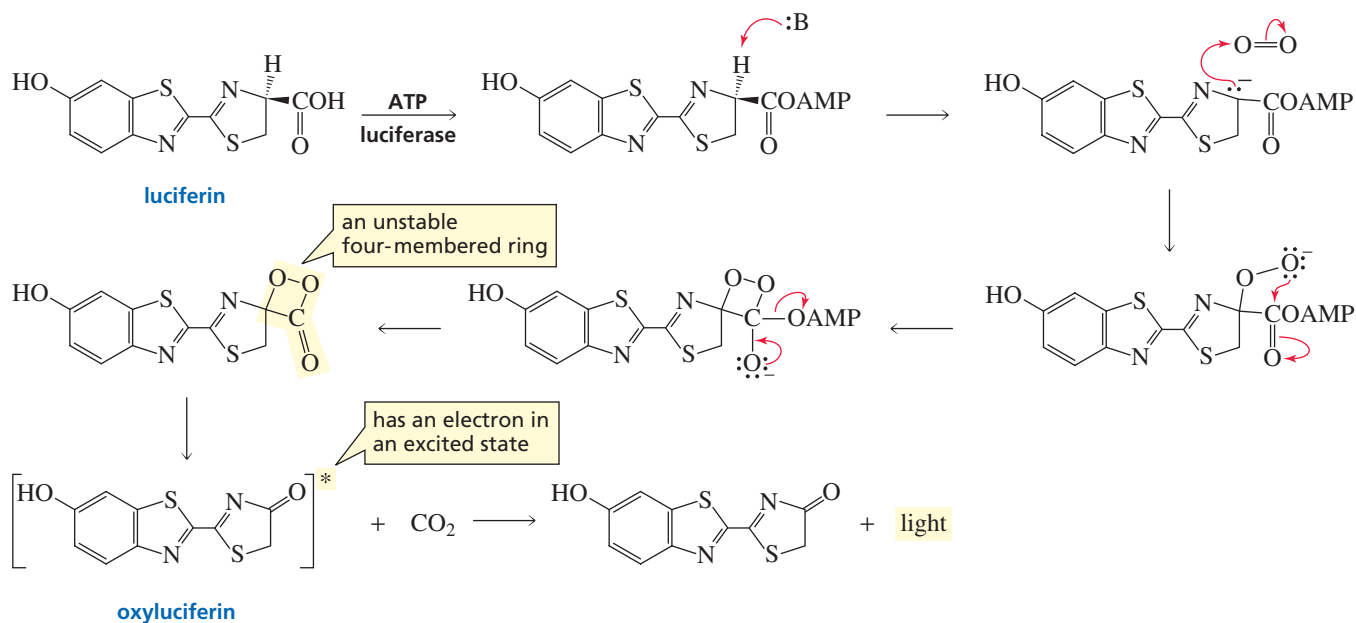
Fireflies are one of several species that emit light as a result of a retro (i.e., reverse) [2 + 2] cycloaddition reaction, similar to the reaction that produces the cold light in light sticks (Section 29.4). Fireflies have an enzyme (luciferase) that catalyzes the reaction between luciferin, ATP, and molecular oxygen that forms a compound with an unstable four-membered ring. When the four-membered ring breaks, an electron in



▲ A firefly with its stomach aglow

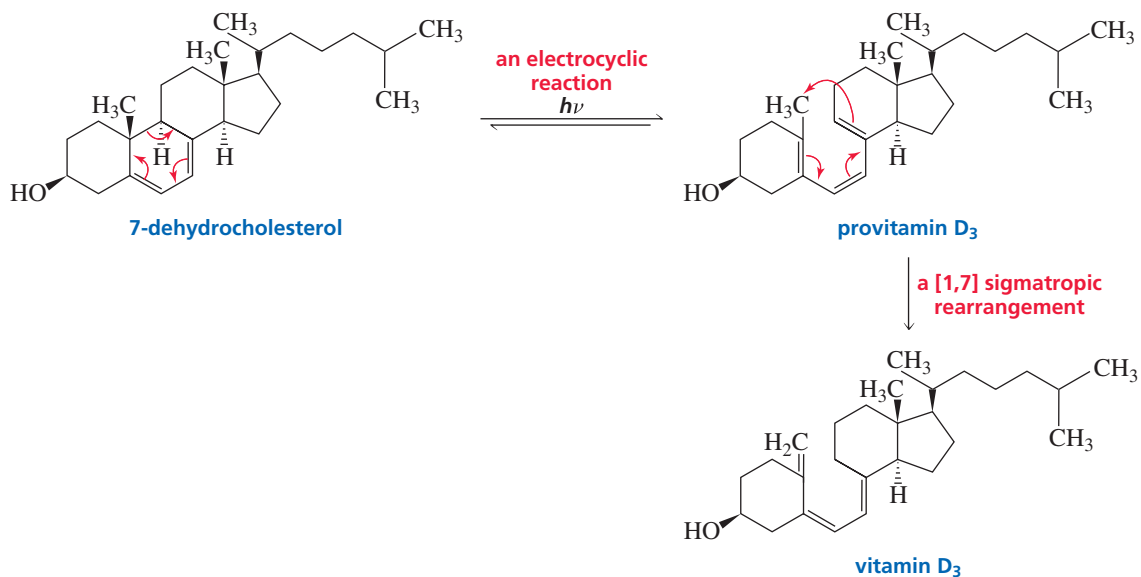
108%

oxyluciferin is promoted to an excited state because suprafacial overlap can occur only under photochemical conditions. When the electron in the excited state drops down to the ground state, a photon of light is released. In this case, the luciferin molecule acts as both the source of the unstable four-membered ring and as the dye molecule that had to be added to the cold-light reaction.



A Biological Reaction Involving an Electrocyclic Reaction and a Sigmatropic Rearrangement

7-Dehydrocholesterol, a steroid found in skin, is converted into vitamin D₃ by two pericyclic reactions. The first is an electrocyclic reaction that opens one of the six-membered rings in the starting material to form provitamin D₃. This reaction occurs under photochemical conditions. The provitamin then undergoes a [1,7] sigmatropic rearrangement to form vitamin D₃. The sigmatropic rearrangement takes place under thermal conditions and is slower than the electrocyclic reaction, so vitamin D₃ continues to be synthesized for several days after exposure to sunlight. Vitamin D₃ is not the active form of the vitamin. The active form requires two successive hydroxylations of vitamin D₃—the first occurs in the liver and the second in the kidneys.



A deficiency in vitamin D, which can be prevented by getting enough sun, causes a disease known as rickets. Rickets is characterized by deformed bones and stunted growth. Too much vitamin D is also harmful because it causes the calcification of soft tissues. It is thought that skin pigmentation evolved to protect the skin from the sun's ultraviolet rays in order to prevent the synthesis of too much vitamin D₃. This agrees with the observation that peoples who are indigenous to countries close to the equator have greater skin pigmentation.

PROBLEM 19♦

Does the [1,7] sigmatropic rearrangement that converts provitamin D₃ to vitamin D₃ involve suprafacial or antarafacial rearrangement?

PROBLEM 20

Explain why photochemical ring closure of provitamin D₃ to form 7-dehydrocholesterol results in the hydrogen and methyl substituents being trans to one another.

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** (**T**hermal/**E**ven) describes the reaction, the outcome *is given* by **AC** (**A**ntarafacial or **C**onrotatory).
- If one of the letters of **TE** is incorrect (it is not **T**hermal/**E**ven but is **T**hermal/**O**dd or **P**hotochemical/**E**ven), the outcome *is not given* by **AC** (the outcome is **S**uprafacial or **D**isrotatory).
- If both of the letters of **TE** are incorrect (**P**hotochemical/**O**dd), the outcome *is given* by **AC** (**A**ntarafacial or **C**onrotatory)—“two negatives make a positive.”

Summary

A **pericyclic reaction** occurs when the electrons in the reactant(s) are reorganized in a cyclic manner. Pericyclic reactions are concerted, highly stereoselective reactions that are generally not affected by catalysts or by a change in solvent. The three most common types of pericyclic reactions are *electrocyclic reactions*, *cycloaddition reactions*, and *sigmatropic rearrangements*. The configuration of the product of a pericyclic reaction depends on the configuration of the reactant, the number of conjugated double bonds or pairs of electrons in the reacting system, and whether the reaction is **thermal** or **photochemical**. The outcome of pericyclic reactions is given by a set of **selection rules**, which can be summarized by **TE-AC**.

The two lobes of a *p* orbital have opposite phases. When two in-phase atomic orbitals interact, a covalent bond is formed; two out-of-phase orbitals interact to create a node. The conservation of orbital symmetry theory states that in-

phase orbitals overlap during the course of a pericyclic reaction; a **symmetry-allowed pathway** is one in which in-phase orbitals overlap. If the *p* orbitals at the ends of the molecular orbital are in-phase, the molecular orbital is **symmetric**. If the two end *p* orbitals are out-of-phase, the molecular orbital is **asymmetric**.

The ground-state **HOMO** of a compound with an even number of conjugated double bonds or an even number of pairs of electrons is **asymmetric**; the ground-state HOMO of a compound with an odd number of conjugated double bonds or an odd number of pairs of electrons is **symmetric**. The **ground-state HOMO** and the **excited-state HOMO** have opposite symmetries.

An **electrocyclic reaction** is an intramolecular reaction in which a new σ (sigma) bond is formed between the ends of a conjugated π (pi) system. To form this new σ bond, *p* orbitals at the ends of the conjugated system rotate so they

can engage in in-phase overlap. If both orbitals rotate in the same direction, ring closure is **conrotatory**; if they rotate in opposite directions, it is **disrotatory**. If the HOMO is asymmetric, conrotatory ring closure occurs: if it is symmetric, disrotatory ring closure occurs.

In a **cycloaddition reaction** two different π bond-containing molecules react to form a cyclic compound by rearranging the π electrons and forming two new σ bonds. Because a cycloaddition reaction involves two molecules, the HOMO of one molecule and the **LUMO** of the other must be considered. Bond formation is **suprafacial** if both

σ bonds form on the same side of the π system; it is **antarafacial** if the two σ bonds form on opposite sides of the π system. Formation of small rings occurs only by suprafacial overlap.

In a **sigmatropic rearrangement**, a σ bond is broken in the reactant, a new σ bond is formed in the product, and the π bonds rearrange. If the migrating group remains on the same face of the π system, the rearrangement is **suprafacial**; if it moves to the opposite face of the π system, it is **antarafacial**.

Key Terms

Author: circled words are not boldface in text. Fix there, or delete here?

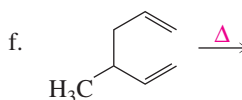
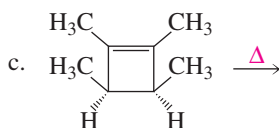
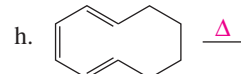
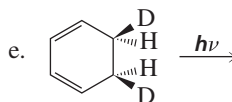
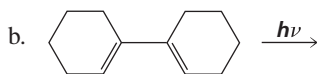
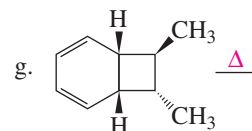
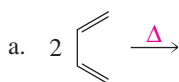
antarafacial **bond formation** (p. 115)
 antarafacial **rearrangement** (p. 119)
 antibonding π^* molecular orbital etc. (p. 105)
 asymmetric molecular orbital (p. 106)
 bonding π molecular orbital (p. 105)
 Claisen rearrangement (p. 120)
 conrotatory **ring closure** (p. 110)
 conservation of orbital symmetry theory (p. 103)
 Cope rearrangement (p. 120)
 cycloaddition reaction (p. 102)
 disrotatory **ring closure** (p. 110)

electrocyclic reaction (p. 101)
 excited state (p. 106)
 frontier orbital analysis (p. 116)
 frontier orbitals (p. 107)
 frontier orbital theory (p. 107)
 ground state (p. 106)
 highest occupied molecular orbital (HOMO) (p. 107)
 linear combination of atomic orbitals (LCAO) (p. 104)
 lowest unoccupied molecular orbital (LUMO) (p. 107)
 molecular orbital (MO) theory (p. 104)

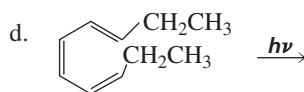
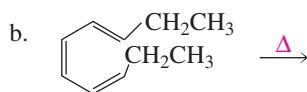
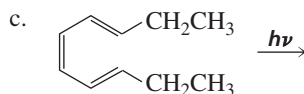
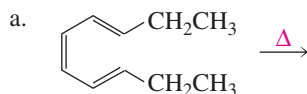
pericyclic reaction (p. 101)
 photochemical reaction (p. 103)
 polar reaction (p. 101)
 radical reaction (p. 101)
 selection rules (p. 112)
 sigmatropic rearrangement (p. 102)
 suprafacial **bond formation** (p. 115)
 suprafacial **rearrangement** (p. 119)
 symmetric molecular orbital (p. 106)
 symmetry-allowed pathway (p. 111)
 symmetry-forbidden pathway (p. 111)
 thermal reaction (p. 103)
 Woodward–Hoffmann rules (p. 112)

Problems

21. Give the product of each of the following reactions:



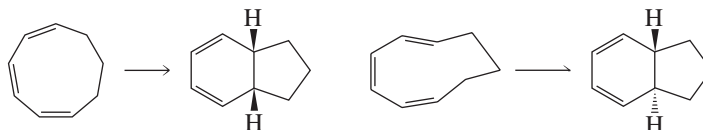
22. Give the product of each of the following reactions:



23. Chorismate mutase is an enzyme that promotes a pericyclic reaction by forcing the substrate to assume the conformation needed for the reaction. The product of the pericyclic reaction is prephenate, which is subsequently converted into the amino acids phenylalanine and tyrosine. What kind of a pericyclic reaction does chorismate mutase catalyze?



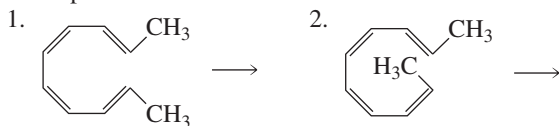
24. Account for the difference in the products of the following reactions:



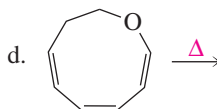
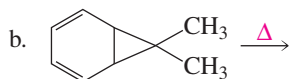
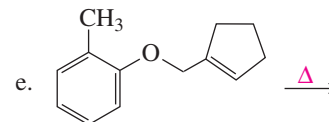
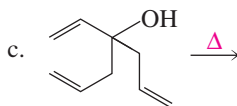
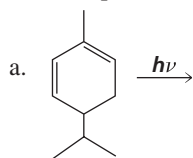
25. Show how norbornane could be prepared from cyclopentadiene.



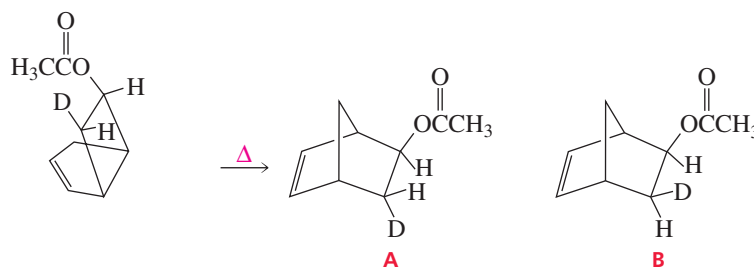
26. Give the product formed when each of the following compounds undergoes an electrocyclic reaction
- under thermal conditions
 - under photochemical conditions



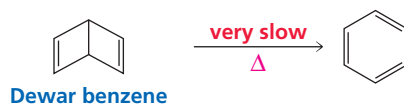
27. Give the product of each of the following reactions:



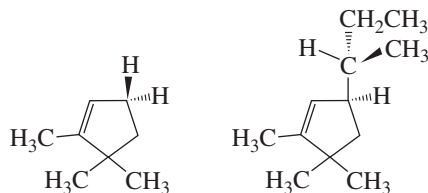
28. Which is the product of the following [1,3] sigmatropic rearrangement, A or B?



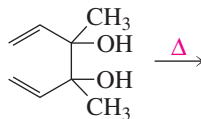
29. Dewar benzene is a highly strained isomer of benzene. In spite of its thermodynamic instability, it is very stable kinetically. It will rearrange to benzene, but only if heated to a very high temperature. Why is it kinetically stable?



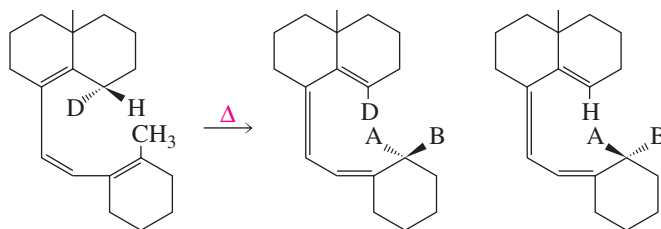
30. If the following compounds are heated, one will form one product from a [1,3] sigmatropic rearrangement and the other will form two products from two different [1,3] sigmatropic rearrangements. Give the products of the reactions.



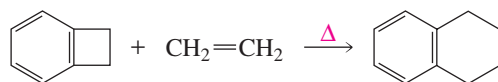
31. When the following compound is heated, a product is formed that shows an infrared absorption band at 1715 cm^{-1} . Draw the structure of the product.



32. Two products are formed in the following [1,7] sigmatropic rearrangement, one due to hydrogen migration and the other to deuterium migration. Show the configuration of the products by replacing A and B with the appropriate substituents (H or D).

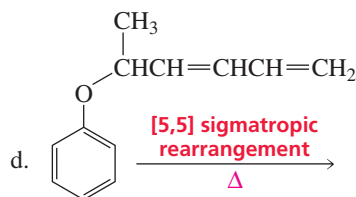
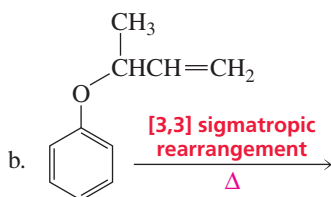
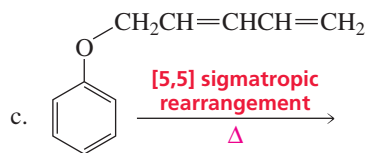
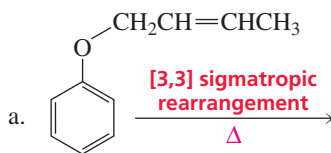


33. a. Propose a mechanism for the following reaction. (*Hint*: An electrocyclic reaction is followed by a Diels–Alder reaction.)
b. What would be the reaction product if *trans*-2-butene were used instead of ethene?

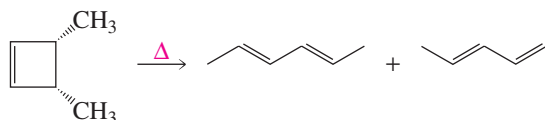


34. Explain why two different products are formed from disrotatory ring closure of (2*E*,4*Z*,6*Z*)-octatriene, but only one product is formed from disrotatory ring closure of (2*E*,4*Z*,6*E*)-octatriene.

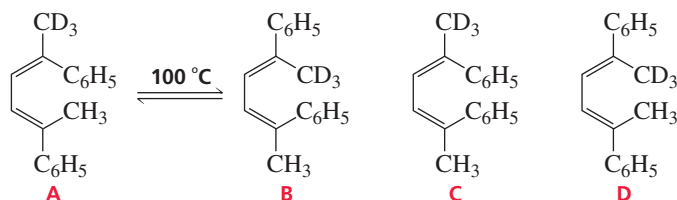
35. Give the product of each of the following sigmatropic rearrangements:



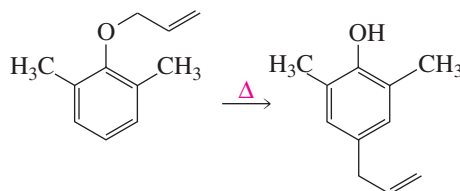
36. *cis*-3,4-Dimethylcyclobutene undergoes thermal ring opening to form the two products shown. One of the products is formed in 99% yield, the other in 1% yield. Which is which?



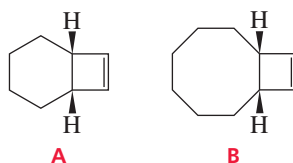
37. If isomer A is heated to about 100 °C, a mixture of isomers A and B is formed. Explain why there is no trace of isomer C or D.



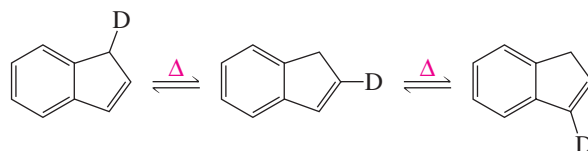
38. Propose a mechanism for the following reaction:



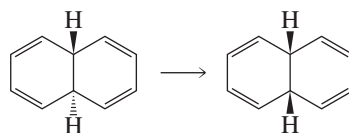
39. Compound A will not undergo a ring-opening reaction under thermal conditions, but compound B will. Explain.



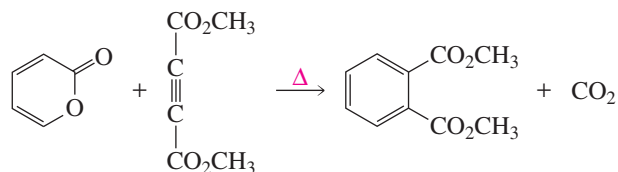
40. Professor Perry C. Click found that heating any one of the following isomers resulted in scrambling of the deuterium to all three positions on the five-membered ring. Propose a mechanism to account for this observation.



41. How could the following transformation be carried out, using only heat or light?



42. Show the steps involved in the following reaction:



43. Propose a mechanism for the following reaction:

