

14

Conjugated Compounds and Ultraviolet Spectroscopy

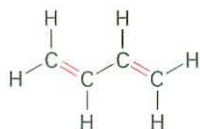
Organic KNOWLEDGE TOOLS

ThomsonNOW Throughout this chapter, sign in at www.thomsonedu.com for online self-study and interactive tutorials based on your level of understanding.

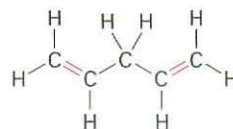


Online homework for this chapter may be assigned in Organic OWL.

The unsaturated compounds we looked at in Chapters 6 and 7 had only one double bond, but many compounds have numerous sites of unsaturation. If the different unsaturations are well separated in a molecule, they react independently, but if they're close together, they may interact with one another. In particular, compounds that have alternating single and double bonds—so-called **conjugated** compounds—have some distinctive characteristics. The conjugated diene 1,3-butadiene, for instance, has some properties quite different from those of the nonconjugated 1,4-pentadiene.



1,3-Butadiene
(conjugated; alternating
double and single bonds)



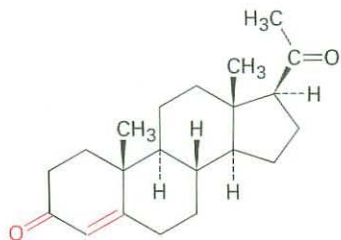
1,4-Pentadiene
(nonconjugated; nonalternating
double and single bonds)

WHY THIS CHAPTER?

Conjugated compounds of many different sorts are common in nature. Many of the pigments responsible for the brilliant colors of fruits and flowers have numerous alternating single and double bonds. Lycopene, for instance, the red pigment found in tomatoes and thought to protect against prostate cancer, is a conjugated *polyene*. Conjugated *enones* (alkene + ketone) are common structural features of many biologically important molecules such as progesterone, the hormone that prepares the uterus for implantation of a fertilized ovum. Cyclic conjugated molecules such as benzene are a major field of study in themselves. In this chapter, we'll look at some of the distinctive properties of conjugated molecules and at the reasons for those properties.



Lycopene, a conjugated polyene

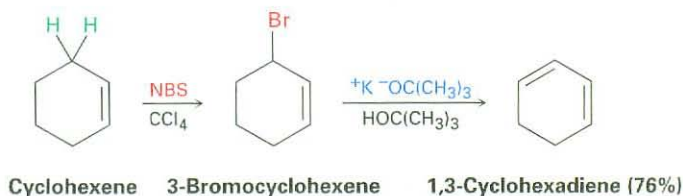


Progesterone, a conjugated enone

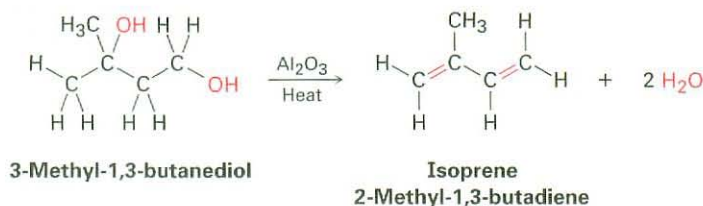
Benzene,
a cyclic conjugated molecule

14.1 Stability of Conjugated Dienes: Molecular Orbital Theory

Conjugated dienes can be prepared by some of the methods previously discussed for preparing alkenes (Sections 11.7–11.10). The base-induced elimination of HX from an allylic halide is one such reaction.

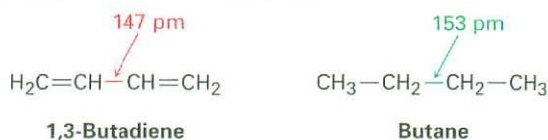


Simple conjugated dienes used in polymer synthesis include 1,3-butadiene, chloroprene (2-chloro-1,3-butadiene), and isoprene (2-methyl-1,3-butadiene). Isoprene has been prepared industrially by several methods, including the acid-catalyzed double dehydration of 3-methyl-1,3-butanediol.



One of the properties that distinguishes conjugated from nonconjugated dienes is the length of the central single bond. The C2–C3 single bond in

1,3-butadiene has a length of 147 pm, some 6 pm shorter than the length of the analogous single bond in butane (153 pm).



Another distinctive property of conjugated dienes is their unusual stability, as evidenced by their heats of hydrogenation (Table 14.1). Recall from Section 6.6 that alkenes with a similar substitution pattern have similar $\Delta H^\circ_{\text{hydrog}}$ values. Monosubstituted alkenes such as 1-butene have $\Delta H^\circ_{\text{hydrog}}$ near -126 kJ/mol (-30.1 kcal/mol), whereas disubstituted alkenes such as 2-methylpropene have $\Delta H^\circ_{\text{hydrog}}$ near -119 kJ/mol (-28.4 kcal/mol), approximately 7 kJ/mol less negative. We concluded from these data that more highly substituted alkenes are more stable than less substituted ones. That is, more highly substituted alkenes release less heat on hydrogenation because they contain less energy to start with. A similar conclusion can be drawn for conjugated dienes.

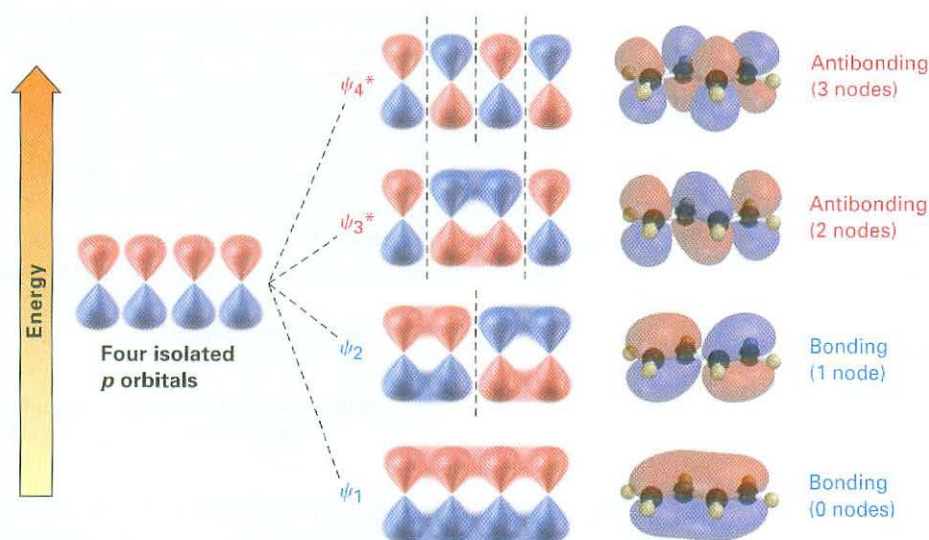
Table 14.1 Heats of Hydrogenation for Some Alkenes and Dienes

Alkene or diene	Product	$\Delta H^\circ_{\text{hydrog}}$	
		(kJ/mol)	(kcal/mol)
$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-126	-30.1
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_3 \end{array}$	-119	-28.4
$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-253	-60.5
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-236	-56.4
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{CH}-\text{C}=\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$	-229	-54.7

Because a monosubstituted alkene has a $\Delta H^\circ_{\text{hydrog}}$ of approximately -126 kJ/mol, we might expect that a compound with two monosubstituted double bonds would have a $\Delta H^\circ_{\text{hydrog}}$ approximately twice that value, or -252 kJ/mol. Nonconjugated dienes, such as 1,4-pentadiene ($\Delta H^\circ_{\text{hydrog}} = -253$ kJ/mol), meet this expectation, but the conjugated diene 1,3-butadiene ($\Delta H^\circ_{\text{hydrog}} = -236$ kJ/mol) does not. 1,3-Butadiene is approximately 16 kJ/mol (3.8 kcal/mol) more stable than expected.

	$\Delta H^\circ_{\text{hydrog}}$ (kJ/mol)	
$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}_2$	$-126 + (-126) = -252$	Expected
1,4-Pentadiene	-253	Observed
	1	Difference
$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$	$-126 + (-126) = -252$	Expected
1,3-Butadiene	-236	Observed
	-16	Difference

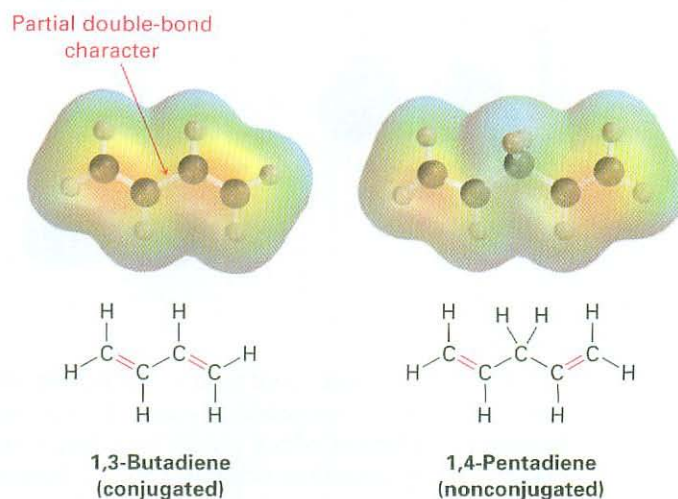
Active Figure 14.2 Four π molecular orbitals in 1,3-butadiene. Note that the number of nodes between nuclei increases as the energy level of the orbital increases. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



antibonding orbitals.) Note that the number of nodes between nuclei increases as the energy level of the orbital increases. The ψ_3^* orbital has two nodes between nuclei, and ψ_4^* , the highest-energy MO, has three nodes between nuclei.

Comparing the π molecular orbitals of 1,3-butadiene (two conjugated double bonds) with those of 1,4-pentadiene (two isolated double bonds) shows why the conjugated diene is more stable. In a conjugated diene, the lowest-energy π MO (ψ_1) has a favorable bonding interaction between C2 and C3 that is absent in a nonconjugated diene. As a result, there is a certain amount of double-bond character to the C2–C3 bond, making that bond both stronger and shorter than a typical single bond. Electrostatic potential maps show clearly the additional electron density in the central bond of 1,3-butadiene, corresponding to partial double-bond character (Figure 14.3).

Figure 14.3 Electrostatic potential maps of 1,3-butadiene (conjugated) and 1,4-pentadiene (nonconjugated) show additional electron density (red) in the central C–C bond of 1,3-butadiene, corresponding to partial double-bond character.



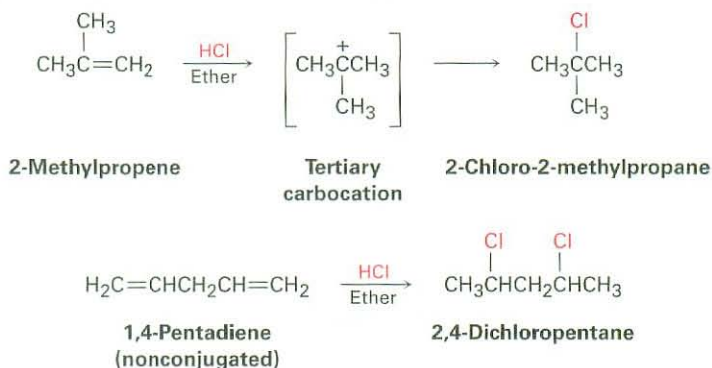
In describing 1,3-butadiene, we say that the π electrons are *spread out*, or *delocalized*, over the entire π framework rather than localized between two

specific nuclei. Electron delocalization and consequent dispersal of charge always lead to lower energy and greater stability.

Problem 14.1 Allene, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, has a heat of hydrogenation of -298 kJ/mol (-71.3 kcal/mol). Rank a conjugated diene, a nonconjugated diene, and an allene in order of stability.

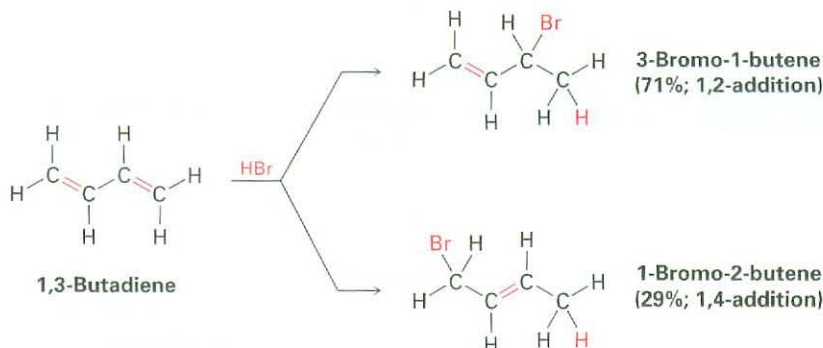
14.2 Electrophilic Additions to Conjugated Dienes: Allylic Carbocations

One of the most striking differences between conjugated dienes and typical alkenes is in their electrophilic addition reactions. To review briefly, the addition of an electrophile to a carbon-carbon double bond is a general reaction of alkenes (Section 6.7). Markovnikov regiochemistry is found because the more stable carbocation is formed as an intermediate. Thus, addition of HCl to 2-methylpropene yields 2-chloro-2-methylpropane rather than 1-chloro-2-methylpropane, and addition of 2 mol equiv of HCl to the nonconjugated diene 1,4-pentadiene yields 2,4-dichloropentane.

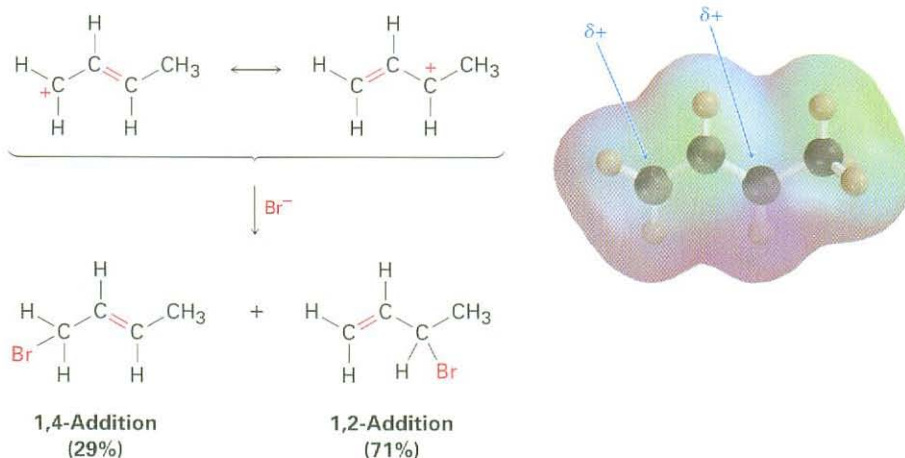


ThomsonNOW Click *Organic Interactive* to use a web-based palette to predict products from electrophilic addition reactions to conjugated dienes.

Conjugated dienes also undergo electrophilic addition reactions readily, but mixtures of products are invariably obtained. Addition of HBr to 1,3-butadiene, for instance, yields a mixture of two products (not counting *cis-trans* isomers). 3-Bromo-1-butene is the typical Markovnikov product of 1,2-addition to a double bond, but 1-bromo-2-butene appears unusual. The double bond in this product has moved to a position between carbons 2 and 3, and HBr has added to carbons 1 and 4, a result described as 1,4-addition.

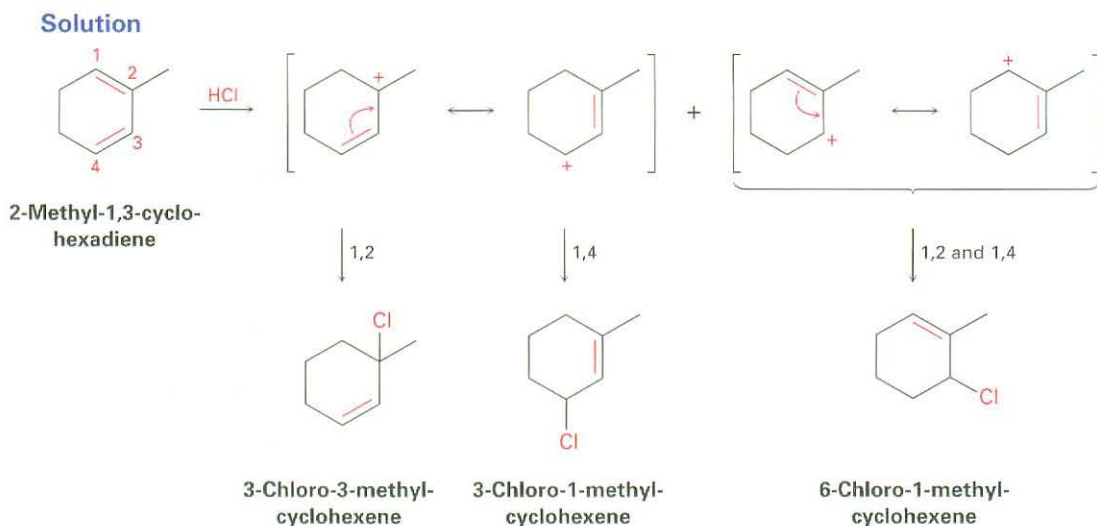


Active Figure 14.4 An electrostatic potential map of the carbocation produced by protonation of 1,3-butadiene shows that the positive charge is shared by carbons 1 and 3. Reaction of Br^- with the more positive carbon (C3; blue) gives predominantly the 1,2-addition product. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



allow each resonance form to react with Cl^- , generating a maximum of four possible products.

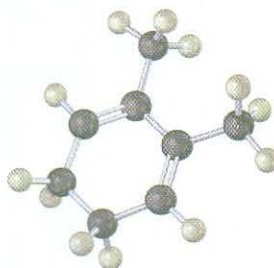
In the present instance, protonation of the C1–C2 double bond gives a carbocation that can react further to give the 1,2 adduct 3-chloro-3-methylcyclohexene and the 1,4 adduct 3-chloro-1-methylcyclohexene. Protonation of the C3–C4 double bond gives a symmetrical carbocation, whose two resonance forms are equivalent. Thus, the 1,2 adduct and the 1,4 adduct have the same structure: 6-chloro-1-methylcyclohexene. Of the two possible modes of protonation, the first is more likely because it yields a tertiary allylic cation rather than a secondary allylic cation.



Problem 14.2 Give the structures of both 1,2 and 1,4 adducts resulting from reaction of 1 equivalent of HCl with 1,3-pentadiene.

Problem 14.3 Look at the possible carbocation intermediates produced during addition of HCl to 1,3-pentadiene (Problem 14.2), and predict which 1,2 adduct predominates. Which 1,4 adduct predominates?

Problem 14.4 Give the structures of both 1,2 and 1,4 adducts resulting from reaction of 1 equivalent of HBr with the following compound:

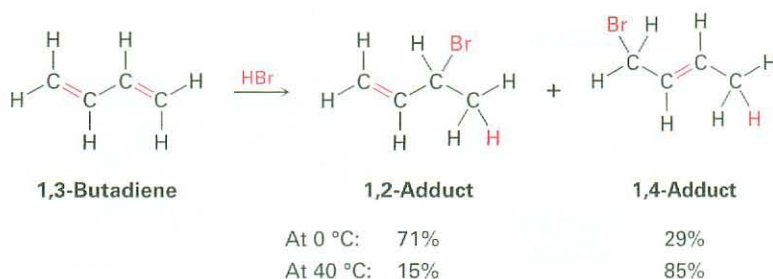


14.3 Kinetic versus Thermodynamic Control of Reactions

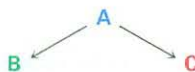
Key IDEAS

Test your knowledge of Key Ideas by using resources in ThomsonNOW or by answering end-of-chapter problems marked with ▲.

Electrophilic addition to a conjugated diene at or below room temperature normally leads to a mixture of products in which the 1,2 adduct predominates over the 1,4 adduct. When the same reaction is carried out at higher temperatures, though, the product ratio often changes and the 1,4 adduct predominates. For example, addition of HBr to 1,3-butadiene at 0 °C yields a 71:29 mixture of 1,2 and 1,4 adducts, but the same reaction carried out at 40 °C yields a 15:85 mixture. Furthermore, when the product mixture formed at 0 °C is heated to 40 °C in the presence of HBr, the ratio of adducts slowly changes from 71:29 to 15:85. Why?



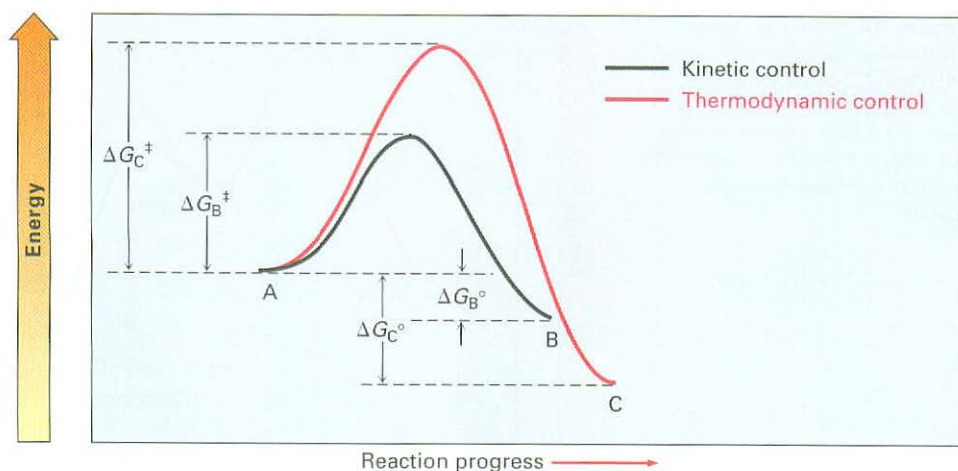
To understand the effect of temperature on product distribution, let's briefly review what we said in Section 5.7 about rates and equilibria. Imagine a reaction that can give either or both of two products, B and C.



Let's assume that B forms faster than C (in other words, $\Delta G^\ddagger_B < \Delta G^\ddagger_C$) but that C is more stable than B (in other words, $\Delta G^\circ_C > \Delta G^\circ_B$). An energy diagram for the two processes might look like that shown in Figure 14.5.

Let's first carry out the reaction at a lower temperature so that both processes are irreversible and no equilibrium is reached. Since B forms faster than C, B is the major product. It doesn't matter that C is more stable than B, because the

Figure 14.5 An energy diagram for two competing reactions in which the less stable product B forms faster than the more stable product C.



two are not in equilibrium. *The product of an irreversible reaction depends only on relative rates, not on product stability.* Such reactions are said to be under **kinetic control**.



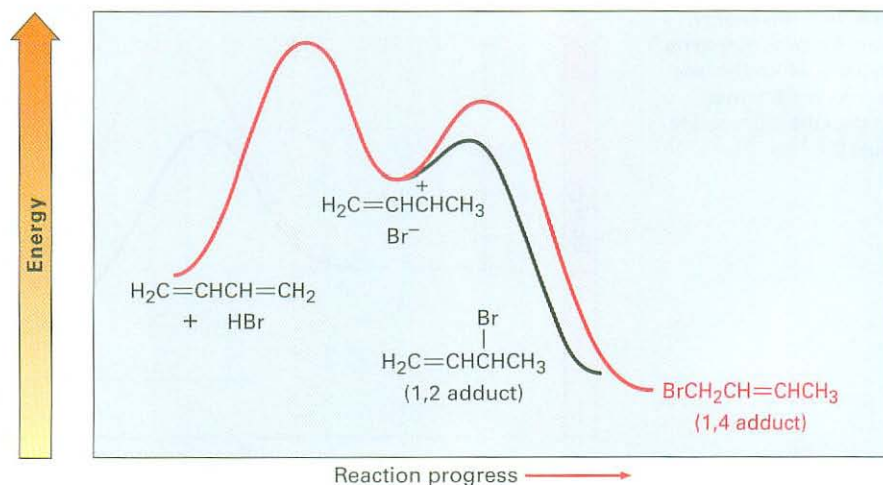
Now let's carry out the same reaction at some higher temperature so that both processes are readily reversible and an equilibrium is reached. Since C is more stable than B, C is the major product obtained. It doesn't matter that C forms more slowly than B, because the two are in equilibrium. *The product of a readily reversible reaction depends only on stability, not on relative rates.* Such reactions are said to be under equilibrium control, or **thermodynamic control**.



We can now explain the effect of temperature on electrophilic addition reactions of conjugated dienes. At low temperature ($0\text{ }^{\circ}\text{C}$), HBr adds to 1,3-butadiene under kinetic control to give a 71:29 mixture of products, with the more rapidly formed 1,2 adduct predominating. Since these mild conditions don't allow the reaction to reach equilibrium, the product that forms faster predominates. At higher temperature ($40\text{ }^{\circ}\text{C}$), however, the reaction occurs under thermodynamic control to give a 15:85 mixture of products, with the more stable 1,4 adduct predominating. The higher temperature allows the addition process to become reversible, and an equilibrium mixture of products therefore results. Figure 14.6 shows the situation in an energy diagram.

The electrophilic addition of HBr to 1,3-butadiene is a good example of how a change in experimental conditions can change the product of a reaction. The concept of thermodynamic control versus kinetic control is a useful one that we can sometimes take advantage of in the laboratory.

Figure 14.6 Energy diagram for the electrophilic addition of HBr to 1,3-butadiene. The 1,2 adduct is the kinetic product because it forms faster, but the 1,4 adduct is the thermodynamic product because it is more stable.

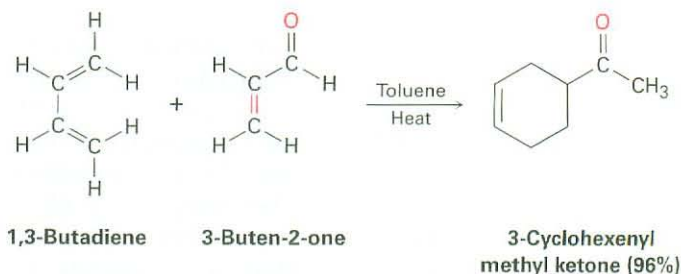


- Problem 14.5** The 1,2 adduct and the 1,4 adduct formed by reaction of HBr with 1,3-butadiene are in equilibrium at 40 °C. Propose a mechanism by which the interconversion of products takes place.
- Problem 14.6** Why do you suppose 1,4 adducts of 1,3-butadiene are generally more stable than 1,2 adducts?

14.4 The Diels–Alder Cycloaddition Reaction

ThomsonNOW Click *Organic Interactive* to use a web-based palette to predict products from cycloaddition reactions.

Perhaps the most striking difference between conjugated and nonconjugated dienes is that conjugated dienes undergo an addition reaction with alkenes to yield substituted cyclohexene products. For example, 1,3-butadiene and 3-buten-2-one give 3-cyclohexenyl methyl ketone.



Otto Paul Hermann Diels

Otto Paul Hermann Diels (1876–1954) was born in Hamburg, Germany, and received his Ph.D. at the University of Berlin working with Emil Fischer. He was professor of chemistry both at the University of Berlin (1906–1916) and at Kiel (1916–1948). His most important discovery was the Diels–Alder reaction, which he developed with one of his research students and for which he received the 1950 Nobel Prize in chemistry.

This process, named the **Diels–Alder cycloaddition reaction** after its discoverers, is extremely useful in organic synthesis because it forms two carbon–carbon bonds in a single step and is one of the few general methods available for making cyclic molecules. (As the name implies, a *cycloaddition* reaction is one in which two reactants add together to give a cyclic product.) The

Kurt Alder

Kurt Alder (1902–1958) was born in Königshütte, Prussia, and moved to Germany after World War I. He received his Ph.D. in 1926 at Kiel working with Otto Diels. He worked first at I. G. Farben on the manufacture of plastics but then became professor at the University of Cologne (1940–1958). He shared the 1950 Nobel Prize in chemistry with his mentor, Otto Diels.

1950 Nobel Prize in chemistry was awarded to Diels and Alder in recognition of the importance of their discovery.

The mechanism of the Diels–Alder cycloaddition is different from that of other reactions we've studied because it is neither polar nor radical. Rather, the Diels–Alder reaction is a *pericyclic* process. Pericyclic reactions, which we'll discuss in more detail in Chapter 30, take place in a single step by a cyclic redistribution of bonding electrons. The two reactants simply join together through a cyclic transition state in which the two new carbon–carbon bonds form at the same time.

We can picture a Diels–Alder addition as occurring by head-on (σ) overlap of the two alkene p orbitals with the two p orbitals on carbons 1 and 4 of the diene (Figure 14.7). This is, of course, a *cyclic* orientation of the reactants.

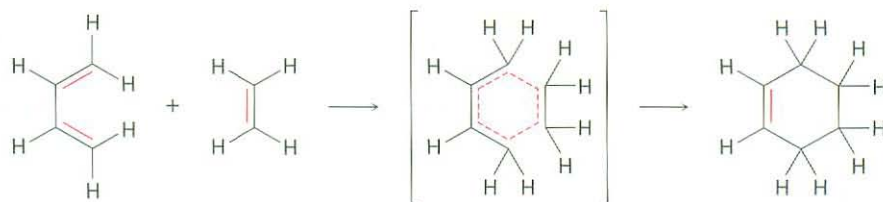
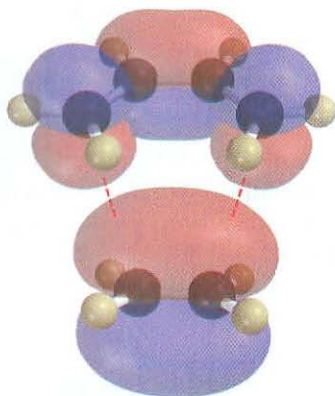


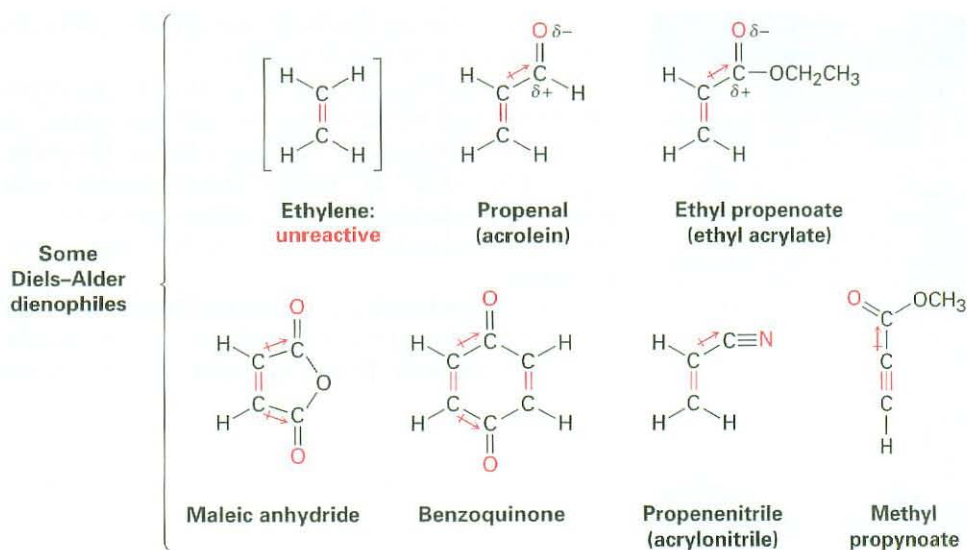
Figure 14.7 Mechanism of the Diels–Alder cycloaddition reaction. The reaction occurs in a single step through a cyclic transition state in which the two new carbon–carbon bonds form simultaneously.

In the Diels–Alder transition state, the two alkene carbons and carbons 1 and 4 of the diene rehybridize from sp^2 to sp^3 to form two new single bonds, while carbons 2 and 3 of the diene remain sp^2 -hybridized to form the new double bond in the cyclohexene product. We'll study this mechanism at greater length in Chapter 30 but will concentrate for the present on learning more about the characteristics and uses of the Diels–Alder reaction.

14.5 Characteristics of the Diels–Alder Reaction

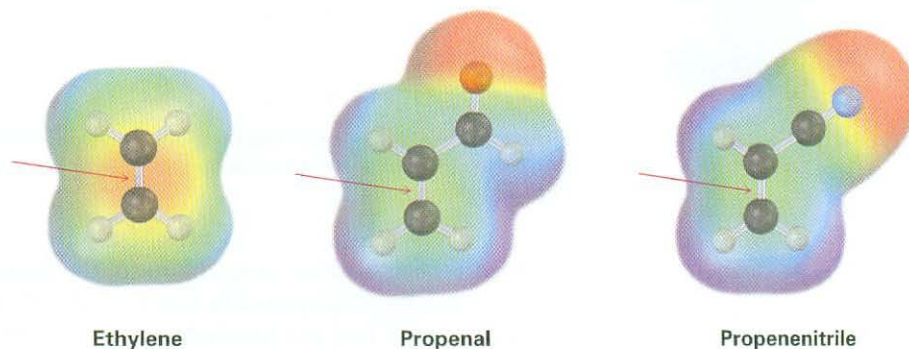
The Dienophile

The Diels–Alder cycloaddition reaction occurs most rapidly if the alkene component, or **dienophile** (“diene lover”), has an electron-withdrawing substituent group. Thus, ethylene itself reacts sluggishly, but propenal, ethyl propenoate, maleic anhydride, benzoquinone, propenenitrile, and similar compounds are highly reactive. Note also that alkynes, such as methyl propynoate, can act as Diels–Alder dienophiles.

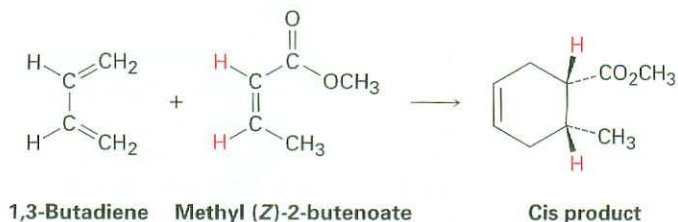


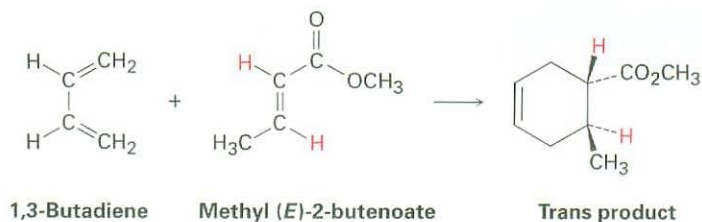
In all the preceding cases, the double or triple bond of the dienophile is next to the positively polarized carbon of an electron-withdrawing substituent. Electrostatic potential maps show that the double-bond carbons are less negative in these substances than in ethylene (Figure 14.8).

Figure 14.8 Electrostatic potential maps of ethylene, propenal, and propenenitrile show that electron-withdrawing groups make the double-bond carbons less negative.

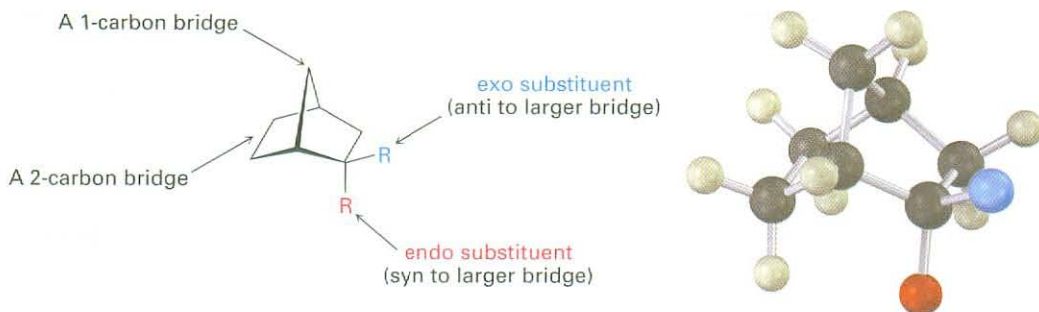


One of the most useful features of the Diels–Alder reaction is that it is *stereospecific*, meaning that a single product stereoisomer is formed. Furthermore, the stereochemistry of the reactant is maintained. If we carry out the cycloaddition with a *cis* dienophile, such as methyl *cis*-2-butenoate, only the *cis*-substituted cyclohexene product is formed. With methyl *trans*-2-butenoate, only the *trans*-substituted cyclohexene product is formed.

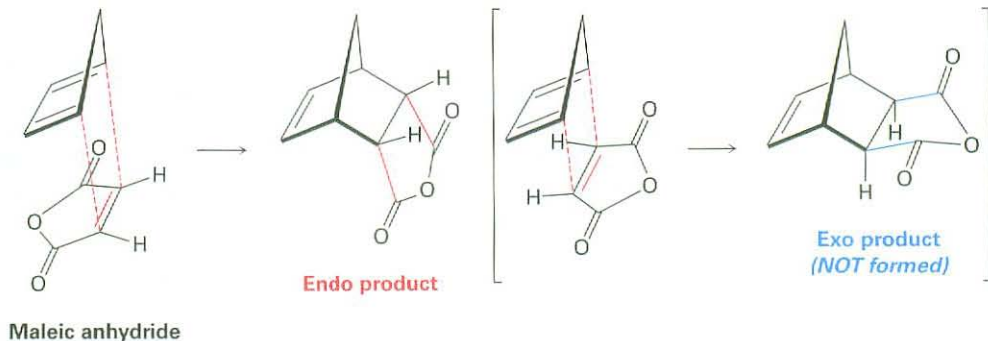




Another stereochemical feature of the Diels–Alder reaction is that the diene and dienophile partners orient so that the *endo* product, rather than the alternative *exo* product, is formed. The words *endo* and *exo* are used to indicate relative stereochemistry when referring to bicyclic structures like substituted norbornanes (Section 4.9). A substituent on one bridge is said to be *exo* if it is *anti* (trans) to the larger of the other two bridges and is said to be *endo* if it is *syn* (cis) to the larger of the other two bridges.



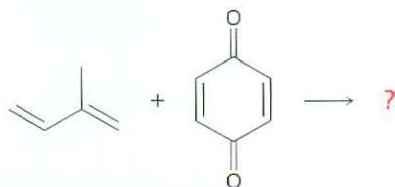
Endo products result from Diels–Alder reactions because the amount of orbital overlap between diene and dienophile is greater when the reactants lie directly on top of one another so that the electron-withdrawing substituent on the dienophile is underneath the diene. In the reaction of 1,3-cyclopentadiene with maleic anhydride, for instance, the following result is obtained:



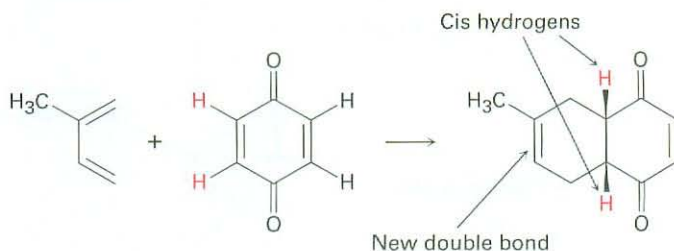
WORKED EXAMPLE 14.2

Predicting the Product of a Diels–Alder Reaction

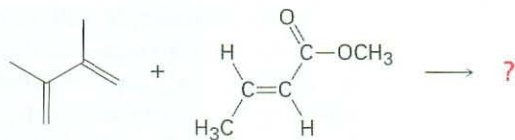
Predict the product of the following Diels–Alder reaction:

**Strategy**

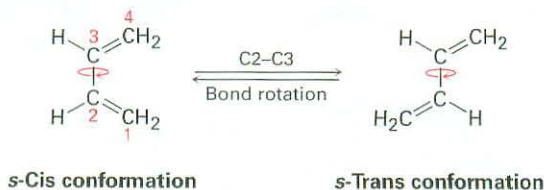
Draw the diene so that the ends of the two double bonds are near the dienophile double bond. Then form two single bonds between the partners, convert the three double bonds into single bonds, and convert the former single bond of the diene into a double bond. Because the dienophile double bond is *cis* to begin with, the two attached hydrogens must remain *cis* in the product.

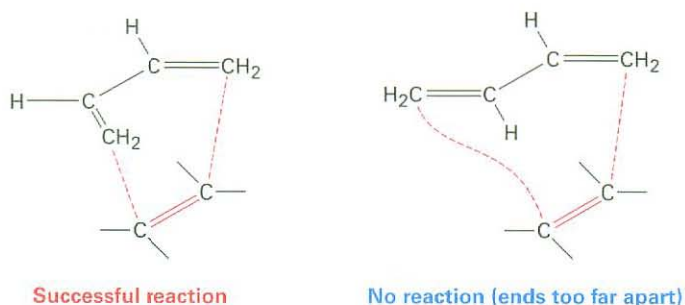
Solution**Problem 14.7**

Predict the product of the following Diels–Alder reaction:

**The Diene**

The diene must adopt what is called an *s-cis conformation*, meaning “cis-like” about the single bond, to undergo a Diels–Alder reaction. Only in the *s-cis* conformation are carbons 1 and 4 of the diene close enough to react through a cyclic transition state. In the alternative *s-trans* conformation, the ends of the diene partner are too far apart to overlap with the dienophile *p* orbitals.



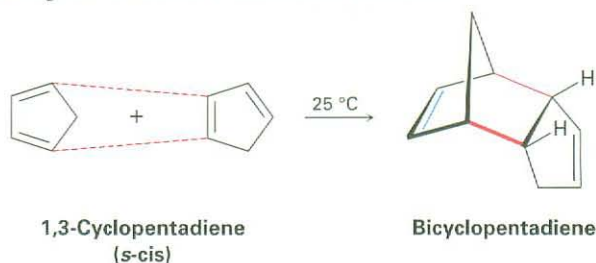


Two examples of dienes that can't adopt an *s-cis* conformation, and thus don't undergo Diels–Alder reactions, are shown in Figure 14.9. In the bicyclic diene, the double bonds are rigidly fixed in an *s-trans* arrangement by geometric constraints of the rings. In (2*Z*,4*Z*)-hexadiene, steric strain between the two methyl groups prevents the molecule from adopting *s-cis* geometry.

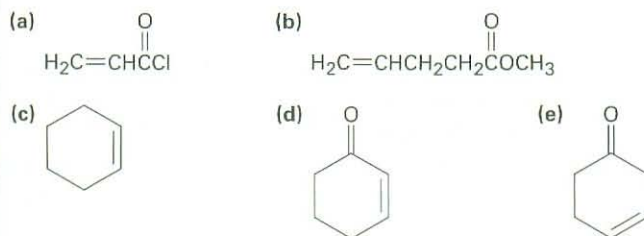
Figure 14.9 Two dienes that can't achieve an *s-cis* conformation and thus can't undergo Diels–Alder reactions.



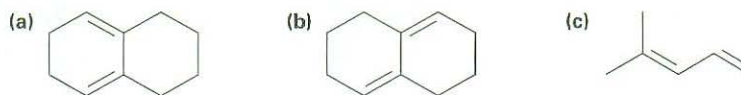
In contrast to those unreactive dienes that can't achieve an *s-cis* conformation, other dienes are fixed only in the correct *s-cis* geometry and are therefore highly reactive in the Diels–Alder cycloaddition reaction. 1,3-Cyclopentadiene, for example, is so reactive that it reacts with itself. At room temperature, 1,3-cyclopentadiene *dimerizes*. One molecule acts as diene and a second molecule acts as dienophile in a self Diels–Alder reaction.



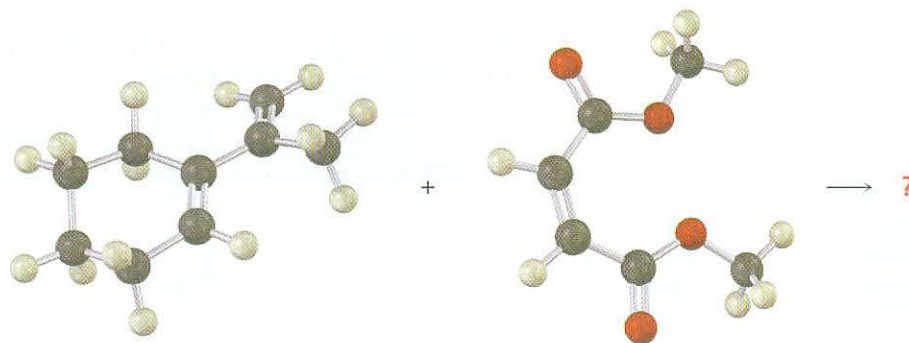
Problem 14.8 Which of the following alkenes would you expect to be good Diels–Alder dienophiles?



Problem 14.9 Which of the following dienes have an *s*-cis conformation, and which have an *s*-trans conformation? Of the *s*-trans dienes, which can readily rotate to *s*-cis?

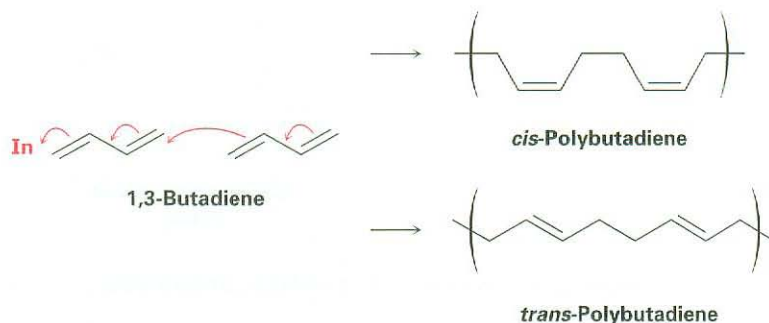


Problem 14.10 Predict the product of the following Diels–Alder reaction:

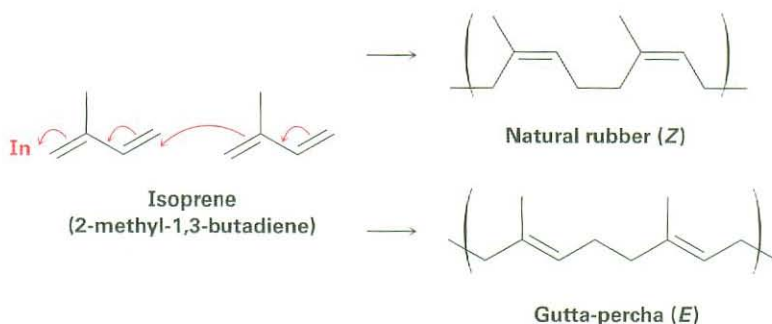


14.6 Diene Polymers: Natural and Synthetic Rubbers

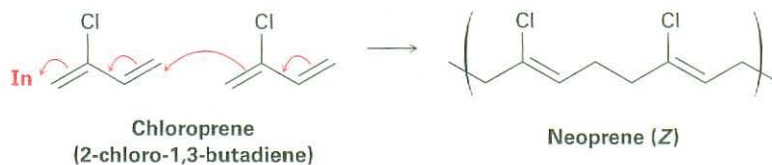
Conjugated dienes can be polymerized just as simple alkenes can (Section 7.10). Diene polymers are structurally more complex than simple alkene polymers, though, because double bonds remain every four carbon atoms along the chain, leading to the possibility of *cis*–*trans* isomers. The initiator (In) for the reaction can be either a radical, as occurs in ethylene polymerization, or an acid. Note that the polymerization is a 1,4-addition of the growing chain to a conjugated diene monomer.



As noted in the Chapter 7 *Focus On*, rubber is a naturally occurring polymer of isoprene, or 2-methyl-1,3-butadiene. The double bonds of rubber have *Z* stereochemistry, but *gutta-percha*, the *E* isomer of rubber, also occurs naturally. Harder and more brittle than rubber, *gutta-percha* has a variety of *minor* applications, including occasional use as the covering on golf balls.

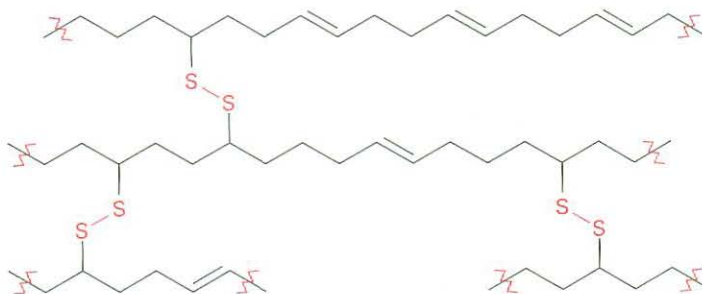


A number of different synthetic rubbers are produced commercially by diene polymerization. Both *cis*- and *trans*-polyisoprene can be made, and the synthetic rubber thus produced is similar to the natural material. Chloroprene (2-chloro-1,3-butadiene) is polymerized to yield neoprene, an excellent, although expensive, synthetic rubber with good weather resistance. Neoprene is used in the production of industrial hoses and gloves, among other things.



Both natural and synthetic rubbers are soft and tacky unless hardened by a process called *vulcanization*. Discovered in 1839 by Charles Goodyear, vulcanization involves heating the crude polymer with a few percent by weight of sulfur. Sulfur forms bridges, or cross-links, between polymer chains, locking the chains together into immense molecules that can no longer slip over one another (Figure 14.10). The result is a much harder rubber with greatly improved resistance to wear and abrasion.

Figure 14.10 Sulfur cross-linked chains resulting from vulcanization of rubber.



Problem 14.11 Draw a segment of the polymer that might be prepared from 2-phenyl-1,3-butadiene.

Problem 14.12 Show the mechanism of the acid-catalyzed polymerization of 1,3-butadiene.

14.7 Structure Determination in Conjugated Systems: Ultraviolet Spectroscopy

Mass spectrometry, infrared spectroscopy, and nuclear magnetic resonance spectroscopy are techniques of structure determination applicable to all organic molecules. In addition to these three generally useful methods, there's a fourth—**ultraviolet (UV) spectroscopy**—that is applicable only to conjugated systems. UV is less commonly used than the other three spectroscopic techniques because of the specialized information it gives, so we'll mention it only briefly.

Mass spectrometry	Molecular size and formula
IR spectroscopy	Functional groups present
NMR spectroscopy	Carbon–hydrogen framework
UV spectroscopy	Nature of conjugated π electron system

The ultraviolet region of the electromagnetic spectrum extends from the short-wavelength end of the visible region (4×10^{-7} m) to the long-wavelength end of the X-ray region (10^{-8} m), but the narrow range from 2×10^{-7} m to 4×10^{-7} m is the portion of greatest interest to organic chemists. Absorptions in this region are usually measured in nanometers (nm), where $1 \text{ nm} = 10^{-9} \text{ m}$. Thus, the ultraviolet range of interest is from 200 to 400 nm (Figure 14.11).

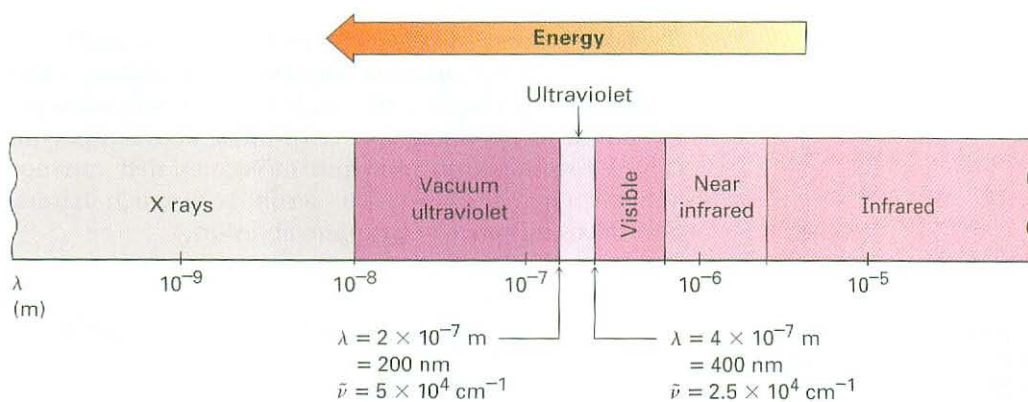


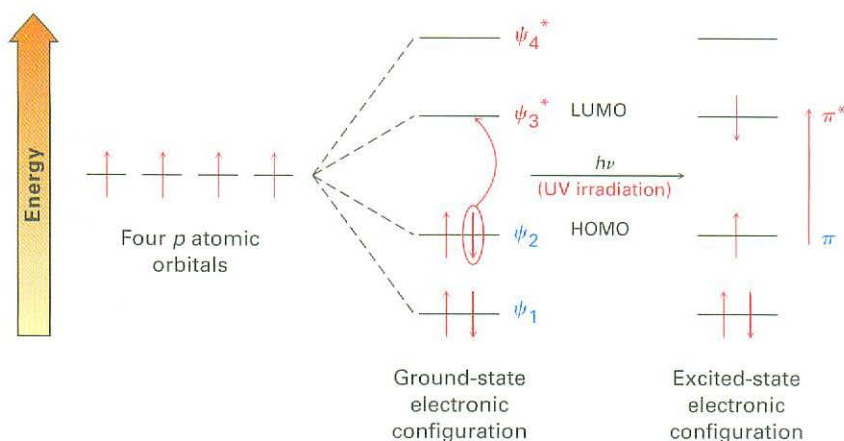
Figure 14.11 The ultraviolet (UV) region of the electromagnetic spectrum.

We saw in Section 12.5 that when an organic molecule is irradiated with electromagnetic energy, the radiation either passes through the sample or is absorbed, depending on its energy. With IR irradiation, the energy absorbed corresponds to the amount necessary to increase molecular vibrations. With UV radiation, the energy absorbed corresponds to the amount necessary to promote an electron from one orbital to another in a conjugated molecule.

The conjugated diene 1,3-butadiene has four π molecular orbitals (Figure 14.2, Section 14.1). The two lower-energy, bonding MOs are occupied in the ground state, and the two higher-energy, antibonding MOs are unoccupied. On irradiation with ultraviolet light ($h\nu$), 1,3-butadiene absorbs energy and a π electron is promoted from the **highest occupied molecular orbital**, or **HOMO**, to the **lowest unoccupied molecular orbital**, or **LUMO**. Since the electron is promoted from a

bonding π molecular orbital to an antibonding π^* molecular orbital, we call this a $\pi \rightarrow \pi^*$ excitation (read as “pi to pi star”). The energy gap between the HOMO and the LUMO of 1,3-butadiene is such that UV light of 217 nm wavelength is required to accomplish the $\pi \rightarrow \pi^*$ electronic transition (Figure 14.12).

Figure 14.12 Ultraviolet excitation of 1,3-butadiene results in the promotion of an electron from ψ_2 , the highest occupied molecular orbital (HOMO), to ψ_3^* , the lowest unoccupied molecular orbital (LUMO).



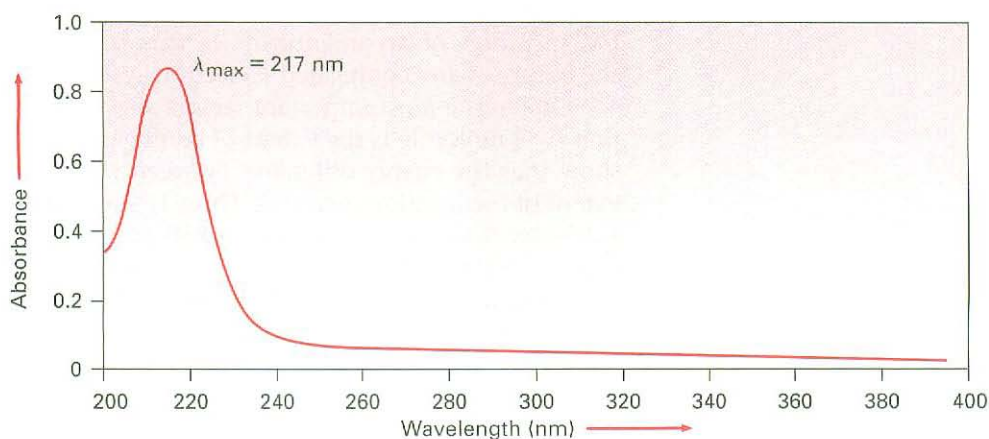
An ultraviolet spectrum is recorded by irradiating the sample with UV light of continuously changing wavelength. When the wavelength corresponds to the energy level required to excite an electron to a higher level, energy is absorbed. This absorption is detected and displayed on a chart that plots wavelength versus *absorbance* (A), defined as

$$A = \frac{I_0}{I}$$

where I_0 is the intensity of the incident light and I is the intensity of the light transmitted through the sample.

Note that UV spectra differ from IR spectra in the way they are presented. For historical reasons, IR spectra are usually displayed so that the baseline corresponding to zero absorption runs across the top of the chart and a valley indicates an absorption, whereas UV spectra are displayed with the baseline at the bottom of the chart so that a peak indicates an absorption (Figure 14.13).

Figure 14.13 The ultraviolet spectrum of 1,3-butadiene, $\lambda_{\max} = 217$ nm.



The amount of UV light absorbed is expressed as the sample's **molar absorptivity** (ϵ), defined by the equation

$$\epsilon = \frac{A}{c \times l}$$

where A = Absorbance
 c = Concentration in mol/L
 l = Sample pathlength in cm

Molar absorptivity is a physical constant, characteristic of the particular substance being observed and thus characteristic of the particular π electron system in the molecule. Typical values for conjugated dienes are in the range $\epsilon = 10,000$ to $25,000$. Note that the units are usually dropped.

Unlike IR and NMR spectra, which show many absorptions for a given molecule, UV spectra are usually quite simple—often only a single peak. The peak is usually broad, and we identify its position by noting the wavelength at the very top of the peak— λ_{max} , read as “lambda max.”

Problem 14.13 Calculate the energy range of electromagnetic radiation in the UV region of the spectrum from 200 to 400 nm. How does this value compare with the values calculated previously for IR and NMR spectroscopy?

Problem 14.14 A knowledge of molar absorptivities is particularly important in biochemistry, where UV spectroscopy can provide an extremely sensitive method of analysis. For example, imagine that you wanted to determine the concentration of vitamin A in a sample. If pure vitamin A has $\lambda_{\text{max}} = 325$ ($\epsilon = 50,100$), what is the vitamin A concentration in a sample whose absorbance at 325 nm is $A = 0.735$ in a cell with a pathlength of 1.00 cm?

14.8 Interpreting Ultraviolet Spectra: The Effect of Conjugation

The wavelength necessary to effect the $\pi \rightarrow \pi^*$ transition in a conjugated molecule depends on the energy gap between HOMO and LUMO, which in turn depends on the nature of the conjugated system. Thus, by measuring the UV spectrum of an unknown, we can derive structural information about the nature of any conjugated π electron system present in a molecule.

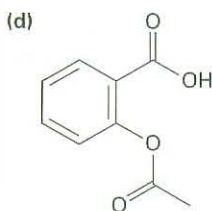
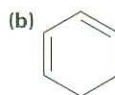
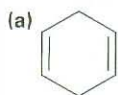
One of the most important factors affecting the wavelength of UV absorption by a molecule is the extent of conjugation. Molecular orbital calculations show that the energy difference between HOMO and LUMO decreases as the extent of conjugation increases. Thus, 1,3-butadiene absorbs at $\lambda_{\text{max}} = 217$ nm, 1,3,5-hexatriene absorbs at $\lambda_{\text{max}} = 258$ nm, and 1,3,5,7-octatetraene absorbs at $\lambda_{\text{max}} = 290$ nm. (Remember: longer wavelength means lower energy.)

Other kinds of conjugated systems, such as conjugated enones and aromatic rings, also have characteristic UV absorptions that are useful in structure determination. The UV absorption maxima of some representative conjugated molecules are given in Table 14.2.

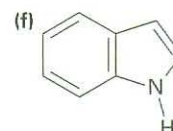
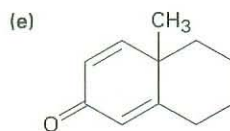
Table 14.2 Ultraviolet Absorptions of Some Conjugated Molecules

Name	Structure	λ_{\max} (nm)
2-Methyl-1,3-butadiene		220
1,3-Cyclohexadiene		256
1,3,5-Hexatriene	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	258
1,3,5,7-Octatetraene	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	290
3-Buten-2-one		219
Benzene		203

Problem 14.15 Which of the following compounds would you expect to show ultraviolet absorptions in the 200 to 400 nm range?



Aspirin



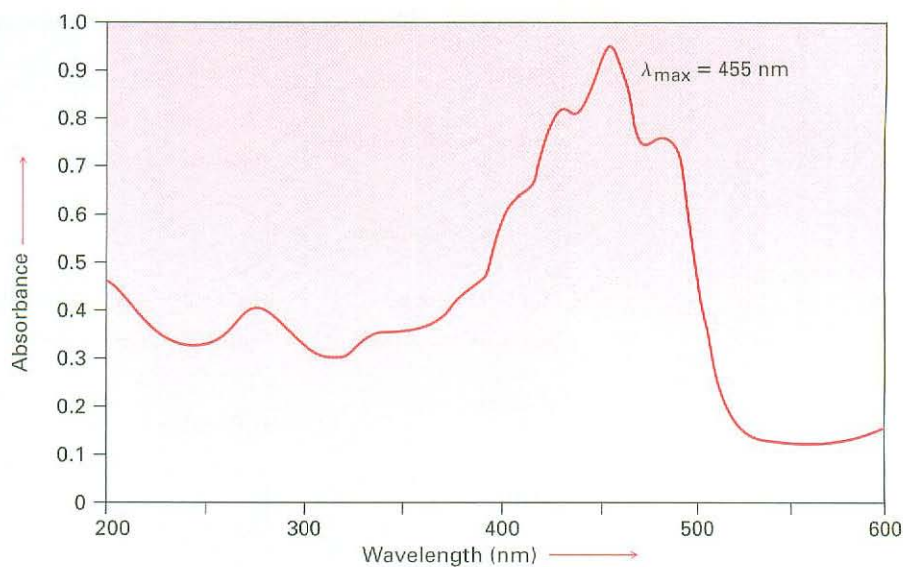
Indole

14.9 Conjugation, Color, and the Chemistry of Vision

Why are some organic compounds colored while others aren't? β -Carotene, the pigment in carrots, is purple-orange, for instance, while cholesterol is colorless. The answer involves both the chemical structures of colored molecules and the way we perceive light.

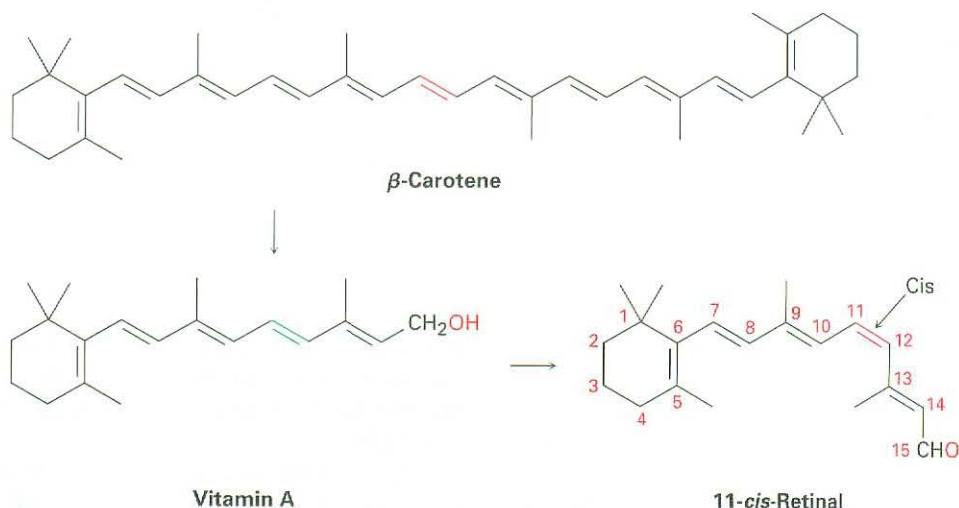
The visible region of the electromagnetic spectrum is adjacent to the ultraviolet region, extending from approximately 400 to 800 nm. Colored compounds have such extended systems of conjugation that their "UV" absorptions extend into the visible region. β -Carotene, for example, has 11 double bonds in conjugation, and its absorption occurs at $\lambda_{\max} = 455$ nm (Figure 14.14).

Figure 14.14 Ultraviolet spectrum of β -carotene, a conjugated molecule with 11 double bonds. The absorption occurs in the visible region.



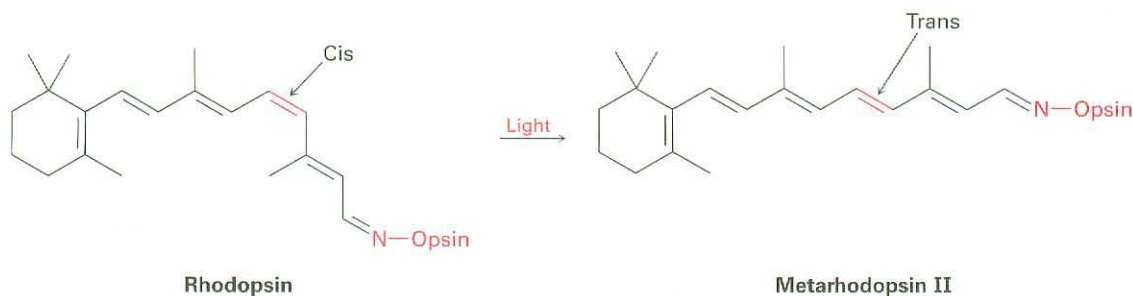
“White” light from the sun or from a lamp consists of all wavelengths in the visible region. When white light strikes β -carotene, the wavelengths from 400 to 500 nm (blue) are absorbed while all other wavelengths are transmitted and can reach our eyes. We therefore see the white light with the blue removed, and we perceive a yellow-orange color for β -carotene.

Conjugation is crucial not only for the colors we see in organic molecules but also for the light-sensitive molecules on which our visual system is based. The key substance for vision is dietary β -carotene, which is converted to vitamin A by enzymes in the liver, oxidized to an aldehyde called 11-*trans*-retinal, and then isomerized by a change in geometry of the C11-C12 double bond to produce 11-*cis*-retinal.



There are two main types of light-sensitive receptor cells in the retina of the human eye, *rod* cells and *cone* cells. The 3 million or so rod cells are

primarily responsible for seeing in dim light, whereas the 100 million cone cells are responsible for seeing in bright light and for the perception of bright colors. In the rod cells of the eye, 11-*cis*-retinal is converted into rhodopsin, a light-sensitive substance formed from the protein opsin and 11-*cis*-retinal. When light strikes the rod cells, isomerization of the C11–C12 double bond occurs and *trans*-rhodopsin, called metarhodopsin II, is produced. In the absence of light, this *cis*–*trans* isomerization takes approximately 1100 years, but in the presence of light, it occurs within 200 *femtoseconds*, or 2×10^{-13} seconds! Isomerization of rhodopsin is accompanied by a change in molecular geometry, which in turn causes a nerve impulse to be sent through the optic nerve to the brain, where it is perceived as vision.

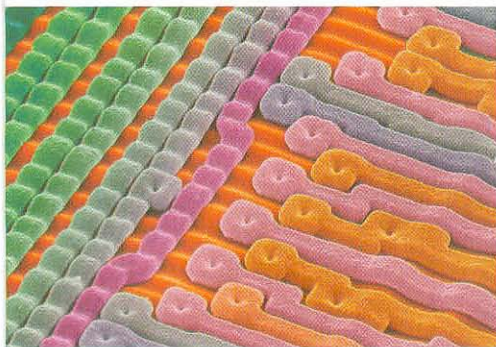


Metarhodopsin II is then recycled back into rhodopsin by a multistep sequence involving cleavage to all-*trans*-retinal and *cis*–*trans* isomerization back to 11-*cis*-retinal.

Focus On . . .



Photolithography



Andrew Syred/Photo Researchers, Inc.

Manufacturing the ultrathin circuitry on this computer chip depends on the organic chemical reactions of special polymers.

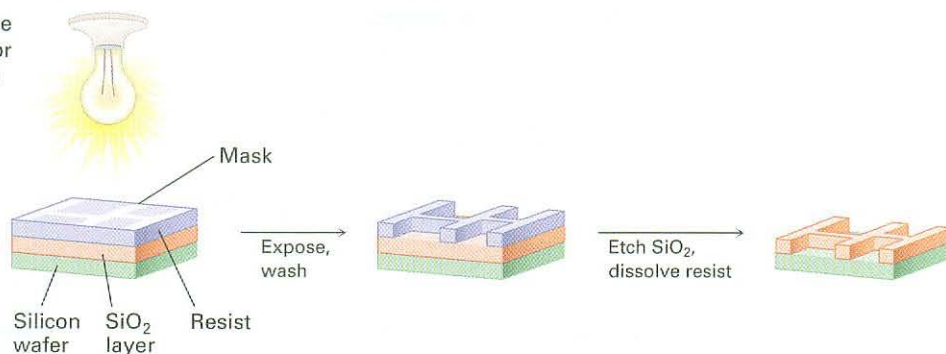
Forty years ago, someone interested in owning a computer would have paid approximately \$150,000 for 16 megabytes of random-access memory that would have occupied a volume the size of a small desk. Today, someone can buy eight times as much computer memory for \$20 and fit the chips into their shirt pocket. The difference between then and now is due to improvements in *photolithography*, the process by which integrated-circuit chips are made.

Photolithography begins by coating a layer of SiO_2 onto a silicon wafer and further coating with a thin (0.5–1.0 μm) film of a light-sensitive organic polymer called a *resist*. A *mask* is then used to cover those parts of the chip that will become a circuit, and the wafer is irradiated with UV light. The nonmasked

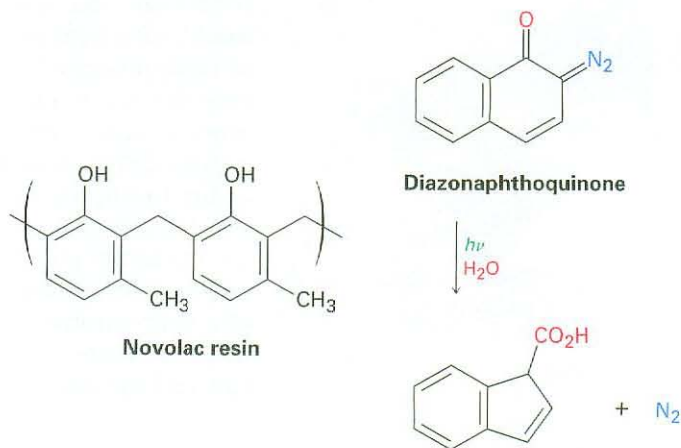
(continued)

sections of the polymer undergo a chemical change when irradiated that makes them more soluble than the masked, unirradiated sections. On washing the irradiated chip with solvent, solubilized polymer is selectively removed from the irradiated areas, exposing the SiO_2 underneath. This SiO_2 is then chemically etched away by reaction with hydrofluoric acid, leaving behind a pattern of polymer-coated SiO_2 . Further washing removes the remaining polymer, leaving a positive image of the mask in the form of exposed ridges of SiO_2 (Figure 14.15). Additional cycles of coating, masking, and etching then produce the completed chips.

Figure 14.15 Outline of the photolithography process for producing integrated circuit chips.



The polymer resist currently used in chip manufacturing is based on the two-component *diazoquinone–novolac system*. Novolac resin is a soft, relatively low-molecular-weight polymer made from methylphenol and formaldehyde, while the diazoquinone is a bicyclic (two-ring) molecule containing a diazo group ($=\text{N}=\text{N}$) adjacent to a ketone carbonyl ($\text{C}=\text{O}$). The diazoquinone–novolac mix is relatively insoluble when fresh, but on exposure to ultraviolet light and water vapor, the diazoquinone component undergoes reaction to yield N_2 and a carboxylic acid, which can be washed away with dilute base. Novolac–diazoquinone technology is capable of producing features as small as $0.5 \mu\text{m}$ ($5 \times 10^{-7} \text{m}$), but still further improvements in miniaturization are being developed.



1,2-addition, 487
 1,4-addition, 487
 conjugated, 482
 Diels–Alder cycloaddition reaction, 492
 dienophile, 493
 highest occupied molecular orbital (HOMO), 500
 kinetic control, 491
 lowest unoccupied molecular orbital (LUMO), 500
 molar absorptivity (ϵ), 502
 thermodynamic control, 491
 ultraviolet (UV) spectroscopy, 500

SUMMARY AND KEY WORDS

A **conjugated** diene or other compound is one that contains alternating double and single bonds. One characteristic of conjugated dienes is that they are more stable than their nonconjugated counterparts. This stability can be explained by a molecular orbital description in which four p atomic orbitals combine to form four π molecular orbitals. Only the two bonding orbitals are occupied; the two antibonding orbitals are unoccupied. A π bonding interaction introduces some partial double-bond character between carbons 2 and 3, thereby strengthening the C2–C3 bond and stabilizing the molecule.

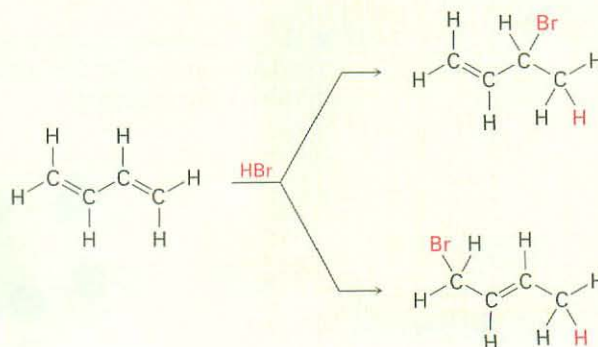
Conjugated dienes undergo several reactions not observed for nonconjugated dienes. One is the 1,4-addition of electrophiles. When a conjugated diene is treated with an electrophile such as HCl, **1,2-** and **1,4-addition** products are formed. Both are formed from the same resonance-stabilized allylic carbocation intermediate and are produced in varying amounts depending on the reaction conditions. The 1,2 adduct is usually formed faster and is said to be the product of **kinetic control**. The 1,4 adduct is usually more stable and is said to be the product of **thermodynamic control**.

Another reaction unique to conjugated dienes is the **Diels–Alder cycloaddition**. Conjugated dienes react with electron-poor alkenes (**dienophiles**) in a single step through a cyclic transition state to yield a cyclohexene product. The reaction is stereospecific, meaning that only a single product stereoisomer is formed, and can occur only if the diene is able to adopt an *s-cis* conformation.

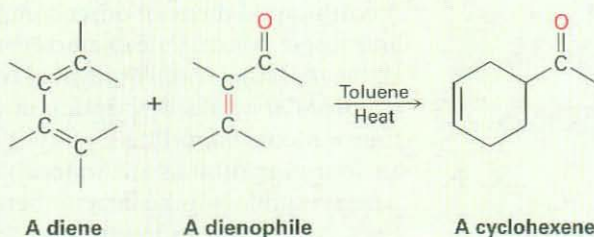
Ultraviolet (UV) spectroscopy is a method of structure determination applicable specifically to conjugated systems. When a conjugated molecule is irradiated with ultraviolet light, energy absorption occurs and a π electron is promoted from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**. For 1,3-butadiene, radiation of $\lambda_{\text{max}} = 217 \text{ nm}$ is required. The greater the extent of conjugation, the less the energy needed and the longer the wavelength of required radiation.

SUMMARY OF REACTIONS

1. Electrophilic addition reactions (Sections 14.2 and 14.3)



2. Diels–Alder cycloaddition reaction (Sections 14.4 and 14.5)



EXERCISES

Organic KNOWLEDGE TOOLS

ThomsonNOW Sign in at www.thomsonedu.com to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.



Online homework for this chapter may be assigned in Organic OWL.

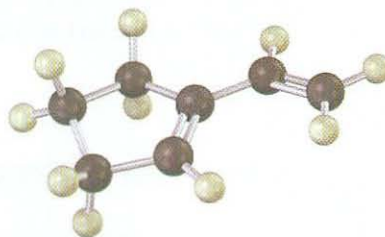
■ indicates problems assignable in Organic OWL.

▲ denotes problems linked to Key Ideas of this chapter and testable in ThomsonNOW.

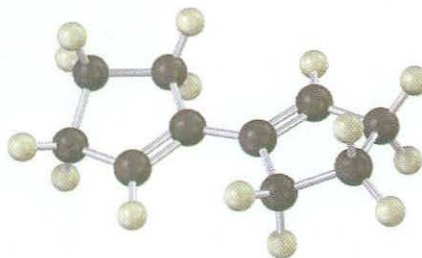
VISUALIZING CHEMISTRY

(Problems 14.1–14.15 appear within the chapter.)

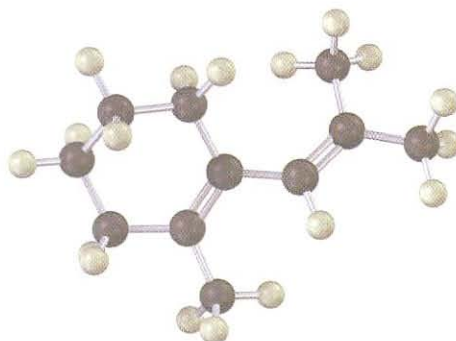
14.16 Show the structures of all possible adducts of the following diene with 1 equivalent of HCl:



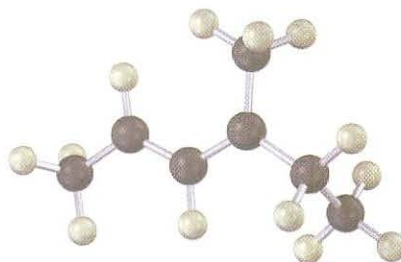
14.17 ■ Show the product of the Diels–Alder reaction of the following diene with 3-buten-2-one, $\text{H}_2\text{C}=\text{CHCOCH}_3$. Make sure you show the full stereochemistry of the reaction product.



14.18 The following diene does not undergo Diels–Alder reactions. Explain.

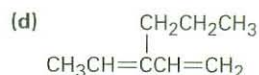
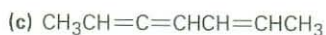
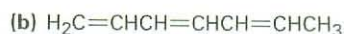
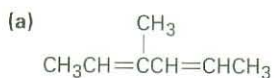


14.19 ■ The following model is that of an allylic carbocation intermediate formed by protonation of a conjugated diene with HBr. Show the structure of the diene and the structures of the final reaction products.



ADDITIONAL PROBLEMS

14.20 ■ Give IUPAC names for the following compounds:

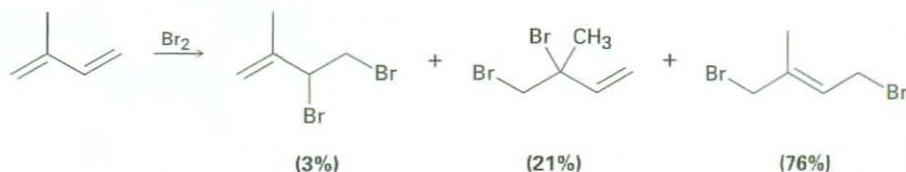


14.21 ■ What product(s) would you expect to obtain from reaction of 1,3-cyclohexadiene with each of the following?

- 1 mol Br_2 in CH_2Cl_2
- O_3 followed by Zn
- 1 mol HCl in ether
- 1 mol DCl in ether
- 3-Buten-2-one ($\text{H}_2\text{C}=\text{CHCOCH}_3$)
- Excess OsO_4 , followed by NaHSO_3

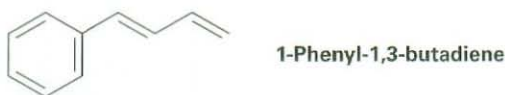
14.22 Draw and name the six possible diene isomers of formula C_5H_8 . Which of the six are conjugated dienes?

- 14.23** Treatment of 3,4-dibromohexane with strong base leads to loss of 2 equivalents of HBr and formation of a product with formula C_6H_{10} . Three products are possible. Name each of the three, and tell how you would use 1H and ^{13}C NMR spectroscopy to help identify them. How would you use UV spectroscopy?
- 14.24** Electrophilic addition of Br_2 to isoprene (2-methyl-1,3-butadiene) yields the following product mixture:

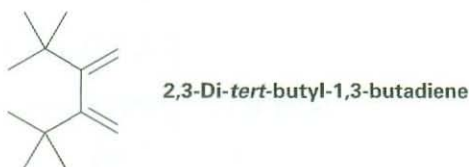


Of the 1,2-addition products, explain why 3,4-dibromo-3-methyl-1-butene (21%) predominates over 3,4-dibromo-2-methyl-1-butene (3%).

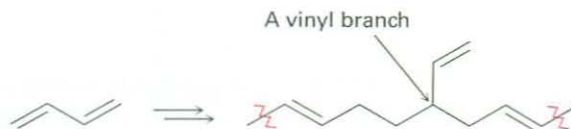
- 14.25** Propose a structure for a conjugated diene that gives the same product from both 1,2- and 1,4-addition of HBr.
- 14.26** ■ Draw the possible products resulting from addition of 1 equivalent of HCl to 1-phenyl-1,3-butadiene. Which would you expect to predominate, and why?



- 14.27** 2,3-Di-*tert*-butyl-1,3-butadiene does not undergo Diels–Alder reactions. Explain.

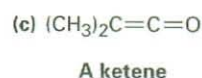
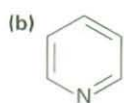
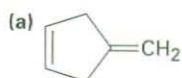


- 14.28** Diene polymers contain occasional vinyl branches along the chain. How do you think these branches might arise?



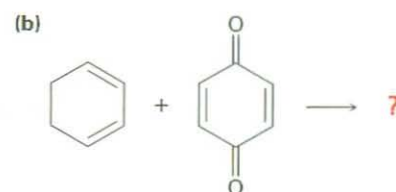
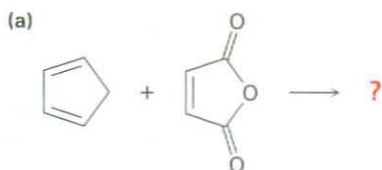
- 14.29** Tires whose sidewalls are made of natural rubber tend to crack and weather rapidly in areas around cities where high levels of ozone and other industrial pollutants are found. Explain.
- 14.30** Would you expect allene, $H_2C=C=CH_2$, to show a UV absorption in the 200 to 400 nm range? Explain.

- 14.31 ■ Which of the following compounds would you expect to have a $\pi \rightarrow \pi^*$ UV absorption in the 200 to 400 nm range?

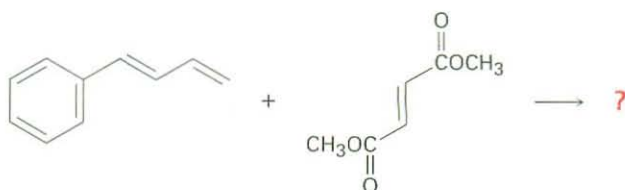


Pyridine

- 14.32 Predict the products of the following Diels–Alder reactions:



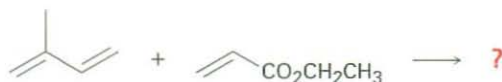
- 14.33 ■ Show the structure, including stereochemistry, of the product from the following Diels–Alder reaction:



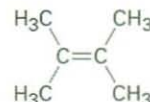
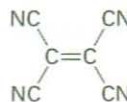
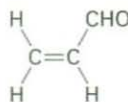
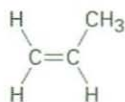
- 14.34 How can you account for the fact that *cis*-1,3-pentadiene is much less reactive than *trans*-1,3-pentadiene in the Diels–Alder reaction?

- 14.35 Would you expect a conjugated diyne such as 1,3-butadiyne to undergo Diels–Alder reaction with a dienophile? Explain.

- 14.36 Reaction of isoprene (2-methyl-1,3-butadiene) with ethyl propenoate gives a mixture of two Diels–Alder adducts. Show the structure of each, and explain why a mixture is formed.



- 14.37 Rank the following dienophiles in order of their expected reactivity in the Diels–Alder reaction.



- 14.38** 1,3-Cyclopentadiene is very reactive in Diels–Alder cycloaddition reactions, but 1,3-cyclohexadiene is less reactive and 1,3-cycloheptadiene is nearly inert. Explain. (Molecular models are helpful.)
- 14.39** 1,3-Pentadiene is much more reactive in Diels–Alder reactions than 2,4-pentadienal. Why might this be?

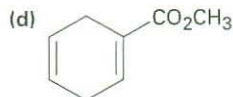
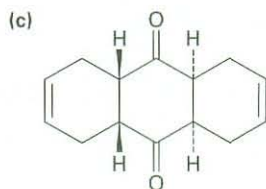
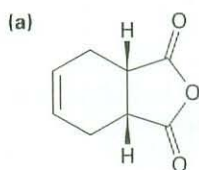


1,3-Pentadiene



2,4-Pentadienal

- 14.40** ■ How could you use Diels–Alder reactions to prepare the following products? Show the starting diene and dienophile in each case.

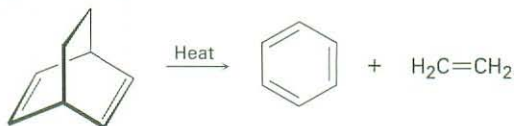


- 14.41** Aldrin, a chlorinated insecticide now banned for use in the United States, can be made by Diels–Alder reaction of hexachloro-1,3-cyclopentadiene with norbornadiene. What is the structure of aldrin?

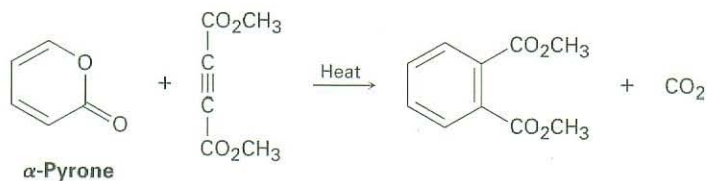


Norbornadiene

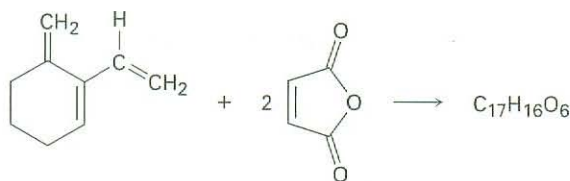
- 14.42** Norbornadiene (Problem 14.41) can be prepared by reaction of chloroethylene with 1,3-cyclopentadiene, followed by treatment of the product with sodium ethoxide. Write the overall scheme, and identify the two kinds of reactions.
- 14.43** ▲ We've seen that the Diels–Alder cycloaddition reaction is a one-step, pericyclic process that occurs through a cyclic transition state. Propose a mechanism for the following reaction:



- 14.44 In light of your answer to Problem 14.43, propose a mechanism for the following reaction:



- 14.45 The triene shown here reacts with 2 equivalents of maleic anhydride to yield a product with the formula $C_{17}H_{16}O_6$. Predict a structure for the product.

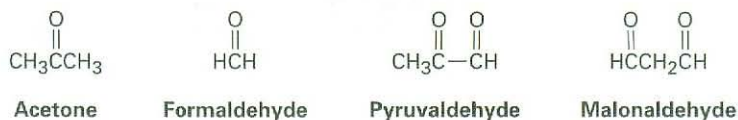


- 14.46 The following ultraviolet absorption maxima have been measured:

1,3-Butadiene	217 nm
2-Methyl-1,3-butadiene	220 nm
1,3-Pentadiene	223 nm
2,3-Dimethyl-1,3-butadiene	226 nm
2,4-Hexadiene	227 nm
2,4-Dimethyl-1,3-pentadiene	232 nm
2,5-Dimethyl-2,4-hexadiene	240 nm

What conclusion can you draw about the effect of alkyl substitution on UV absorption maxima? Approximately what effect does each added alkyl group have?

- 14.47 1,3,5-Hexatriene has $\lambda_{\text{max}} = 258$ nm. In light of your answer to Problem 14.46, approximately where would you expect 2,3-dimethyl-1,3,5-hexatriene to absorb?
- 14.48 ■ β -Ocimene is a pleasant-smelling hydrocarbon found in the leaves of certain herbs. It has the molecular formula $C_{10}H_{16}$ and a UV absorption maximum at 232 nm. On hydrogenation with a palladium catalyst, 2,6-dimethyloctane is obtained. Ozonolysis of β -ocimene, followed by treatment with zinc and acetic acid, produces the following four fragments:



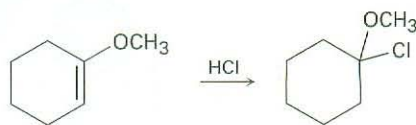
- How many double bonds does β -ocimene have?
- Is β -ocimene conjugated or nonconjugated?
- Propose a structure for β -ocimene.
- Write the reactions, showing starting material and products.

- 14.49** ■ Myrcene, $C_{10}H_{16}$, is found in oil of bay leaves and is isomeric with β -ocimene (Problem 14.48). It has an ultraviolet absorption at 226 nm and can be catalytically hydrogenated to yield 2,6-dimethyloctane. On ozonolysis followed by zinc/acetic acid treatment, myrcene yields formaldehyde, acetone, and 2-oxopentanedial:

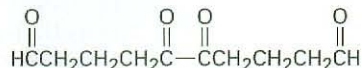


Propose a structure for myrcene, and write the reactions, showing starting material and products.

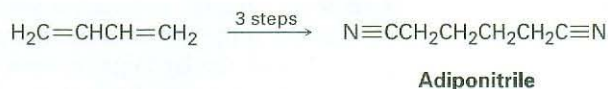
- 14.50** Addition of HCl to 1-methoxycyclohexene yields 1-chloro-1-methoxycyclohexane as the sole product. Use resonance structures to explain why none of the other regioisomer is formed.



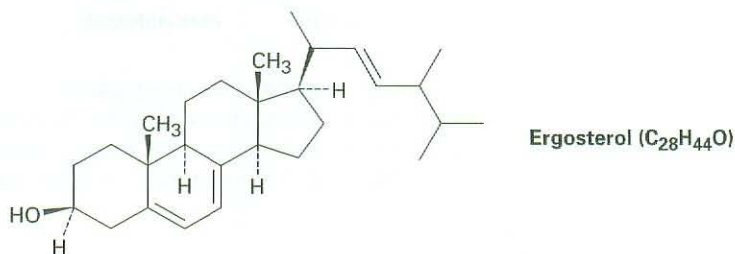
- 14.51** ■ Hydrocarbon A, $C_{10}H_{14}$, has a UV absorption at $\lambda_{\text{max}} = 236$ nm and gives hydrocarbon B, $C_{10}H_{18}$, on catalytic hydrogenation. Ozonolysis of A followed by zinc/acetic acid treatment yields the following diketo dialdehyde:



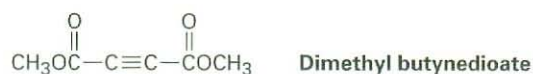
- (a) Propose two possible structures for A.
 (b) Hydrocarbon A reacts with maleic anhydride to yield a Diels–Alder adduct. Which of your structures for A is correct?
 (c) Write the reactions, showing starting material and products.
- 14.52** Adiponitrile, a starting material used in the manufacture of nylon, can be prepared in three steps from 1,3-butadiene. How would you carry out this synthesis?



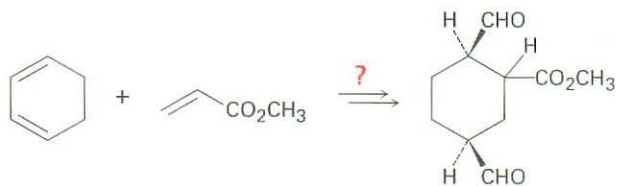
- 14.53** ■ Ergosterol, a precursor of vitamin D, has $\lambda_{\text{max}} = 282$ nm and molar absorptivity $\epsilon = 11,900$. What is the concentration of ergosterol in a solution whose absorbance $A = 0.065$ with a sample pathlength $l = 1.00$ cm?



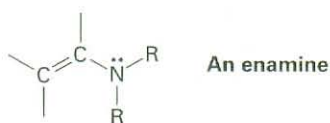
- 14.54 ▲ 1,3-Cyclopentadiene polymerizes slowly at room temperature to yield a polymer that has no double bonds except on the ends. On heating, the polymer breaks down to regenerate 1,3-cyclopentadiene. Propose a structure for the product.
- 14.55 ■ ▲ Dimethyl butynedioate undergoes a Diels–Alder reaction with (2*E*,4*E*)-hexadiene. Show the structure and stereochemistry of the product.



- 14.56 ■ Dimethyl butynedioate also undergoes a Diels–Alder reaction with (2*E*,4*Z*)-hexadiene, but the stereochemistry of the product is different from that of the (2*E*,4*E*) isomer (Problem 14.55). Explain.
- 14.57 How would you carry out the following synthesis (more than one step is required)? What stereochemical relationship between the $-\text{CO}_2\text{CH}_3$ group attached to the cyclohexane ring and the $-\text{CHO}$ groups would your synthesis produce?



- 14.58 The double bond of an *enamine* (alkene + *amine*) is much more nucleophilic than a typical alkene double bond. Assuming that the nitrogen atom in an enamine is sp^2 -hybridized, draw an orbital picture of an enamine, and explain why the double bond is electron-rich.



- 14.59 Benzene has an ultraviolet absorption at $\lambda_{\text{max}} = 204 \text{ nm}$, and *para*-toluidine has $\lambda_{\text{max}} = 235 \text{ nm}$. How do you account for this difference?

