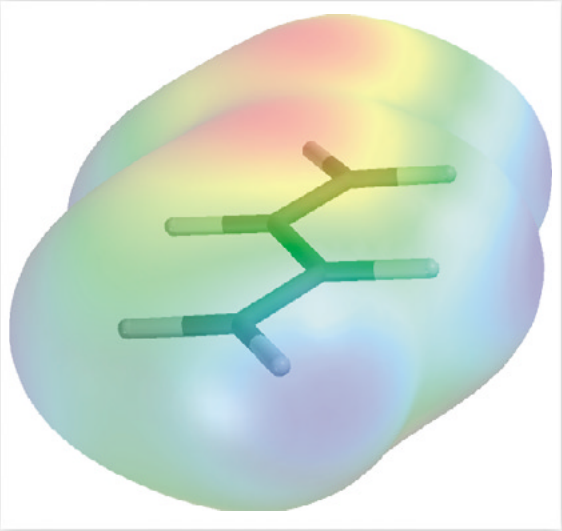
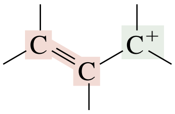


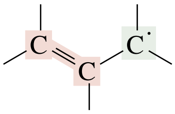
CHAPTER 10

CONJUGATION IN ALKADIENES AND ALLYLIC SYSTEMS

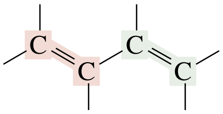
Not all the properties of alkenes are revealed by focusing exclusively on the functional group behavior of the double bond. A double bond can affect the properties of a second functional unit to which it is directly attached. It can be a substituent, for example, on a positively charged carbon in an **allylic carbocation,** or on a carbon that bears an unpaired electron in an **allylic free radical,** or it can be a substituent on a second double bond in a **conjugated diene.**



Allylic carbocation



Allylic free radical



Conjugated diene

Conjugare is a Latin verb meaning "to link or yoke together," and allylic carbocations, allylic free radicals, and conjugated dienes are all examples of **conjugated systems.** In this chapter we'll see how conjugation permits two functional units within a molecule to display a kind of reactivity that is qualitatively different from that of either unit alone.

10.1 THE ALLYL GROUP

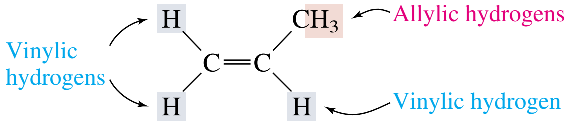
The group $CH_2{=}CHCH_2{-}$ is known as **allyl*,** which is both a common name and a permissible IUPAC name. It is most often encountered in functionally substituted derivatives, and the following compounds containing this group are much better known by their functional class IUPAC names than by their substitutive ones:

---

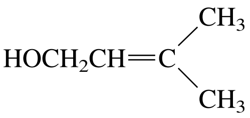
*"Allyl" is derived from the botanical name for garlic (*Allium sativum*). It was found in 1892 that the major component obtained by distilling garlic oil is $CH_2{=}CHCH_2SSCH_2CH{=}CH_2$, and the word "allyl" was coined for the $CH_2{=}CHCH_2{-}$ group on the basis of this origin.

$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2Cl$	$CH_2{=}CHCH_2Br$
Allyl alcohol (2-propen-1-ol)	Allyl chloride (3-chloro-1-propene)	Allyl bromide (3-bromo-1-propene)

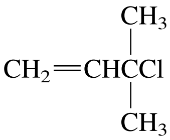
The term “allylic” refers to a $C{=}C{-}C$ unit. Its sp^3-hybridized carbon is called the **allylic carbon,** and an **allylic substituent** is one that is attached to an allylic carbon. Conversely, the sp^2-hybridized carbons of a carbon–carbon double bond are called **vinylic carbons,** and substituents attached to either one of them are referred to as **vinylic substituents.**



“Allylic” is often used as a general term for molecules that have a functional group at an allylic position. Thus, the following compounds represent an *allylic alcohol* and an *allylic chloride,* respectively.



3-Methyl-2-buten-1-ol
(an allylic alcohol)



$$CH_2{=}CH\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}Cl$$

3-Chloro-3-methyl-1-butene
(an allylic chloride)

10.2 ALLYLIC CARBOCATIONS

Allylic carbocations are carbocations in which the positive charge is on an allylic carbon. Allyl cation is the simplest allylic carbocation.

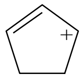
Representative allylic carbocations

$$CH_2{=}CH\overset{+}{C}H_2$$

Allyl cation

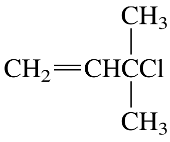
$$CH_3CH{=}CH\overset{+}{C}HCH_3$$

1-Methyl-2-butenyl cation



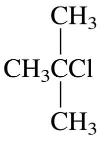
2-Cyclopentenyl cation

A substantial body of evidence indicates that allylic carbocations are more stable than simple alkyl cations. For example, the rate of solvolysis of a chloride that is both tertiary and allylic is much faster than that of a typical tertiary alkyl chloride.



$$CH_2{=}CH\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}Cl$$

3-Chloro-3-methyl-1-butene
More reactive: k(rel) 123

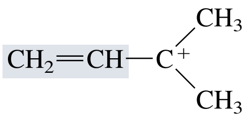


$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}Cl$$

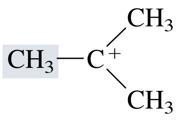
tert-Butyl chloride
Less reactive: k(rel) 1.0

The first-order rate constant for ethanolysis of the allylic chloride 3-chloro-3-methyl-1-butene is over 100 times greater than that of *tert*-butyl chloride at the same temperature.

Both compounds react by an S_N1 mechanism, and their relative rates reflect their activation energies for carbocation formation. Since the allylic chloride is more reactive, we reason that it ionizes more rapidly because it forms a more stable carbocation. Structurally, the two carbocations differ in that the allylic carbocation has a vinyl substituent on its positively charged carbon in place of one of the methyl groups of *tert*-butyl cation.



1,1-Dimethylallyl cation
(more stable)

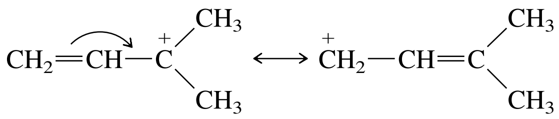


tert-Butyl cation
(less stable)

A vinyl group stabilizes a carbocation more than does a methyl group. Why?

A vinyl group is an extremely effective electron-releasing substituent. A resonance interaction of the type shown permits the π electrons of the double bond to be delocalized and disperses the positive charge.

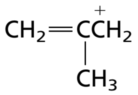
A rule of thumb is that a C=C substituent stabilizes a carbocation about as well as two alkyl groups. Although allyl cation ($CH_2{=}CHCH_2^+$) is a primary carbocation, it is about as stable as a typical secondary carbocation such as isopropyl cation, $(CH_3)_2CH^+$.

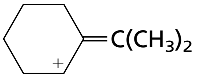


It's important to recognize that the positive charge is shared by the two end carbons in the $C{=}C{-}C^+$ unit; the center carbon does not bear a positive charge in either of the resonance structures that we just wrote. Keep that fact in mind as you answer Problem 10.1.

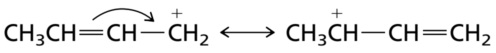
PROBLEM 10.1 Write a second resonance structure for each of the following carbocations:

(a) $CH_3CH{=}CH\overset{+}{C}H_2$

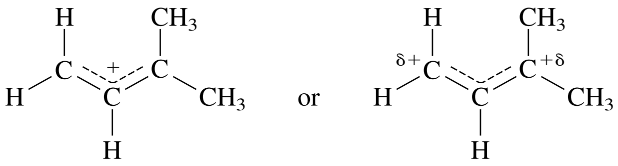
(b)

$CH_2{=}\overset{+}{C}(CH_3)H_2$

(c)


SAMPLE SOLUTION (a) When writing resonance forms of carbocations, electrons are moved in pairs from sites of high electron density toward the positively charged carbon.

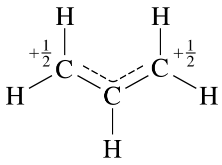

$$CH_3CH{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}H{-}CH{=}CH_2$$

Electron delocalization in allylic carbocations can be indicated using a dashed line to show the sharing of a pair of π electrons by the three carbons. The structural formula is completed by placing a positive charge above the dashed line or by adding partial positive charges to the carbons at the end of the allylic system.



Two dashed-line representations of 1,1-dimethylallyl cation

In the case of the parent cation $CH_2{=}CH{-}CH_2^+$ both the terminal carbons are equivalently substituted, and so each bears exactly half of a unit positive charge.

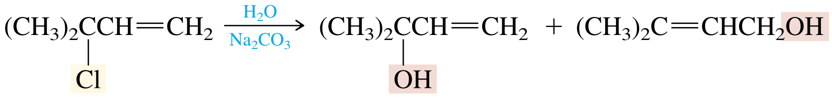


Allyl cation

This same sharing of positive charge between the first and third carbons in $CH_2{=}CH{-}CH_2^+$ is shown by the use of colors in an electrostatic potential map (Figure 10.1).

An orbital overlap description of electron delocalization in 1,1-dimethylallyl cation $CH_2{=}CH{-}\overset{+}{C}(CH_3)_2$ is given in Figure 10.2. Figure 10.2*a* shows the π bond and the vacant *p* orbital as independent units. Figure 10.2*b* shows how the units can overlap to give an extended π orbital that encompasses all three carbons. This permits the two π electrons to be delocalized over three carbons and disperses the positive charge.

Since the positive charge in an allylic carbocation is shared by two carbons, there are two potential sites for attack by a nucleophile. Thus, hydrolysis of 3-chloro-3-methyl-1-butene gives a mixture of two allylic alcohols:



$$(CH_3)_2\underset{\underset{\displaystyle Cl}{|}}{C}CH{=}CH_2 \xrightarrow[Na_2CO_3]{H_2O} (CH_3)_2\underset{\underset{\displaystyle OH}{|}}{C}CH{=}CH_2 + (CH_3)_2C{=}CHCH_2OH$$

3-Chloro-3-methyl-1-butene

2-Methyl-3-buten-2-ol (85%)

3-Methyl-2-buten-1-ol (15%)

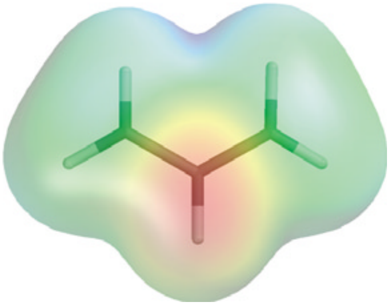


FIGURE 10.1 An electrostatic potential map for allyl cation. The middle carbon (red region) has the least positive charge of the three carbons; the end carbons (blue regions) have the most positive charge.

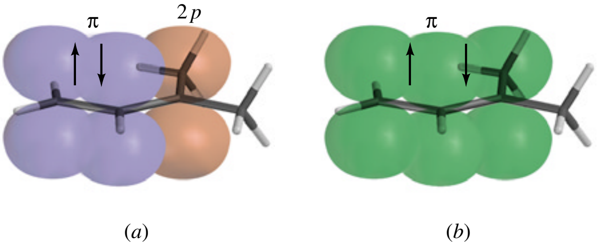
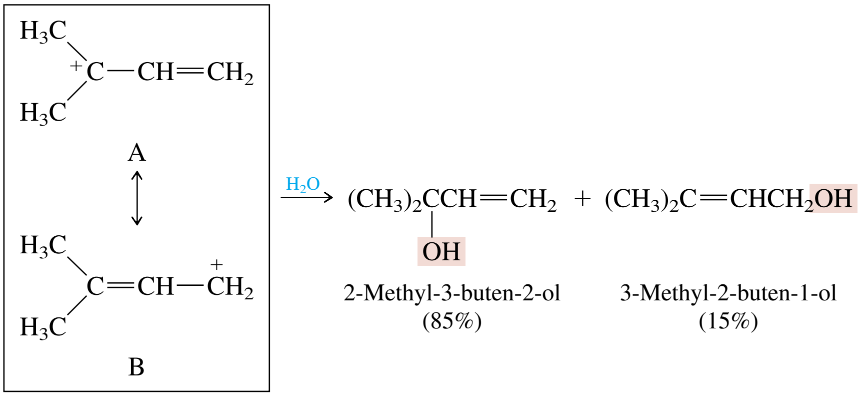


FIGURE 10.2 Electron delocalization in an allylic carbocation. (*a*) The π orbital of the double bond, and the vacant 2*p* orbital of the positively charged carbon. (*b*) Overlap of the π orbital and the 2*p* orbital gives an extended π orbital that encompasses all three carbons. The two electrons in the π bond are delocalized over two carbons in (*a*) and over three carbons in (*b*).

Both alcohols are formed from the same carbocation. Water may react with the carbocation to give either a primary alcohol or a tertiary alcohol.



$$\xrightarrow{H_2O} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH{=}CH_2 + (CH_3)_2C{=}CHCH_2OH$$

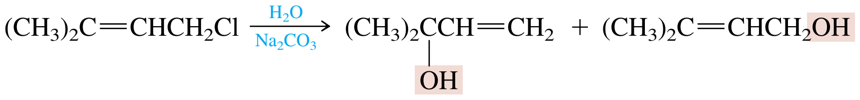
2-Methyl-3-buten-2-ol (85%)

3-Methyl-2-buten-1-ol (15%)

Use *Learning By Modeling* to view the carbocation represented by resonance structures A and B. How is the positive charge distributed among its carbons?

It must be emphasized that we are not dealing with an equilibrium between two isomeric carbocations. *There is only one carbocation.* Its structure is not adequately represented by either of the individual resonance forms but is a hybrid having qualities of both of them. The carbocation has more of the character of A than B because resonance structure A is more stable than B. Water attacks faster at the tertiary carbon because it bears more of the positive charge.

The same two alcohols are formed in the hydrolysis of 1-chloro-3-methyl-2-butene:



$$(CH_3)_2C{=}CHCH_2Cl \xrightarrow[Na_2CO_3]{H_2O} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH{=}CH_2 + (CH_3)_2C{=}CHCH_2OH$$

1-Chloro-3-methyl-2-butene

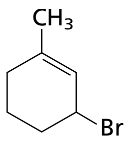
2-Methyl-3-buten-2-ol (85%)

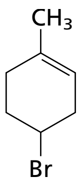
3-Methyl-2-buten-1-ol (15%)

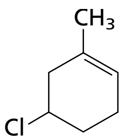
The carbocation formed on ionization of 1-chloro-3-methyl-2-butene is the same allylic carbocation as the one formed on ionization of 3-chloro-3-methyl-1-butene and gives the same mixture of products.

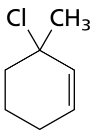
Reactions of allylic systems that yield products in which double-bond migration has occurred are said to have proceeded with **allylic rearrangement,** or by way of an **allylic shift.**

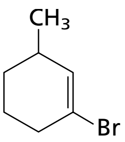
PROBLEM 10.2 From among the following compounds, choose the two that yield the same carbocation on ionization.







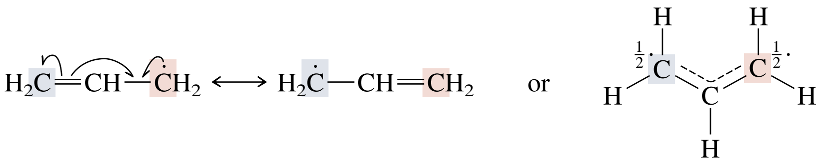




Later in this chapter we'll see how allylic carbocations are involved in electrophilic addition to dienes and how the principles developed in this section apply there as well.

10.3 ALLYLIC FREE RADICALS

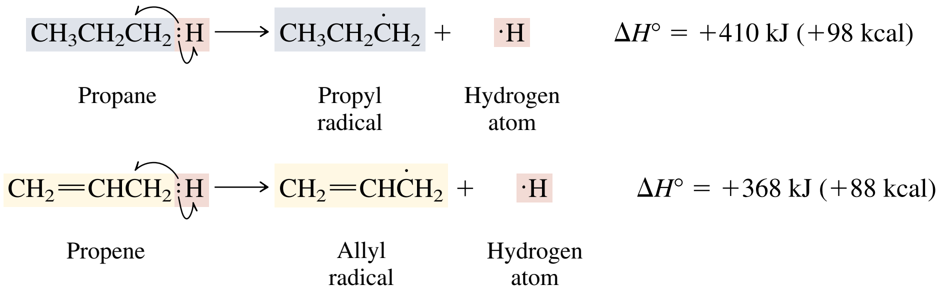
Just as allyl cation is stabilized by electron delocalization, so is allyl radical:



Allyl radical

Allyl radical is a conjugated system in which three electrons are delocalized over three carbons. The unpaired electron has an equal probability of being found at C-1 or C-3.

Reactions that generate allylic radicals occur more readily than those involving simple alkyl radicals. Compare the bond dissociation energies of the primary C—H bonds of propane and propene:



$$CH_3CH_2CH_2\!:\!H \longrightarrow CH_3CH_2\dot{C}H_2 + \cdot H \qquad \Delta H^\circ = +410\text{ kJ }(+98\text{ kcal})$$

Propane | Propyl radical | Hydrogen atom

$$CH_2{=}CHCH_2\!:\!H \longrightarrow CH_2{=}CH\dot{C}H_2 + \cdot H \qquad \Delta H^\circ = +368\text{ kJ }(+88\text{ kcal})$$

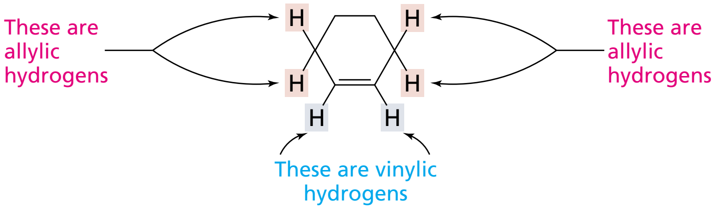
Propene | Allyl radical | Hydrogen atom

It requires less energy, by 42 kJ/mol (10 kcal/mol), to break a bond to a primary hydrogen atom in propene than in propane. The free radical produced from propene is allylic and stabilized by electron delocalization; the one from propane is not.

PROBLEM 10.3 Identify the allylic hydrogens in

(a) Cyclohexene
(b) 1-Methylcyclohexene
(c) 2,3,3-Trimethyl-1-butene
(d) 1-Octene

SAMPLE SOLUTION (a) Allylic hydrogens are bonded to an allylic carbon. An allylic carbon is an sp^3-hybridized carbon that is attached directly to an sp^2-hybridized carbon of an alkene. Cyclohexene has four allylic hydrogens.



10.4 ALLYLIC HALOGENATION

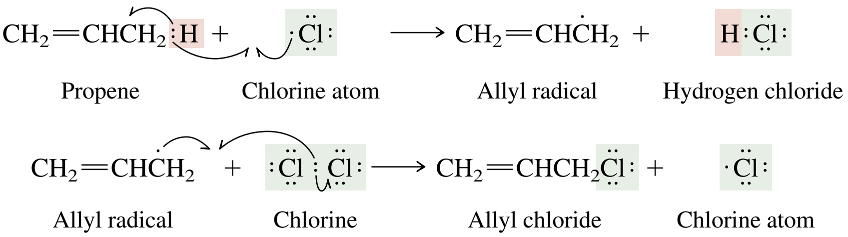
Of the reactions that involve carbon radicals, the most familiar are the chlorination and bromination of alkanes (Sections 4.15 through 4.19):

$$\underset{\text{Alkane}}{RH} + \underset{\text{Halogen}}{X_2} \xrightarrow[\text{light}]{\text{heat or}} \underset{\text{halide}}{\underset{\text{Alkyl}}{RX}} + \underset{\text{halide}}{\underset{\text{Hydrogen}}{HX}}$$

Although alkenes typically react with chlorine and bromine by *addition* at room temperature and below (Section 6.14), *substitution* becomes competitive at higher temperatures, especially when the concentration of the halogen is low. When substitution does occur, it is highly selective for the allylic position. This forms the basis of an industrial preparation of allyl chloride:

$$\underset{\text{Propene}}{CH_2{=}CHCH_3} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{500°C} \underset{(80\text{–}85\%)}{\underset{\text{Allyl chloride}}{CH_2{=}CHCH_2Cl}} + \underset{\text{Hydrogen chloride}}{HCl}$$

The reaction proceeds by a free-radical chain mechanism, involving the following propagation steps:

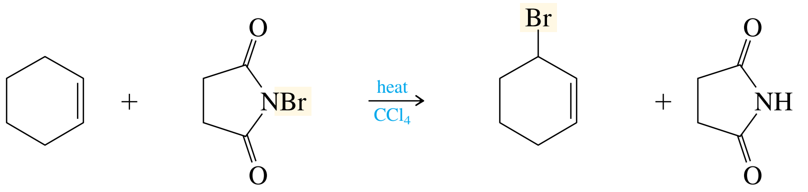


$$\underset{\text{Propene}}{CH_2{=}CHCH_2{:}H} + \underset{\text{Chlorine atom}}{\cdot\ddot{\underset{..}{Cl}}{:}} \longrightarrow \underset{\text{Allyl radical}}{CH_2{=}CH\dot{C}H_2} + \underset{\text{Hydrogen chloride}}{H{:}\ddot{\underset{..}{Cl}}{:}}$$

$$\underset{\text{Allyl radical}}{CH_2{=}CH\dot{C}H_2} + \underset{\text{Chlorine}}{{:}\ddot{\underset{..}{Cl}}{:}\ddot{\underset{..}{Cl}}{:}} \longrightarrow \underset{\text{Allyl chloride}}{CH_2{=}CHCH_2\ddot{\underset{..}{Cl}}{:}} + \underset{\text{Chlorine atom}}{\cdot\ddot{\underset{..}{Cl}}{:}}$$

Allyl chloride is quite reactive toward nucleophilic substitutions, especially those that proceed by the S_N2 mechanism, and is used as a starting material in the synthesis of a variety of drugs and agricultural and industrial chemicals.

Allylic brominations are normally carried out using one of a number of specialized reagents developed for that purpose. *N*-Bromosuccinimide (NBS) is the most frequently used of these reagents. An alkene is dissolved in carbon tetrachloride, *N*-bromosuccinimide is added, and the reaction mixture is heated, illuminated with a sunlamp, or both. The products are an allylic halide and succinimide.



Cyclohexene *N*-Bromosuccinimide (NBS) 3-Bromocyclohexene (82–87%) Succinimide

N-Bromosuccinimide will be seen again as a reagent for selective bromination in Section 11.12.

N-Bromosuccinimide provides a low concentration of molecular bromine, which reacts with alkenes by a mechanism analogous to that of other free-radical halogenations.

PROBLEM 10.4 Assume that *N*-bromosuccinimide serves as a source of Br_2, and write equations for the propagation steps in the formation of 3-bromocyclohexene by allylic bromination of cyclohexene.

Although allylic brominations and chlorinations offer a method for attaching a reactive functional group to a hydrocarbon framework, we need to be aware of two important limitations. For allylic halogenation to be effective in a particular synthesis:

1. All the allylic hydrogens in the starting alkene must be equivalent.
2. Both resonance forms of the allylic radical must be equivalent.

In the two examples cited so far, the chlorination of propene and the bromination of cyclohexene, both criteria are met.

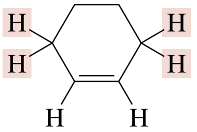
All the allylic hydrogens of propene are equivalent.

$CH_2{=}CH{-}CH_3$

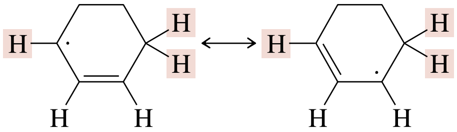
The two resonance forms of allyl radical are equivalent.

$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$

All the allylic hydrogens of cyclohexene are equivalent.



The two resonance forms of 2-cyclohexenyl radical are equivalent.



Unless both criteria are met, mixtures of constitutionally isomeric allylic halides result.

PROBLEM 10.5 The two alkenes 2,3,3-trimethyl-1-butene and 1-octene were each subjected to allylic halogenation with *N*-bromosuccinimide. One of these alkenes yielded a single allylic bromide, whereas the other gave a mixture of two constitutionally isomeric allylic bromides. Match the chemical behavior to the correct alkene and give the structure of the allylic bromide(s) formed from each.

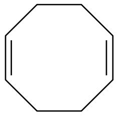
10.5 CLASSES OF DIENES

Allylic carbocations and allylic radicals are conjugated systems involved as reactive intermediates in chemical reactions. The third type of conjugated system that we will examine, **conjugated dienes,** consists of stable molecules.

A hydrocarbon that contains two double bonds is called an **alkadiene,** and the relationship between the double bonds may be described as *isolated, conjugated,* or *cumulated.* **Isolated diene** units are those in which two carbon–carbon double bond units are separated from each other by one or more sp^3-hybridized carbon atoms. 1,4-Pentadiene and 1,5-cyclooctadiene have isolated double bonds:

$CH_2{=}CHCH_2CH{=}CH_2$

1,4-Pentadiene

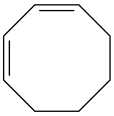


1,5-Cyclooctadiene

Conjugated dienes are those in which two carbon–carbon double bond units are directly connected to each other by a single bond. 1,3-Pentadiene and 1,3-cyclooctadiene contain conjugated double bonds:

$\mathrm{CH_2{=}CH{-}CH{=}CHCH_3}$

1,3-Pentadiene



1,3-Cyclooctadiene

Cumulated dienes are those in which one carbon atom is common to two carbon–carbon double bonds. The simplest cumulated diene is 1,2-propadiene, also called *allene*, and compounds of this class are generally referred to as *allenes.*

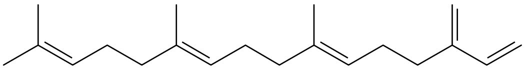
Allene is an acceptable IUPAC name for 1,2-propadiene.

$$\mathrm{CH_2{=}C{=}CH_2}$$

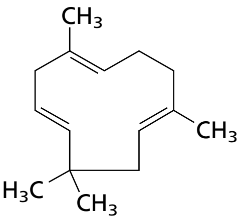
1,2-Propadiene

PROBLEM 10.6 Many naturally occurring substances contain several carbon–carbon double bonds: some isolated, some conjugated, and some cumulated. Identify the types of carbon–carbon double bonds found in each of the following substances:

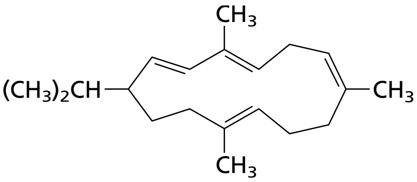
(a) β-Springene (a scent substance from the dorsal gland of springboks)



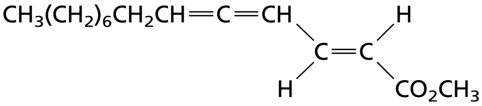
(b) Humulene (found in hops and oil of cloves)



(c) Cembrene (occurs in pine resin)

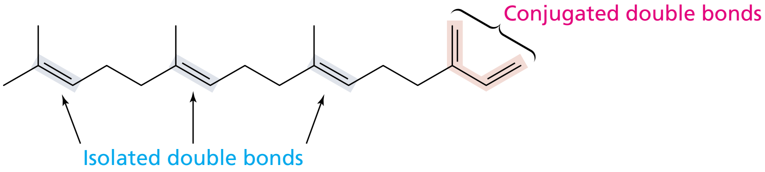


(d) The sex attractant of the male dried-bean beetle



$$\mathrm{CH_3(CH_2)_6CH_2CH{=}C{=}CH{-}CH{=}CH{-}CO_2CH_3}$$

SAMPLE SOLUTION (a) β-Springene has three isolated double bonds and a pair of conjugated double bonds:



Isolated double bonds are separated from other double bonds by at least one sp^3-hybridized carbon. Conjugated double bonds are joined by a single bond.

Alkadienes are named according to the IUPAC rules by replacing the *-ane* ending of an alkane with *-adiene* and locating the position of each double bond by number. Compounds with three carbon–carbon double bonds are called *alkatrienes* and named accordingly, those with four double bonds are *alkatetraenes,* and so on.

10.6 RELATIVE STABILITIES OF DIENES

Which is the most stable arrangement of double bonds in an alkadiene—isolated, conjugated, or cumulated?

As we saw in Chapter 6, the stabilities of alkenes may be assessed by comparing their heats of hydrogenation. Figure 10.3 depicts the heats of hydrogenation of an isolated diene (1,4-pentadiene) and a conjugated diene (1,3-pentadiene), along with the alkenes 1-pentene and (*E*)-2-pentene. The figure shows that an isolated pair of double bonds behaves much like two independent alkene units. The measured heat of hydrogenation of the two double bonds in 1,4-pentadiene is 252 kJ/mol (60.2 kcal/mol), exactly twice the heat of hydrogenation of 1-pentene. Furthermore, the heat evolved on hydrogenation of each double bond must be 126 kJ/mol (30.1 kcal/mol), since 1-pentene is an intermediate in the hydrogenation of 1,4-pentadiene to pentane.

By the same reasoning, hydrogenation of the terminal double bond in the conjugated diene (*E*)-1,3-pentadiene releases only 111 kJ/mol (26.5 kcal/mol) when it is hydrogenated to (*E*)-2-pentene. Hydrogenation of the terminal double bond in the conjugated diene evolves 15 kJ/mol (3.6 kcal/mol) less heat than hydrogenation of a terminal double bond in the diene with isolated double bonds. *A conjugated double bond is 15 kJ/mol (3.6 kcal/mol) more stable than a simple double bond.* We call this increased stability due to conjugation the **delocalization energy, resonance energy,** or **conjugation energy.**

The cumulated double bonds of an allenic system are of relatively high energy. The heat of hydrogenation of allene is more than twice that of propene.

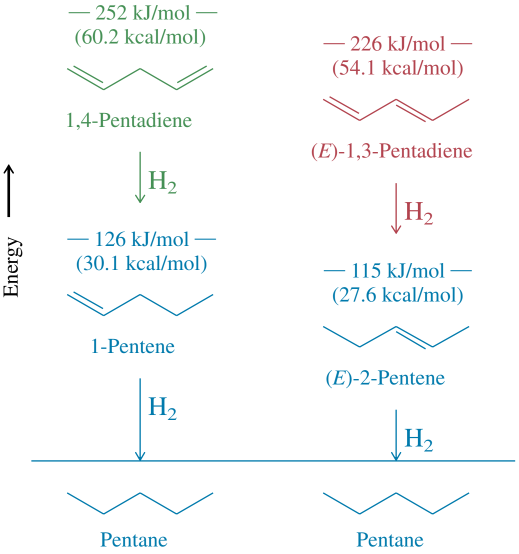


FIGURE 10.3 Heats of hydrogenation of some C_5H_{10} alkenes and C_5H_8 alkadienes.

$$\underset{\text{Allene}}{CH_2{=}C{=}CH_2} + \underset{\text{Hydrogen}}{2H_2} \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} \qquad \Delta H° = -295\text{ kJ } (-70.5\text{ kcal})$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Hydrogen}}{H_2} \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} \qquad \Delta H° = -125\text{ kJ } (-29.9\text{ kcal})$$

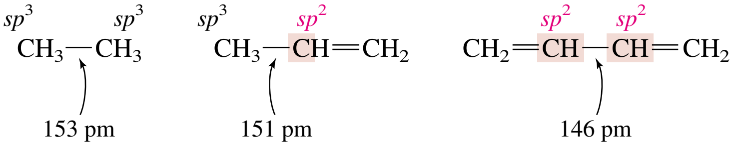
PROBLEM 10.7 Another way in which energies of isomers may be compared is by their heats of combustion. Match the heat of combustion with the appropriate diene.

Dienes:	1,2-Pentadiene, (*E*)-1,3-pentadiene, 1,4-pentadiene
Heats of combustion:	3186 kJ/mol, 3217 kJ/mol, 3251 kJ/mol 761.6 kcal/mol, 768.9 kcal/mol, 777.1 kcal/mol

Thus, the order of alkadiene stability decreases in the order: conjugated diene (most stable) → isolated diene → cumulated diene (least stable). To understand this ranking, we need to look at structure and bonding in alkadienes in more detail.

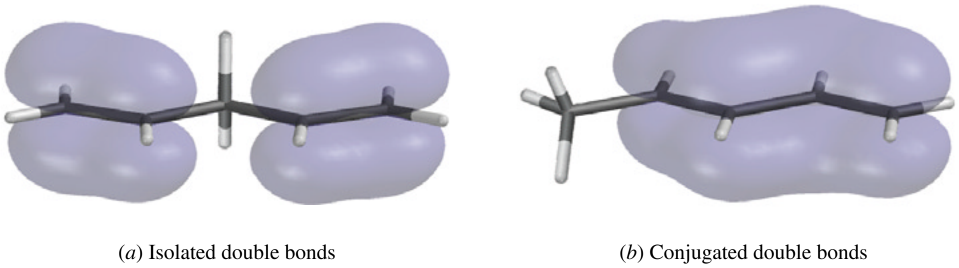
10.7 BONDING IN CONJUGATED DIENES

At 146 pm the C-2—C-3 distance in 1,3-butadiene is relatively short for a carbon–carbon single bond. This is most reasonably seen as a hybridization effect. In ethane both carbons are sp^3-hybridized and are separated by a distance of 153 pm. The carbon–carbon single bond in propene unites sp^3- and sp^2-hybridized carbons and is shorter than that of ethane. Both C-2 and C-3 are sp^2-hybridized in 1,3-butadiene, and a decrease in bond distance between them reflects the tendency of carbon to attract electrons more strongly as its *s* character increases.



$$\overset{sp^3}{CH_3}\underset{153\text{ pm}}{—}\overset{sp^3}{CH_3} \qquad \overset{sp^3}{CH_3}\underset{151\text{ pm}}{—}\overset{sp^2}{CH}{=}CH_2 \qquad CH_2{=}\overset{sp^2}{CH}\underset{146\text{ pm}}{—}\overset{sp^2}{CH}{=}CH_2$$

The factor most responsible for the increased stability of conjugated double bonds is the greater delocalization of their π electrons compared with the π electrons of isolated double bonds. As shown in Figure 10.4*a*, the π electrons of an isolated diene system occupy, in pairs, two noninteracting π orbitals. Each of these π orbitals encompasses two carbon atoms. An sp^3-hybridized carbon isolates the two π orbitals from each other, preventing the exchange of electrons between them. In a conjugated diene, however, mutual overlap of the two π orbitals, represented in Figure 10.4*b*, gives an orbital system in which each π electron is delocalized over four carbon atoms. Delocalization of electrons lowers their energy and gives a more stable molecule.

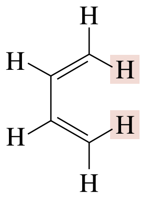


(*a*) Isolated double bonds

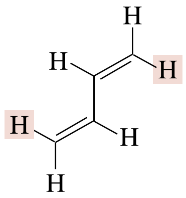
(*b*) Conjugated double bonds

FIGURE 10.4 (*a*) Isolated double bonds are separated from each other by one or more sp^3-hybridized carbons and cannot overlap to give an extended π orbital. (*b*) In a conjugated diene, overlap of two π orbitals gives an extended π system encompassing four carbon atoms.

Additional evidence for electron delocalization in 1,3-butadiene can be obtained by considering its conformations. Overlap of the two π electron systems is optimal when the four carbon atoms are coplanar. Two conformations allow this coplanarity: they are called the *s*-cis and *s*-trans conformations.



s-Cis conformation of 1,3-butadiene



s-Trans conformation of 1,3-butadiene

The letter *s* in *s*-cis and *s*-trans refers to conformations around the C—C single bond in the diene. The *s*-trans conformation of 1,3-butadiene is 12 kJ/mol (2.8 kcal/mol) more

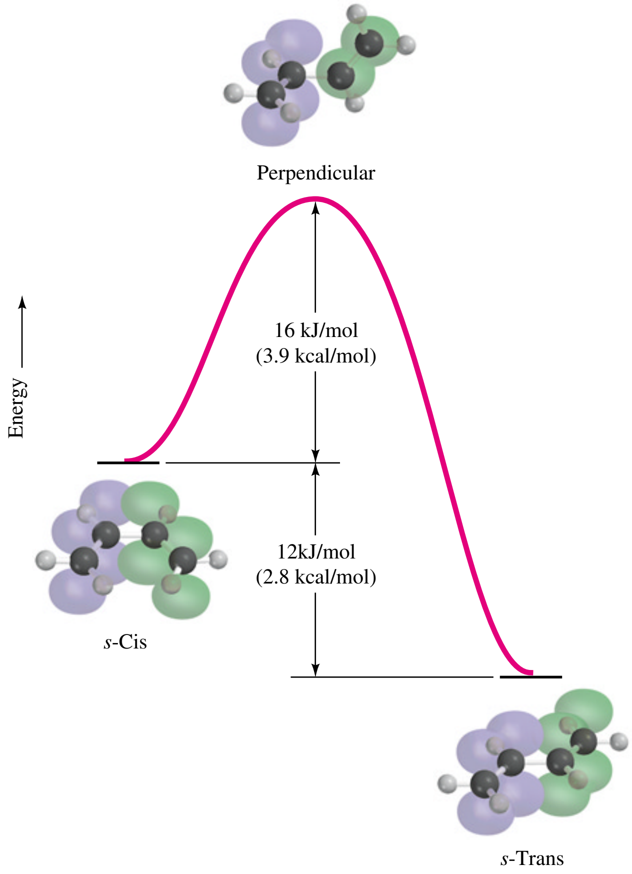


FIGURE 10.5 Conformations and electron delocalization in 1,3-butadiene. The *s*-cis and the *s*-trans conformations permit the 2*p* orbitals to be aligned parallel to one another for maximum π electron delocalization. The *s*-trans conformation is more stable than the *s*-cis. Stabilization resulting from π electron delocalization is least in the perpendicular conformation, which is a transition state for rotation about the C-2—C-3 single bond.

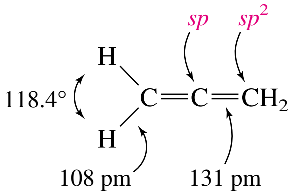
stable than the *s*-cis, which is destabilized by van der Waals strain between the hydrogens at C-1 and C-4.

The *s*-cis and *s*-trans conformations of 1,3-butadiene interconvert by rotation around the C-2—C-3 bond, as illustrated in Figure 10.5. The conformation at the midpoint of this rotation, the *perpendicular conformation,* has its 2*p* orbitals in a geometry that prevents extended conjugation. It has localized double bonds. The main contributor to the energy of activation for rotation about the single bond in 1,3-butadiene is the decrease in electron delocalization that attends conversion of the *s*-cis or *s*-trans conformation to the perpendicular conformation.

Return to the models of 1,3-butadiene in Figure 10.5 on *Learning By Modeling* and compare space-filling models of the *s*-cis and *s*-trans conformation.

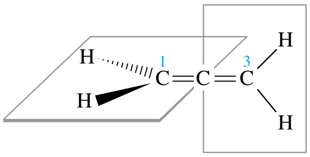
10.8 BONDING IN ALLENES

The three carbons of allene lie in a straight line, with relatively short carbon–carbon bond distances of 131 pm. The central carbon, since it bears only two substituents, is *sp*-hybridized. The terminal carbons of allene are sp^2-hybridized.

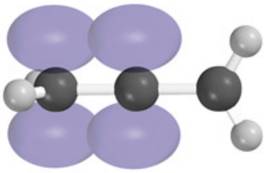


Allene

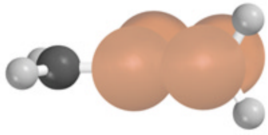
Structural studies show allene to be nonplanar. As Figure 10.6 illustrates, the plane of one HCH unit is perpendicular to the plane of the other. Figure 10.6 also portrays the



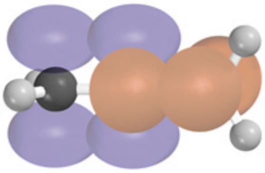
(*a*) Planes defined by H(C-1)H and H(C-3)H are mutually perpendicular.



(*b*) The *p* orbital of C-1 and one of the *p* orbitals of C-2 can overlap so as to participate in π bonding.



(*c*) The *p* orbital of C-3 and one of the *p* orbitals of C-2 can overlap so as to participate in a second π orbital perpendicular to the one in (*b*).



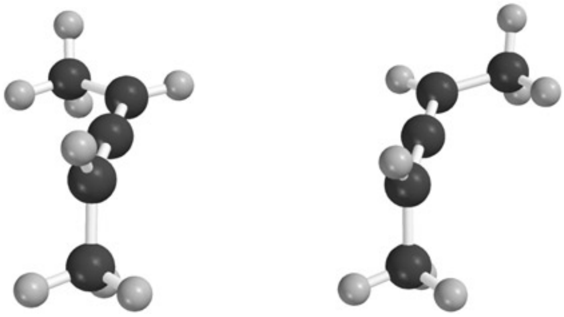
(*d*) Allene is a nonplanar molecule characterized by a linear carbon chain and two mutually perpendicular π bonds.

FIGURE 10.6 Bonding and geometry in 1,2-propadiene (allene).

reason for the molecular geometry of allene. The 2*p* orbital of each of the terminal carbons overlaps with a different 2*p* orbital of the central carbon. Since the 2*p* orbitals of the central carbon are perpendicular to each other, the perpendicular nature of the two HCH units follows naturally.

The nonplanarity of allenes has an interesting stereochemical consequence. 1,3-Disubstituted allenes are chiral; they are not superposable on their mirror images. Even an allene as simple as 2,3-pentadiene ($CH_3CH{=}C{=}CHCH_3$) has been obtained as separate enantiomers.

Examine models of both enantiomers of 2,3-pentadiene to verify that they are nonsuperposable.



(+)-2,3-Pentadiene (−)-2,3-Pentadiene

The enantiomers shown are related as a right-hand and left-hand screw, respectively.

Chiral allenes are examples of a small group of molecules that are chiral, but don't have a stereogenic center. What they do have is a **stereogenic axis,** also called a **chiral axis,** which in the case of 2,3-pentadiene is a line passing through the three carbons of the allene unit (carbons 2, 3, and 4).

The Cahn–Ingold–Prelog *R,S* notation has been extended to chiral allenes and other molecules that have a stereogenic axis. Such compounds are so infrequently encountered, however, we will not cover the rules for specifying their stereochemistry in this text.

PROBLEM 10.8 Is 2-methyl-2,3-pentadiene chiral? What about 2-chloro-2,3-pentadiene?

Because of the linear geometry required of cumulated dienes, cyclic allenes, like cycloalkynes, are strained unless the rings are fairly large. 1,2-Cyclononadiene is the smallest cyclic allene that is sufficiently stable to be isolated and stored conveniently.

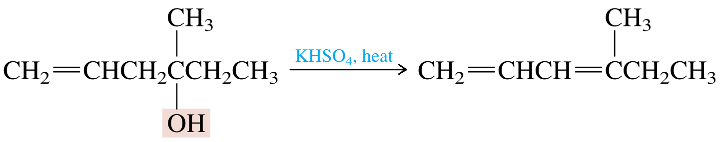
10.9 PREPARATION OF DIENES

The use of 1,3-butadiene in the preparation of synthetic rubber is discussed in the boxed essay "Diene Polymers" that appears later in this chapter.

The conjugated diene 1,3-butadiene is used in the manufacture of synthetic rubber and is prepared on an industrial scale in vast quantities. Production in the United States is currently 4×10^9 lb/year. One industrial process is similar to that used for the preparation of ethylene: in the presence of a suitable catalyst, butane undergoes thermal dehydrogenation to yield 1,3-butadiene.

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{chromia–alumina}]{590–675°C} CH_2{=}CHCH{=}CH_2 + 2H_2$$

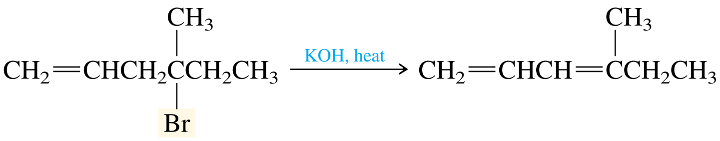
Laboratory syntheses of conjugated dienes can be achieved by elimination reactions of unsaturated alcohols and alkyl halides. In the two examples that follow, the conjugated diene is produced in high yield even though an isolated diene is also possible.



$$CH_2{=}CHCH_2\overset{CH_3}{\underset{OH}{C}}CH_2CH_3 \xrightarrow{KHSO_4,\ heat} CH_2{=}CHCH{=}\overset{CH_3}{C}CH_2CH_3$$

3-Methyl-5-hexen-3-ol

4-Methyl-1,3-hexadiene (88%)



$$CH_2{=}CHCH_2\overset{CH_3}{\underset{Br}{C}}CH_2CH_3 \xrightarrow{KOH,\ heat} CH_2{=}CHCH{=}\overset{CH_3}{C}CH_2CH_3$$

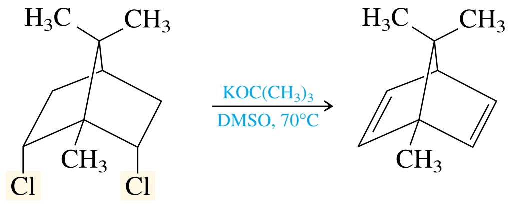
4-Bromo-4-methyl-1-hexene

4-Methyl-1,3-hexadiene (78%)

As we saw earlier, dehydrations and dehydrohalogenations are typically regioselective in the direction that leads to the most stable double bond. Conjugated dienes are more stable than isolated dienes and are formed faster via a lower energy transition state.

PROBLEM 10.9 What dienes containing isolated double bonds are capable of being formed, but are not observed, in the two preceding equations describing elimination in 3-methyl-5-hexen-3-ol and 4-bromo-4-methyl-1-hexene?

Dienes with isolated double bonds can be formed when the structure of the substrate doesn't permit the formation of a conjugated diene.



2,6-Dichlorocamphane

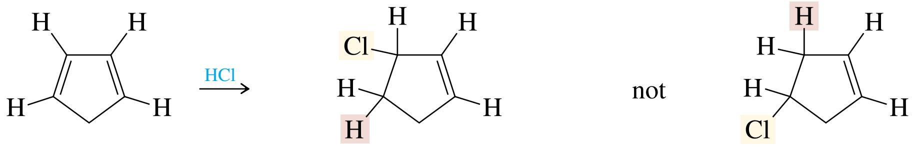
Bornadiene (83%)

We will not discuss the preparation of cumulated dienes. They are prepared less readily than isolated or conjugated dienes and require special methods.

10.10 ADDITION OF HYDROGEN HALIDES TO CONJUGATED DIENES

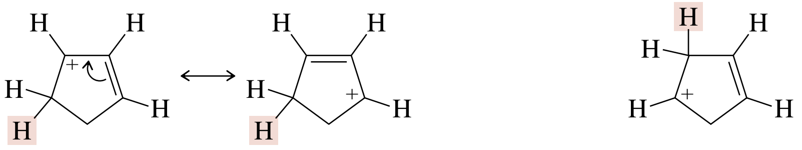
Our discussion of chemical reactions of alkadienes will be limited to those of conjugated dienes. The reactions of isolated dienes are essentially the same as those of individual alkenes. The reactions of cumulated dienes are—like their preparation—so specialized that their treatment is better suited to an advanced course in organic chemistry.

Electrophilic addition is the characteristic chemical reaction of alkenes, and conjugated dienes undergo addition reactions with the same electrophiles that react with alkenes, and by similar mechanisms. As we saw in the reaction of hydrogen halides with alkenes (Section 6.5), the regioselectivity of electrophilic addition is governed by protonation of the double bond in the direction that gives the more stable of two possible carbocations. With conjugated dienes it is one of the terminal carbons that is protonated, because the species that results is an allylic carbocation which is stabilized by electron delocalization. Thus, when 1,3-cyclopentadiene reacts with hydrogen chloride, the product is 3-chlorocyclopentene.



1,3-Cyclopentadiene 3-Chlorocyclopentene (70–90%) 4-Chlorocyclopentene

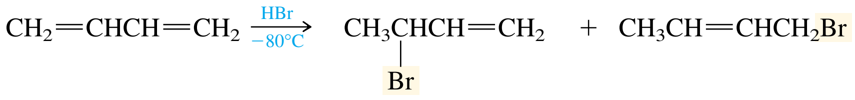
The carbocation that leads to the observed product is secondary and allylic; the other is secondary but not allylic.



Protonation at end of diene unit gives a carbocation that is both secondary and allylic; product is formed from this carbocation.

Protonation at C-2 gives a carbocation that is secondary but not allylic; less stable carbocation; not formed as rapidly.

Both resonance forms of the allylic carbocation from 1,3-cyclopentadiene are equivalent, and so attack at either of the carbons that share the positive charge gives the same product, 3-chlorocyclopentene. This is not the case with 1,3-butadiene, and so hydrogen halides add to 1,3-butadiene to give a mixture of two regioisomeric allylic halides. For the case of electrophilic addition of hydrogen bromide,



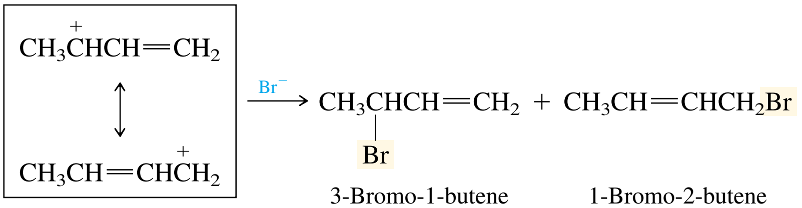
$$\mathrm{CH_2{=}CHCH{=}CH_2} \xrightarrow[-80°\mathrm{C}]{\mathrm{HBr}} \mathrm{CH_3}\underset{\overset{|}{\mathrm{Br}}}{\mathrm{C}}\mathrm{HCH{=}CH_2} + \mathrm{CH_3CH{=}CHCH_2Br}$$

1,3-Butadiene 3-Bromo-1-butene (81%) 1-Bromo-2-butene (19%)

The major product corresponds to addition of a proton at C-1 and bromide at C-2. This mode of addition is called **1,2 addition,** or **direct addition.** The minor product has its proton and bromide at C-1 and C-4, respectively, of the original diene system. This mode of addition is called **1,4 addition,** or **conjugate addition.** The double bond that was between C-3 and C-4 in the starting material remains there in the product from 1,2 addition but migrates to a position between C-2 and C-3 in the product from 1,4 addition.

Both the 1,2-addition product and the 1,4-addition product are derived from the same allylic carbocation.

Use *Learning By Modeling* to view the charge distribution in the allylic carbocation shown in the equation.



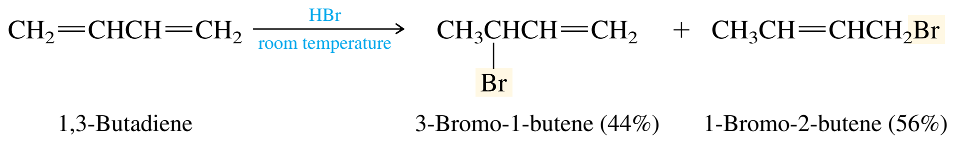
$$\boxed{\begin{array}{c}\mathrm{CH_3\overset{+}{C}HCH{=}CH_2}\\ \updownarrow \\ \mathrm{CH_3CH{=}CH\overset{+}{C}H_2}\end{array}} \xrightarrow{\mathrm{Br^-}} \mathrm{CH_3}\underset{\overset{|}{\mathrm{Br}}}{\mathrm{C}}\mathrm{HCH{=}CH_2} + \mathrm{CH_3CH{=}CHCH_2Br}$$

3-Bromo-1-butene (major) 1-Bromo-2-butene (minor)

The secondary carbon bears more of the positive charge than does the primary carbon, and attack by the nucleophilic bromide ion is faster there. Hence, the major product is the secondary bromide.

When the major product of a reaction is the one that is formed at the fastest rate, we say that the reaction is governed by **kinetic control.** Most organic reactions fall into this category, and the electrophilic addition of hydrogen bromide to 1,3-butadiene at low temperature is a kinetically controlled reaction.

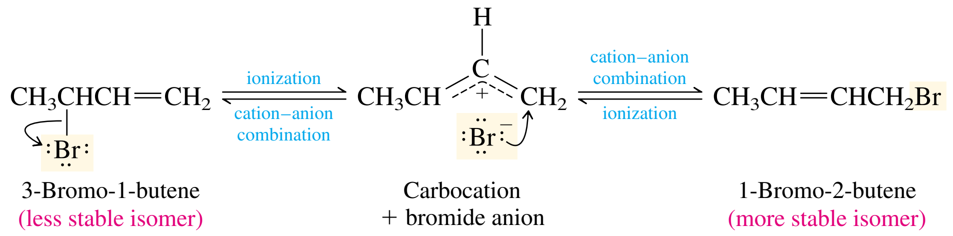
When, however, the ionic addition of hydrogen bromide to 1,3-butadiene is carried out at room temperature, the ratio of isomeric allylic bromides observed is different from that which is formed at −80°C. At room temperature, the 1,4-addition product predominates.



$$CH_2{=}CHCH{=}CH_2 \xrightarrow[\text{room temperature}]{HBr} \underset{\underset{\displaystyle Br}{|}}{CH_3CH}CH{=}CH_2 + CH_3CH{=}CHCH_2Br$$

1,3-Butadiene 3-Bromo-1-butene (44%) 1-Bromo-2-butene (56%)

Clearly, the temperature at which the reaction occurs exerts a major influence on the product composition. To understand why, an important fact must be added. The 1,2- and 1,4-addition products *interconvert rapidly* by allylic rearrangement at elevated temperature in the presence of hydrogen bromide. Heating the product mixture to 45°C in the presence of hydrogen bromide leads to a mixture in which the ratio of 3-bromo-1-butene to 1-bromo-2-butene is 15:85.



The product of 1,4 addition, 1-bromo-2-butene, contains an internal double bond and so is *more stable* than the product of 1,2 addition, 3-bromo-l-butene, which has a terminal double bond.

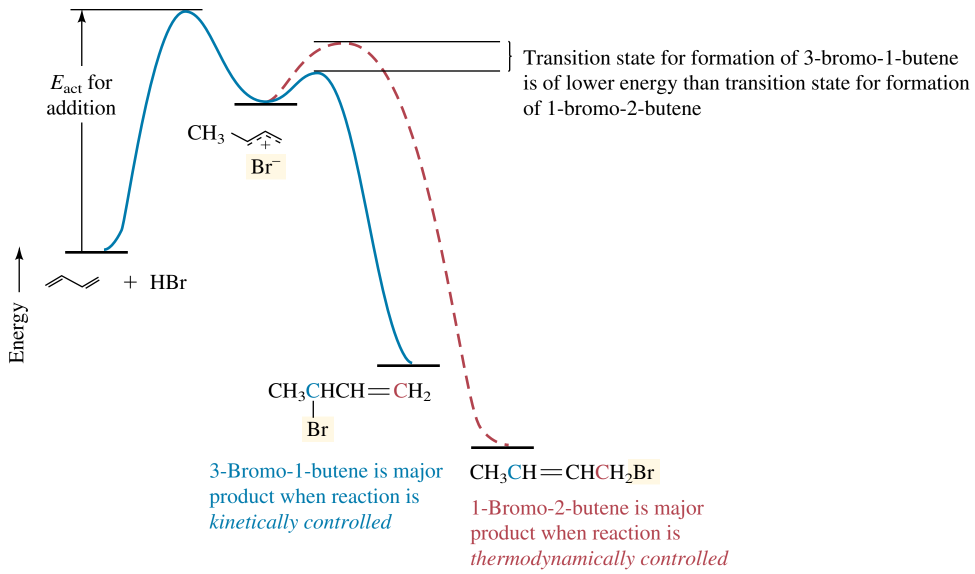


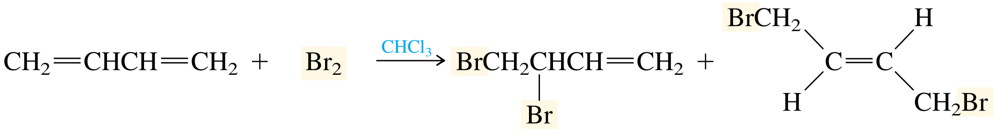
FIGURE 10.7 Energy diagram showing relationship of kinetic control to thermodynamic control in addition of hydrogen bromide to 1,3-butadiene.

When addition occurs under conditions in which the products can equilibrate, the composition of the reaction mixture no longer reflects the relative rates of formation of the products but tends to reflect their *relative stabilities.* Reactions of this type are said to be governed by **thermodynamic control.** One way to illustrate kinetic and thermodynamic control in the addition of hydrogen bromide to 1,3-butadiene is by way of the energy diagram of Figure 10.7. At low temperature, addition takes place irreversibly. Isomerization is slow because insufficient thermal energy is available to permit the products to surmount the energy barrier for ionization. At higher temperatures isomerization is possible, and the more stable product predominates.

PROBLEM 10.10 Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?

10.11 HALOGEN ADDITION TO DIENES

Mixtures of 1,2- and 1,4-addition products are obtained when 1,3-butadiene reacts with chlorine or bromine.



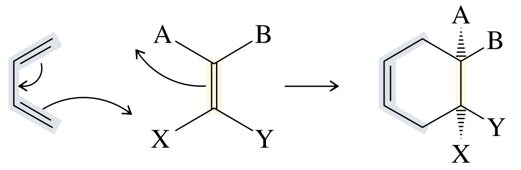
1,3-Butadiene   Bromine   3,4-Dibromo-1-butene (37%)   (*E*)-1,4-Dibromo-2-butene (63%)

The tendency for conjugate addition is pronounced, and *E* double bonds are generated almost exclusively.

PROBLEM 10.11 Exclusive of stereoisomers, how many products are possible in the electrophilic addition of 1 eq of bromine to 2-methyl-1,3-butadiene?

10.12 THE DIELS–ALDER REACTION

A particular kind of conjugate addition reaction earned the Nobel Prize in chemistry for Otto Diels and Kurt Alder of the University of Kiel (Germany) in 1950. The Diels–Alder reaction is the *conjugate addition of an alkene to a diene.* Using 1,3-butadiene as a typical diene, the Diels–Alder reaction may be represented by the general equation:



1,3-Butadiene   Dienophile   Diels–Alder adduct

For an animation of this reaction, see *Learning By Modeling.*

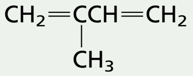
The alkene that adds to the diene is called the **dienophile.** Because the Diels–Alder reaction leads to the formation of a ring, it is termed a **cycloaddition** reaction. The product contains a cyclohexene ring as a structural unit.

Epoxidation of alkenes (Section 6.18) is another example of a cycloaddition.

The Diels–Alder cycloaddition is one example of a **pericyclic reaction.** A pericyclic reaction is a one-step reaction that proceeds through a cyclic transition state. Bond

DIENE POLYMERS

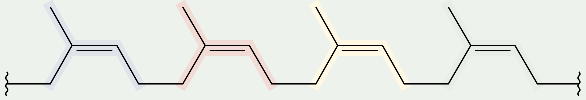
Some 500 years ago during Columbus's second voyage to what are now the Americas, he and his crew saw children playing with balls made from the latex of trees that grew there. Later, Joseph Priestley called this material "rubber" to describe its ability to erase pencil marks by rubbing, and in 1823 Charles Macintosh demonstrated how rubber could be used to make waterproof coats and shoes. Shortly thereafter Michael Faraday determined an empirical formula of C_5H_8 for rubber. It was eventually determined that rubber is a polymer of 2-methyl-1,3-butadiene.



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH{=}CH_2$$

2-Methyl-1,3-butadiene (common name: *isoprene*)

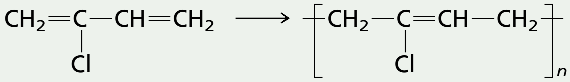
The structure of rubber corresponds to 1,4 addition of several thousand isoprene units to one another:



All the double bonds in rubber have the *Z* (or cis) configuration. A different polymer of isoprene, called *gutta-percha,* has shorter polymer chains and *E* (or trans) double bonds. Gutta-percha is a tough, horn-like substance once used as a material for golf ball covers.*

In natural rubber the attractive forces between neighboring polymer chains are relatively weak, and there is little overall structural order. The chains slide easily past one another when stretched and return, in time, to their disordered state when the distorting force is removed. The ability of a substance to recover its original shape after distortion is its *elasticity.* The elasticity of natural rubber is satisfactory only within a limited temperature range; it is too rigid when cold and too sticky when warm to be very useful. Rubber's elasticity is improved by *vulcanization,* a process discovered by Charles Goodyear in 1839. When natural rubber is heated with sulfur, a chemical reaction occurs in which neighboring polyisoprene chains become connected through covalent bonds to sulfur. Although these sulfur "bridges" permit only limited movement of one chain with respect to another, their presence ensures that the rubber will snap back to its original shape once the distorting force is removed.

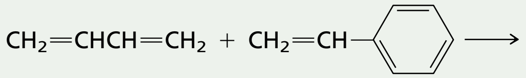
As the demand for rubber increased, so did the chemical industry's efforts to prepare a synthetic substitute. One of the first **elastomers** (a synthetic polymer that possesses elasticity) to find a commercial niche was *neoprene,* discovered by chemists at Du Pont in 1931. Neoprene is produced by free-radical polymerization of 2-chloro-1,3-butadiene and has the greatest variety of applications of any elastomer. Some uses include electrical insulation, conveyer belts, hoses, and weather balloons.



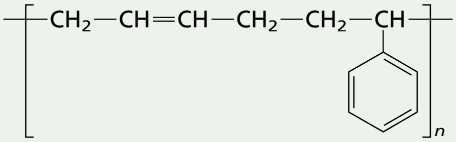
$$CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \longrightarrow \left[CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2\right]_n$$

2-Chloro-1,3-butadiene Neoprene

The elastomer produced in greatest amount is *styrene-butadiene rubber* (SBR). Annually, just under 10^9 lb of SBR is produced in the United States, and almost all of it is used in automobile tires. As its name suggests, SBR is prepared from styrene and 1,3-butadiene. It is an example of a **copolymer,** a polymer assembled from two or more different monomers. Free-radical polymerization of a mixture of styrene and 1,3-butadiene gives SBR.



1,3-Butadiene Styrene



Styrene-butadiene rubber

Coordination polymerization of isoprene using Ziegler–Natta catalyst systems (Section 6.21) gives a material similar in properties to natural rubber, as does polymerization of 1,3-butadiene. Poly(1,3-butadiene) is produced in about two thirds the quantity of SBR each year. It, too, finds its principal use in tires.

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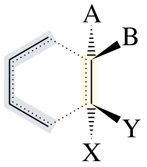
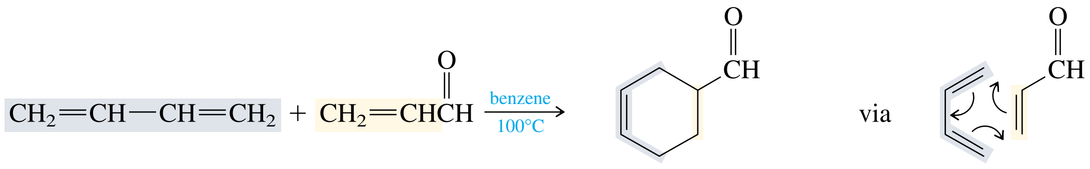
[*] A detailed discussion of the history, structure, and applications of natural rubber appears in the May 1990 issue of the *Journal of Chemical Education.*

formation occurs at both ends of the diene system, and the Diels–Alder transition state involves a cyclic array of six carbons and six π electrons. The diene must adopt the *s*-cis conformation in the transition state.



Transition state for
Diels–Alder cycloaddition

The simplest of all Diels–Alder reactions, cycloaddition of ethylene to 1,3-butadiene, does not proceed readily. It has a high activation energy and a low reaction rate. Substituents such as C═O or C≡N, however, when *directly* attached to the double bond of the dienophile, increase its reactivity, and compounds of this type give high yields of Diels–Alder adducts at modest temperatures.

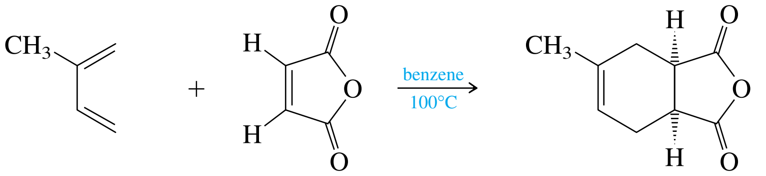


1,3-Butadiene

Acrolein

Cyclohexene-4-carboxaldehyde (100%)

The product of a Diels–Alder cycloaddition always contains one more ring than was present in the reactants. The dienophile *maleic anhydride* contains one ring, so the product of its addition to a diene contains two.

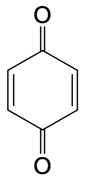


2-Methyl-1,3-butadiene

Maleic anhydride

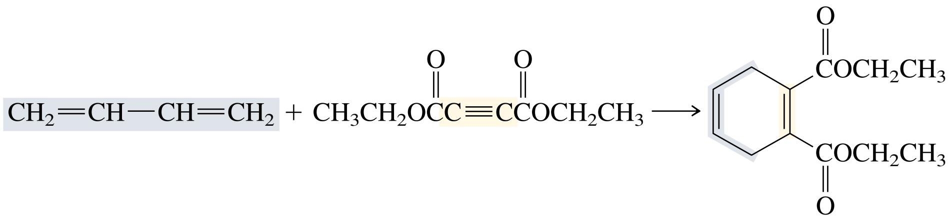
1-Methylcyclohexene-4,5-dicarboxylic anhydride (100%)

PROBLEM 10.12 Benzoquinone is a very reactive dienophile. It reacts with 2-chloro-1,3-butadiene to give a single product, $C_{10}H_9ClO_2$, in 95% yield. Write a structural formula for this product.



Benzoquinone

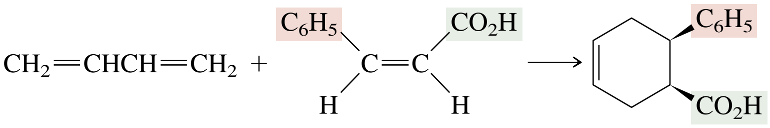
Acetylene, like ethylene, is a poor dienophile, but alkynes that bear C═O or C≡N substituents react readily with dienes. A cyclohexadiene derivative is the product.



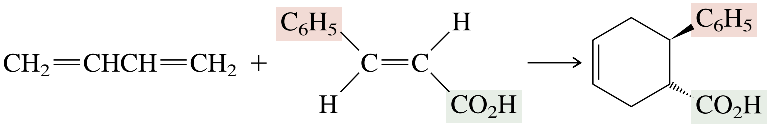
$CH_2{=}CH{-}CH{=}CH_2 + CH_3CH_2OCC{\equiv}CCOCH_2CH_3 \longrightarrow$

1,3-Butadiene Diethyl acetylenedicarboxylate Diethyl 1,4-cyclohexadiene-1,2-dicarboxylate (98%)

The Diels–Alder reaction is stereospecific. Substituents that are cis in the dienophile remain cis in the product; substituents that are trans in the dienophile remain trans in the product.



1,3-Butadiene *cis*-Cinnamic acid Only product

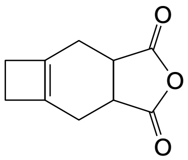


1,3-Butadiene *trans*-Cinnamic acid Only product

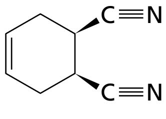
Recall from Section 7.13 that a stereospecific reaction is one in which each stereoisomer of a particular starting material yields a different stereoisomeric form of the reaction product. In the examples shown, the product from Diels–Alder cycloaddition of 1,3-butadiene to *cis*-cinnamic acid is a stereoisomer of the product from *trans*-cinnamic acid. Each product, although chiral, is formed as a racemic mixture.

PROBLEM 10.13 What combination of diene and dienophile would you choose in order to prepare each of the following compounds?

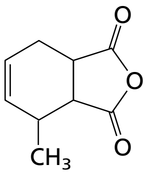
(a)



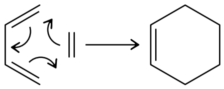
(b)



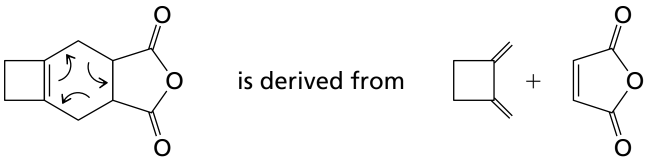
(c)



SAMPLE SOLUTION (a) Using curved arrows, we represent a Diels–Alder reaction as

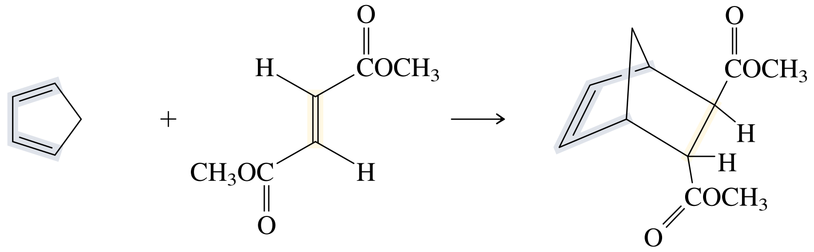


To deduce the identity of the diene and dienophile that lead to a particular Diels–Alder adduct, we use curved arrows in the reverse fashion to "undo" the cyclohexene derivative. Start with the π component of the double bond in the six-membered ring, and move electrons in pairs.

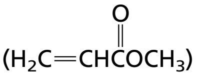


Diels–Alder adduct Diene Dienophile

Cyclic dienes yield bridged bicyclic Diels–Alder adducts.



1,3-Cyclopentadiene Dimethyl fumarate Dimethylbicyclo[2.2.1]hept-2-ene-*trans*-5,6-dicarboxylate

PROBLEM 10.14 The Diels–Alder reaction of 1,3-cyclopentadiene with methyl acrylate ( $H_2C{=}CH\overset{\overset{O}{\|}}{C}OCH_3$) gives a mixture of two diastereomers. Write their structural formulas.

The importance of the Diels–Alder reaction is in synthesis. It gives us a method to form *two* new carbon–carbon bonds in a single operation and requires no reagents, such as acids or bases, that might affect other functional groups in the molecule.

The mechanism of the Diels–Alder reaction is best understood on the basis of a molecular orbital approach. To understand this approach we need to take a more detailed look at the π orbitals of alkenes and dienes.

10.13 THE π MOLECULAR ORBITALS OF ETHYLENE AND 1,3-BUTADIENE

The valence bond approach has served us well to this point as a tool to probe structure and reactivity in organic chemistry. An appreciation for the delocalization of π electrons through a system of overlapping *p* orbitals has given us insights into conjugated systems that are richer in detail than those obtained by examining Lewis formulas. An even deeper understanding can be gained by applying qualitative molecular orbital theory to these π electron systems. We shall see that useful information can be gained by directing attention to what are called the **frontier orbitals** of molecules. The frontier orbitals are the *highest occupied molecular orbital* (the *HOMO*) and the *lowest unoccupied molecular orbital* (the *LUMO*). When electrons are transferred *from* a molecule, it is the electrons in the HOMO that are involved, because they are the most weakly held. When electrons are transferred *to* a molecule, they go into the LUMO, because that is the lowest energy orbital available.

Ethylene. Let's begin by examining the π molecular orbitals of ethylene. Recall from Section 1.14 that the number of molecular orbitals is equal to the number of atomic orbitals that combine to form them. We saw that the 1*s* orbitals of two hydrogen atoms overlap to give both a bonding (σ) and an antibonding (σ*) orbital. The same principle applies to π orbitals. As Figure 10.8 illustrates for the case of ethylene, the 2*p* orbitals of adjacent carbons overlap to give both a bonding (π) and an antibonding (π*) orbital. Notice that the σ electrons are not explicitly considered in Figure 10.8. These electrons are strongly held, and the collection of σ bonds can be thought of as an inert framework that supports the valence electrons of the π orbital.

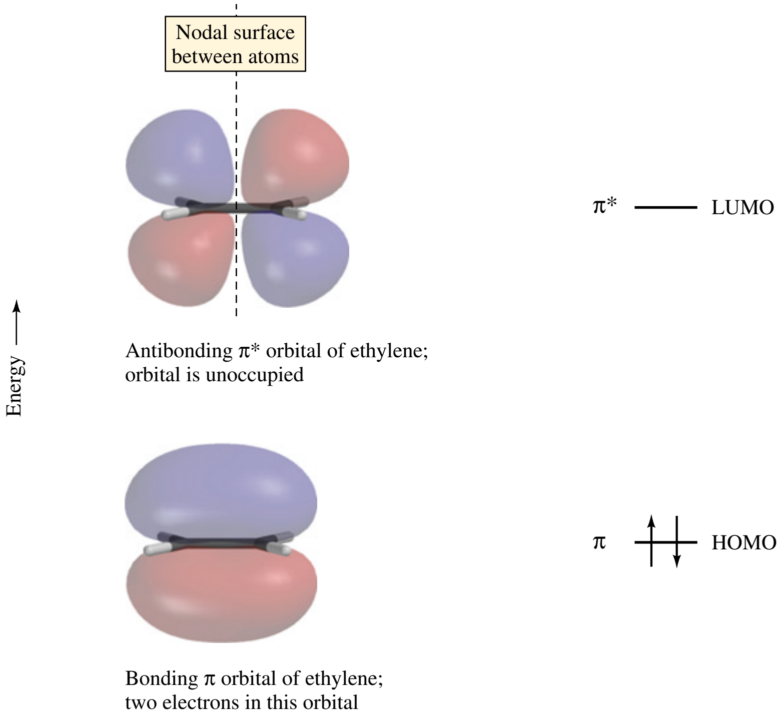


FIGURE 10.8 The bonding (π) and antibonding (π*) molecular orbitals of ethylene. The wave function changes sign (red to blue) on passing through a nodal surface. The plane of the molecule is a nodal surface in both orbitals; the antibonding orbital has an additional nodal surface perpendicular to the plane of the molecule.

Both the π and π* molecular orbitals of ethylene are *antisymmetric* with respect to the plane of the molecule. By this we mean that the wave function changes sign on passing through the molecular plane. It's convenient to designate the signs of *p* orbital wave functions by shading one lobe of a *p* orbital in red and the other in blue instead of using plus (+) and minus (−) signs that might be confused with electronic charges. The plane of the molecule corresponds to a nodal plane where the probability of finding the π electrons is zero. The bonding π orbital has no nodes other than this plane, whereas the antibonding π* orbital has a nodal plane between the two carbons. The more nodes an orbital has, the higher is its energy.

As is true for all orbitals, a π orbital may contain a maximum of two electrons. Ethylene has two π electrons, and these occupy the bonding π molecular orbital, which is the HOMO. The antibonding π* molecular orbital is vacant, and is the LUMO.

PROBLEM 10.15 Which molecular orbital of ethylene (π or π*) is the most important one to look at in a reaction in which ethylene is attacked by an electrophile?

1,3-Butadiene. The π molecular orbitals of 1,3-butadiene are shown in Figure 10.9. The four sp^2-hybridized carbons contribute four 2*p* atomic orbitals, and their overlap leads to four π molecular orbitals. Two are bonding (π_1 and π_2) and two are antibonding (π_3^* and π_4^*). Each π molecular orbital encompasses all four carbons of the diene. There are four π electrons, and these are distributed in pairs between the two orbitals of lowest energy (π_1 and π_2). Both bonding orbitals are occupied; π_2 is the HOMO. Both antibonding orbitals are vacant; π_3^* is the LUMO.

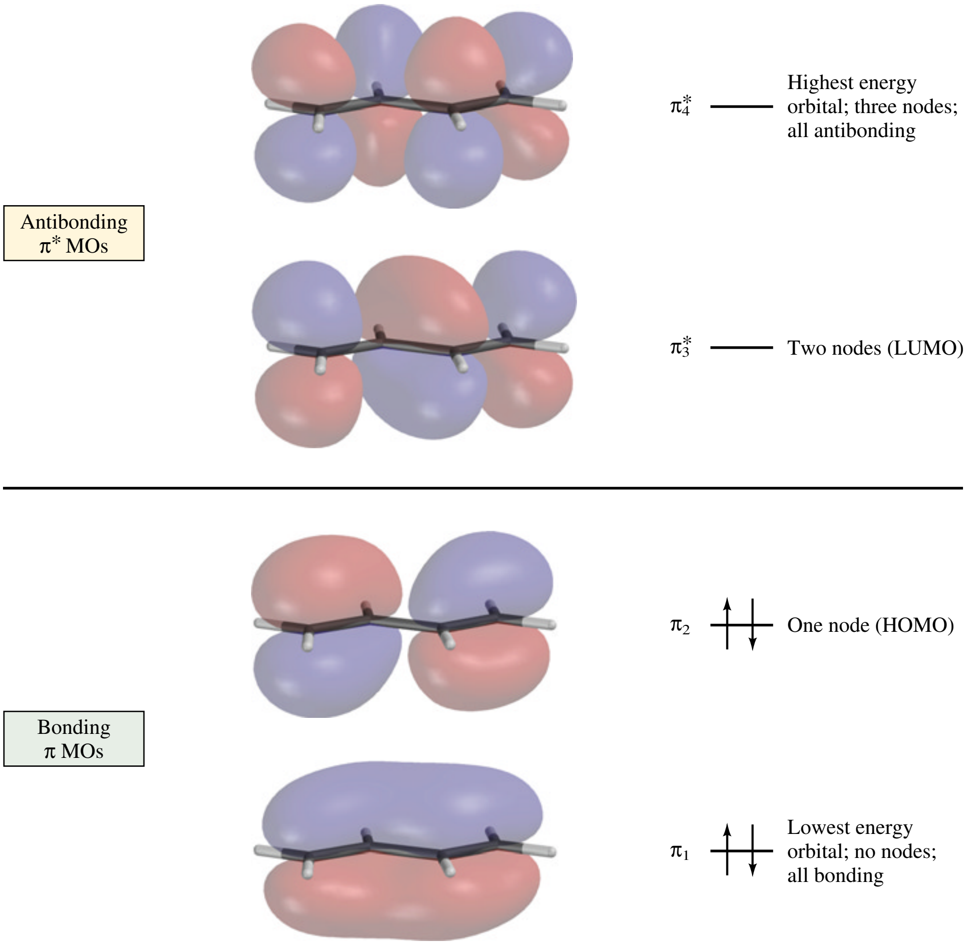


FIGURE 10.9 The π molecular orbitals of 1,3-butadiene.

10.14 A π MOLECULAR ORBITAL ANALYSIS OF THE DIELS–ALDER REACTION

Let us now examine the Diels–Alder cycloaddition from a molecular orbital perspective. Chemical experience, such as the observation that the substituents that increase the reactivity of a dienophile tend to be those that attract electrons, suggests that electrons flow from the diene to the dienophile during the reaction. Thus, the orbitals to be considered are the HOMO of the diene and the LUMO of the dienophile. As shown in Figure 10.10 for the case of ethylene and 1,3-butadiene, the symmetry properties of the HOMO of the diene and the LUMO of the dienophile permit bond formation between the ends of the diene system and the two carbons of the dienophile double bond because the necessary orbitals overlap "in phase" with each other. Cycloaddition of a diene and an alkene is said to be a **symmetry-allowed** reaction.

Contrast the Diels–Alder reaction with a cycloaddition reaction that looks superficially similar, the combination of two ethylene molecules to give cyclobutane.

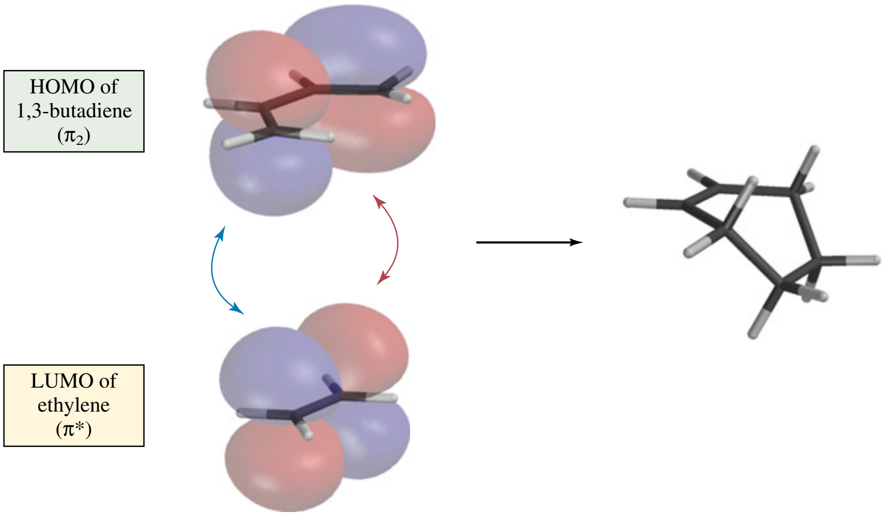
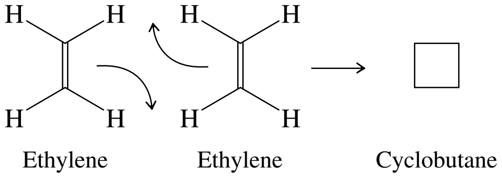


FIGURE 10.10 The HOMO of 1,3-butadiene and the LUMO of ethylene have the proper symmetry to allow σ bond formation to occur at both ends of the diene chain in the same transition state.



Reactions of this type are rather rare and seem to proceed in a stepwise fashion rather than by way of a concerted mechanism involving a single transition state.

Figure 10.11 shows the interaction between the HOMO of one ethylene molecule and the LUMO of another. In particular, notice that two of the carbons that are to become

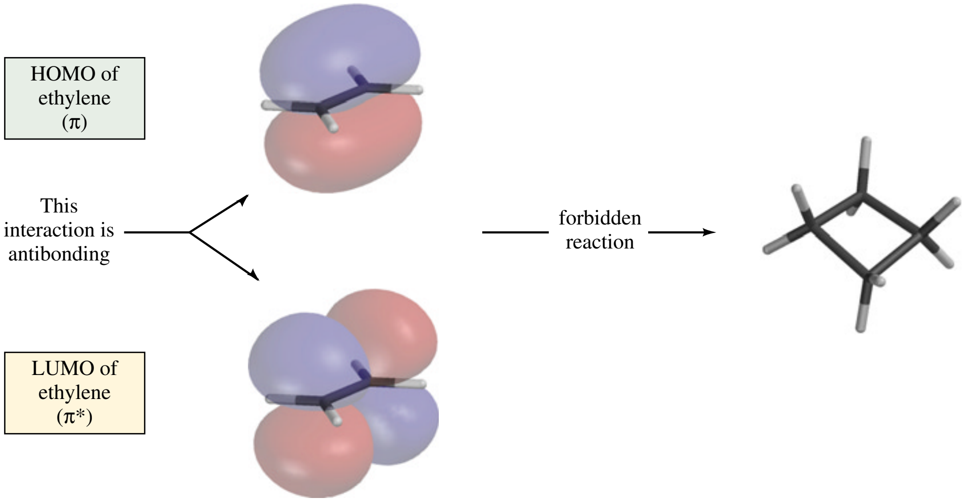
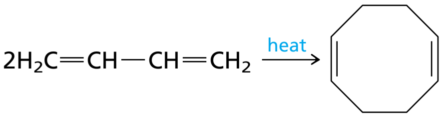


FIGURE 10.11 The HOMO of one ethylene molecule and the LUMO of another do not have the proper symmetry to permit two σ bonds to be formed in the same transition state for concerted cycloaddition.

σ-bonded to each other in the product experience an antibonding interaction during the cycloaddition process. This raises the activation energy for cycloaddition and leads the reaction to be classified as a **symmetry-forbidden** reaction. Reaction, were it to occur, would take place slowly and by a mechanism in which the two new σ bonds are formed in separate steps rather than by way of a concerted process involving a single transition state.

PROBLEM 10.16 Use frontier orbital analysis to decide whether the dimerization of 1,3-butadiene shown here is allowed or forbidden.

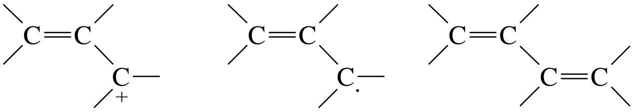


Frontier orbital analysis is a powerful theory that aids our understanding of a great number of organic reactions. Its early development is attributed to Professor Kenichi Fukui of Kyoto University, Japan. The application of frontier orbital methods to Diels–Alder reactions represents one part of what organic chemists refer to as the *Woodward–Hoffmann rules,* a beautifully simple analysis of organic reactions by Professor R. B. Woodward of Harvard University and Professor Roald Hoffmann of Cornell University. Professors Fukui and Hoffmann were corecipients of the 1981 Nobel Prize in chemistry for their work.

Woodward's death in 1979 prevented his being considered for a share of the 1981 prize with Fukui and Hoffmann. Woodward had earlier won a Nobel Prize (1965) for his achievements in organic synthesis.

10.15 SUMMARY

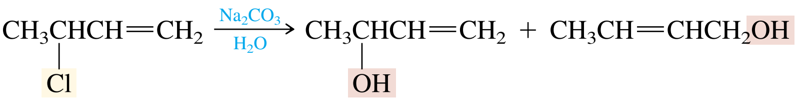
This chapter focused on the effect of a carbon–carbon double bond as a stabilizing substituent on a positively charged carbon in an **allylic carbocation,** on a carbon bearing an odd electron in an **allylic free radical,** and on a second double bond as in a **conjugated diene.**



Allylic carbocation Allylic radical Conjugated diene

Section 10.1 **Allyl** is the common name of the parent group $CH_2{=}CHCH_2{-}$ and is an acceptable name in IUPAC nomenclature.

Section 10.2 The carbocations formed as intermediates when allylic halides undergo S_N1 reactions have their positive charge shared by the two end carbons of the allylic system and may be attacked by nucleophiles at either site. Products may be formed with the same pattern of bonds as the starting allylic halide or with *allylic rearrangement.*

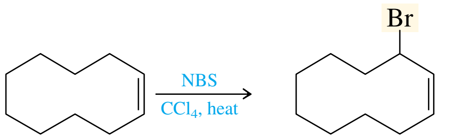


$$\underset{\displaystyle Cl}{CH_3CH}CH{=}CH_2 \xrightarrow[H_2O]{Na_2CO_3} \underset{\displaystyle OH}{CH_3CH}CH{=}CH_2 + CH_3CH{=}CHCH_2OH$$

3-Chloro-1-butene 3-Buten-2-ol (65%) 2-Buten-1-ol (35%)

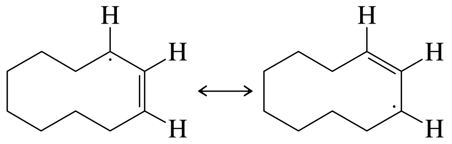
via: $CH_3\overset{+}{C}H{-}CH{=}CH_2 \longleftrightarrow CH_3CH{=}CH{-}\overset{+}{C}H_2$

Sections 10.3–10.4 Alkenes react with *N*-bromosuccinimide (NBS) to give allylic bromides. NBS serves as a source of Br_2, and substitution occurs by a free-radical mechanism. The reaction is used for synthetic purposes only when the two resonance forms of the allylic radical are equivalent. Otherwise a mixture of isomeric allylic bromides is produced.

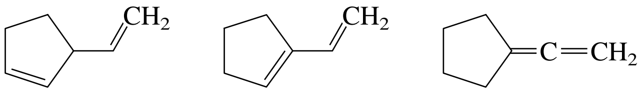


Cyclodecene 3-Bromocyclodecene (56%)

via:



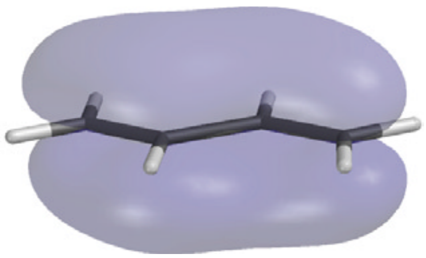
Section 10.5 Dienes are classified as having **isolated, conjugated,** or **cumulated** double bonds.



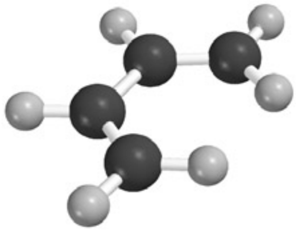
Isolated Conjugated Cumulated

Section 10.6 Conjugated dienes are more stable than isolated dienes, and cumulated dienes are the least stable of all.

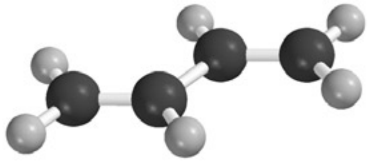
Section 10.7 Conjugated dienes are stabilized by electron delocalization to the extent of 12–16 kJ/mol (3–4 kcal/mol). Overlap of the *p* orbitals of four adjacent sp^2-hybridized carbons in a conjugated diene gives an extended π system through which the electrons are delocalized.



The two most stable conformations of conjugated dienes are the *s*-cis and *s*-trans. The *s*-trans conformation is normally more stable than the *s*-cis. Both conformations are planar, which allows the *p* orbitals to overlap to give an extended π system.



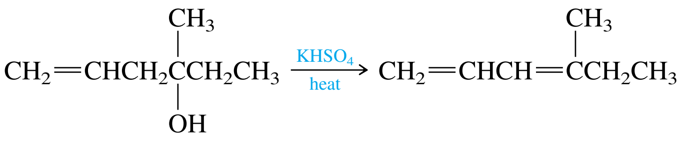
s-cis



s-trans

Section 10.8 1,2-Propadiene ($CH_2{=}C{=}CH_2$), also called **allene,** is the simplest cumulated diene. The two π bonds in an allene share an *sp*-hybridized carbon and are at right angles to each other. Certain allenes such as 2,3-pentadiene ($CH_3CH{=}C{=}CHCH_3$) possess a *stereogenic axis* and are chiral.

Section 10.9 1,3-Butadiene is an industrial chemical and is prepared by dehydrogenation of butane. Elimination reactions such as dehydration and dehydrohalogenation are common routes to alkadienes.

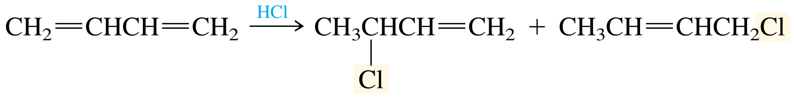


$$CH_2{=}CHCH_2\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_2CH_3 \xrightarrow[\text{heat}]{KHSO_4} CH_2{=}CHCH{=}\overset{\overset{CH_3}{|}}{C}CH_2CH_3$$

3-Methyl-5-hexen-3-ol 4-Methyl-1,3-hexadiene (88%)

Elimination is typically regioselective and gives a conjugated diene rather than an isolated or cumulated diene system of double bonds.

Section 10.10 Protonation at the terminal carbon of a conjugated diene system gives an allylic carbocation that can be captured by the halide nucleophile at either of the two sites that share the positive charge. Nucleophilic attack at the carbon adjacent to the one that is protonated gives the product of *direct addition* (*1,2 addition*). Capture at the other site gives the product of *conjugate addition* (*1,4 addition*).



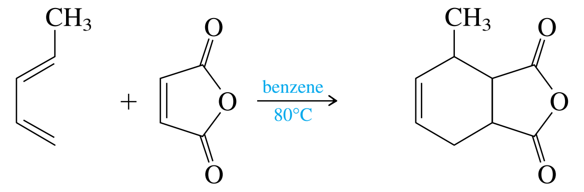
$$CH_2{=}CHCH{=}CH_2 \xrightarrow{HCl} CH_3\underset{\underset{Cl}{|}}{C}HCH{=}CH_2 + CH_3CH{=}CHCH_2Cl$$

1,3-Butadiene 3-Chloro-1-butene (78%) 1-Chloro-2-butene (22%)

$$\textit{via:}\quad CH_3\overset{+}{C}H{-}CH{=}CH_2 \longleftrightarrow CH_3CH{=}CH{-}\overset{+}{C}H_2$$

Section 10.11 1,4-Addition predominates when Cl_2 and Br_2 add to conjugated dienes.

Section 10.12 Conjugate addition of an alkene (the *dienophile*) to a conjugated diene gives a cyclohexene derivative in a process called the *Diels–Alder reaction.* It is concerted and stereospecific; substituents that are cis to each other on the dienophile remain cis in the product.



trans-1,3-Pentadiene

Maleic anhydride

3-Methylcyclohexene-4,5-dicarboxylic anhydride (81%)

Sections 10.13–10.14 The Diels–Alder reaction is believed to proceed in a single step. A deeper level of understanding of the bonding changes in the transition state can be obtained by examining the nodal properties of the highest occupied molecular orbital (HOMO) of the diene and the lowest unoccupied molecular orbital (LUMO) of the dienophile.

PROBLEMS

10.17 Write structural formulas for each of the following:

(a) 3,4-Octadiene

(b) (*E*,*E*)-3,5-Octadiene

(c) (*Z*,*Z*)-1,3-Cyclooctadiene

(d) (*Z*,*Z*)-1,4-Cyclooctadiene

(e) (*E*,*E*)-1,5-Cyclooctadiene

(f) (2*E*,4*Z*,6*E*)-2,4,6-Octatriene

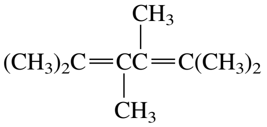
(g) 5-Allyl-1,3-cyclopentadiene

(h) *trans*-1,2-Divinylcyclopropane

(i) 2,4-Dimethyl-1,3-pentadiene

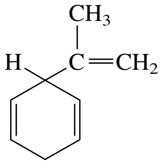
10.18 Give the IUPAC names for each of the following compounds:

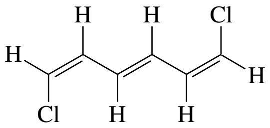
(a) $CH_2{=}CH(CH_2)_5CH{=}CH_2$

(b) 

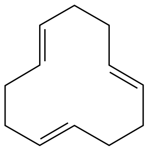
$(CH_3)_2C{=}\overset{CH_3}{\underset{CH_3}{C}}C{=}C(CH_3)_2$

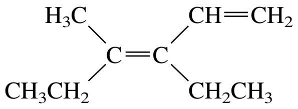
(c) $(CH_2{=}CH)_3CH$

(d) 

(e) 

(f) $CH_2{=}C{=}CHCH{=}CHCH_3$

(g) 

(h) 

10.19 (a) What compound of molecular formula C_6H_{10} gives 2,3-dimethylbutane on catalytic hydrogenation over platinum?

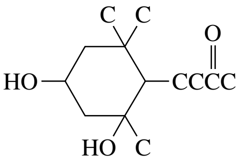
(b) What two compounds of molecular formula $C_{11}H_{20}$ give 2,2,6,6-tetramethylheptane on catalytic hydrogenation over platinum?

10.20 Write structural formulas for all the

(a) Conjugated dienes (b) Isolated dienes (c) Cumulated dienes

that give 2,4-dimethylpentane on catalytic hydrogenation.

10.21 A certain species of grasshopper secretes an allenic substance of molecular formula $C_{13}H_{20}O_3$ that acts as an ant repellent. The carbon skeleton and location of various substituents in this substance are indicated in the partial structure shown. Complete the structure, adding double bonds where appropriate.

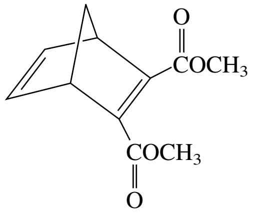


10.22 Show how you could prepare each of the following compounds from propene and any necessary organic or inorganic reagents:

(a) Allyl bromide
(b) 1,2-Dibromopropane
(c) 1,3-Dibromopropane
(d) 1-Bromo-2-chloropropane
(e) 1,2,3-Tribromopropane
(f) Allyl alcohol
(g) 1-Penten-4-yne ($CH_2{=}CHCH_2C{\equiv}CH$)
(h) 1,4-Pentadiene

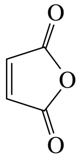
10.23 Show, by writing a suitable sequence of chemical equations, how you could prepare each of the following compounds from cyclopentene and any necessary organic or inorganic reagents:

(a) 2-Cyclopenten-1-ol
(b) 3-Iodocyclopentene
(c) 3-Cyanocyclopentene
(d) 1,3-Cyclopentadiene
(e)



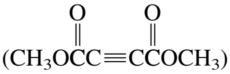
10.24 Give the structure, exclusive of stereochemistry, of the principal organic product formed on reaction of 2,3-dimethyl-1,3-butadiene with each of the following:

(a) 2 mol H_2, platinum catalyst
(b) 1 mol HCl (product of direct addition)
(c) 1 mol HCl (product of conjugate addition)
(d) 1 mol Br_2 (product of direct addition)
(e) 1 mol Br_2 (product of conjugate addition)
(f) 2 mol Br_2
(g)



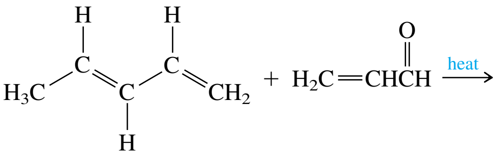
10.25 Repeat the previous problem for the reactions of 1,3-cyclohexadiene.

10.26 Give the structure of the Diels–Alder adduct of 1,3-cyclohexadiene and dimethyl acetylenedicarboxylate.

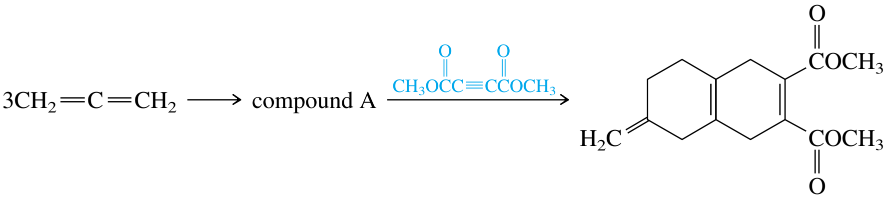


$(CH_3O\overset{O}{\overset{\|}{C}}C{\equiv}C\overset{O}{\overset{\|}{C}}OCH_3)$

10.27 Two constitutional isomers of molecular formula $C_8H_{12}O$ are formed in the following reaction. Ignoring stereochemistry suggest reasonable structures for these Diels–Alder adducts.

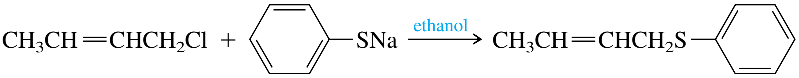


10.28 Allene can be converted to a trimer (compound A) of molecular formula C_9H_{12}. Compound A reacts with dimethyl acetylenedicarboxylate to give compound B. Deduce the structure of compound A.



Compound B

10.29 The following reaction gives only the product indicated. By what mechanism does this reaction most likely occur?



10.30 Suggest reasonable explanations for each of the following observations:

(a) The first-order rate constant for the solvolysis of $(CH_3)_2C{=}CHCH_2Cl$ in ethanol is over 6000 times greater than that of allyl chloride (25°C).

(b) After a solution of 3-buten-2-ol in aqueous sulfuric acid had been allowed to stand for 1 week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol.

(c) Treatment of $CH_3CH{=}CHCH_2OH$ with hydrogen bromide gave a mixture of 1-bromo-2-butene and 3-bromo-1-butene.

(d) Treatment of 3-buten-2-ol with hydrogen bromide gave the same mixture of bromides as in part (c).

(e) The major product in parts (c) and (d) was 1-bromo-2-butene.

10.31 2-Chloro-1,3-butadiene (chloroprene) is the monomer from which the elastomer *neoprene* is prepared. 2-Chloro-1,3-butadiene is the thermodynamically controlled product formed by addition of hydrogen chloride to vinylacetylene ($CH_2{=}CHC{\equiv}CH$). The principal product under conditions of kinetic control is the allenic chloride 4-chloro-1,2-butadiene. Suggest a mechanism to account for the formation of each product.

10.32 (a) Write equations expressing the *s*-trans $\rightleftharpoons$ *s*-cis conformational equilibrium for (*E*)-1,3-pentadiene and for (*Z*)-1,3-pentadiene.

(b) For which stereoisomer will the equilibrium favor the *s*-trans conformation more strongly? Why? Support your prediction by making molecular models.

10.33 Which of the following are chiral?

(a) 2-Methyl-2,3-hexadiene

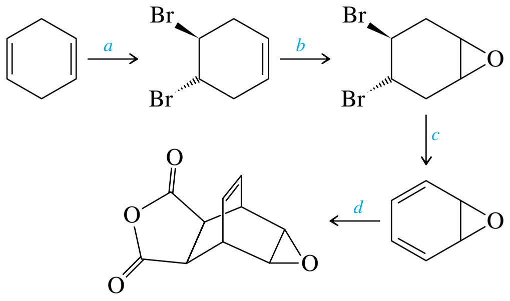
(b) 4-Methyl-2,3-hexadiene

(c) 2,4-Dimethyl-2,3-pentadiene

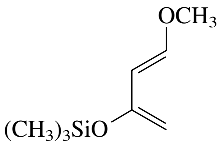
10.34 (a) Describe the molecular geometry expected for 1,2,3-butatriene ($CH_2{=}C{=}C{=}CH_2$).

(b) Two stereoisomers are expected for 2,3,4-hexatriene ($CH_3CH{=}C{=}C{=}CHCH_3$). What should be the relationship between these two stereoisomers?

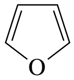
10.35 Suggest reagents suitable for carrying out each step in the following synthetic sequence:



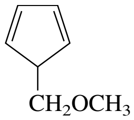
10.36 A very large number of Diels–Alder reactions are recorded in the chemical literature, many of which involve relatively complicated dienes, dienophiles, or both. On the basis of your knowledge of Diels–Alder reactions, predict the constitution of the Diels–Alder adduct that you would expect to be formed from the following combinations of dienes and dienophiles:

(a) 

$+ \ CH_3O_2CC{\equiv}CCO_2CH_3$

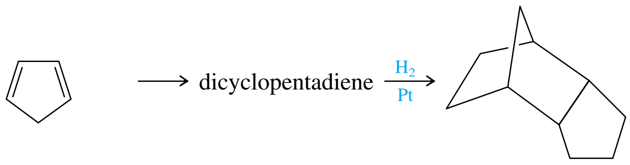
(b) 

$+ \ CH_3O_2CC{\equiv}CCO_2CH_3$

(c) 

$+ \ CH_2{=}CHNO_2$

10.37 On standing, 1,3-cyclopentadiene is transformed into a new compound called *dicyclopentadiene,* having the molecular formula $C_{10}H_{12}$. Hydrogenation of dicyclopentadiene gives the compound shown. Suggest a structure for dicyclopentadiene. What kind of reaction is occurring in its formation?

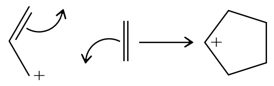


$\longrightarrow$ dicyclopentadiene $\xrightarrow[Pt]{H_2}$

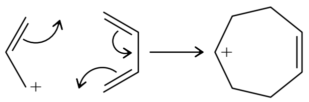
1,3-Cyclopentadiene $\quad$ $C_{10}H_{12}$ $\quad$ $C_{10}H_{16}$

10.38 Refer to the molecular orbital diagrams of allyl cation (Figure 10.12) and those presented earlier in this chapter for ethylene and 1,3-butadiene (Figures 10.8 and 10.9) to decide which of the following cycloaddition reactions are allowed and which are forbidden according to the Woodward–Hoffmann rules.

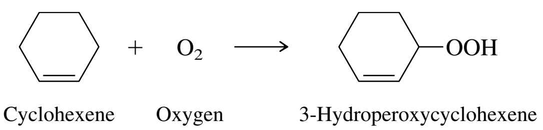
(a)



(b)



10.39 Alkenes slowly undergo a reaction in air called *autoxidation* in which allylic hydroperoxides are formed.



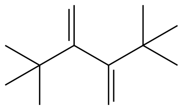
Keeping in mind that oxygen has two unpaired electrons $(\cdot\ddot{\underset{\cdot\cdot}{O}}{:}\ddot{\underset{\cdot\cdot}{O}}\cdot)$, suggest a reasonable mechanism for this reaction.

10.40 Make molecular models of:

(a) 1,2-Pentadiene
(b) (*E*)-1,3-Pentadiene
(c) 1,4-Pentadiene

Examine the C—C bond distances in these substances. Is there a correlation with the hybridization states of the bonded carbons?

10.41 The compound shown is quite unreactive in Diels–Alder reactions. Make a space-filling model of it in the conformation required for the Diels–Alder reaction to see why.



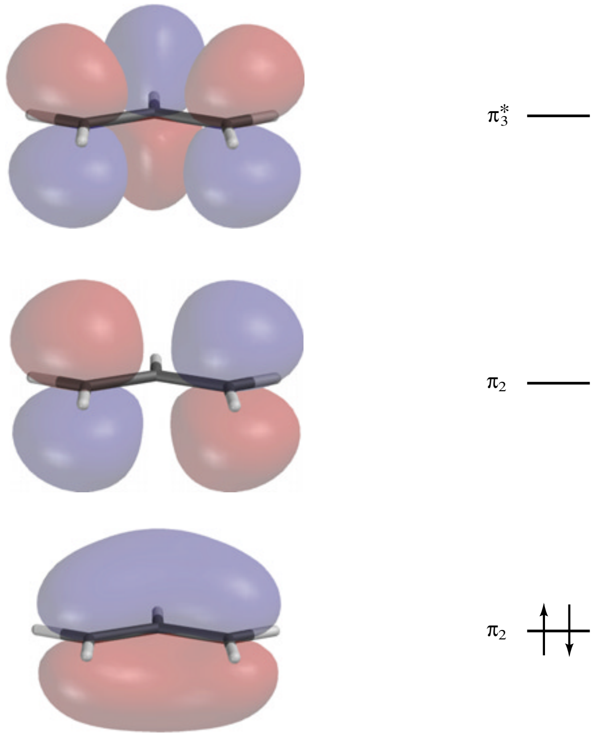


FIGURE 10.12 The π molecular orbitals of allyl cation. Allyl cation has two π electrons, and they are in the orbital marked π_1.