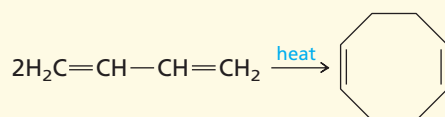


FIGURE 10.12 The HOMO of one ethylene molecule and the LUMO of another do not have the proper symmetry to permit two σ bonds to be formed in the same transition state for concerted cycloaddition.

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 10.12 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 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 10.17 Use frontier orbital analysis to decide whether the dimerization of 1,3-butadiene shown here is symmetry allowed or forbidden.



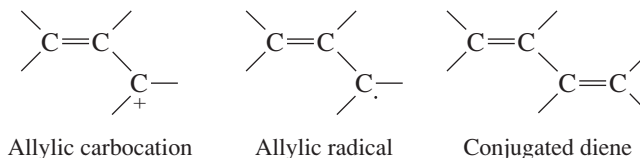
Frontier orbital analysis is a powerful theory that aids our understanding of a great number of organic reactions. Its early development is attributed to Professor Kenichi Fukui of Kyoto University, Japan. The application of frontier orbital methods to Diels–Alder reactions represents one part of what 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

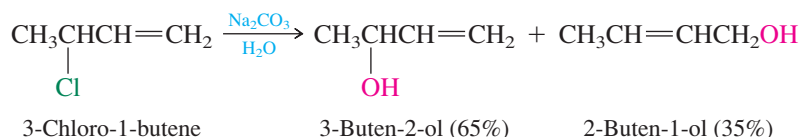
This chapter focused on the effect of a carbon–carbon double bond as a stabilizing substituent on a positively charged carbon in an **allylic carbocation**, on a carbon bearing

an odd electron in an **allylic free radical**, and on a second double bond as in a **conjugated diene**.



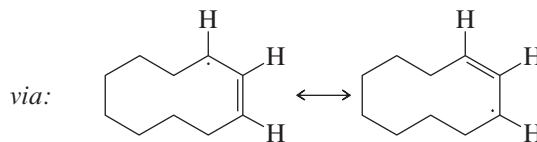
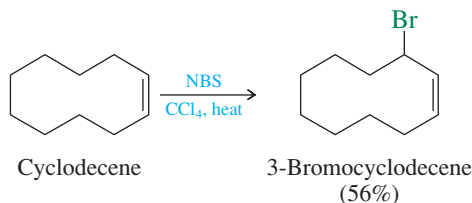
Section 10.1 **Allyl** is the common name of the parent group $\text{H}_2\text{C}=\text{CHCH}_2-$ and is an acceptable name in IUPAC nomenclature.

Section 10.2 The carbocations formed as intermediates when allylic halides undergo $\text{S}_{\text{N}}1$ 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*.

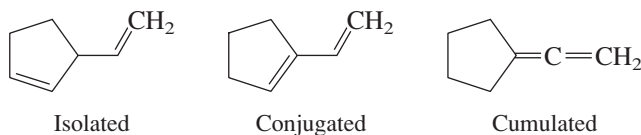


Sections
10.3–10.4

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.

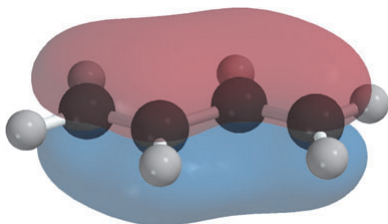


Section 10.5 Dienes are classified as having **isolated**, **conjugated**, or **cumulated** double bonds.

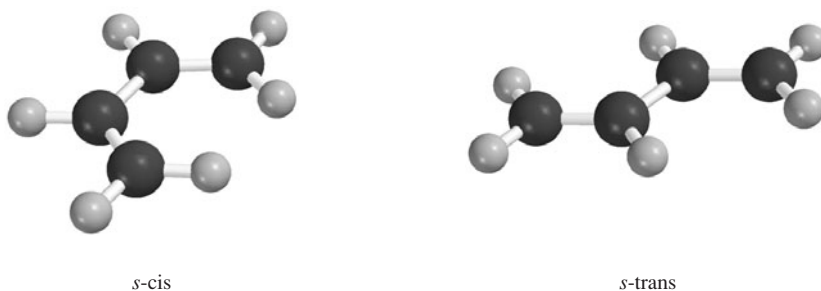


Section 10.6 Conjugated dienes are more stable than isolated dienes, and cumulated dienes are the least stable of all.

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.

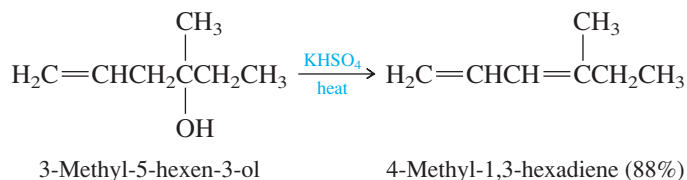


The two most stable conformations of conjugated dienes are the *s*-cis and *s*-trans. The *s*-trans conformation is normally more stable than the *s*-cis. Both conformations are planar, which allows the p orbitals to overlap to give an extended π system.



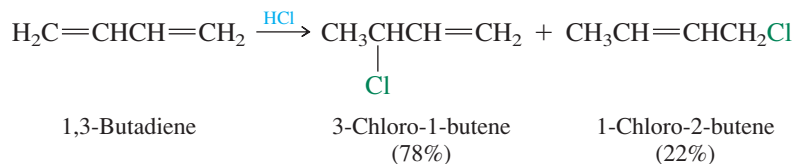
Section 10.8 1,2-Propadiene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$), also called **allene**, is the simplest cumulated diene. The two π bonds in an allene share an sp -hybridized carbon and are at right angles to each other. Certain allenes such as 2,3-pentadiene ($\text{CH}_3\text{CH}=\text{C}=\text{CHCH}_3$) possess a *chirality 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.



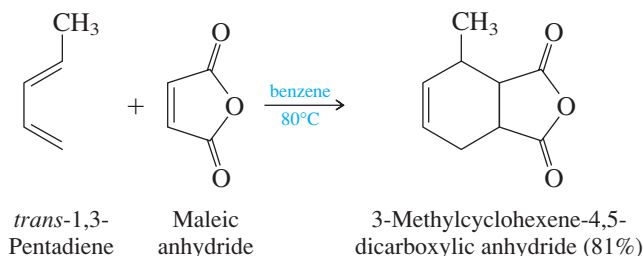
Elimination is typically regioselective and gives a conjugated diene rather than an isolated or cumulated diene system of double bonds.

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).



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.



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

10.18 Write structural formulas for each of the following:

- | | |
|---------------------------------------|--|
| (a) 3,4-Octadiene | (f) (2 <i>E</i> ,4 <i>Z</i> ,6 <i>E</i>)-2,4,6-Octatriene |
| (b) (<i>E,E</i>)-3,5-Octadiene | (g) 5-Allyl-1,3-cyclopentadiene |
| (c) (<i>Z,Z</i>)-1,3-Cyclooctadiene | (h) <i>trans</i> -1,2-Divinylcyclopropane |
| (d) (<i>Z,Z</i>)-1,4-Cyclooctadiene | (i) 2,4-Dimethyl-1,3-pentadiene |
| (e) (<i>E,E</i>)-1,5-Cyclooctadiene | |

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

- | | |
|--|---|
| (a) $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}=\text{CH}_2$ | (d) |
| (b) | (e) |
| (c) $(\text{H}_2\text{C}=\text{CH})_3\text{CH}$ | (f) $\text{H}_2\text{C}=\text{C}=\text{CHCH}=\text{CHCH}_3$ |