15.18 Give the structures of the starting materials that would yield each of the compounds below in Diels–Alder reactions. Pay careful attention to stereochemistry, where appropriate.

(a) ![Structure](image)

(b) ![Structure](image)

(c) ![Structure](image)

(d) ![Structure](image)

15.19 (a) In the products of Eq. 15.13, the observed stereochemistry at the ring fusion is not specified. Show this stereochemistry, assuming that the Diels–Alder reaction gives the endo product.

(b) Sketch diagrams like the one in Fig. 15.8 (without the orbitals) that shows the approach of the diene and dienophile leading to both endo and exo products in part (a). Pay careful attention to the relative positions of substituent groups.

15.20 Assuming endo stereochemistry of the product, give the structure of the compound formed when 1,3-cyclohexadiene reacts with maleic anhydride. (The structure of maleic anhydride is shown in Eq. 15.12a.)

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**ADDITION OF HYDROGEN HALIDES TO CONJUGATED DIENES**

### A. 1,2- and 1,4-Additions

Conjugated dienes, like ordinary alkenes (Sec. 4.7), react with hydrogen halides; however, conjugated dienes give two types of addition product:

\[
\text{CH}_3\text{CH}═\text{CH}═\text{CHCH}_3 + \text{HBr} \xrightarrow{-20 ^\circ C} \text{CH}_3\text{CH}═\text{CH}═\text{CHCH}_3 + \text{CH}_3\text{CHCH}═\text{CHCH}_3 \quad \text{(15.16)}
\]

The major product is a 1,2-addition product. (We’ll address why this is the major product in Sec. 15.4C.) The term 1,2-addition means that addition (of HBr in this case) occurs at adjacent carbons. The minor product results from 1,4-addition, or conjugate addition. In a 1,4-addition, or conjugate addition, addition occurs to carbons that have a 1,4-relationship. (The terms 1,2-addition and 1,4-addition have nothing to do with systematic nomenclature.)

The 1,2-addition reaction is analogous to the reaction of HBr with an ordinary alkene. But how can we account for the conjugate-addition product? As in HBr addition to ordinary alkenes, the first mechanistic step is protonation of a double bond. Protonation of the diene in Eq. 15.16 at either of the equivalent carbons 2 or 5 gives a resonance-stabilized carbocation:
15.4 ADDITION OF HYDROGEN HALIDES TO CONJUGATED DIENES

The resonance structures for this carbocation show that the positive charge in this ion is not localized, but is instead shared by two different carbons. Two constitutional isomers are formed in Eq. 15.16 because the bromide ion can react at either of the electron-deficient carbons:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}^+\text{CH} &= \text{CHCH}_3 & &\rightarrow & &\text{CH}_3\text{CH}_2\text{CH} &= \text{CHCH}^+\text{CHCH}_3
\end{align*}
\] (15.17)

Protonation at carbon-3 would give a different carbocation, which would react with the bromide ion to give an alkyl halide that is different from those obtained experimentally:

\[
\begin{align*}
\text{CH}_3\text{CH} &= \text{CHCH}_3 & &\rightarrow & &\text{CH}_3\text{CH} &= \text{CHCH}^+\text{CHCH}_3
\end{align*}
\] (15.18)

The course of addition to conjugated alkenes is suggested by Hammond’s postulate (Sec. 4.8D), which predicts that the reaction pathway that involves the more stable carbocation occurs more rapidly. Because the carbocation in Eq. 15.17 is more stable, it is formed more rapidly; therefore, the products derived from this carbocation are the ones observed. Although both possible carbocations are secondary, the carbocation in Eq. 15.17 is resonance-stabilized, but the carbocation in Eq. 15.19 is not:

\[
\begin{align*}
\text{CH}_3\text{CH} &= \text{CHCH}_3 & &\rightarrow & &\text{CH}_3\text{CH} &= \text{CHCH}^+\text{CHCH}_3 & &\text{CH}_3\text{CH} &= \text{CHCHCH}_3
\end{align*}
\] (not formed) (15.19)

In other words, resonance accounts for the greater stability of the carbocation intermediate that is formed.
In Sec. 1.4, we stated as a fact that resonance is a stabilizing effect. We’ve seen other examples (Eq. 14.3b, p. 653, and Eq. 14.6c, p. 655) in which the resonance stabilization of a carbocation intermediate determines the course of the reaction. Now we’re going to consider why resonance should be a stabilizing effect. Understanding the connection between resonance and stability is the subject of the Sec. 15.4B.

**PROBLEMS**

15.21. Use the reaction mechanism, including the resonance structures of the carbocation intermediates, to predict the products of the following reactions.

(a) 1,3-butadiene + HCl

(b) S_N1 solvolysis of 3-chloro-1-methylcyclohexene in ethanol

15.22. Suggest a mechanism for each of the following reactions that accounts for both products.

(a)  
\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{C}==\text{CH}==\text{CH}_3 + \text{H}_3\text{O} & \quad \rightarrow \\
\text{(CH}_3\text{)}_2\text{C}==\text{CH}==\text{CH}_3 + \text{(CH}_3\text{)}_2\text{C}==\text{CH}==\text{CH}_3 & + \text{HCl} \nonumber
\end{align*}
\]

(b)  
\[
\begin{align*}
\text{CH}_3\text{CH}==\text{CHCH}_2\text{OH} & + \text{HBr} \quad \rightarrow \\
\text{CH}_3\text{CH}==\text{CHCH}_2\text{Br} + \text{CH}_3\text{CHCH}==\text{CH}_2 & \quad \text{OH \ OH \ OH} \\
\text{CH}_3\text{CH}==\text{CHCH}==\text{CH}_2 & \quad \text{Br} \quad \text{(84%)} \quad \text{(16%)}
\end{align*}
\]

**B. Allylic Carbocations. The Connection between Resonance and Stability**

To explore the connection between resonance and stability, we’ll use a carbocation similar to the one involved in HBr addition to conjugated alkenes (Eq. 15.17). This is an example of an **allylic carbocation**: a carbocation in which the positively charged, electron-deficient carbon is adjacent to a double bond.

The word **allylic** is a generic term applied to any functional group at a carbon adjacent to a double bond.

Allylic carbocations are more stable than comparably branched nonallylic alkyl carbocations. Roughly speaking, an allylic carbocation is about as stable as a nonallylic alkyl carbocation with one additional alkyl branch. Thus, a secondary allylic carbocation is about as stable as a tertiary nonallylic one. To summarize:
Stability of carbocations:

The reason for the stability of allylic carbocations lies in their electronic structures. The π-electron structure of the allyl cation, \( \text{H}_2\text{C}═\text{CH}═\text{CH}_2 \) (the simplest allylic cation), is shown in Fig. 15.9. The electron-deficient carbon and the carbons of the double bond are all \( sp^2\)-hybridized; each carbon has a \( 2p \) orbital (Fig. 15.9a). The overlap of these three \( 2p \) orbitals results in three \( \pi \) molecular orbitals. The MO of lowest energy, \( \pi_1 \), is bonding with an energy of +1.41\( \beta \), and it has no nodes. The next MO, \( \pi_2 \), has the same energy as an isolated \( 2p \) orbital (0\( \beta \)). An MO that has the same energy as an isolated \( 2p \) orbital is called a nonbonding MO (NBMO). This MO has one node. Because nodes must be placed symmetrically, this node is placed in the center of the molecule (Fig. 15.9b).

Figure 15.9 (a) An orbital interaction diagram that shows the arrangement of \( 2p \) orbitals in the allyl cation, the simplest allylic carbocation. Notice that the axes of the \( 2p \) orbitals are parallel and thus properly aligned for overlap. (b) Interaction of the three \( 2p \) orbitals (dashed lines) gives three \( \pi \) MOs. Nodal planes are shown in gray. The two \( 2p \) electrons both go into \( \pi_1 \), the bonding MO. The violet arrows and numbers show the relative energies of the MOs in \( \beta \) units, and the relative energies of the ethylene bonding MO is shown in red. The absence of electrons in \( \pi_2 \) accounts for the positive charge. The nodal plane in \( \pi_2 \) cuts through the central carbon; as a result, there is no positive charge on this carbon.
goes through the central carbon. The position of this node determines the location of the positive charge, as we’ll see shortly. The MO of highest energy, $\pi_3^*$, is antibonding. It has two nodes—one between each carbon.

The allyl cation has two electrons; both reside in $\pi_1$. Each $\pi$ electron contributes $+1.41\beta$ to the energy of the molecule, for a total of $+2.82\beta$. The delocalization energy (Sec. 15.1A) of the allyl cation is the difference between this energy and the energies of an isolated ethylene ($+2.00\beta$) and an isolated $2p$ orbital ($0\beta$). The allyl cation, then, has a delocalization energy of $0.82\beta$. Because the source of this stabilization is the “nodeless” $\pi_1$ MO, the stabilization of the allyl cation arises from the delocalization of $\pi$ electrons across the entire molecule. This delocalization, then, is a source of additional bonding in the allyl cation that would not be present if the alkene $\pi$ bond and the carbocation could not interact.

Here is the connection between molecular stability and resonance: *Resonance structures provide a device to show electron delocalization with Lewis structures.* For example, the allyl cation has two equivalent resonance structures.

\[
\begin{array}{c}
\text{C} = \text{C} = \text{C}^+ & \text{or} \\
\text{or} & \\
\text{C} = \text{C}^+ = \text{C} \\
\end{array}
\]

\begin{align}
\text{an allylic carbocation} & \quad \text{hybrid structure} \\
\end{align}

The two structures show the sharing of $\pi$-electron density and charge—in other words, electron delocalization. The hybrid structure shows the same delocalization with dashed bonds and partial charges. In summary, the logic of resonance stabilization is as follows:

1. Resonance structures symbolize electron delocalization.
2. Electron delocalization is stabilizing because it results in additional bonding associated with the formation of low-energy bonding MOs.
3. Resonance, therefore, is a stabilizing effect.

Because resonance describes electron delocalization, *delocalization energy* (Sec. 15.1B), the energetic advantage of electron delocalization, is also referred to as *resonance energy*. In Sec. 1.4 we learned that resonance-stabilized molecules are more stable than any of their fictional contributors. The resonance energy is a quantitative measure of this additional stability.

One other important aspect of resonance structures emerges from a consideration of the positive-charge distribution in the allyl cation. Notice in the resonance structures that, although the $\pi$ electrons are delocalized across the entire molecule, the positive charge resides on only two of the three carbons; *there is no positive charge on the central carbon of an allylic cation*. This charge distribution is consistent with the molecular orbital description of the cation, shown in Fig. 15.9b. The charge is due to the absence of a third $\pi$ electron. If a third $\pi$ electron were present, it would occupy the NBMO $\pi_2$. Thus, the picture of $\pi_2$ describes the distribution of the “missing electron”—the positive charge. Because $\pi_3$ has a node on the central carbon, this carbon bears no charge. This charge distribution is shown graphically in the EPM of the allyl cation, which is calculated from MO theory. Notice that the terminal carbons have more positive charge (*blue*) than the central carbon (*red*):

\[ \star = \text{sites of positive charge} \]

EPM of the allyl cation
Resonance structures are useful because they give us the qualitative results of MO theory without any calculations!

**PROBLEM 15.23**

(a) The allyl anion has an unshared electron pair on the allylic carbon:

\[ H_2C=CH-CH_2^- \]

allyl anion

This anion has two more \( \pi \) electrons than the allyl cation. Use the molecular orbital diagram in Fig. 15.9b to decide which molecular orbital these “extra electrons” occupy.

(b) According to the molecular orbital description, which carbons of the allyl anion bear the negative charge?

(c) Show that the same conclusion can be reached by drawing resonance structures of the allyl anion. Use the curved-arrow notation.

### C. Kinetic and Thermodynamic Control

Naively, we might expect that when a reaction can give products that differ in stability, the more stable product should be formed in greater amount. However, this is often not the case. Consider, for example, the addition of hydrogen halides to conjugated dienes. When a conjugated diene reacts with a hydrogen halide to give a mixture of 1,2- and 1,4-addition products, the 1,2-addition product predominates at low temperature:

\[ H_2C=CH=CH=CH_2 + HCl \rightarrow \text{products} \]

(See Eq. 15.16, p. 700, for another example.) We learned in Sec. 4.5B that alkenes with internal double bonds are more stable than their isomers with terminal double bonds, because the internal double bonds have more alkyl branches. Hence, in Eq. 15.22, the major product is the less stable one. This can be demonstrated experimentally by bringing the two alkyl halide products to equilibrium with heat and Lewis acids:

\[ H_3C=CH=CH=CH_2 \overset{\text{heat, } FeCl_3}{\rightarrow} \text{products} \]

Because the more stable isomer always predominates in an equilibrium (Sec. 3.5), the result in Eq. 15.23 shows that the 1,4-addition product is more stable than the 1,2-addition product, as expected.

When the less stable product of a reaction is the major product, then two things must be true. First, the less stable product must form more rapidly than the other products. Recall from Sec. 4.8 that a reaction in which two products form from the same starting material is in reality two competing reactions. Consequently, the reaction that forms the less stable product is...
faster. Second, the products must not come to equilibrium under the reaction conditions, because otherwise the more stable compound would be present in larger amount. Thus, in the addition of HCl to conjugated dienes, the predominance of the less stable product (Eq. 15.22) shows that 1,2-addition, which gives the less stable product, is faster than 1,4-addition:

When the products of a reaction do not come to equilibrium under the reaction conditions, the reaction is said to be **kinetically controlled**. In a kinetically controlled reaction, the relative proportions of products are controlled solely by the relative rates at which they are formed. Thus, the addition of hydrogen halides to conjugated dienes is a kinetically controlled reaction. On the other hand, if the products of a reaction come to equilibrium under the reaction conditions, the reaction is said to be **thermodynamically controlled**.

It is possible that a given kinetically controlled reaction might give about the same distribution of products as would be obtained if the products were allowed to come to equilibrium. However, it is **impossible** for a thermodynamically controlled reaction to give a product distribution other than the equilibrium distribution. Hence, when we obtain a product distribution that is clearly different from that obtained at equilibrium (as occurs in the addition of HCl to conjugated dienes), we know immediately that the reaction must be kinetically controlled.

**An Analogy for Kinetic Control**

Imagine a very disoriented steer stumbling randomly around a pasture with a shallow watering hole and a deep well with a high fence around it. Where is he likely to end up? Certainly the deep well is the state of lowest potential energy. However, because of the fence around the well, it is simply less likely that the animal will fall into the well; he is much more likely to wander into the watering hole.

Now, if you imagine a large herd of similarly disoriented steers staggering around the same (very large) pasture, you should get a reasonably good image of kinetic control. Most of the animals wander into the watering hole, even though this is not the state of lowest potential energy.

Likewise with molecules: It is possible for the formation of a more stable product to have a greater standard free energy of activation (a greater energy barrier) than the formation of a less stable product. In such a case, the less stable product forms more rapidly and in greater amount.

In hydrogen halide addition to a conjugated diene, the first and rate-limiting step in the formation of both 1,2- and 1,4-addition products is the same—protonation of the double bond. Consequently, the product distribution must be determined by the relative rates of the **product-determining steps** (Sec. 9.6B): the nucleophilic reaction of the halide ion at one or the other of the electron-deficient carbons of the allylic carbocation intermediate.
Why is the 1,2-addition product formed more rapidly? The diene reacts with undissociated HCl; consequently, the carbocation and its chloride counterion, when first formed, exist as an ion pair (Fig. 8.2, p. 344). That is, the chloride ion and the carbocation are closely associated. Addition is completed, therefore, at the nearer site of positive charge, giving the 1,2-addition product.

(The very elegant experiment that suggested this explanation is described in Problem 15.56.) The reason for kinetic control varies from reaction to reaction. Whatever the reason, the relative amounts of products in a kinetically controlled reaction are determined by the relative free energies of the transition states for each of the product-determining steps and not by the relative free energies of the products.

**PROBLEM**

15.24 Suggest structures for the two constitutional isomers formed when 1,3-butadiene reacts with one equivalent of Br₂. (Ignore any stereochemical issues.) Which of these products would predominate if the two were brought to equilibrium?