s-trans conformation. However, dienes locked into s-cis conformations have higher values of \( \lambda_{\text{max}} \) and lower extinction coefficients than comparably substituted s-trans compounds:

A third variable that affects \( \lambda_{\text{max}} \) in a less dramatic yet predictable way is the presence of substituent groups on the double bond. For example, each alkyl group on a conjugated double bond adds about 5 nm to the \( \lambda_{\text{max}} \) of a conjugated alkene. Thus, the two methyl groups of 2,3-dimethyl-1,3-butadiene add \((2 \times 5) = 10\) nm to the \( \lambda_{\text{max}} \) of 1,3-butadiene, which is 217 nm (Table 15.2). The predicted \( \lambda_{\text{max}} \) is \((217 + 10) = 227\) nm; the observed value is 226 nm.

Although other structural features affect the \( \lambda_{\text{max}} \) of a conjugated alkene, the two most important points to remember are:

1. The \( \lambda_{\text{max}} \) is greater for compounds containing more conjugated double bonds.
2. The \( \lambda_{\text{max}} \) is affected by substituents, conformation, and other structural characteristics of the conjugated \( \pi \)-electron system.

**PROBLEM 15.10** Predict \( \lambda_{\text{max}} \) for the UV absorption of each of the following compounds.

(a) ![Chemical structure](attachment:a.png)

(b) ![Chemical structure](attachment:b.png)

### 15.3 THE DIELS–ALDER REACTION

#### A. Reaction of Conjugated Dienes with Alkenes

Conjugated dienes undergo several unique reactions. One of these was discovered in 1928, when two German chemists, Otto Diels (1876–1954) and Kurt Alder (1902–1958), showed that many conjugated dienes undergo addition reactions with certain alkenes or alkynes. The following reaction is typical:
This type of reaction between a conjugated diene and an alkene is called the Diels–Alder reaction. For their extensive work on this reaction, Diels and Alder shared the 1950 Nobel Prize in Chemistry.

The Diels–Alder reaction is an example of a cycloaddition reaction—an addition reaction that results in the formation of a ring. Indeed, the Diels–Alder reaction is an important method for making rings, as the example in Eq. 15.4 illustrates.

The Diels–Alder reaction is also an example of a 1,4-addition or conjugate addition. In such a reaction, addition occurs across the outer carbons (carbons 1 and 4) of the diene. Conjugate addition is a characteristic type of reaction of conjugated dienes. In the Diels–Alder reaction, conjugate addition also results in the formation of a double bond between carbons 2 and 3. (The numbers indicate the relative locations of the carbons involved in the addition; it has nothing to do with the numbering of the diene used in its substitutive nomenclature.)

When discussing the reactants in the Diels–Alder reaction, we employ the following terminology, which is illustrated in Eq. 15.5. The conjugated diene reactant is referred to simply as the diene, and the alkene with which it reacts is called the dienophile (literally, “diene-loving molecule”). The diene in 1,3-butadiene is used as the diene for simplicity in Eq. 15.5, but as you’ll see shortly, a wide variety of dienes can be used in this reaction.

Mechanistically, the Diels–Alder reaction occurs in a single step involving a cyclic flow of electrons. The curved arrows for this mechanism can be drawn in either a clockwise or counterclockwise direction.

(The best evidence for a concerted rather than a stepwise mechanism for the Diels–Alder reaction comes from the stereochemistry of the reaction, which we’ll consider in Secs. 15.3B and 15.3C.) A concerted reaction that involves a cyclic flow of electrons is called a pericyclic reaction. The Diels–Alder reaction is a pericyclic reaction, as is the hydroboration of alkenes (Sec. 5.4B). However, hydroboration is not a cycloaddition, because no ring is formed. (Pericyclic reactions as a class are discussed from the perspective of MO theory in Chapter 27.)
Some of the dienophiles that react most rapidly in the Diels–Alder reaction, as in Eq. 15.4, bear substituent groups such as esters (—CO₂R), nitriles (—CN), or certain other unsaturated, electronegative groups. However, these substituents are not strictly necessary because the reactions of many other alkenes can be promoted by heat or pressure. Some alkynes can also serve as dienophiles.

\[
\begin{array}{c}
\text{CH}_3\begin{array}{c}
\text{CO}_2\text{CH}_3
\end{array}
\end{array} \quad 140-150 \degree C \quad \begin{array}{c}
\text{CH}_3\begin{array}{c}
\text{CO}_2\text{CH}_3
\end{array}
\end{array}
\]

(15.7)

As you have already learned, when a simple diene is used in the Diels–Alder reaction, a new ring is formed. When the diene is cyclic, a second ring is formed. In other words, the Diels–Alder reaction can be used to prepare certain bicyclic compounds (Sec. 7.6A).

\[
\begin{array}{c}
\text{a cyclic diene}
\end{array} \quad \begin{array}{c}
\text{CN}
\end{array} \quad \text{or} \quad \begin{array}{c}
\text{CN}
\end{array}
\]

(15.8)

different representations of the bicyclic product

**Study Problem 15.1**

Give the structure of the diene and dienophile that would react in a Diels–Alder reaction to give the following product:

\[
\begin{array}{c}
\text{CO}_2\text{CH}_3
\end{array}
\]

**Solution** In the product of a Diels–Alder reaction, the two carbons of the double bond and the two adjacent carbons originate from the diene. These carbons are numbered 1 through 4 in the following structure:

\[
\begin{array}{c}
\text{CO}_2\text{CH}_3
\end{array}
\]

The two new single bonds formed in the reaction connect carbons 1 and 4 of the diene to the carbons of the dienophile double bond, which (because they are part of the same double bond) must be adjacent in the dienophile. This analysis reveals two possibilities, A and B, for the bonds formed in the Diels–Alder reaction:
Because the product is bicyclic, the diene in either case is a cyclic diene. The double bonds in the diene are between carbons 1 and 2 and between carbons 3 and 4. Thus, to derive the starting materials in each case, follow these steps:

1. Disconnect the bonds between carbons 1 and 4 and their adjacent dienophile carbons.
2. Complete the diene structure by eliminating the double bond between carbons 2 and 3 and by adding the C1–C2 and C3–C4 double bonds.
3. Complete the dienophile structure by adding the double bond between its carbons.

By following these steps we find that the starting materials for possibilities A and B are as follows: (The carbon skeleton of the diene unit is first drawn exactly as it looks in the product (even though this is a distorted conformation), and then it is drawn in the more conventional way.)

In principle, either combination A or B could serve as the starting materials in a Diels–Alder reaction. Recall, however, that dienophiles with ester groups (or other electronegative groups) react faster than those without such groups. Hence, the reactants in B would be preferred.

PROBLEMS

15.11 What products are formed in the Diels–Alder reactions of the following dienes and dienophiles?

(a) 

(b)
15.12 Give the diene and dienophile that would react in a Diels–Alder reaction to give each of the following products.

(a)  
(b) 

15.13 (a) What product would be expected from the Diels–Alder reaction of 1,3-butadiene and ethylene?

(b) This product is actually not observed because 1,3-butadiene reacts with itself faster than it does with ethylene. In this reaction, one molecule of 1,3-butadiene acts as the diene component and the other as the dienophile. Give the product of this reaction.

15.14 (a) Explain why two constitutional isomers are formed in the following Diels–Alder reaction:

(b) What two constitutional isomers could be formed in the following Diels–Alder reaction?

B. Effect of Diene Conformation on the Diels–Alder Reaction

Dienes that are “locked” into s-trans conformations are unreactive in Diels–Alder reactions:

The reason is that if such dienes were to form Diels–Alder products, the s-trans single bond of the diene would become a trans double bond in the Diels–Alder product. This means that the Diels–Alder product would contain a trans double bond in a six-membered ring. For example, consider the following reaction:
The product is a bicyclic compound containing a bridgehead double bond. As discussed in Sec. 7.6C, the bridgehead double bond (red in the preceding equation) has trans stereochemistry within one of the rings joined at the bridges, and therefore the product violates Bredt’s rule and is too strained to exist. (For a graphic demonstration, try building a model of the product, but don’t break your models.)

In contrast, dienes locked into $s$-cis conformations are considerably more reactive than the corresponding noncyclic dienes:

![Figure 15.8](image)

For example, 1,3-cyclopentadiene, which is locked in an $s$-cis conformation, reacts with typical dienophiles hundreds of times more rapidly than 1,3-butadiene, which exists primarily in the $s$-trans conformation.

These observations are consistent with a transition state in which the diene component of the reaction has assumed an $s$-cis conformation. This transition state is shown in Fig. 15.8 for the reaction of 1,3-butadiene and ethylene. In this transition state, the diene and the dienophile approach in parallel planes. The $2p$ orbitals on the dienophile interact with the $2p$ orbitals on the outer carbons of the diene to form the new $\sigma$ bonds. Because 1,3-butadiene prefers the $s$-trans conformation (Fig. 15.1, p. 679), the energy required for it to assume the $s$-cis conformation in the transition state becomes part of the energy barrier for the reaction. In contrast, a diene that is locked by its structure into an $s$-cis conformation, such as 1,3-cyclopentadiene, does not have this additional energy barrier to climb before it can react; hence, it reacts more rapidly.

The importance of the $s$-cis diene conformation can have some fairly drastic consequences for the reactivity of some noncyclic dienes. Thus, the $E$ isomer of 1,3-pentadiene reacts 12,600 times faster than the $Z$ isomer.
times more rapidly than the Z isomer of the same diene with tetracyanoethylene (TCNE), a very reactive dienophile:

\[
\begin{align*}
\text{(E)-1,3-pentadiene} & \quad \text{reactive with TCNE} \\
\text{(Z)-1,3-pentadiene} & \quad \text{much less reactive with TCNE}
\end{align*}
\]

As Eq. 15.9b shows, the \(s\)-cis conformation of the cis diene is destabilized by a significant van der Waals repulsion between the methyl group and a diene hydrogen. The transition states for the Diels–Alder reactions of this diene, which require an \(s\)-cis conformation, are destabilized by the same effect. Consequently, the Diels–Alder reactions of the cis diene are much slower than the corresponding reactions of the trans diene, in which the destabilizing repulsion in its \(s\)-cis conformation is between hydrogens and is much less severe.

**PROBLEMS**

15.15 A mixture of 0.1 mole of (2\(E\),4\(E\))-2,4-hexadiene and 0.1 mole of (2\(E\),4\(Z\))-2,4-hexadiene was allowed to react with 0.1 mole of TCNE. After the reaction, the unreacted diene was found to consist of only one of the starting 2,4-hexadiene isomers. Which isomer did not react? Explain.

15.16 Complete the following Diels–Alder reaction.

\[
\begin{align*}
\text{C. Stereochemistry of the Diels–Alder Reaction}
\end{align*}
\]

If the Diels–Alder reaction takes place in a single step without reactive intermediates, and if the transition-state picture of Fig. 15.8 is correct, then the diene should undergo a \(s\text{yn}\)-addition.
to the dienophile. Likewise, the dienophile should undergo a 1,4-syn-addition to the diene. Each component adds to the other at one face of the π system.

The stereochemistry of the Diels–Alder reaction is completely consistent with these predictions. If we use a dienophile that is a cis alkene, groups that are cis in the alkene starting material are also cis in the product.

![Diels-Alder Reaction Example](image)

Use of the trans isomer of this dienophile gives the complementary result:

Although one enantiomer of the product is shown in Eq. 15.10b, the product is the racemate, because both starting materials are achiral (Sec. 7.8A).

Syn-addition to the diene is revealed if the terminal carbons of the diene unit are stereocenters. To assist in the analysis of stereochemistry, let’s first draw the diene in its s-cis conformation and then classify the groups at the terminal carbons as inner substituents (Rᵢ) or outer substituents (Rₒ):

![Stereochemistry Classification](image)

A syn-addition requires that in the Diels–Alder product, the two inner substituents always have a cis relationship; the two outer substituents are also cis; and an inner substituent on one carbon is always trans to an outer substituent on the other.
The following reactions of the stereoisomeric 2,4-hexadienes with the dienophile maleic anhydride demonstrate these points.

In Eq. 15.12a, the methyl groups in the diene are both outer substituents, and they are cis in the product. In Eq. 15.12b, one methyl group in the diene is outer and the other is inner; consequently, they are trans in the product.

Notice, incidentally, the different reaction conditions required for reactions of the two dienes in Eqs. 15.12a and 15.12b. The latter reaction requires much more drastic conditions. Why? (See Eq. 15.9b.)

One other stereochemical issue arises in the reactions of Eqs. 15.12a–15.12b: the stereochemistry at the ring junction. Because maleic anhydride is a cis alkene, and because the Diels–Alder reaction is a syn-addition, we know that the stereochemistry at the ring junction must be cis. However, for a given diene and dienophile, two diastereomeric syn-addition products are possible. The reaction of Eq. 15.12a illustrates this point:

This issue arises when both the terminal carbons of the diene and the carbons of the dienophile are stereocenters.

Let’s classify these two possibilities with a more general equation in which a cis alkene reacts with a diene:
Following the diagram in Eq. 15.11a, we have drawn the diene in its s-cis conformation and have labeled the groups at the terminal carbons as outer or inner substituents. The product in which the alkene substituents R are cis to the outer diene substituents R° is said to have endo stereochemistry. The product in which the alkene substituents R are trans to the outer diene substituents R° is said to have exo stereochemistry. (The terms endo and exo are from Greek roots meaning “inside” and “outside,” respectively.)

In many cases, the endo products are formed more rapidly than the exo products, although exceptions occur. (A theoretical explanation for this observation exists, but we won’t consider that here.) If this is so, which product would be favored in Eq. 15.13? (See Problem 15.19.)

The preference for endo products extends to cases in which cyclic dienes are used and bicyclic products are formed:

Be sure you see the correspondence between Eq. 15.15 and Eq. 15.14. The —CH₂— group of the diene (red) represents the inner groups R’ (tied together in one group as part of the ring); the hydrogens in blue are the outer groups R°. You can see from this equation that, in the predominant, or endo, product, the —CO₂CH₃ group is cis to R° and trans to R’.

PROBLEMS

15.17 Give the products formed when each of the following pairs reacts in a Diels–Alder reaction; show the relative stereochemistry of the substituent groups where appropriate. In part (b), show both exo and endo products and label them.

(a) OAc + H₂C═C—CO₂CH₃

(b) CH₃ + H₂C═C—CO₂CH₃

(c) + HC═C—CO₂CH₃
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) 
(b) 
(c) 
(d) 

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:

\[
\text{CH}_3\text{CH}=\text{CH}=\text{CHCH}_3 + \text{HBr} \xrightarrow{20^\circ C} \text{CH}_3\text{CH} = \text{CH} = \text{CHCH}_3 + \text{CH}_3\text{CH} = \text{CH} = \text{CHCH}_3
\]

(15.16)

The major product is a 1,2-\textit{addition} product. (We’ll address why this is the major product in Sec. 15.4C.) The term 1,2-\textit{addition} means that addition (of HBr in this case) occurs at adjacent carbons. The minor product results from 1,4-\textit{addition}, or conjugate addition. In a 1,4-\textit{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: