Chapter 4

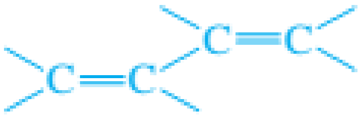
Part III

Conjugated Dienes

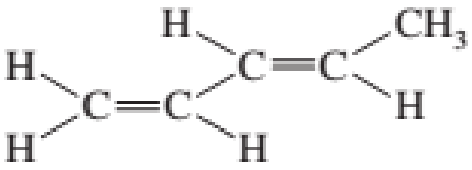
Nomenclature, Structure and Properties

Structures of dienes

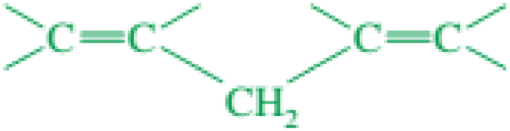
- Double bonds can interact with each other if they are separated by just one single bond. Such interacting double bonds are said to be **conjugated.**
- Double bonds with two or more single bonds separating them have little interaction and are called **isolated double bonds.**
- For example, penta-1,3-diene has conjugated double bonds, while penta-1,4-diene has isolated double bonds.



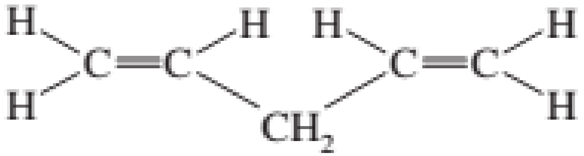
conjugated double bonds
(more stable than isolated double bonds)



penta-1,3-diene



isolated double bonds



penta-1,4-diene

Because of the interaction between the double bonds, systems containing conjugated double bonds tend to be more stable than similar systems with isolated double bonds.

Structure and Bonding of Buta-1,3-diene

- The heat of hydrogenation of buta-1,3-diene is about 17 kJ mol (4.0 kcal mol) less than twice that of but-1-ene, showing that buta-1,3-diene has a resonance energy of 17 kJ mol.

$$H_2C{=}CH{-}CH{=}CH_2 \xrightarrow{2\ H_2,\ Pt} CH_3{-}CH_2{-}CH_2{-}CH_3 \qquad \Delta H^\circ = -237\ \text{kJ}\ (-56.6\ \text{kcal})$$

buta-1,3-diene

$$H_2C{=}CH{-}CH_2{-}CH_3 \xrightarrow{H_2,\ Pt} CH_3{-}CH_2{-}CH_2{-}CH_3 \quad \Delta H^\circ = -127\ \text{kJ}\ (-30.3\ \text{kcal})$$

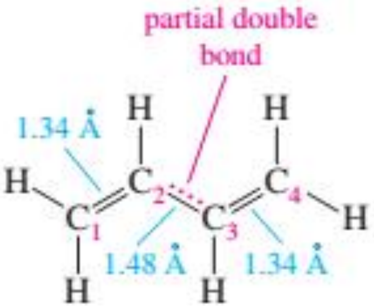
$$\times\ 2 = -254\ \text{kJ}\ (-60.6\ \text{kcal})$$

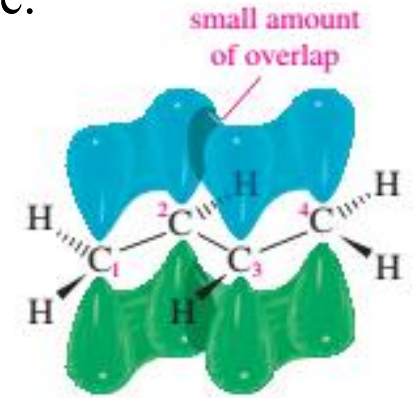
but-1-ene

$$\text{resonance energy of buta-1,3-diene} = 254\ \text{kJ} - 237\ \text{kJ} = 17\ \text{kJ} \quad (4.0\ \text{kcal})$$

Structure and Bonding of Buta-1,3-diene

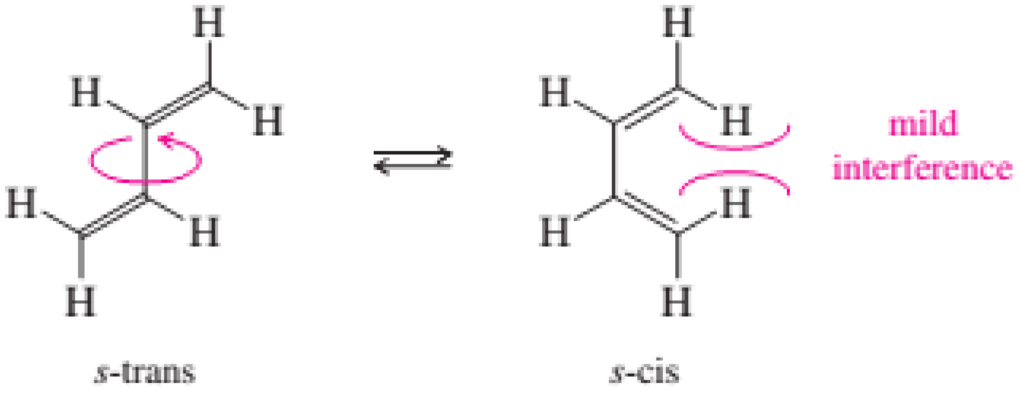
- The bond in buta-1,3-diene (1.48 Å) is shorter than a carbon–carbon single bond in an alkane (1.54 Å). This bond is shortened slightly by the increased *s* character of the hybrid orbitals, but the most important cause of this short bond is its pi bonding overlap and partial double-bond character.
- The planar conformation, with the *p* orbitals of the two double bonds aligned, allows overlap between the pi bonds.
- In effect, the electrons in the double bonds are **delocalized** over the entire molecule, creating some pi overlap and pi bonding in the bond. The length of this bond is intermediate between the normal length of a single bond and that of a double bond.
- Lewis structures are inadequate to represent delocalized molecules such as buta-1,3-diene. To represent the bonding in conjugated systems accurately, we must consider molecular orbitals that represent the entire conjugated pi system, and not just one bond at a time.





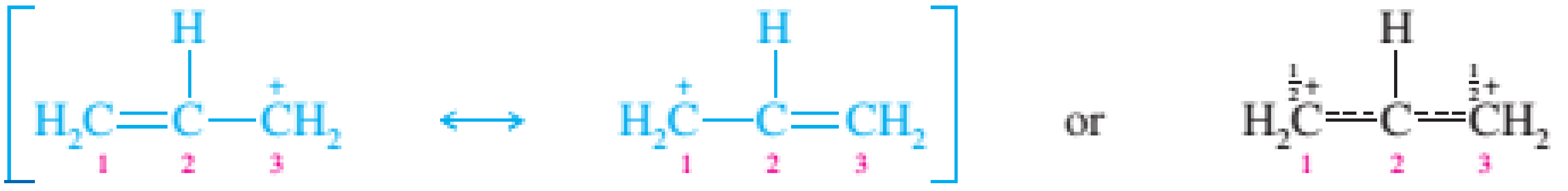
Structure and Bonding of Buta-1,3-diene

- The *s*-trans conformation is 12 kJ mol (2.8 kcal mol) more stable than the *s*-cis conformation, which shows interference between the two nearby hydrogen atoms.
- The barrier for rotation about the bond from *s*-trans to *s*-cis is only about 29 kJ mol (about 7 kcal mol) compared with about 250 kJ mol (60 kcal mol) for rotation of a double bond in an alkene. The *s*-cis and *s*-trans conformers of butadiene (and all the skew conformations in between) easily interconvert at room temperature.



Delocalization of the allyl cation

- We can represent a delocalized ion such as the allyl cation either by resonance forms, as shown on the left in the following figure, or by a combined structure, as shown on the right.



$$\left[\underset{1}{H_2C}{=}\overset{\displaystyle H}{\underset{2}{C}}{-}\underset{3}{\overset{+}{C}H_2} \longleftrightarrow \underset{1}{H_2\overset{+}{C}}{-}\overset{\displaystyle H}{\underset{2}{C}}{=}\underset{3}{CH_2}\right] \quad \text{or} \quad \underset{1}{H_2\overset{\frac{1}{2}+}{C}}{\cdots}\overset{\displaystyle H}{\underset{2}{C}}{\cdots}\underset{3}{\overset{\frac{1}{2}+}{C}H_2}$$

resonance forms

combined representation

- Because of its resonance stabilization, the (primary) allyl cation is about as stable as a simple secondary carbocation, such as the isopropyl cation.
- Most substituted allylic cations have at least one secondary carbon atom bearing part of the positive charge. They are about as stable as simple tertiary carbocations such as the *tert*-butyl cation.

1,2 and 1,4 addition of HBr to buta-1,3-diene

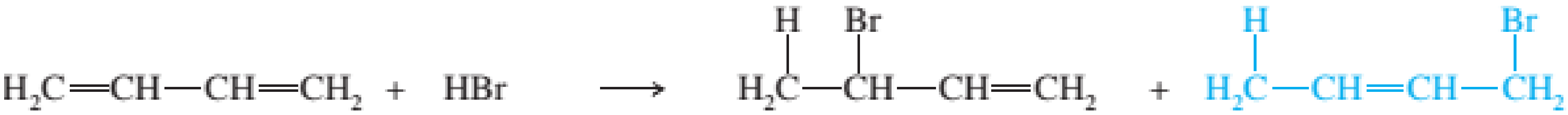
➢ Electrophilic additions to conjugated dienes usually involve allylic cations as intermediates.

➢ Unlike simple carbocations, an allylic cation can react with a nucleophile at either of its positive centers.

➢ In the addition reaction of HBr to buta-1,3-diene, an electrophilic addition that produces a mixture of two constitutional isomers.

+ One product, 3-bromobut-1-ene, results from Markovnikov addition across one of the double bonds.

+ In the other product, 1-bromobut-2-ene, the double bond shifts to the C2-C3 position.



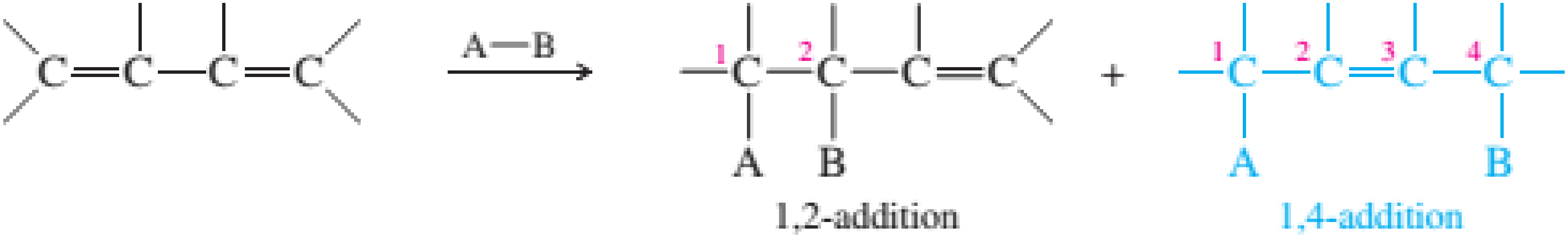
$$\mathrm{H_2C{=}CH{-}CH{=}CH_2 + HBr \longrightarrow H_2\overset{H}{\overset{|}{C}}{-}\overset{Br}{\overset{|}{C}}H{-}CH{=}CH_2 + H_2\overset{H}{\overset{|}{C}}{-}CH{=}CH{-}\overset{Br}{\overset{|}{C}}H_2}$$

3-bromobut-1-ene
1,2-addition

1-bromobut-2-ene
1,4-addition

1,2 and 1,4 addition of HBr to buta-1,3-diene

- The first product results from electrophilic addition of HBr across a double bond. This process is called a **1,2-addition**.
- In the second product, the proton and bromide ion add at the two ends of the conjugated system to carbon atoms with a 1,4-relationship. Such an addition is called a **1,4-addition**.



- The mechanism is similar to other electrophilic additions to alkenes.

\+ The proton is the electrophile, adding to the alkene to give the most stable carbocation.

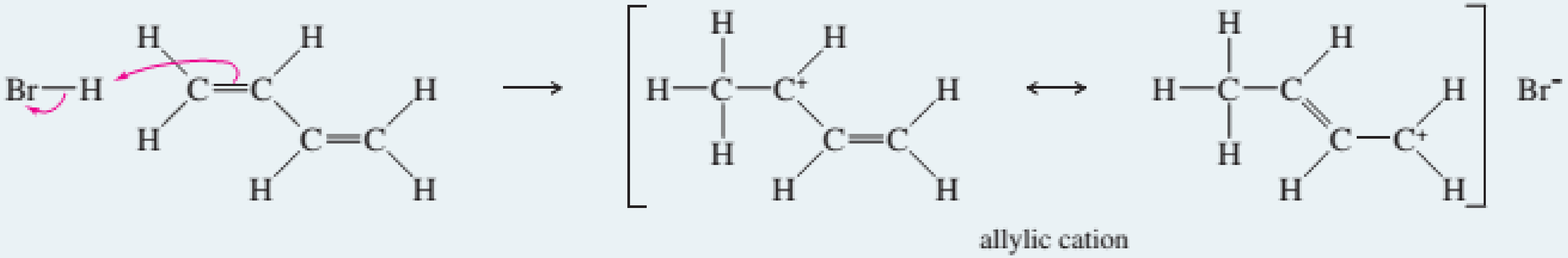
\+ Protonation of buta-1,3-diene gives an allylic cation, which is stabilized by resonance delocalization of the positive charge over two carbon atoms.

\+ Bromide can attack this resonance-stabilized intermediate at either of the two carbon atoms sharing the positive charge: Attack at the secondary carbon gives 1,2-addition; attack at the primary carbon gives 1,4-addition.

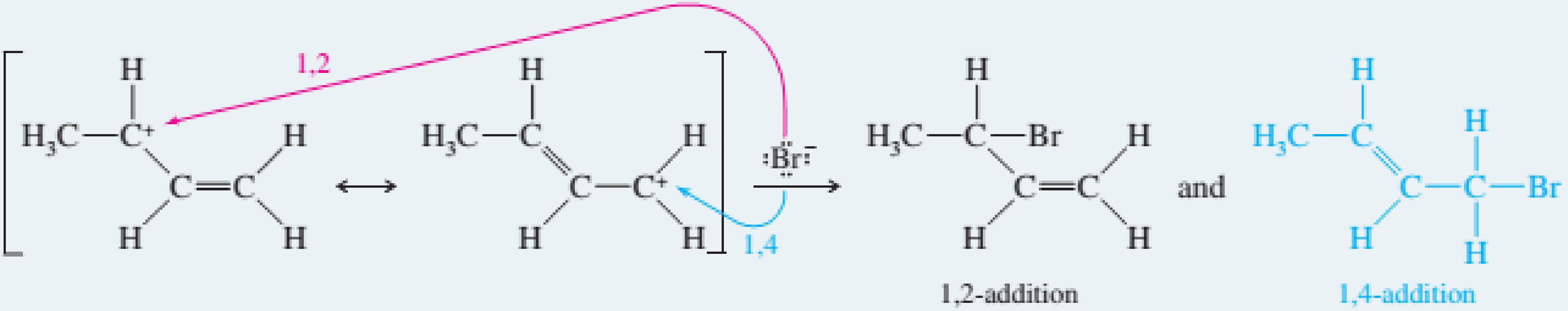
1,2 and 1,4 –addition to a conjugated diene

MECHANISM 15-1 1,2- and 1,4-Addition to a Conjugated Diene

Step 1: Protonation of one of the double bonds forms a resonance-stabilized allylic cation.



Step 2: A nucleophile attacks at either electrophilic carbon atom.



Problems

PROBLEM 15-6

Treatment of an alkyl halide with alcoholic $AgNO_3$ often promotes ionization.

$$Ag^+ + R-Cl \longrightarrow AgCl + R^+$$

When 4-chloro-2-methylhex-2-ene reacts with $AgNO_3$ in ethanol, two isomeric ethers are formed. Suggest structures, and propose a mechanism for their formation.

PROBLEM 15-7

Propose a mechanism for each reaction, showing explicitly how the observed mixtures of products are formed.

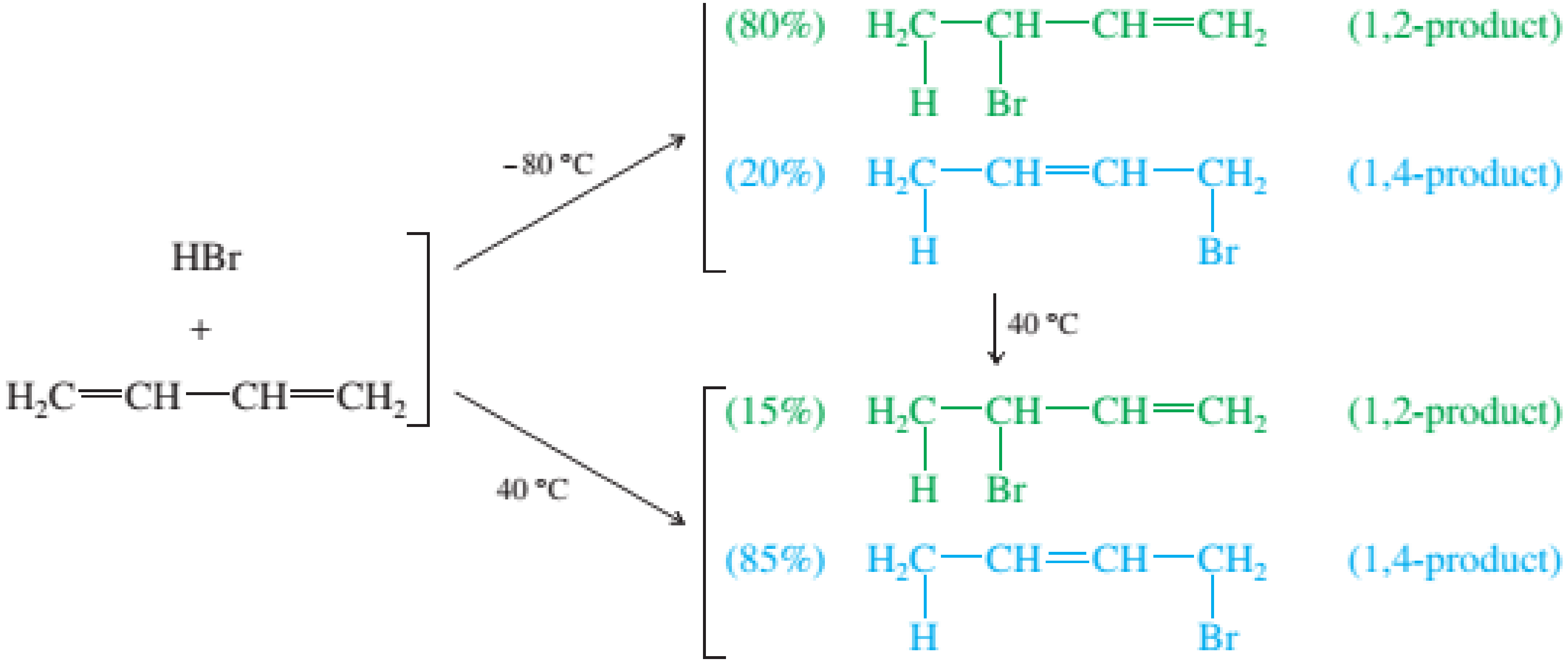
(a) 3-methylbut-2-en-1-ol + HBr → 1-bromo-3-methylbut-2-ene + 3-bromo-3-methylbut-1-ene
(b) 2-methylbut-3-en-2-ol + HBr → 1-bromo-3-methylbut-2-ene + 3-bromo-3-methylbut-1-ene
(c) cyclopenta-1,3-diene + Br_2 → 3,4-dibromocyclopent-1-ene + 3,5-dibromocyclopent-1-ene
(d) 1-chlorobut-2-ene + $AgNO_3$, H_2O → but-2-en-1-ol + but-3-en-2-ol
(e) 3-chlorobut-1-ene + $AgNO_3$, H_2O → but-2-en-1-ol + but-3-en-2-ol

Kinetic versus Thermodynamic control in the addition of HBr to buta- 1,4 -diene

- One of the interesting peculiarities of the reaction of buta-1,3-diene with HBr is the effect of temperature on the products.

+ If the reagents are allowed to react briefly at -80 °C, the 1,2-addition product predominates.

+ If this reaction mixture is later allowed to warm to 40 °C, however, or if the original reaction is carried out at 40 °C, the composition favors the 1,4-addition product.



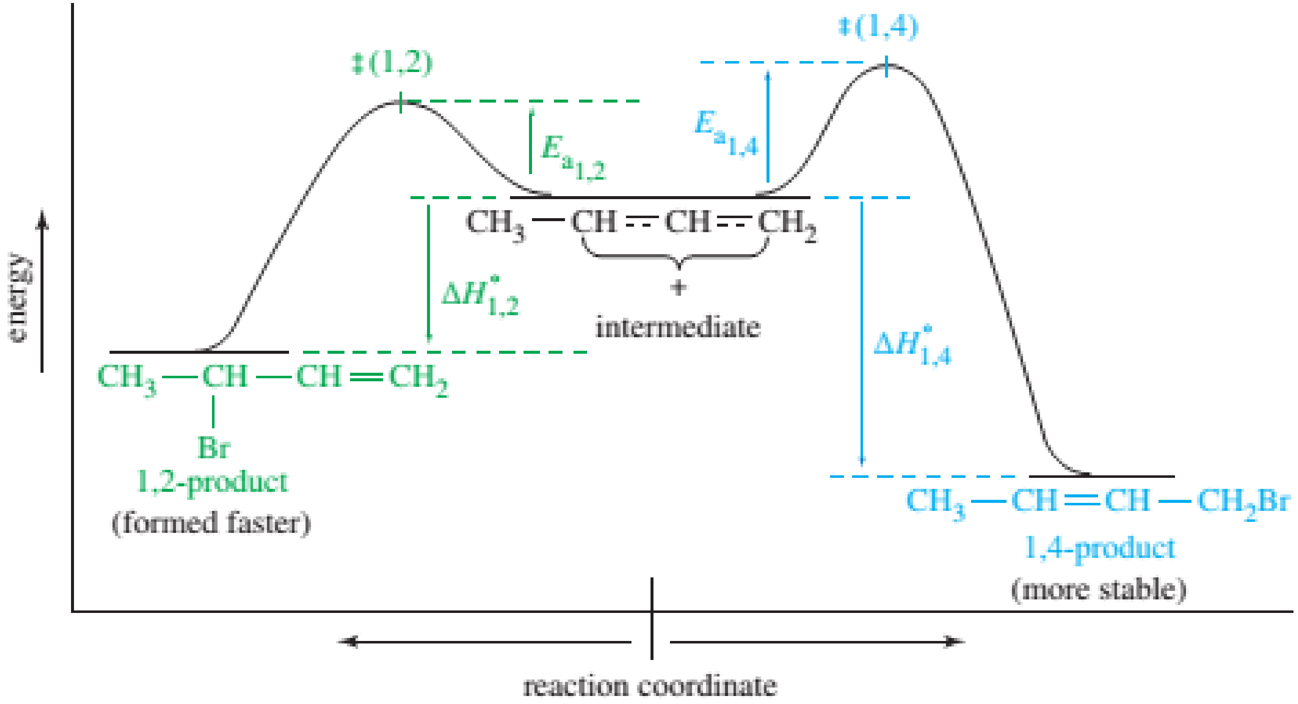
Kinetic versus Thermodynamic control in the addition of HBr to buta- 1,4 -diene

- ➢ This variation in product composition reminds us that the most stable product is not always the major product. Of the two products, we expect 1-bromobut-2-ene (the 1,4-product) to be more stable, since it has the more substituted double bond. This prediction is supported by the fact that this isomer predominates when the reaction mixture is warmed to 40 °C and allowed to equilibrate.
- ➢ A reaction-energy diagram for the second step of this reaction helps to show why one product is favored at low temperatures and another at higher temperatures.

+ The allylic cation is in the center of the diagram; it can react toward the left to give the 1,2-product or toward the right to give the 1,4-product.

+ The initial product depends on where bromide attacks the resonance-stabilized allylic cation. Bromide can attack at either of the two carbon atoms that share the positive charge. Attack at the secondary carbon gives 1,2-addition, and attack at the primary carbon gives 1,4-addition.

Kinetic versus Thermodynamic control in the addition of HBr to buta- 1,4 -diene

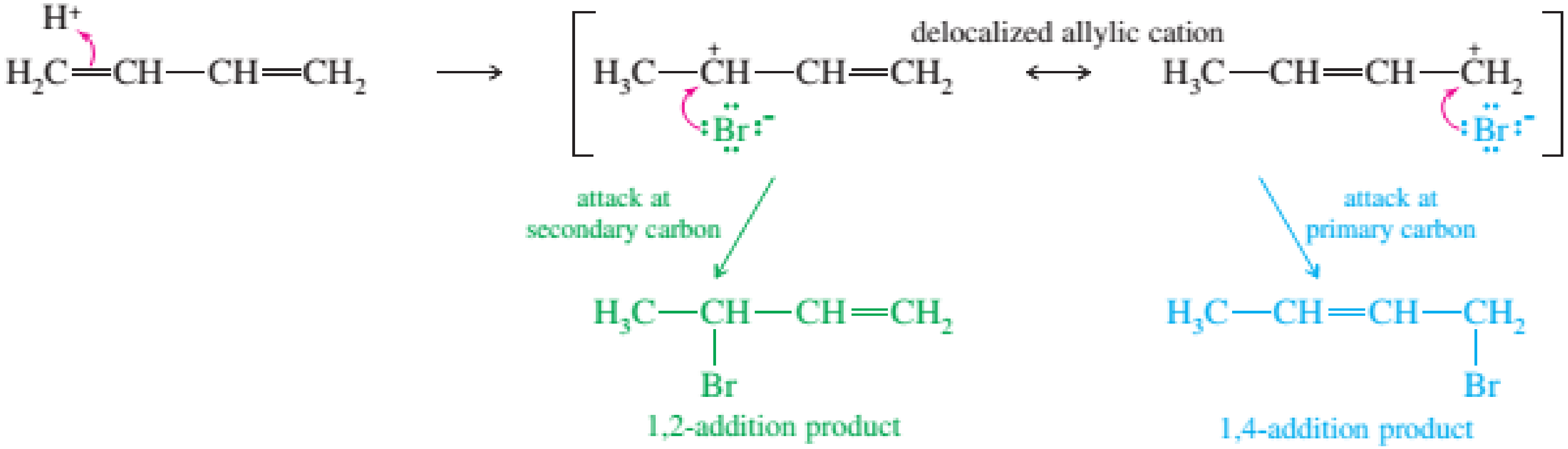


- Reaction-energy diagram for the second step of the addition of HBr to buta-1,3-diene. The allylic carbocation (center) can react at either of its electrophilic carbon atoms.

+ The transition state (‡) leading to 1,2-addition has a lower energy than that leading to the 1,4- product, so the 1,2-product is formed faster (kinetic product).

+The 1,2- product is not as stable as the 1,4- product, however. If equilibrium is reached, the 1,4-product predominates (thermodynamic product).

Kinetic versus Thermodynamic control in the addition of HBr to buta- 1,4 -diene



Kinetic Control at -80 °C

- ➢ The transition state for 1,2-addition has a lower energy than the transition state for 1,4-addition, giving the 1,2-addition a lower activation energy (E_a). This is not surprising, because 1,2-addition results from bromide attack at the more substituted secondary carbon, which bears more of the positive charge because it is better stabilized than the primary carbon.
- ➢ Because the 1,2-addition has a lower activation energy than the 1,4-addition, the 1,2-addition takes place faster (at *all* temperatures).
- ➢ Attack by bromide on the allylic cation is a strongly exothermic process, so the reverse reaction has a large activation energy. At few collisions take place with this much energy, and the rate of the reverse reaction is practically zero. Under these conditions, the product that is formed faster predominates.
- ➢ Because the kinetics of the reaction determine the results, this situation is called **kinetic control** of the reaction. The 1,2 product, favored under these conditions, is

Molecular formulas of alkenes

Thermodynamic Control at 40 °C

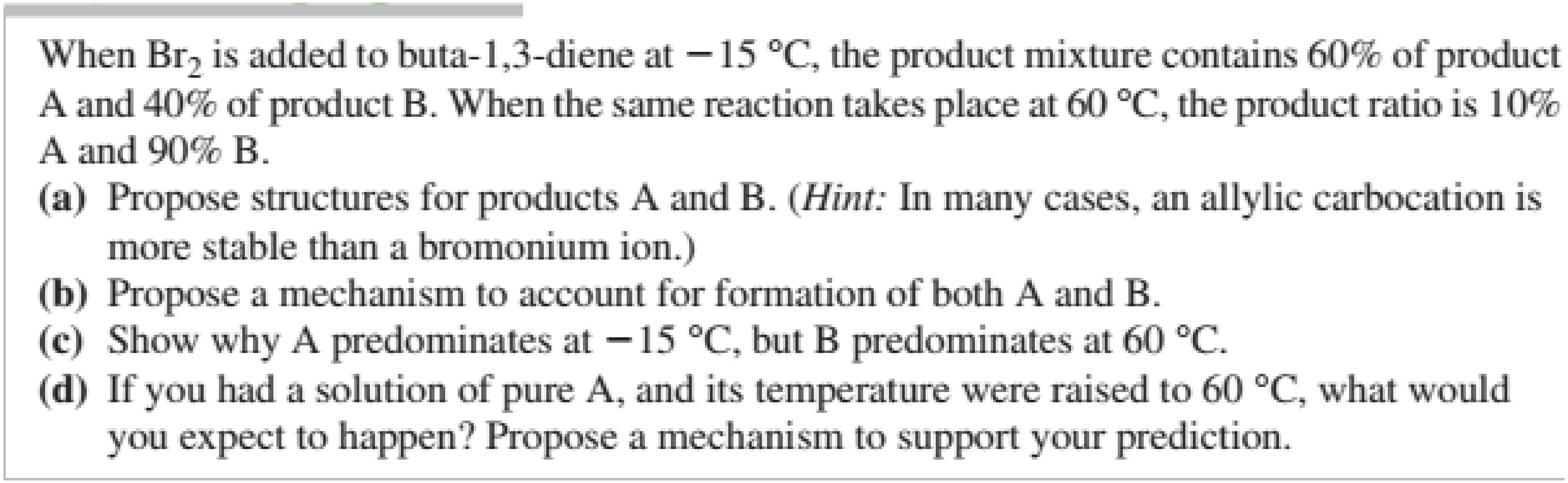
- At 40 °C, a significant fraction of molecular collisions have enough energy for reverse reactions to occur.
- Notice that the activation energy for the reverse of the 1,2-addition is less than that for the reverse of the 1,4-addition.
- Although the 1,2-product is still formed faster, it also reverts to the allylic cation faster than the 1,4-product does.
- At 40 °C, an equilibrium is set up, and the relative energy of each species determines its concentration.

\+ The 1,4-product is the most stable species, and it predominates.

\+ Since thermodynamics determine the results, this situation is called **thermodynamic control** (or **equilibrium control**) of the reaction.

\+ The 1,4-product, favored under these conditions, is called the **thermodynamic product.**

Problems



When Br_2 is added to buta-1,3-diene at −15 °C, the product mixture contains 60% of product A and 40% of product B. When the same reaction takes place at 60 °C, the product ratio is 10% A and 90% B.

(a) Propose structures for products A and B. (*Hint:* In many cases, an allylic carbocation is more stable than a bromonium ion.)

(b) Propose a mechanism to account for formation of both A and B.

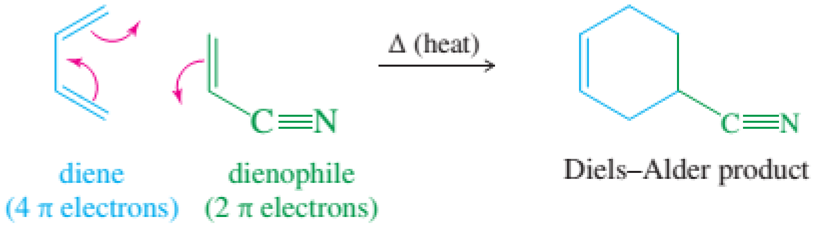
(c) Show why A predominates at −15 °C, but B predominates at 60 °C.

(d) If you had a solution of pure A, and its temperature were raised to 60 °C, what would you expect to happen? Propose a mechanism to support your prediction.

The Diels – Alder reaction

- In 1928, German chemists Otto Diels and Kurt Alder discovered that alkenes and alkynes with electron-withdrawing groups add to conjugated dienes to form six-membered rings.
- The **Diels–Alder reaction** has proven to be a useful synthetic tool, providing one of the best ways to make six-membered rings with diverse functionality and controlled stereochemistry. Diels and Alder were awarded the Nobel Prize in 1950 for their work.

The Diels–Alder Reaction:



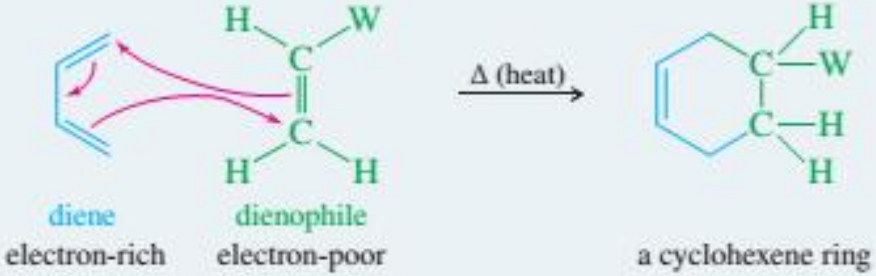
- The Diels–Alder reaction is called a **cycloaddition** because a ring is formed by the interaction of four pi electrons in the diene with two pi electrons of the alkene or alkyne.
- Since the electron-poor alkene or alkyne is prone to react with a diene, it is called a **dienophile** (“lover of dienes”).
- We can symbolize the Diels–Alder reaction by using three arrows to show the movement of three pairs of electrons. This electron movement is **concerted,** with three pairs of electrons moving simultaneously.

The Diels – Alder reaction

KEY MECHANISM 15-3 The Diels–Alder Reaction

The Diels–Alder is a one-step, concerted mechanism.

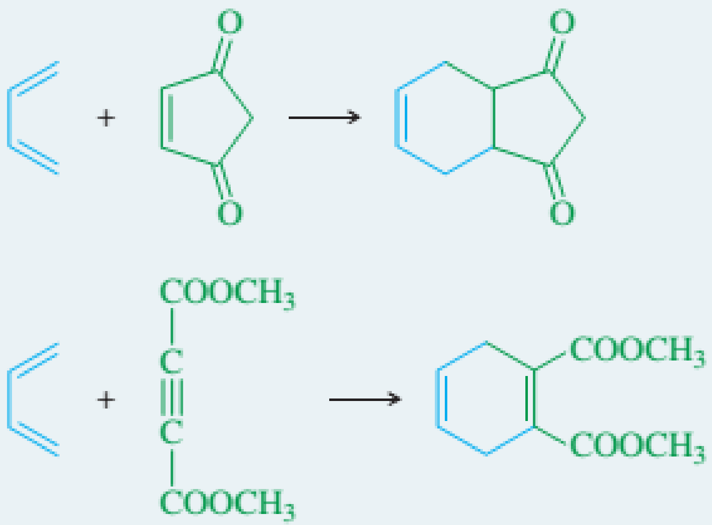
A diene reacts with an electron-poor alkene to give a new cyclohexene ring. (W is an electron-withdrawing group.)



A diene reacts with an electron-poor alkyne to give a cyclohexadiene.

The Diels – Alder reaction

EXAMPLES:



The Diels – Alder reaction

➢ The Diels–Alder reaction is like a nucleophile–electrophile reaction.

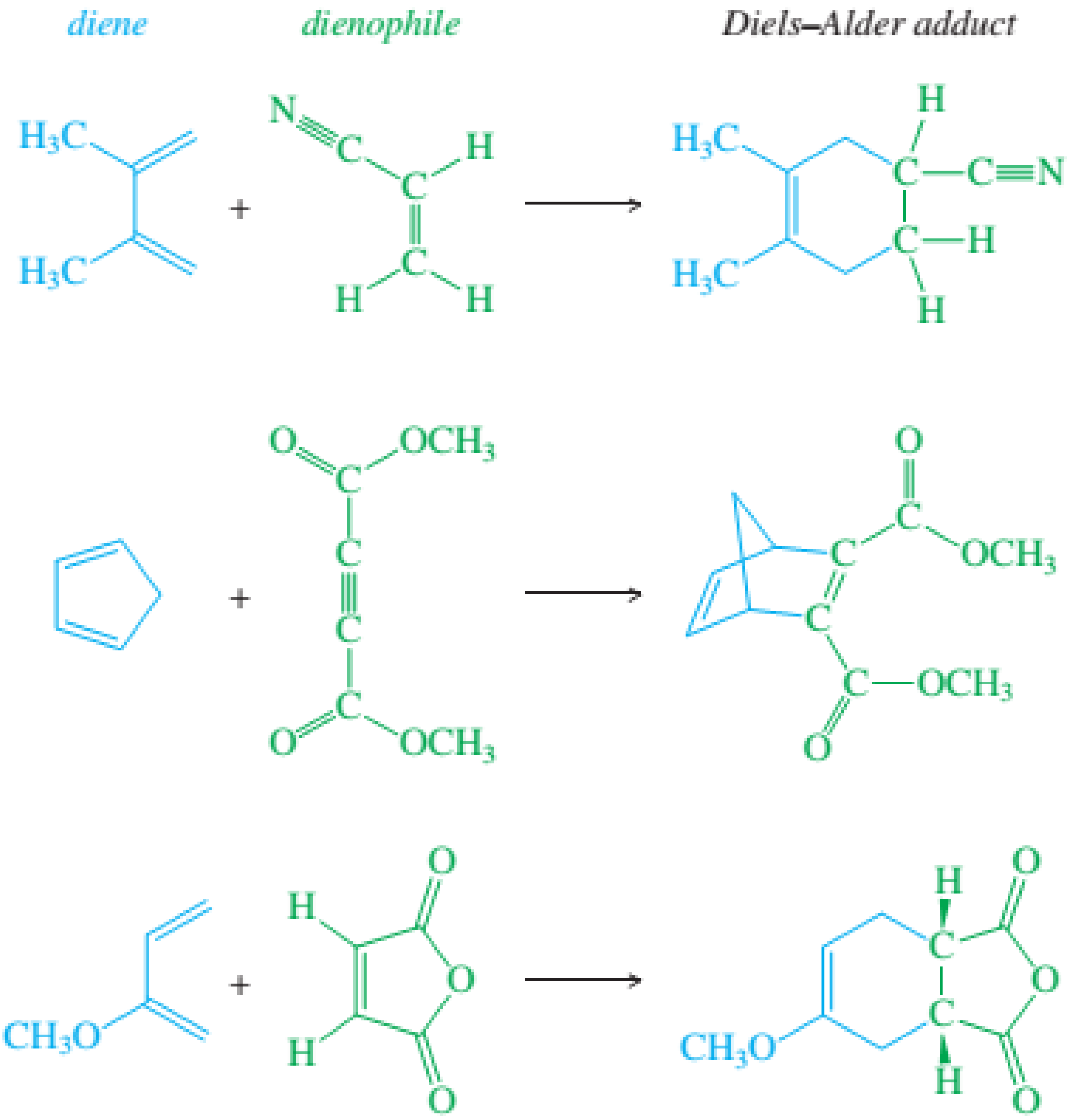
+ The diene is electron-rich, and the dienophile is electron-poor.

+ Simple dienes such as buta-1,3-diene are sufficiently electron-rich to be effective dienes for the Diels–Alder reaction.

+ The presence of electron-donating (-D) groups, such as alkyl groups or alkoxy (-OR) groups, may further enhance the reactivity of the diene.

+ Simple alkenes and alkynes such as ethene and ethyne are poor dienophiles, however. A good dienophile generally has one or more electron-withdrawing groups (-W) pulling electron density away from the pi bond. Dienophiles commonly have carbonyl-containing (C=O) groups or cyano (-C≡N) groups to enhance their Diels–Alder reactivity.

The Diels – Alder reaction

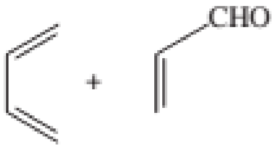


Problems

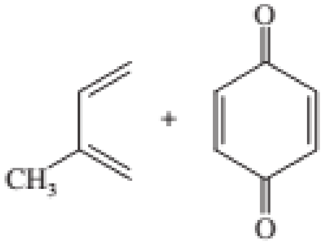
PROBLEM 15-14

Predict the products of the following proposed Diels–Alder reactions.

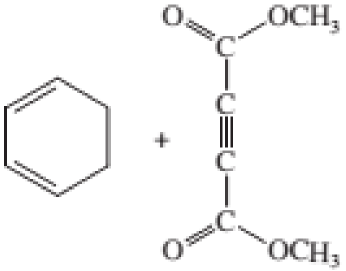
(a)



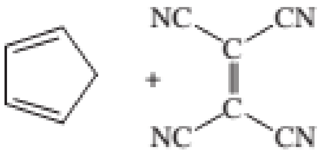
(b)



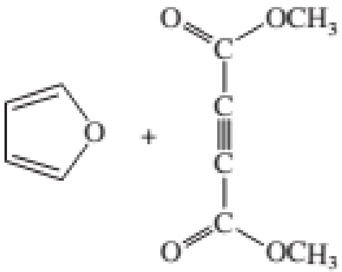
(c)



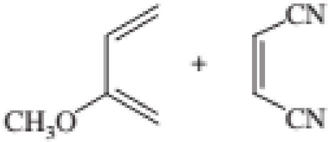
(d)



(e)



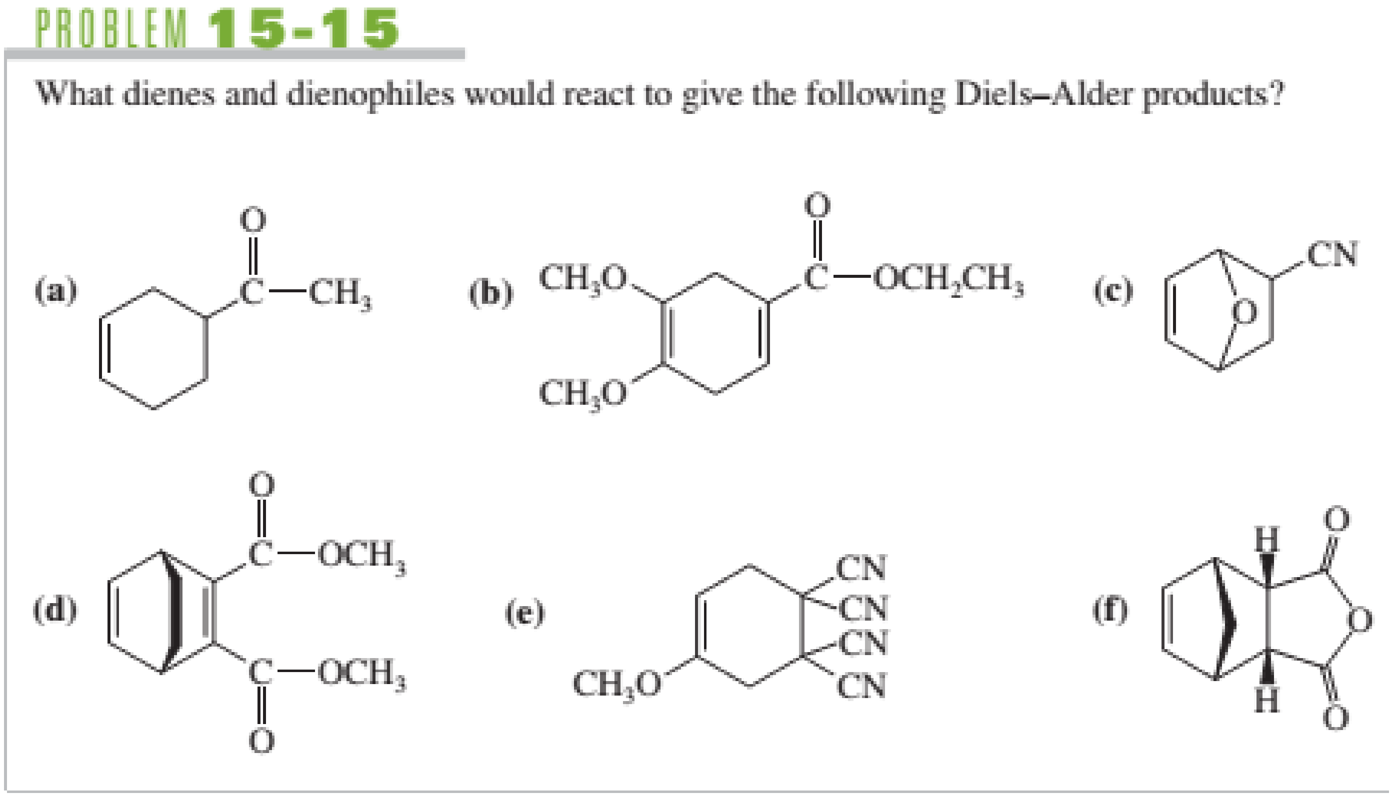
(f)



Problem-solving Hint

A Diels–Alder product always contains one more ring than the reactants. The two ends of the diene form new bonds to the ends of the dienophile. The center (formerly single) bond of the diene becomes a double bond. The dienophile's double bond becomes a single bond (or its triple bond becomes a double bond).

Problems



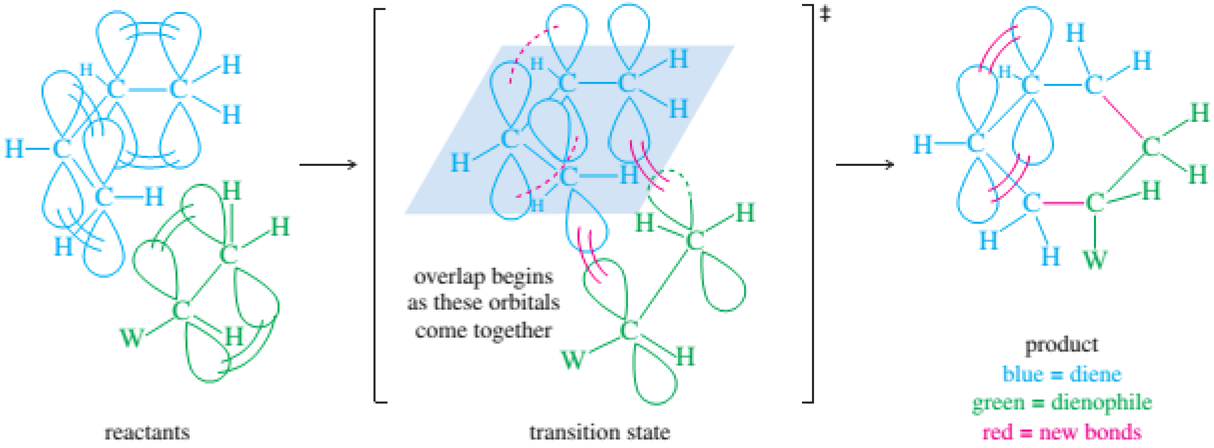
PROBLEM 15-15

What dienes and dienophiles would react to give the following Diels–Alder products?

Stereochemical Requirements of the Diels–Alder Transition State

The mechanism of the Diels–Alder reaction is a concerted cyclic movement of six electrons: four in the diene and two in the dienophile. For the three pairs of electrons to move simultaneously, the transition state must have a geometry that allows overlap of the two end *p* orbitals of the diene with those of the dienophile.

The geometry of the Diels–Alder transition state explains why some isomers react differently from others, and it enables us to predict the stereochemistry of the product

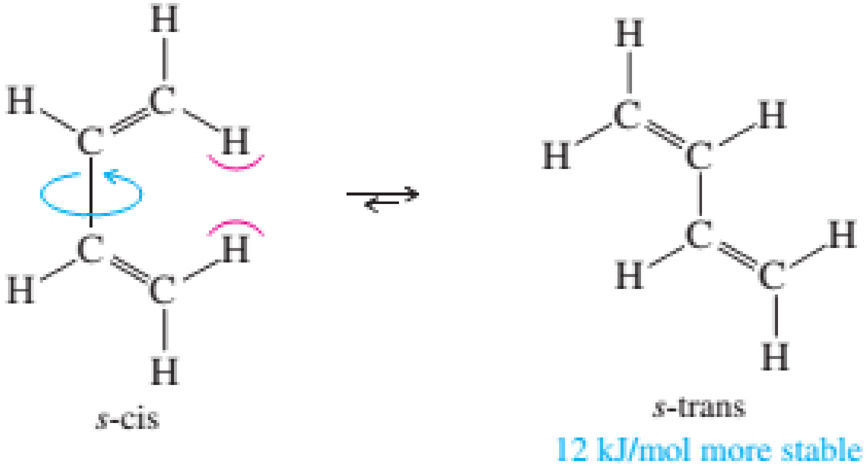


The geometry of the Diels–Alder transition state. The Diels–Alder reaction has a concerted mechanism, with all the bond making and bond breaking occurring in a single step. Three pairs of electrons move simultaneously, requiring a transition state with overlap between the end *p* orbitals of the diene and those of the dienophile.

Stereochemical requirements of the Diels–Alder transition state

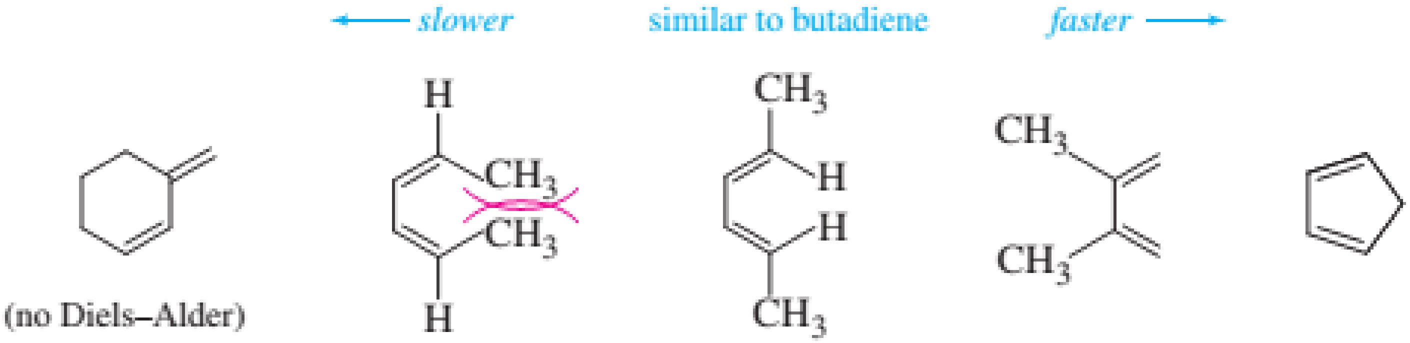
Three stereochemical features of the Diels–Alder reaction are controlled by the requirements of the transition state:

s-cis Conformation of the Diene The diene must be in the *s*-cis conformation to react. When the diene is in the *s*-trans conformation, the end *p* orbitals are too far apart to overlap with the *p* orbitals of the dienophile. The *s*-trans conformation usually has a lower energy than the *s*-cis, but this energy difference is not enough to prevent most dienes from undergoing Diels–Alder reactions. For example, the *s*-trans conformation of butadiene is only 9.6 kJ mol (2.3 kcal mol) lower in energy than the *s*-cis conformation.



Stereochemical requirements of the Diels–Alder transition state

Structural features that aid or hinder the diene in achieving the *s*-cis conformation affect its ability to participate in Diels–Alder reactions. Figure 15-16 shows that dienes with functional groups that hinder the *s*-cis conformation react more slowly than butadiene. Dienes with functional groups that hinder the *s*-trans conformation react faster than butadiene.

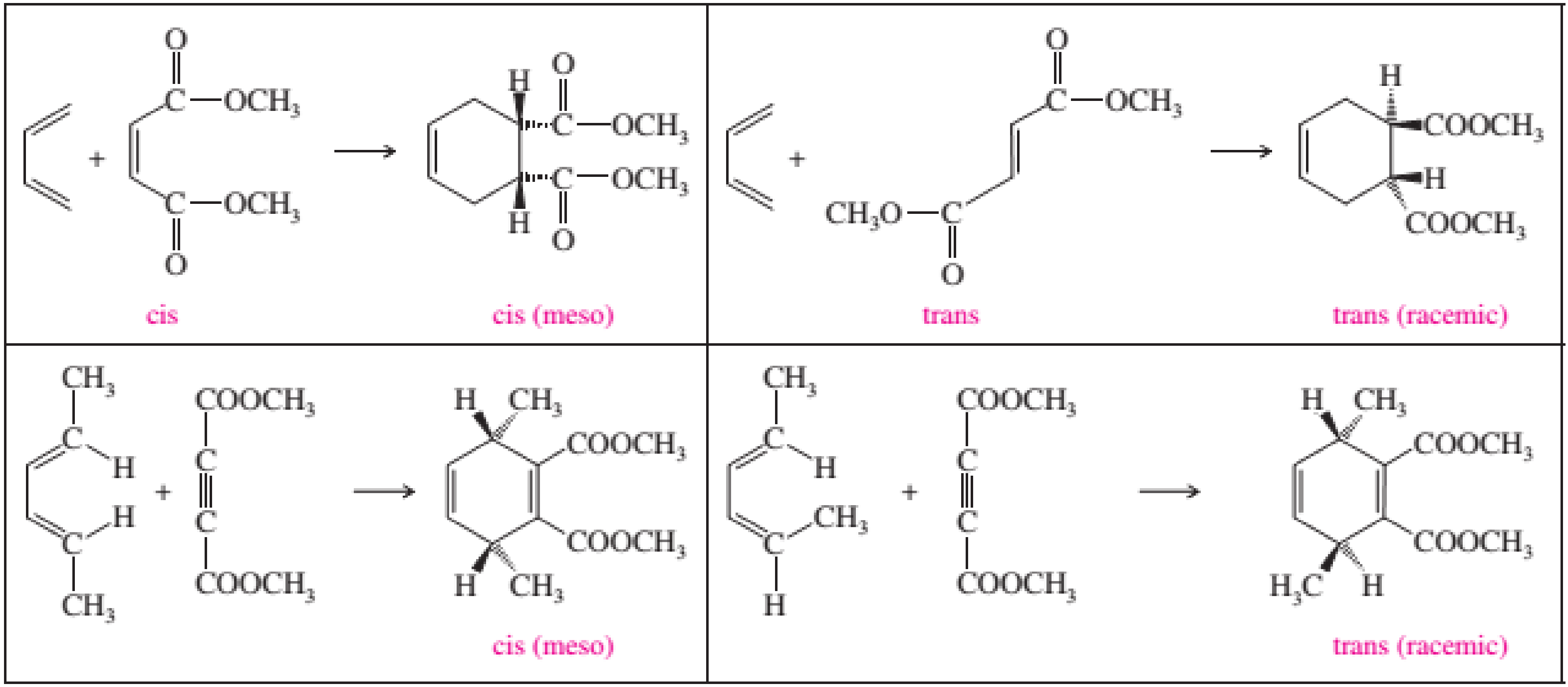


Diels–Alder rate compared with that of buta-1,3-diene

Dienes that easily adopt the *s*-cis conformation undergo the Diels–Alder reaction more readily.

Stereochemical requirements of the Diels–Alder transition state

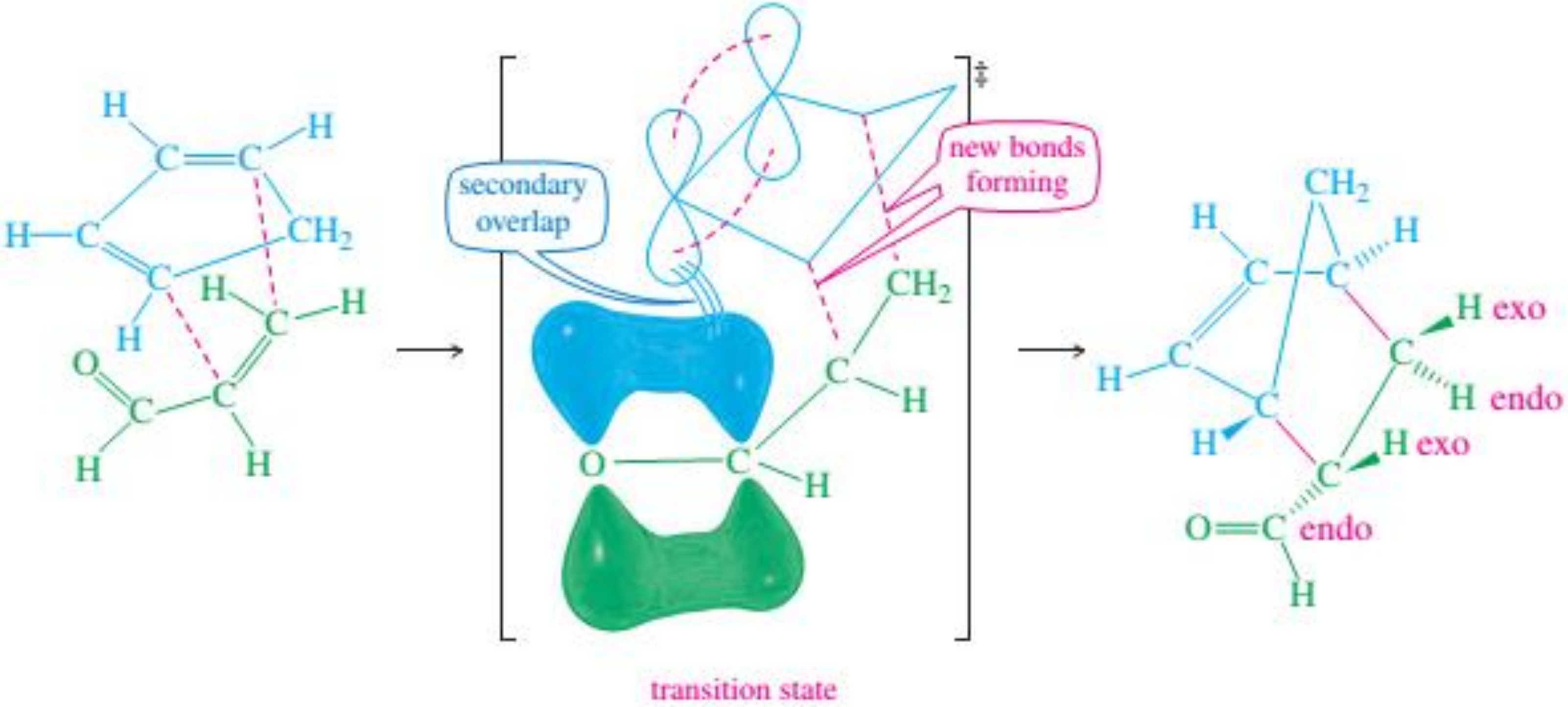
syn Stereochemistry The Diels–Alder reaction is a syn addition with respect to both the diene and the dienophile. The dienophile adds to one face of the diene, and the diene adds to one face of the dienophile. As you can see from the transition state in Figure 15-15, there is no opportunity for any of the substituents to change their stereochemical positions during the course of the reaction. Substituents that are on the same side of the diene or dienophile will be cis on the newly formed ring. The following examples show the results of this syn addition.



Stereochemical requirements of the Diels–Alder transition state

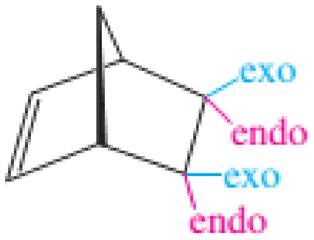
The Endo Rule When the dienophile has a pi bond in its electron-withdrawing group (as in a carbonyl group or a cyano group), the *p* orbitals in that electron-withdrawing group approach one of the central carbon atoms (C2 or C3) of the diene. This proximity results in **secondary overlap:** an overlap of the *p* orbitals of the electron-withdrawing group with the *p* orbitals of C2 and C3 of the diene. Secondary overlap helps to stabilize the transition state. The influence of secondary overlap was first observed in reactions using cyclopentadiene to form bicyclic ring systems. In the bicyclic product (called *norbornene*), the electron-withdrawing substituent occupies the stereochemical position closest to the central atoms of the diene. This position is called the **endo position** because the substituent seems to be inside the pocket formed by the six-membered ring of norbornene. This stereochemical preference for the electron-withdrawing substituent to appear in the endo position is called the **endo rule.**

Stereochemical requirements of the Diels–Alder transition state

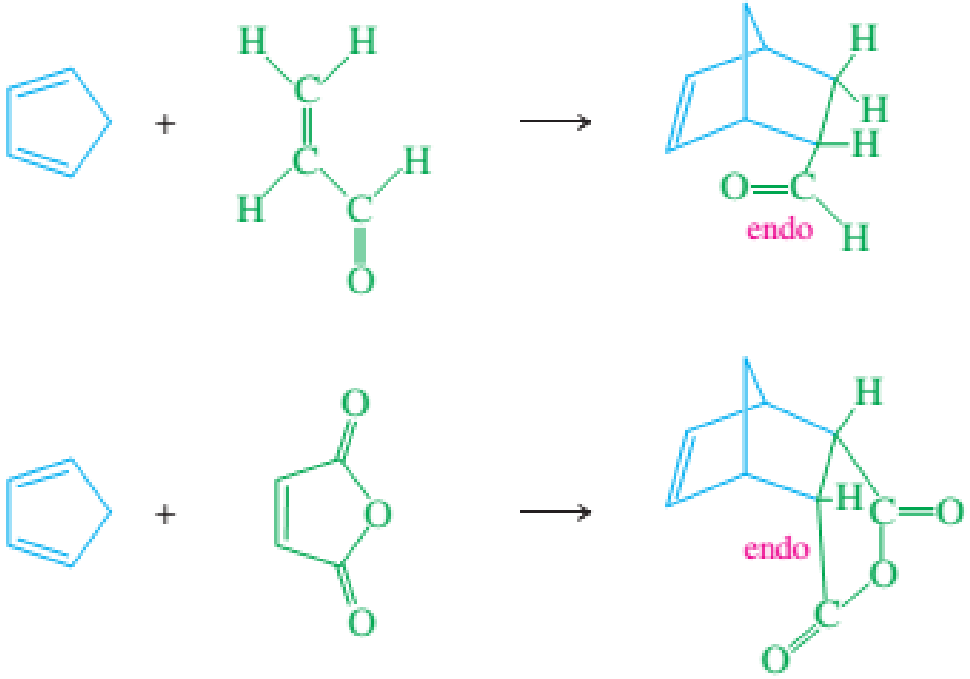


In most Diels–Alder reactions, there is *secondary overlap* between the *p* orbitals of the electron-withdrawing group and one of the central carbon atoms of the diene. Secondary overlap stabilizes the transition state, and it favors products having the electron-withdrawing groups in *endo* positions.

Stereochemical requirements of the Diels–Alder transition state



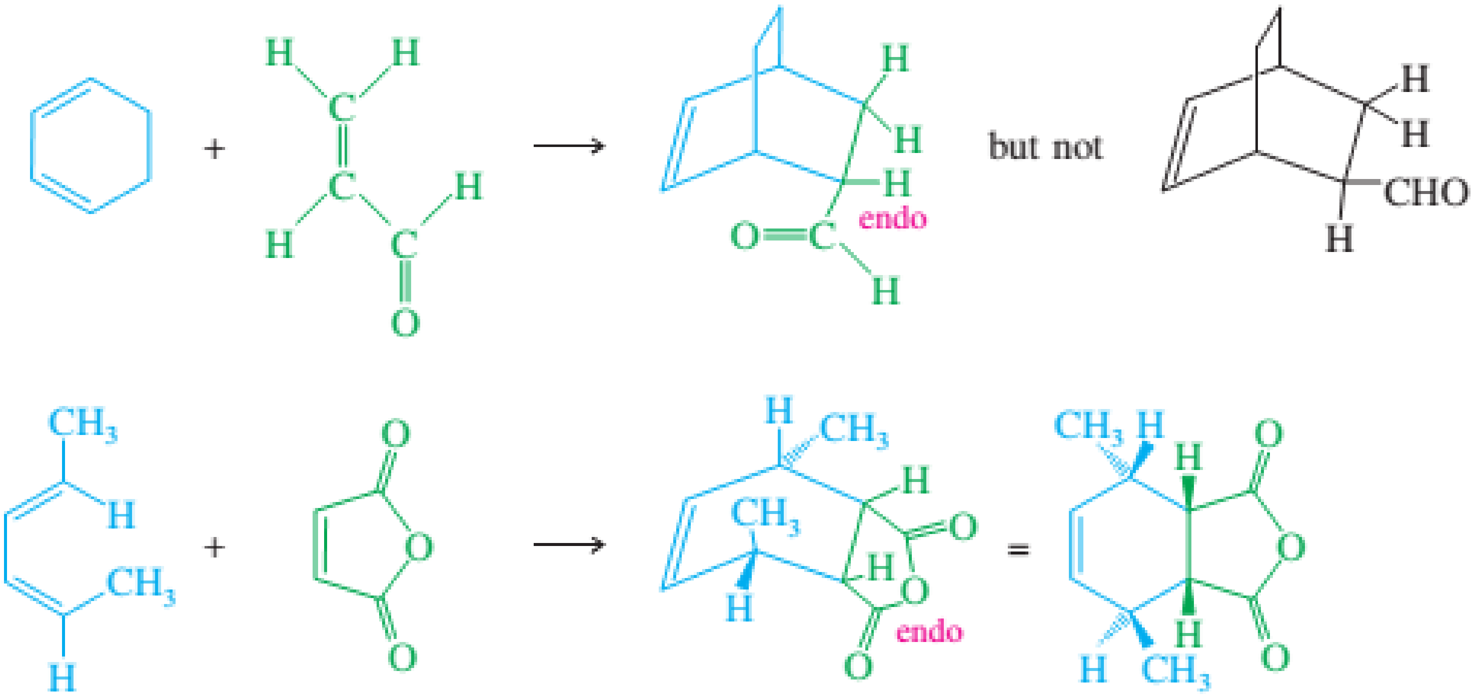
stereochemical positions of norbornene



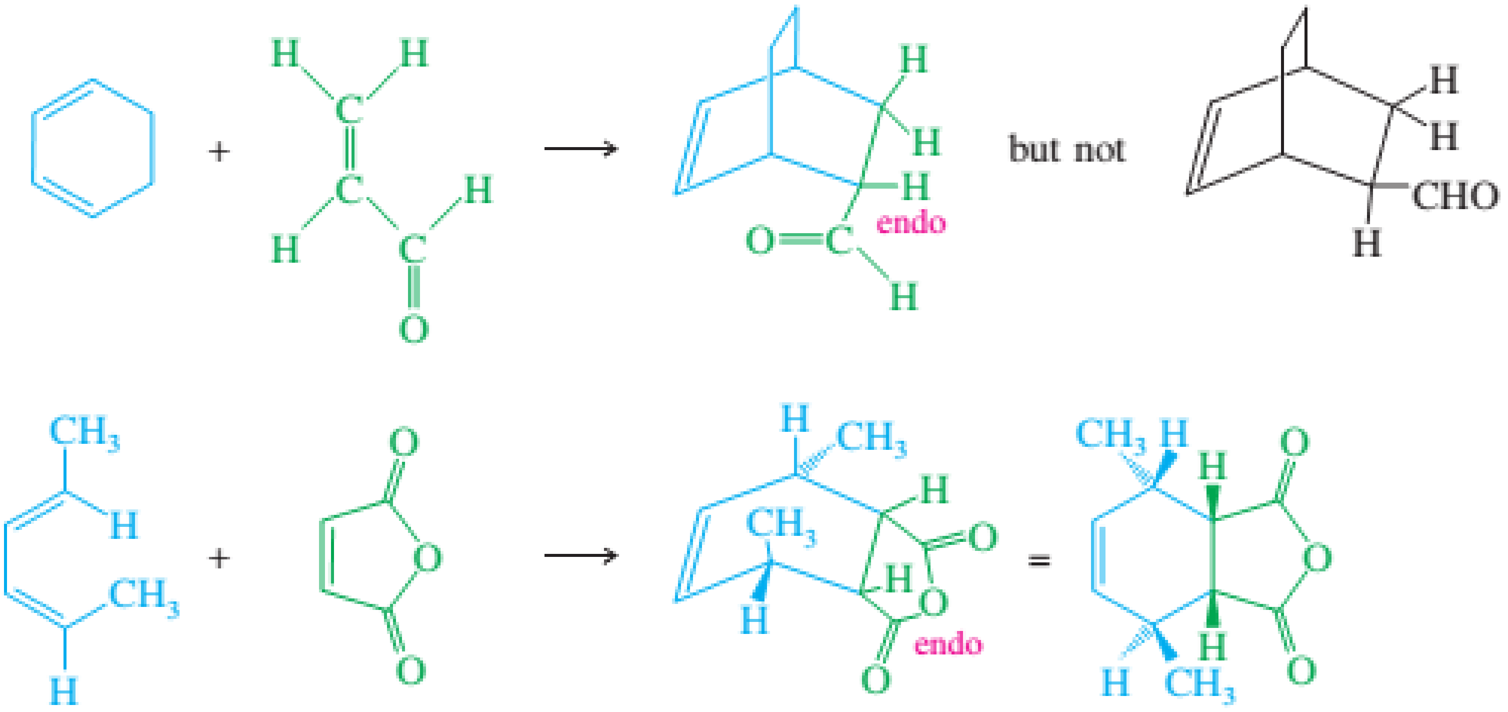
Stereochemical requirements of the Diels–Alder transition state

The endo rule is useful for predicting the products of many types of Diels–Alderreactions, regardless of whether they use cyclopentadiene to form norbornene systems.

The following examples show the use of the endo rule with other types of Diels–Alder reactions.



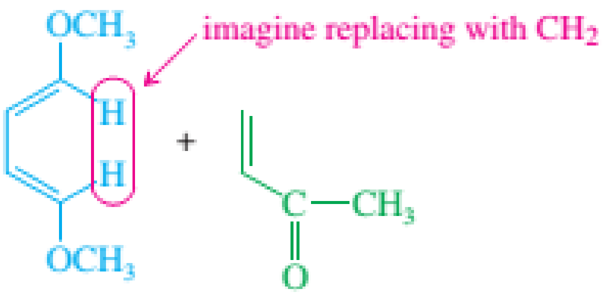
Stereochemical requirements of the Diels–Alder transition state



Chapter 4

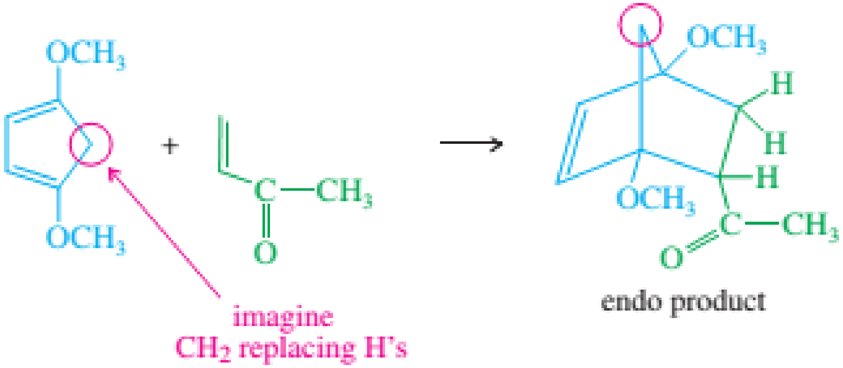
SOLVED PROBLEM 15-1

Use the endo rule to predict the product of the following cycloaddition.



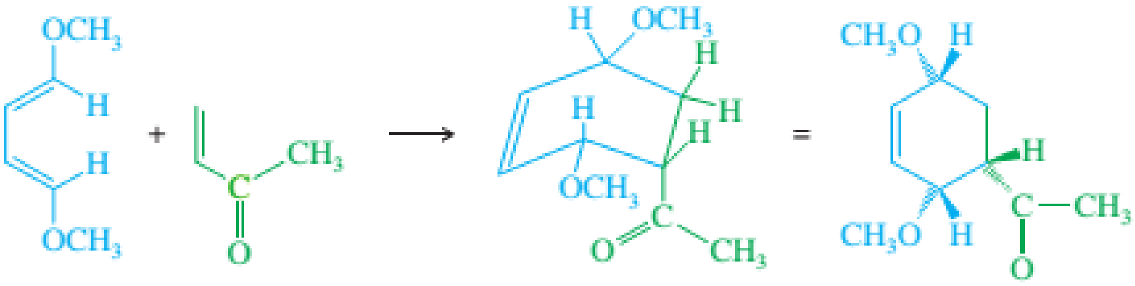
SOLUTION

Imagine this diene to be a substituted cyclopentadiene; the endo product will be formed.

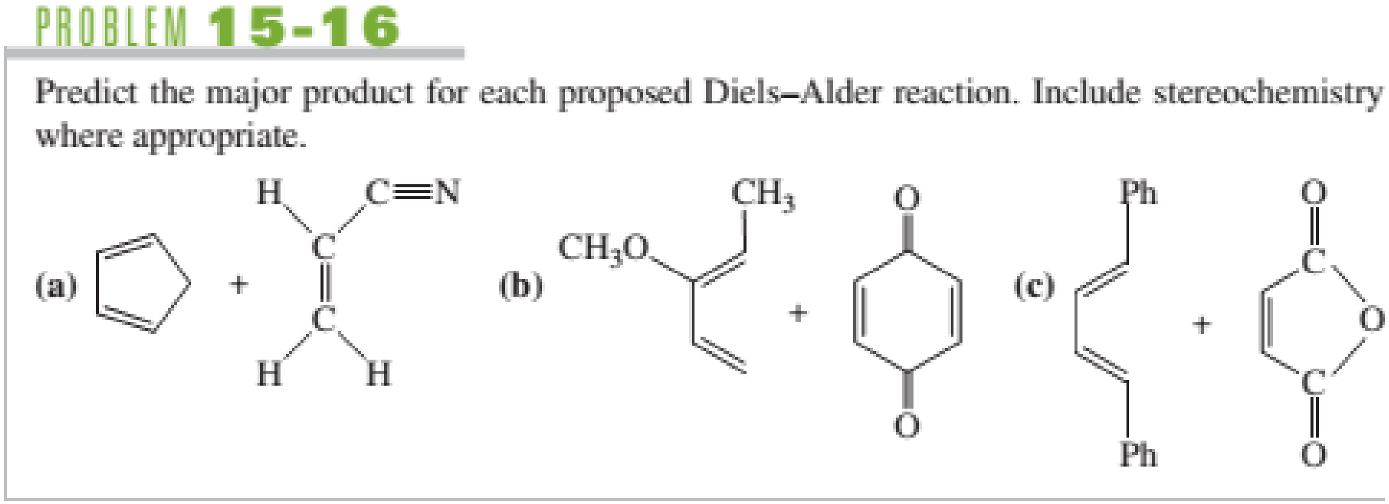


(Continued)

In the imaginary reaction, we replaced the two inside hydrogens with the rest of the cyclopentadiene ring. Now we put them back and draw the actual product.



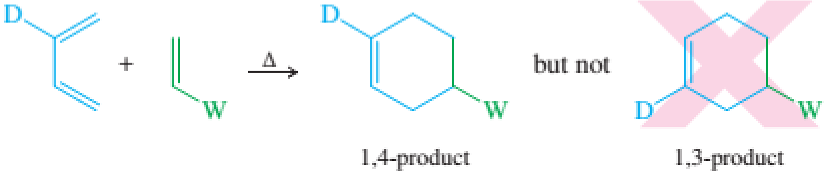
endo product



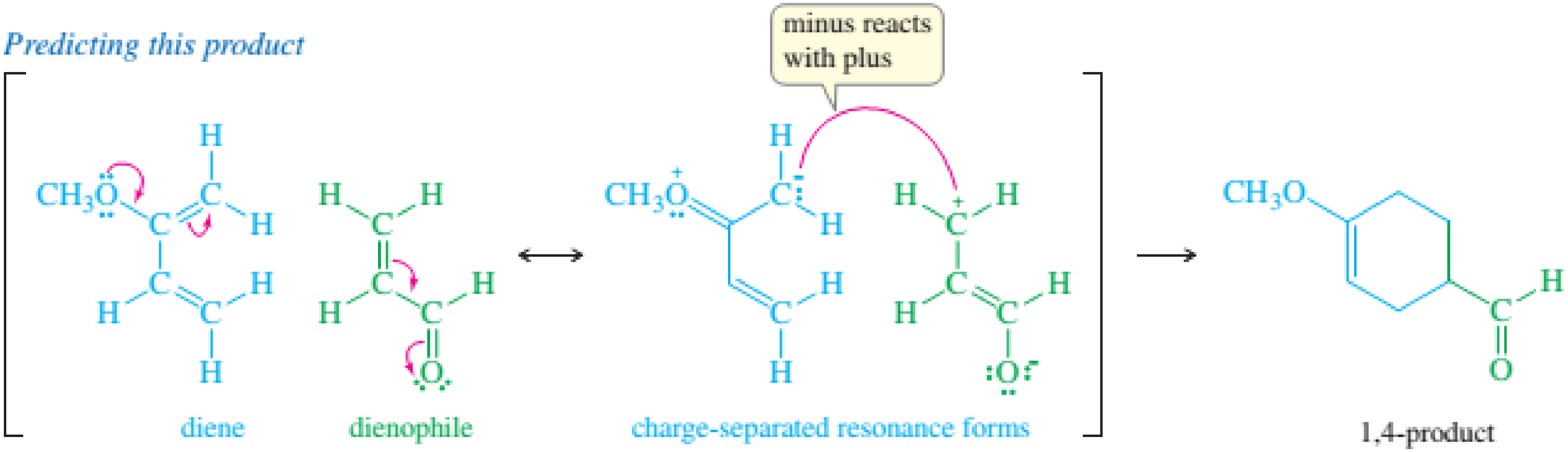
PROBLEM 15-16

Predict the major product for each proposed Diels–Alder reaction. Include stereochemistry where appropriate.

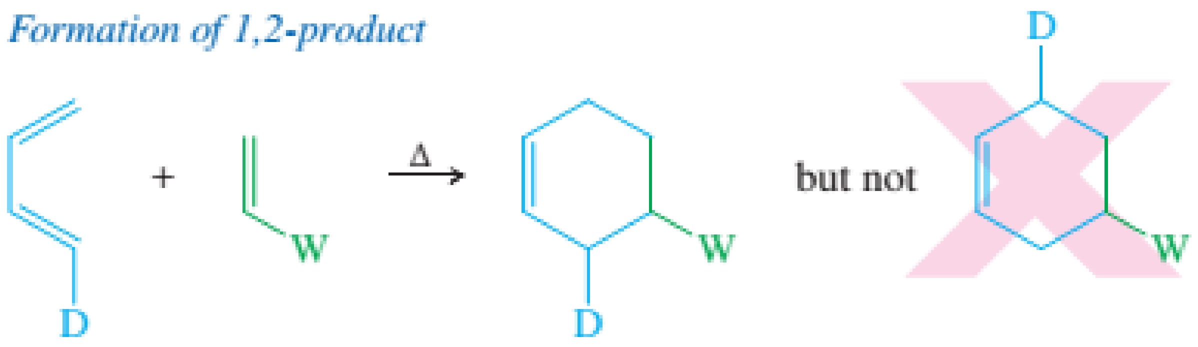
Formation of 1,4-product



Predicting this product



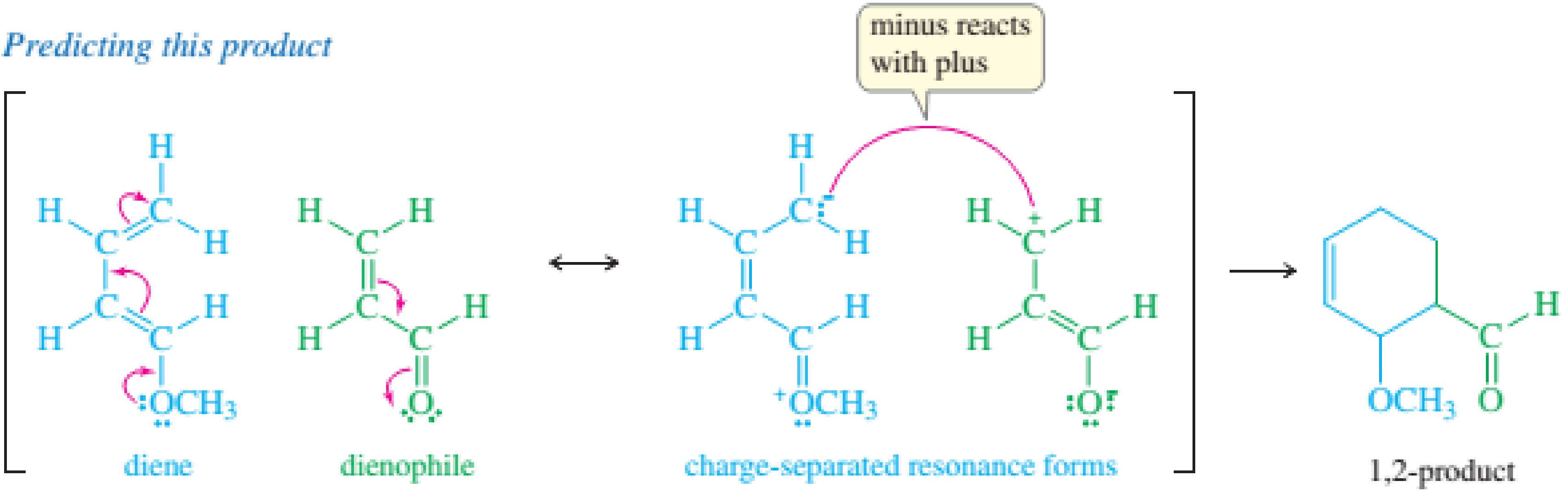
Formation of 1,2-product



1,2-product

1,3-product

Predicting this product



diene

dienophile

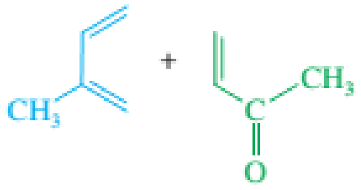
charge-separated resonance forms

1,2-product

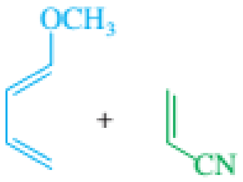
SOLVED PROBLEM 15-2

Predict the products of the following proposed Diels–Alder reactions.

(a)

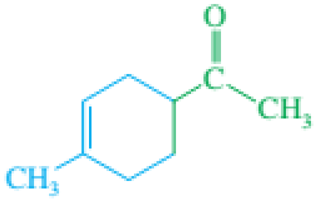


(b)

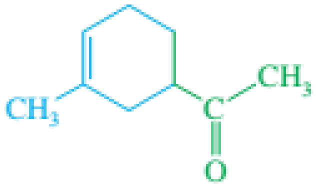


SOL

(a) The methyl group is weakly electron-donating to the diene, and the carbonyl group is electron-withdrawing from the dienophile. The two possible orientations place these groups in a 1,4-relationship or a 1,3-relationship. We select the 1,4-relationship for our predicted product. (Experimental results show a 70:30 preference for the 1,4-product.)

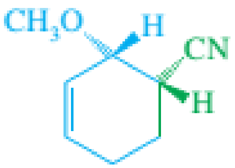


1,4-relationship (major)
(70%)

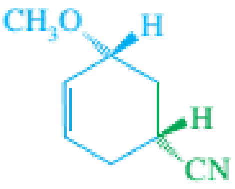


1,3-relationship (minor)
(30%)

(b) The methoxy group ($-OCH_3$) is strongly electron-donating to the diene, and the cyano group ($-C{\equiv}N$) is electron-withdrawing from the dienophile. Depending on the orientation of addition, the product has either a 1,2- or a 1,3-relationship of these two groups. We select the 1,2-relationship, and the endo rule predicts cis stereochemistry of the two substituents.



1,2-relationship (product)



1,3-relationship (not formed)

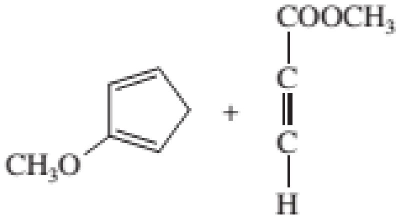
PROBLEM 15-17

In Solved Problem 15-2, we simply predicted that the products would have a 1,2- or 1,4-relationship of the proper substituents. Draw the charge-separated resonance forms of the reactants to support these predictions.

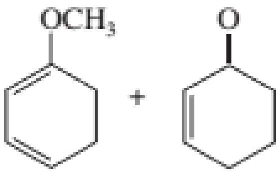
PROBLEM 15-18

Predict the products of the following Diels–Alder reactions.

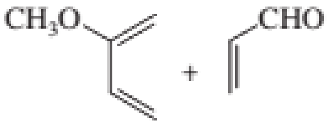
(a)



(b)



(c)



***(d)**