

Chapter 15

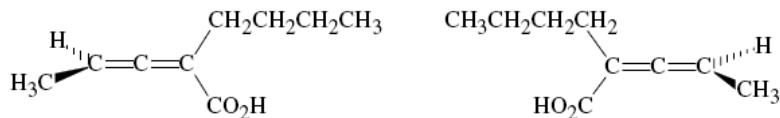
Dienes, Resonance, and Aromaticity

Solutions to In-Text Problems

- 15.2 The delocalization energy is the energy of each MO times the number of electrons in that MO, minus the same energy for three ethylenes:

$$\text{delocalization energy} = 2(1.80\beta) + 2(1.25\beta) + 2(0.44\beta) - (3)(2)(1.00\beta) = 0.98\beta$$

- 15.5 (a) The two enantiomers of an allene:



- (b) Because enantiomers have specific rotations of equal magnitudes and opposite signs, the other enantiomer has a specific rotation of +30.7°.

- 15.6 (b) The calculation is identical to that in part (a) with different numbers:

$$E = \frac{hc}{\lambda} = \frac{(3.99 \times 10^{-13} \text{ kJ s mol}^{-1})(3.00 \times 10^8 \text{ m s}^{-1})}{250 \times 10^{-9} \text{ m}} = 479 \text{ kJ mol}^{-1}$$

(The corresponding value in kcal mol⁻¹ is 114.)

- 15.7 (b) Use Eq. 15.1 on text p. 685 with $(I_0/I) = 2$. Thus, $A = \log(2) = 0.30$.

- 15.8 The piece with greater absorbance transmits less of the incident radiation. Therefore, the thick piece of glass has greater absorbance.

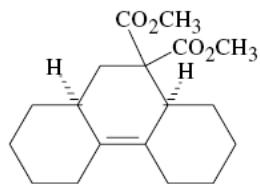
- 15.9 (b) The absorbance of the isoprene sample in Fig. 15.5 on text p. 684 at 235 nm is 0.225. With the concentration determined from part (a), Beer's law gives $A = 0.225$ absorbance units = $\epsilon(7.44 \times 10^{-5} \text{ mol L}^{-1})(1 \text{ cm})$, or $\epsilon = 3.02 \times 10^3$ absorbance units L mol⁻¹ cm⁻¹. Another way to determine the extinction coefficient at a different wavelength is based on the fact that the ratio of absorbances at different wavelengths equals the ratio of the extinction coefficients. Hence, the extinction coefficient at 235 nm is

$$\epsilon_{235} = \epsilon_{225} \frac{A_{235}}{A_{225}} = (10,750 \text{ absorbance units L mol}^{-1} \text{ cm}^{-1}) \left(\frac{0.225 \text{ absorbance units}}{0.800 \text{ absorbance units}} \right)$$

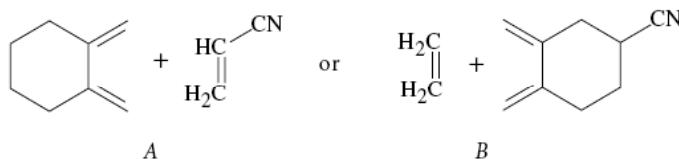
or $\epsilon_{235} = 3.02 \times 10^3 = 3023$ absorbance units L mol⁻¹ cm⁻¹.

- 15.10 (a) The two alkyl substituents contribute +10 nm to the base λ_{\max} of 217 for a predicted λ_{\max} value of 227 nm.

15.11 (b)

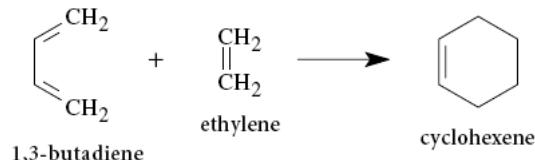


15.12 (a) An analysis like that employed in Study Problem 15.1 (text p. 692) suggests two possibilities.

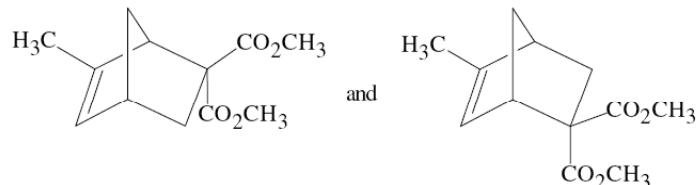
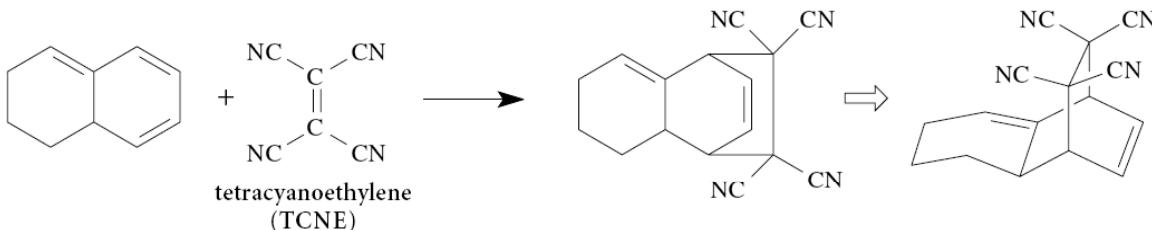


Pair *A* is preferred because, in many cases, the most reactive dienophiles are those with conjugated electronegative substituents. But if your answer was pair *B*, you have analyzed the problem correctly.

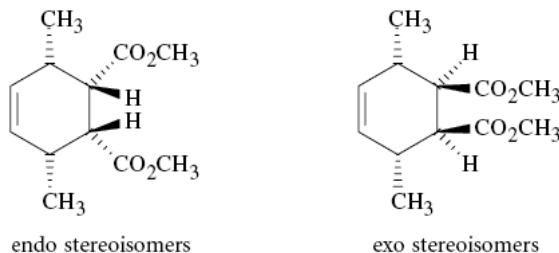
15.13 (a) With 1,3-butadiene as the diene and ethylene as the dienophile, the product would be cyclohexene.



15.14 (b) As in part (a), two possible orientations of the diene and dienophile lead to the following two possible constitutional isomers:

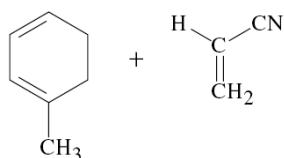
15.16 The triene contains two diene units with one double bond common to both. The dienophile reacts with the diene unit that is locked in an *s*-cis conformation.

15.17 (b) The two products correspond to the two possibilities in Eq. 15.14 on text p. 699. They result from addition of the diene at either of the two faces of the alkene (or the alkene at either of the two faces of the diene).

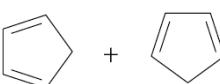


Notice that both stereoisomers result from *syn*-addition. In other words, there are *two* possible modes of *syn*-addition.

- 15.18 (b) (d)

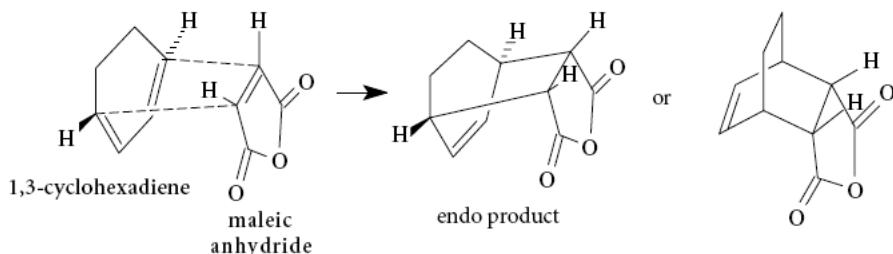


- (d)

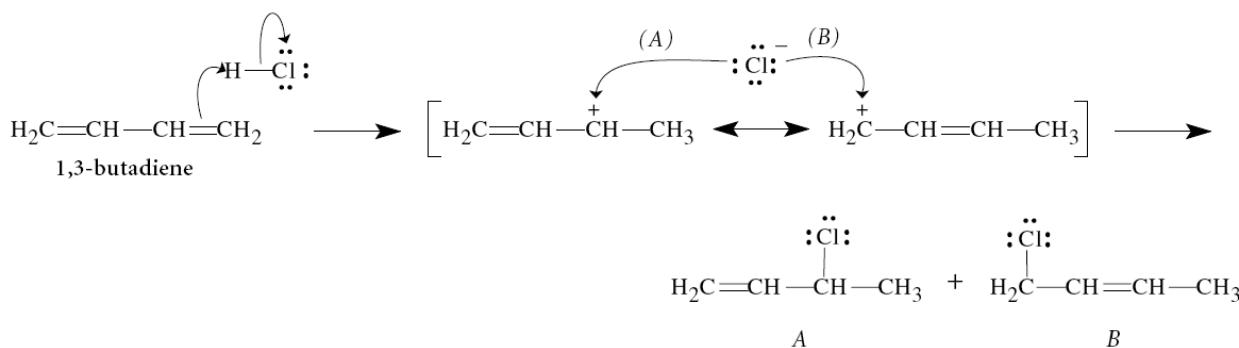


(that is, the reaction of two 1,3-cyclopentadiene molecules)

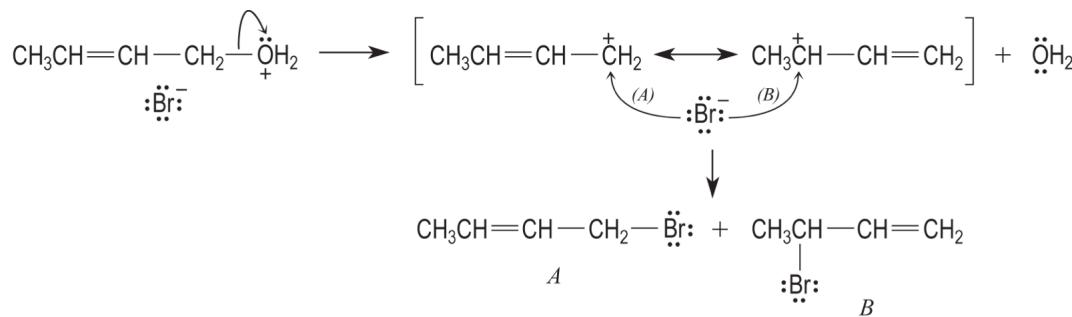
- 15.20 We'll use a diagram like the one in the solution to Problem 15.19:



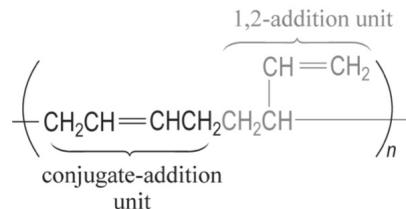
- 15.21 (a) The carbocation intermediate in the addition of HCl has two sites of electron deficiency, either of which can undergo a Lewis acid–base association reaction with the chloride ion.



- 15.22 (b) An allylic carbocation intermediate undergoes a Lewis acid–base association reaction with bromide ion at the two sites of electron deficiency.



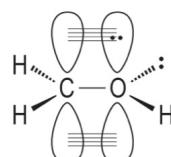
- 15.26 The structure of polybutadiene if every other unit of the polymer resulted from 1,2-addition:



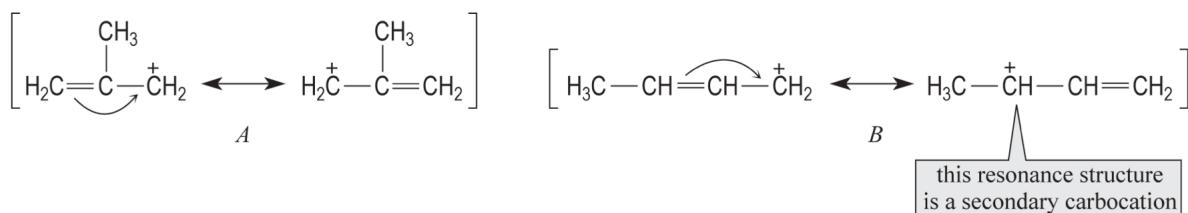
- 15.27 (b) The second structure is more important because every atom has an octet; however, the first structure has some importance because it assigns positive charge to the more electropositive atom, carbon.



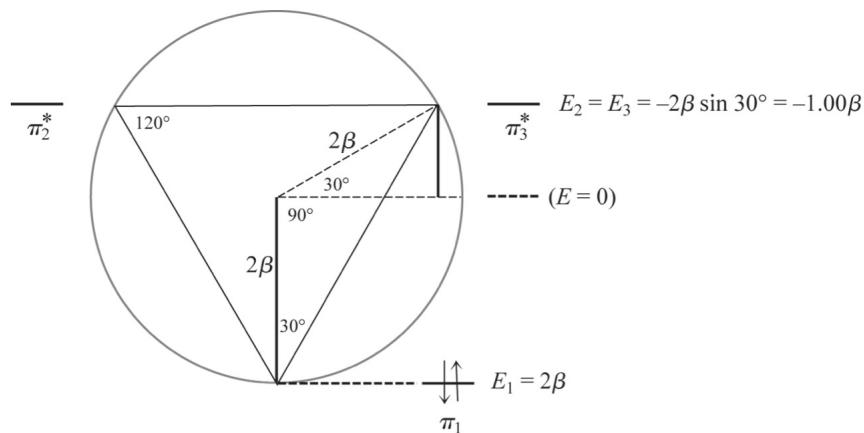
- 15.28 The electron-deficient carbon has an empty $2p$ orbital that overlaps with a filled $2p$ orbital on the oxygen. The other oxygen electron pair in an sp^2 orbital.



- 15.29 (c) Both ions have two resonance structures. However, the ion on the right (ion *B* below) is more stable because one of its resonance contributors is a secondary carbocation, whereas both contributors for the ion on the left (ion *A* below) are primary carbocations.



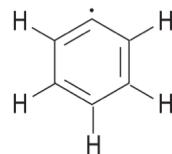
- 15.31 (b) The Frost circle construction for the cyclopropenyl cation is as follows:



This cation contains two π electrons, which both occupy the bonding MO π_1 . From Fig. 15.9, text p. 703, the π -electron energy of the allyl cation is $2(1.41\beta) = 2.82\beta$. The energy of cyclopropenyl is 4.0β . (Remember, β is a negative number.) The extra stabilization, 1.18β , is the contribution of aromaticity. (This does not take into account the destabilizing contribution of ring strain.)

- 15.34 An aromatic compound *cannot* have a single unpaired electron as part of its π -electron system, because the number of π -electrons required for aromaticity, $4n + 2$, must be an even number; a single unpaired electron would result in an odd number of electrons.

However, a free radical could certainly be aromatic if the unpaired electron were not part of the π -electron system. An example is the *phenyl radical*, which could be formed conceptually by abstraction of a hydrogen atom from benzene:



phenyl radical

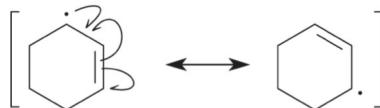
However, in such a radical, the unpaired electron itself does not contribute to the aromatic stability because it is not part of the $4n + 2$ π -electron system.

- 15.35 (b) This ion contains $4n$, not $4n + 2$, π electrons, and is therefore not aromatic.
 (d) Isoxazole is aromatic. Each double bond contributes two electrons to the π -electron system. One electron pair on the oxygen is also part of the π -electron system, but the other electron pair on the oxygen is not. (See the solution to Problem 15.33.) The electron pair on the nitrogen is vinylic and, like the electron pair in pyridine, it is not part of the π -electron system.
 (f) This compound is not aromatic because it has $4n$ rather than $4n + 2$ π electrons. The empty p orbital on boron, although part of the π -electron system, contributes no electrons.

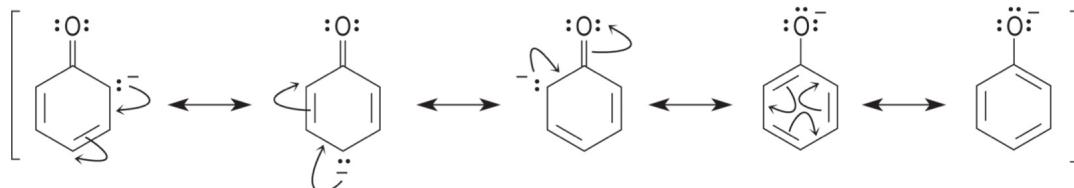
- 15.37 Compounds (b) and (f) contain $4n$ π electrons and are in principle antiaromatic.

Solutions to Additional Problems

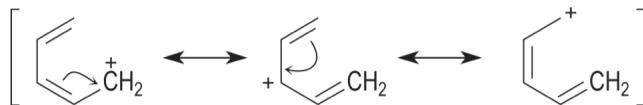
- 15.38 (b) The structures are identical; they are of equal importance.



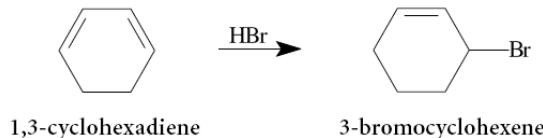
- (d) The fourth and fifth structures are most important because they are aromatic and because they have the negative charge on the most electronegative atom.



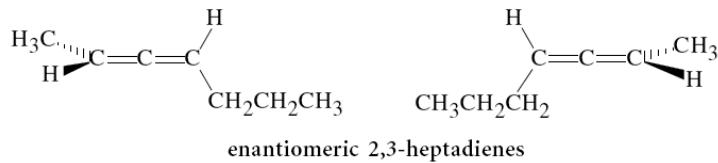
- (f) The second structure is somewhat more important because it places electron deficiency (and positive charge) on a secondary carbon. (The first and third structures are identical, although only one of the carbons is written out explicitly.)



- 15.40 1,3-Cyclohexadiene gives 3-bromocyclohexene by either 1,2- or 1,4-addition of HBr.

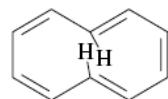


- 15.41 (a) Since the perpendicular relationship is necessary for chirality of a cumulene, allenes, as well as other cumulenes with an even number of cumulated double bonds, can be chiral. Indeed, 2,3-heptadiene is a chiral allene, and therefore exists as a pair of enantiomers that can in principle be separated by an enantiomeric resolution.

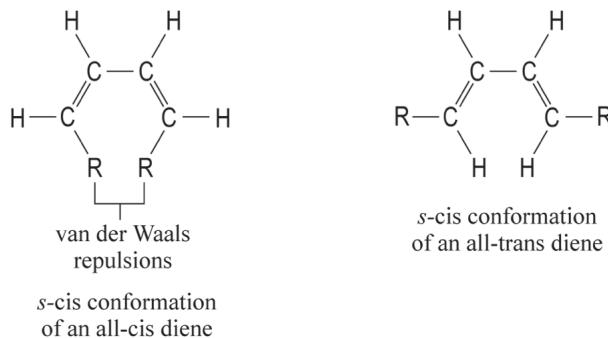


- 15.42 (b) This radical has three π electrons: two from the double bond and one from the unpaired electron. It is therefore not aromatic.
 (d) This anion has ten π electrons: two from each of the four double bonds and two from the anionic carbon. It is likely to be aromatic.

- 15.44 Severe van der Waals repulsions between the inner hydrogens (shown in the following structure) force the compound out of planarity. These van der Waals repulsions are so great in the planar conformation that not even aromaticity can compensate for the resulting destabilization.

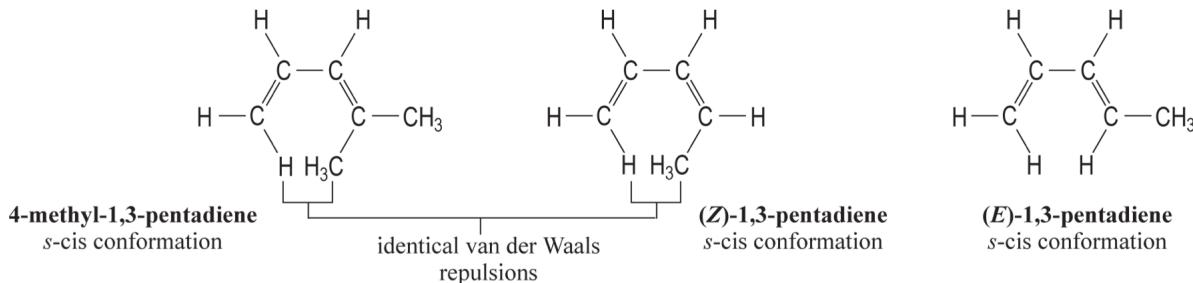


- 15.45 (b) *Heats of formation:* $3 < 1 < 2$. *Reasons:* Compound (3) is most stable because it is aromatic. Compound (1) is more stable than compound (2) because conjugated alkenes are more stable than isomeric alkynes.
- 15.46 (b) The first compound has three alkyl substituents on conjugated double bonds; the second compound has two. Hence, the λ_{\max} of the first compound should be about 5 nm greater than the λ_{\max} of the second.
 (d) The first compound has three conjugated double bonds, whereas the second compound has two; one double bond is not conjugated with the other two. Hence, the first compound should have a considerably greater λ_{\max} than the second.
- 15.48 The color of β -carotene is due to its chromophore of extensively conjugated double bonds. Catalytic hydrogenation would result in addition of hydrogen to these double bonds; hence, catalytic hydrogenation of a β -carotene sample would convert it from a red-orange conjugated alkene into a colorless alkane.
- 15.50 Although mycomycin has no asymmetric carbons, it does contain stereocenters: the outer carbons of the allene unit. Evidently, mycomycin is one enantiomer of this chiral allene. The chirality of certain allenes is discussed in Sec. 15.1C on text p. 682.)
- 15.52 The analysis in Eqs. 15.9a–b on text p. 654 shows that the *s*-cis conformations of dienes with cis double bonds are destabilized by van der Waals repulsions, whereas the *s*-cis conformations of dienes with trans double bonds do not suffer the same repulsions.



These van der Waals repulsions also destabilize the transition states of Diels–Alder reactions, which require *s*-cis conformations of the reacting dienes. Because the diene in the problem undergoes the Diels–Alder reaction under mild conditions, it is probably the all-trans diene.

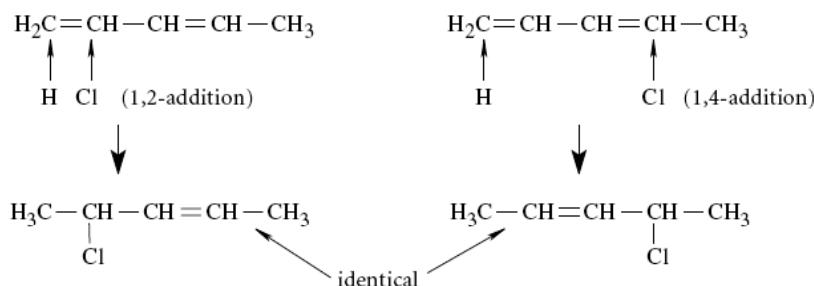
- 15.54 The answer to this problem lies in the *s*-cis conformations of the three dienes, which are as follows:



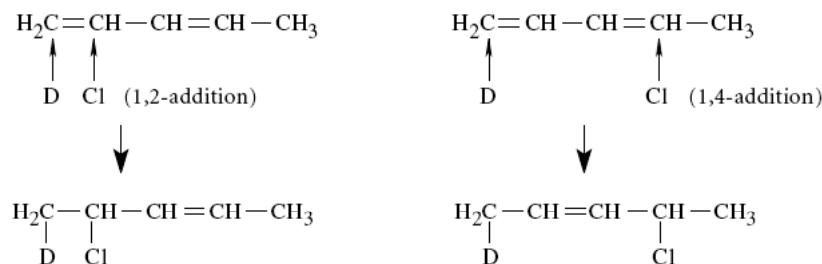
The reactivities of these three dienes in the Diels–Alder reactions correlates nicely with the accessibility of their *s*-cis conformations. (Remember, the transition state of the Diels–Alder reaction involves the *s*-cis conformation of

the diene.) The van der Waals repulsions shown above destabilize the *s*-*cis* conformations of both 4-methyl-1,3-pentadiene and (*Z*)-1,3-pentadiene to the same extent because the interacting groups are identical. Hence, their reactivity is reduced by about the same amount relative to that of (*E*)-1,3-pentadiene, whose *s*-*cis* conformation has no such repulsions.

- 15.56 (a) The 1,2- and 1,4-addition products formed in the reaction of 1,3-pentadiene and HCl are identical if we assume that all double bonds retain their *E* stereochemistry.



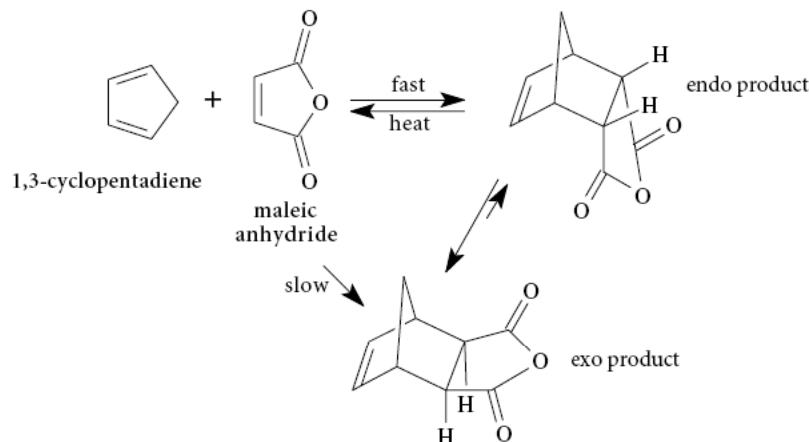
- (b) There can be no preference for 1,2- versus 1,4-addition on the basis of the product stability, because, as shown in part (a), the products are the same. The problem is that we can't tell one mode of addition from the other! The use of D—Cl, however, solves this problem. The use of deuterium allows us to distinguish between the hydrogen that has added and the ones that were originally in the diene.



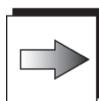
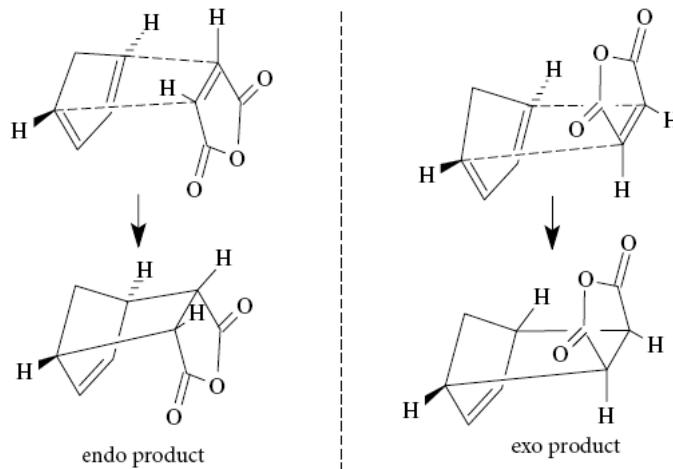
The two products are different, if only subtly so. The isotope has a negligible effect on product stability.

- (c) According to the text, the product of 1,2-addition is preferred, and it is shown in the solution to part (b). In fact, this was observed experimentally. The actual ratio is about 70:30 in favor of 1,2-addition. (How would we tell one product from the other?) This experiment, reported in 1979 by J. E. Nordlander of Case Western Reserve University, established clearly that product stability has nothing to do with the kinetic preference. The arguments in the text are the only reasonable alternative.

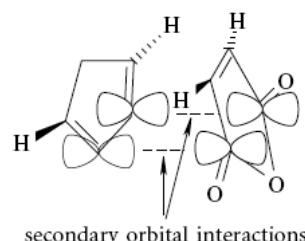
- 15.58 (a) The transformations involved in the reaction between 1,3-cyclopentadiene and maleic anhydride:



- (b) Because the initially formed product distribution is markedly different from the equilibrium distribution, the reaction is kinetically controlled.
- (c) At low temperature, the formation of product is kinetically controlled. The problem tells us that the endo stereoisomer is the major one formed. The transition state for this process is shown on the left side of the following diagram. The transition state for the other process is shown at right.

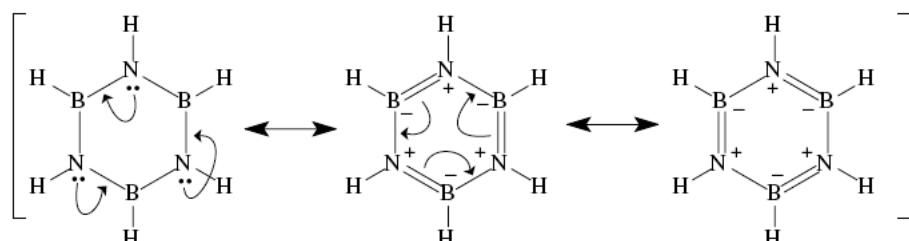


It has been suggested that kinetic control in the Diels–Alder reaction is due to “maximum accumulation of unsaturation,” or “secondary orbital interactions.” You can see that in the endo transition state, the $2p$ orbitals of the anhydride carbonyl groups and some of the $2p$ orbitals of the diene unit are “face-to-face.”

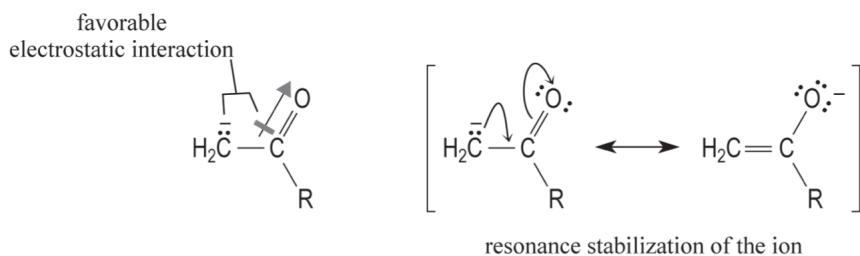


The interaction between these orbitals evidently stabilizes the transition state. The endo product is formed almost exclusively. However, when the two products are allowed to come to equilibrium, there is little difference in their stabilities.

- 15.63 Borazole is very stable because it is aromatic; each nitrogen contributes two π electrons and each boron contributes zero electrons, for a total of six π electrons in the aromatic system. The resemblance of borazole to benzene is more obvious from its other two resonance structures:

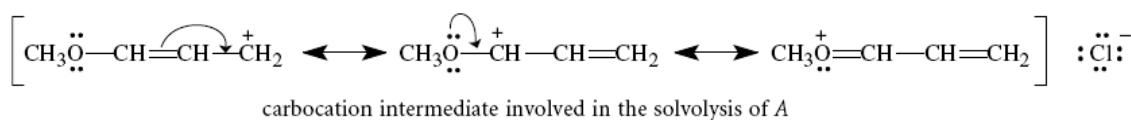


- 15.65 (a) The conjugate-base enolate ion is stabilized by the polar (electron-withdrawing) effect of the nearby carbonyl bond dipole as well as by resonance:



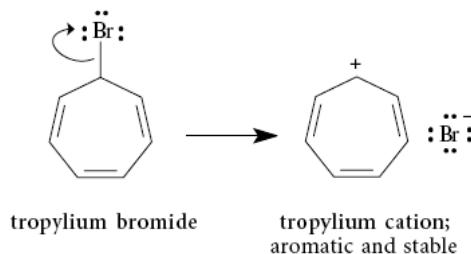
Recall (Sec. 3.6, text p. 113) that stabilization of a conjugate base increases the acidity of its conjugate acid.

- 15.66 Compound *A* should react much more rapidly because the carbocation intermediate (shown below) has three important resonance contributors. In particular, an unshared pair of electrons on the oxygen can be delocalized in this cation; in the solvolysis of the other compound, the unshared pairs on oxygen have no resonance interaction with the positive charge in the carbocation.



By Hammond's postulate, the reaction involving the more stable carbocation intermediate is faster.

- 15.68 This compound behaves like a salt because it *is* a salt. Tropylium bromide ionizes readily to bromide ion and the *tropylium cation*, which, because it has a continuous cycle of six ($4n + 2$, $n = 1$) π electrons, is aromatic, very stable, and very easily formed.



- 15.72 The structure of spiropentadiene is shown below; it undergoes a Diels–Alder reaction with two molar equivalents of 1,3-cyclopentadiene. Spiropentadiene is unstable because of its great ring strain. Although cyclopropane rings are retained in the product, they contain less ring strain than cyclopropene rings. (Why?)



- 15.73 (a) The mechanism below is shown beginning with the protonated alcohol, which is formed under the strongly acidic conditions.

