

Chapter 14 – Conjugated Dienes and Ultraviolet Spectroscopy

Chapter Outline

I. Conjugated Dienes (Sections 14.1 – 14.6).

A. Preparation and stability of conjugated dienes (Section 14.1).

1. Base-induced elimination of allylic halides is the most common method.
2. The C2–C3 bond length of 1,3-butadiene is 5 pm shorter than a C–C single bond.
3. Stability of conjugated dienes.
 - a. Heats of hydrogenation show that conjugated dienes are somewhat more stable than nonconjugated dienes.
 - b. Because conjugated dienes are more stable and contain less energy, they release less heat on hydrogenation.
4. Molecular orbital description of 1,3-butadiene.
 - a. The stability of 1,3-butadiene may be due to the greater amount of *s* character of the C–C single bond between the double bonds.
 - b. Molecular orbital theory offers another explanation.
 - i. If we combine 4 adjacent *p* orbitals, we generate a set of 4 molecular orbitals.
 - ii. Bonding electrons go into the lower two MOs.
 - iii. The lowest MO has a bonding interaction between C2 and C3 that gives that bond partial double-bond character.
 - iv. The π electrons of butadiene are delocalized over the entire π framework.

C. Reactions of conjugated dienes (Sections 14.2 – 14.6).

1. Electrophilic addition to conjugated dienes (Sections 14.2 – 14.3).

- a. Conjugated dienes react in electrophilic addition reactions to give products of both 1,2-addition and 1,4-addition (Section 14.2).
 - i. Addition of an electrophile gives an allylic carbocation intermediate that is resonance-stabilized.
 - ii. Addition of the nucleophile in the second step of the reaction can occur at either end of the allylic carbocation to yield two products.
- b. The ratio of products can vary if the reaction is carried out under conditions of kinetic control or of thermodynamic control (Section 14.3).
 - i. Under conditions of kinetic control (lower temperature), the product whose formation has the lower energy of activation forms in greater amounts.
 - ii. Under conditions of thermodynamic control (high temperature), the more stable product (the product whose formation has a larger negative value of ΔG°) forms in greater amounts.
 - iii. In electrophilic addition reactions of conjugated dienes, the 1,2 adduct forms preferentially at low T, and the 1,4 adduct forms preferentially at high temperature.

2. The Diels–Alder reaction (Sections 14.4 – 14.5).

- a. How the reaction occurs (Section 14.4).
 - i. A diene can react with certain alkenes to form a cyclic product.
 - ii. This reaction, the Diels–Alder reaction, forms two C–C bonds in a single step.
 - iii. The reaction occurs by a pericyclic mechanism, which takes place in a single step by a cyclic redistribution of electrons.
 - iv. In the reaction, σ overlap occurs between the two alkene *p* orbitals and the two *p* orbitals on carbons 1 and 4 of the diene.

- v. The two alkene carbons and C1 and C4 of the diene rehybridize from sp^2 to sp^3 , and C2 and C3 of the diene remain sp^2 hybridized.
- b. The dienophile (Section 14.5).
 - i. The dienophile must have an electron-withdrawing group and may contain a triple bond.
 - ii. The stereochemistry of the dienophile is maintained during the reaction.
 - iii. Only endo product is formed because orbital overlap is greater in the transition state than for exo product.

A substituent in a bicyclic ring system is endo if it is syn to the larger of the other two bridges.
- c. The diene.
 - i. A diene must adopt an *s*-cis conformation in order to undergo the Diels-Alder reaction.
 - ii. Some dienes can rotate to achieve an *s*-cis conformation; those that are rigid can't react.
 - iii. Dienes that have fixed *s*-cis geometry are very reactive.
- 3. Diene polymers (Section 14.6).
 - a. Like simple alkenes, conjugated dienes can polymerize.
 - i. Because double bonds remain in the polymer, cis-trans isomerism is possible.
 - ii. Polymerization can be initiated by either a radical or by acid.
 - iii. Polymerization occurs by 1,4-addition.
 - b. Natural rubber is a polymer of isoprene with *Z* double-bond stereochemistry, and *gutta-percha* is a polymer of isoprene with *E* double-bond stereochemistry.
 - c. Synthetic rubber and neoprene (a polymer of chloroprene) are also diene polymers.
 - d. Rubber needs to be hardened by vulcanization.

Heating rubber with sulfur forms cross-links that lock the chains together.

II. Ultraviolet spectroscopy (Sections 14.7 – 14.9).

- A. Principles of ultraviolet spectroscopy (Section 14.7).
 - 1. The ultraviolet region of interest is between the wavelengths 200 nm and 400 nm.
 - 2. The energy absorbed is used to promote a π electron in a conjugated system from one orbital to another.
- B. Ultraviolet spectrum of 1,3-butadiene.
 - 1. When 1,3-butadiene is irradiated with ultraviolet light, a π electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital.
 - 2. UV radiation of 217 nm is necessary to promote this transition.
 - 3. This transition is known as a $\pi \rightarrow \pi^*$ transition.
- C. The ultraviolet spectrum.
 - 1. A UV spectrum is a plot of absorbance vs. wavelength.
 - a. The absorbance is $A = \log [I_0/I]$.
 - b. I_0 = intensity of incident light.
 - c. I = intensity of transmitted light.
 - d. The baseline is zero absorbance.
 - 2. For a specific substance, A is related to the molar absorptivity (ϵ).
 - a. Molar absorptivity is the absorbance of a sample whose concentration is 1 mol/L with a path length of 1 cm..
 - b. $A = \epsilon \times c \times l$.
 - c. The range of ϵ is 10,000 – 25,000 L/mol·cm.
 - 3. UV spectra usually consist of a single broad peak, whose maximum is λ_{max} .

D. Interpreting UV spectra (Section 14.8).

1. The wavelength necessary for a $\pi \rightarrow \pi^*$ transition depends on the energy difference between HOMO and LUMO.
2. By measuring this difference, it is possible to learn about the extent of conjugation in a molecule.
3. As the extent of conjugation increases, λ_{max} increases.
4. Different types of conjugated systems have characteristic values of λ_{max} .

F. Colored organic compounds (Section 14.9).

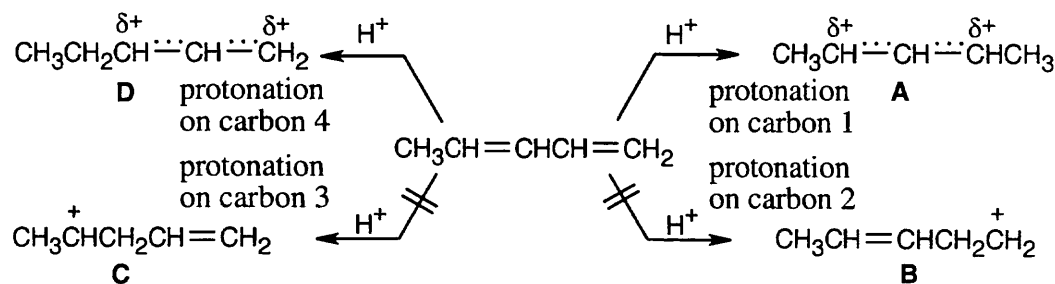
Compounds with extensive systems of conjugated bonds absorb in the visible range of the electromagnetic spectrum (400 – 800 nm).

Solutions to Problems

- 14.1** We would expect $\Delta H_{\text{hydrog}} = -126 + (-126) = -252$ kJ/mol for allene if the heat of hydrogenation for each double bond were the same as that for an isolated double bond. The measured ΔH_{hydrog} , -298 kJ/mol, is 46 kJ/mol more negative than the expected value. Thus, allene is higher in energy (less stable) than a nonconjugated diene, which in turn is less stable than a conjugated diene.

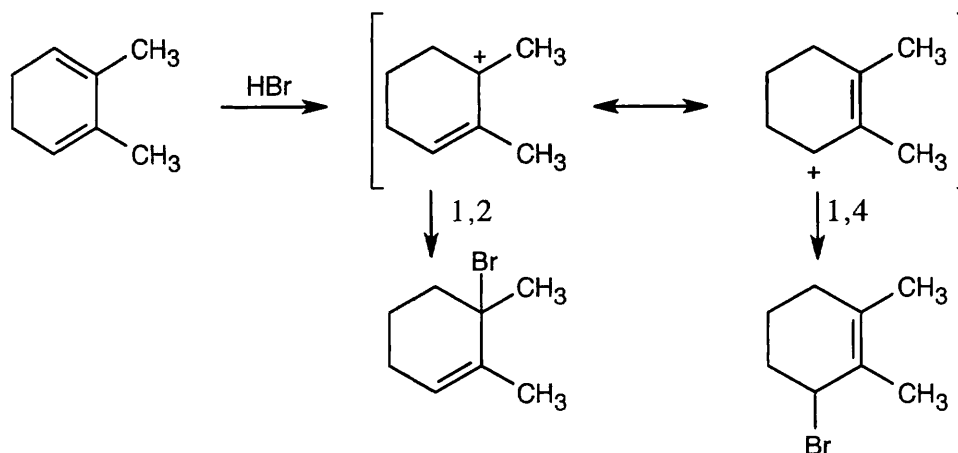
14.2

Product	Name	Results from:
$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3\text{CH}=\text{CHCHCH}_3 \end{array}$	4-Chloro-2-pentene	1,2 addition 1,4 addition
$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3\text{CH}_2\text{CHCH}=\text{CH}_2 \end{array}$	3-Chloro-1-pentene	1,2 addition
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{Cl}$	1-Chloro-2-pentene	1,4 addition

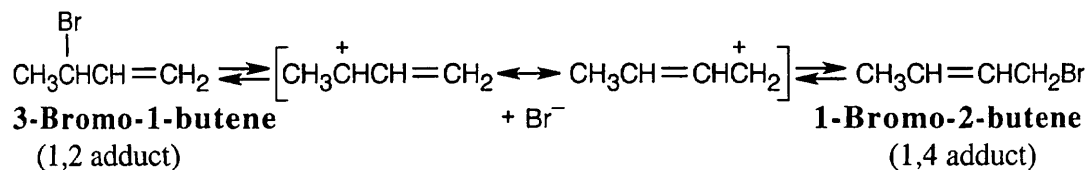
14.3

A and **D**, which are resonance-stabilized, are formed in preference to **B** and **C**, which are not. The positive charge of allylic carbocation **A** is delocalized over two secondary carbons, while the positive charge of carbocation **D** is delocalized over one secondary and one primary carbon. We therefore predict that carbocation **A** is the major intermediate formed, and that 4-chloro-2-pentene predominates. Note that this product results from both 1,2 and 1,4 addition.

14.4

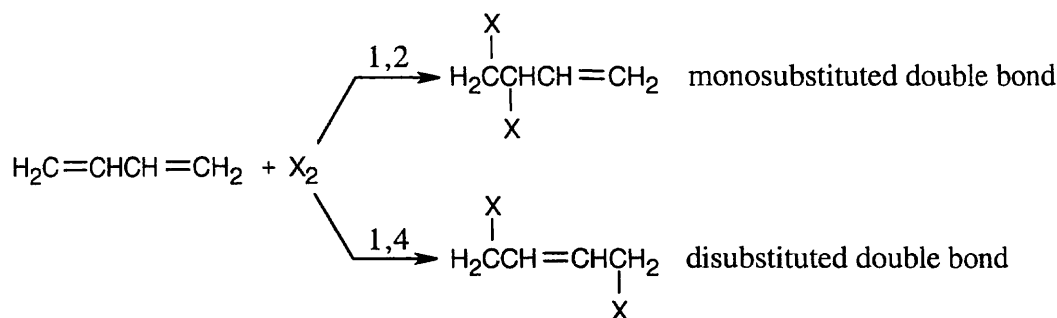


14.5



Allylic halides can undergo slow dissociation to form stabilized carbocations ($\text{S}_{\text{N}}1$ reaction). Both 3-bromo-1-butene and 1-bromo-2-butene form the same allylic carbocation, pictured above, on dissociation. Addition of bromide ion to the allylic carbocation then occurs to form a mixture of bromobutenes. Since the reaction is run under equilibrium conditions, the thermodynamically more stable 1-bromo-2-butene predominates.

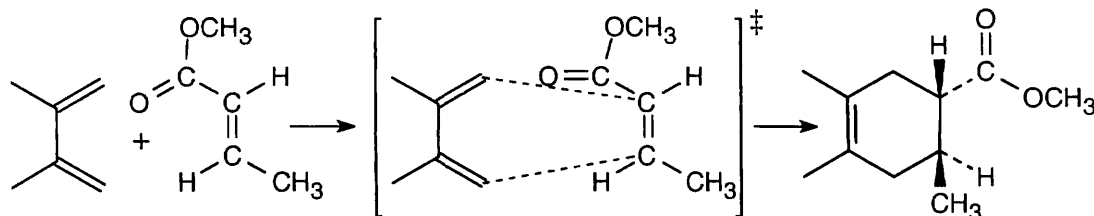
14.6



1,4 adducts are more stable than 1,2 adducts because disubstituted double bonds are more stable than monosubstituted double bonds (see Chapter 6).

14.7 Strategy: Draw the reactants in an orientation that shows where the new bonds will form. Form the new bonds by connecting the two reactants, removing two double bonds, and relocating the remaining double bond so that it lies between carbon 2 and carbon 3 of the diene. The substituents on the dienophile retain their trans relationship in the product. The product is a racemic mixture.

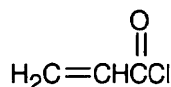
Solution:



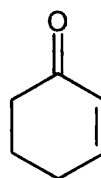
14.8 Strategy: Good dienophiles have an electron-withdrawing group conjugated with a double bond.

Solution:

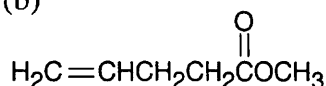
Good dienophiles: (a)



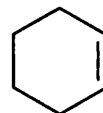
(d)



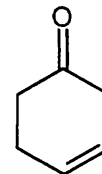
Poor dienophiles: (b)



(c)



(e)

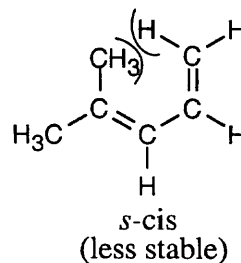
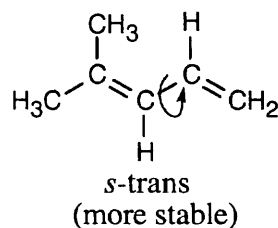


Compound (a) and (d) are good dienophiles because they have electron-withdrawing groups conjugated with a carbon-carbon double bond. Alkene (c) is a poor dienophile because it has no electron-withdrawing functional group. Compounds (b) and (e) are poor dienophiles because their electron-withdrawing groups are not conjugated with the double bond.

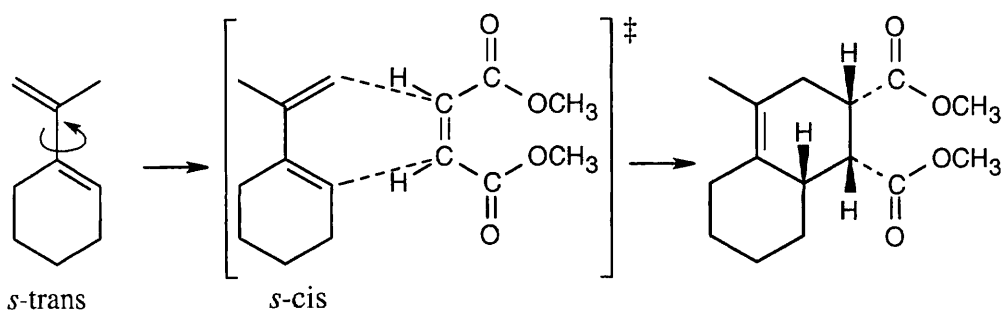
14.9 (a) This diene has an *s*-cis conformation and should undergo Diels-Alder cycloaddition.

(b) This diene has an *s*-trans conformation. Because the double bonds are in a fused ring system, it is not possible for them to rotate to an *s*-cis conformation.

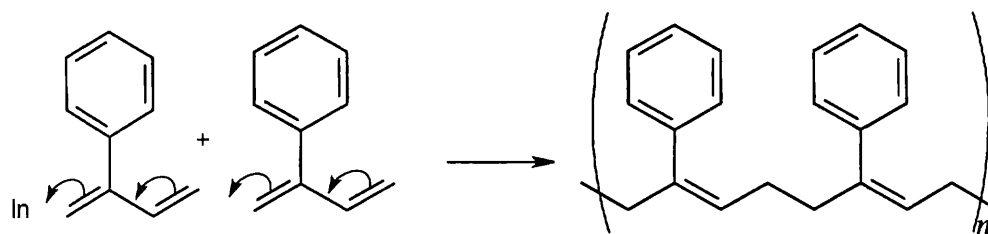
(c) Rotation can occur about the single bond of this *s*-trans diene. The resulting *s*-cis conformation, however, has an unfavorable steric interaction of a methyl group with a hydrogen at carbon 1. Rotation to the *s*-cis conformation is therefore not favored energetically.



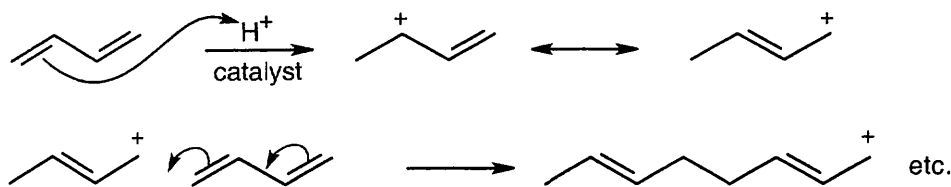
14.10 Rotation of the diene to the *s*-cis conformation must occur in order for reaction to take place.



14.11 The initiator may be either a radical or a cation. Diene polymerization is a 1,4 addition process that forms a polymer whose monomer units have a 4 carbon chain that contains a double bond every 4 bonds.



14.12



14.13

$$200 \text{ nm} = 200 \times 10^{-9} \text{ m} = 2 \times 10^{-7} \text{ m}$$

$$400 \text{ nm} = 400 \times 10^{-9} \text{ m} = 4 \times 10^{-7} \text{ m}$$

for $\lambda = 2 \times 10^{-7} \text{ m}$:

$$E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{\lambda \text{ (in m)}} = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{2.0 \times 10^{-7}} = 6.0 \times 10^2 \text{ kJ/mol}$$

for $\lambda = 4 \times 10^{-7} \text{ m}$:

$$E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{\lambda \text{ (in m)}} = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{4.0 \times 10^{-7}} = 3.0 \times 10^2 \text{ kJ/mol}$$

The energy of electromagnetic radiation in the region of the spectrum from 200 nm to 400 nm is 300–600 kJ/mol.

	UV	IR	^1H NMR (at 200 MHz)
Energy (in kJ/mol)	300–600	4.8–48	8.0×10^{-5}

The energy required for UV transitions is greater than the energy required for IR or ^1H NMR transitions.

14.14

$$\epsilon = \frac{A}{c \times l}$$

In this problem:

$$\epsilon = 50,100 = 5.01 \times 10^4 \text{ L/mol} \cdot \text{cm}$$

$$l = 1.00 \text{ cm}$$

$$A = 0.735$$

$$c = \frac{A}{\epsilon \times l} = \frac{0.735}{5.01 \times 10^4 \text{ L/mol} \cdot \text{cm} \times 1.00 \text{ cm}} = 1.47 \times 10^{-5} \text{ M}$$

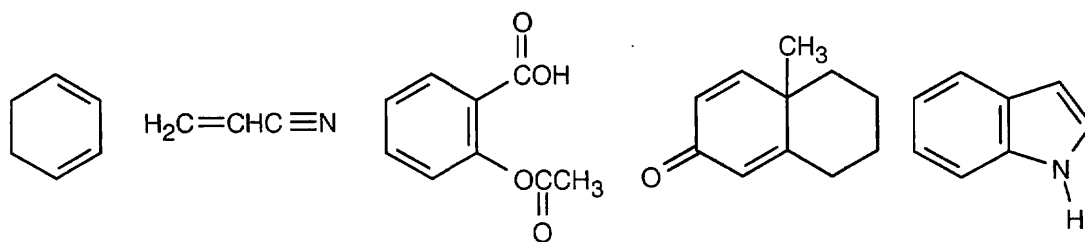
Where ϵ = molar absorptivity (in L/mol·cm)

A = absorbance

l = sample pathlength (in cm)

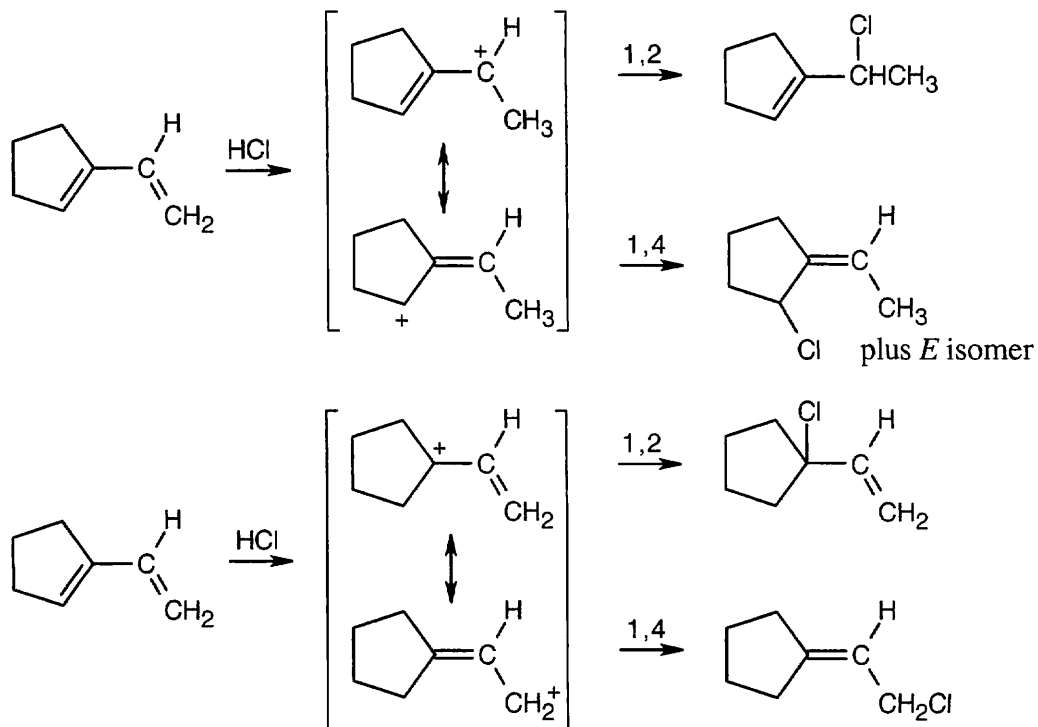
c = concentration (in mol/L)

14.15 All compounds having alternating single and multiple bonds should show ultraviolet absorption in the range 200–400 nm. Only compound (a) is not UV-active. All of the compounds pictured below show UV absorptions.

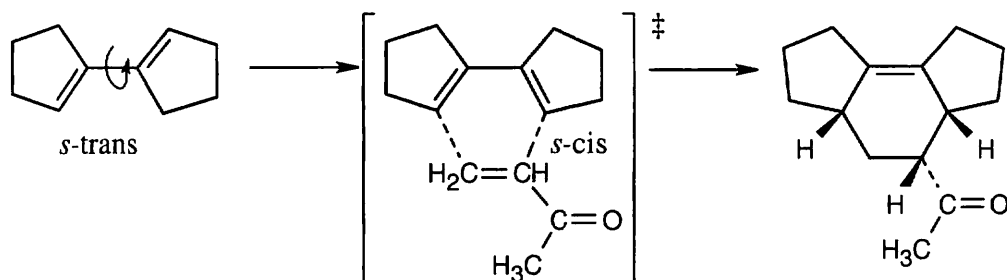


Visualizing Chemistry

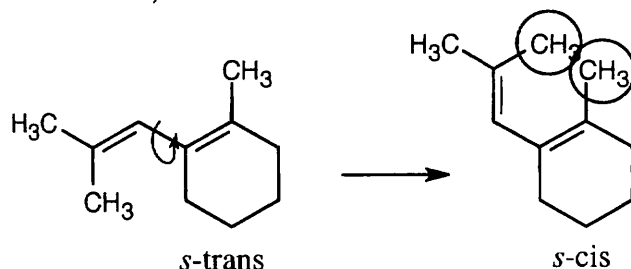
14.16



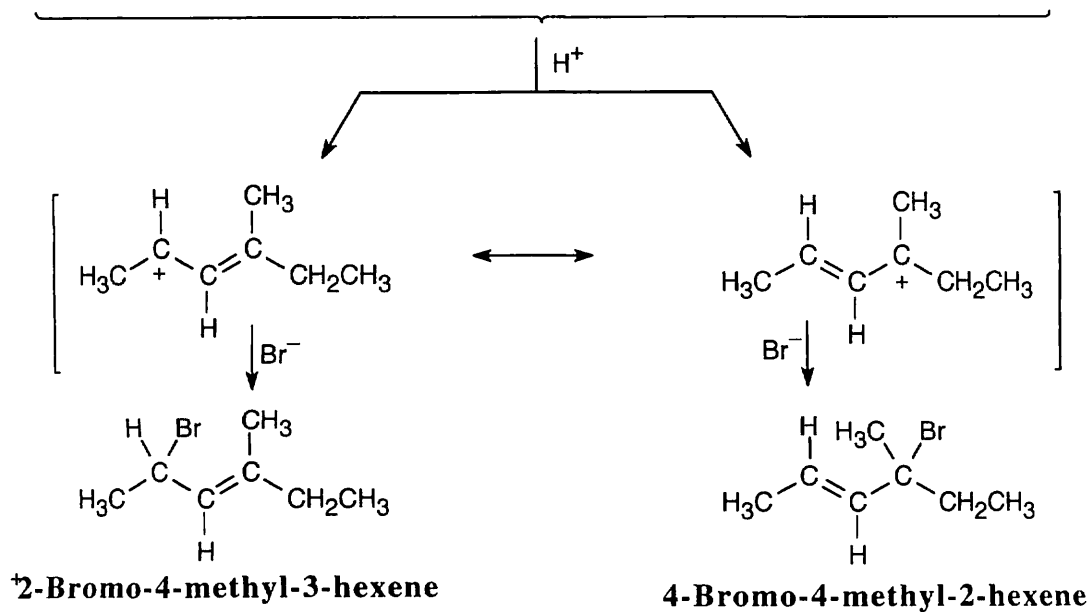
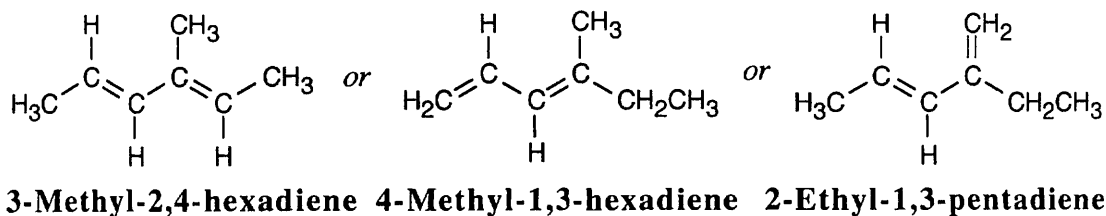
14.17



14.18 In order to undergo Diels–Alder reaction, this *s-trans* diene would have to rotate to an *s-cis* arrangement. In an *s-cis* conformation, however, the two circled methyl groups experience steric strain by being too close to each other, preventing the molecule from adopting this conformation. Thus, Diels–Alder reaction doesn't occur.



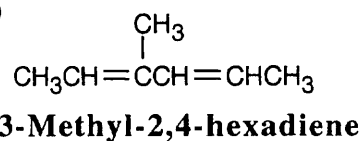
14.19



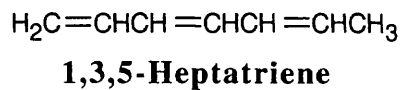
Additional Problems

14.20 All of these compounds can exhibit *E/Z* isomerism.

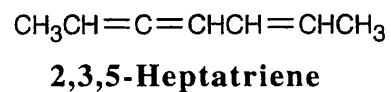
(a)



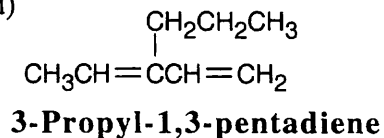
(b)



(c)

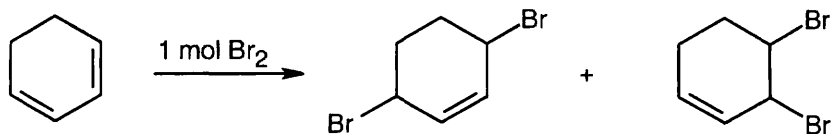


(d)

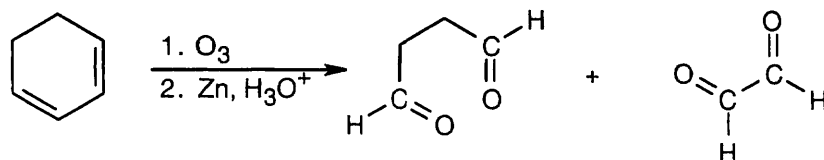


14.21

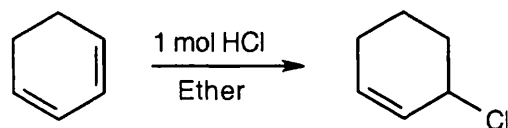
(a)



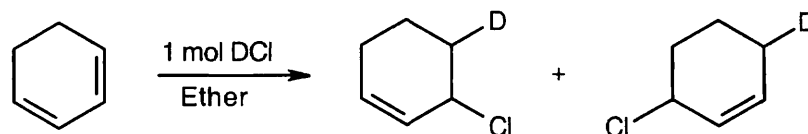
(b)



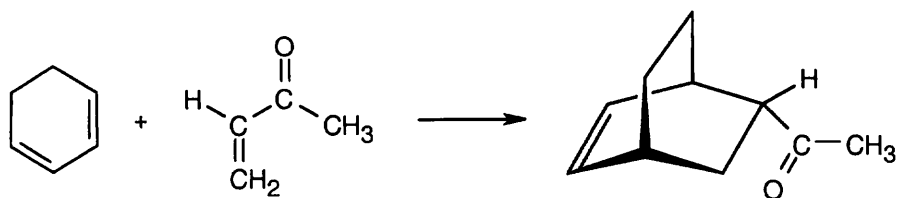
(c)



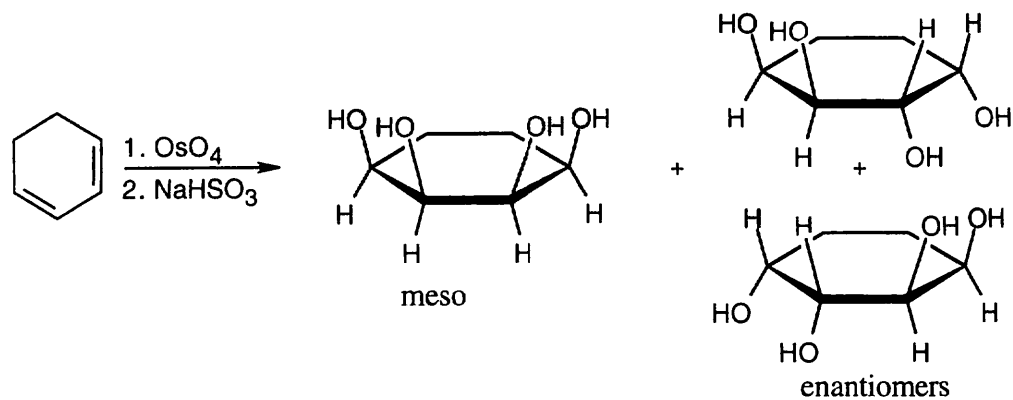
(d)



(e)

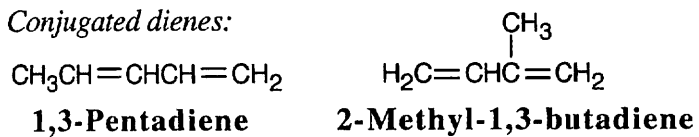


(f)

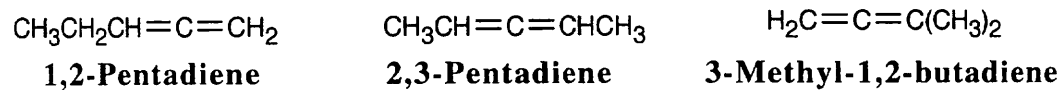


14.22 Excluding double-bond isomers:

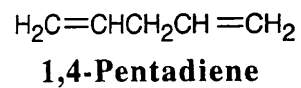
Conjugated dienes:



Cumulated dienes:



Nonconjugated diene:

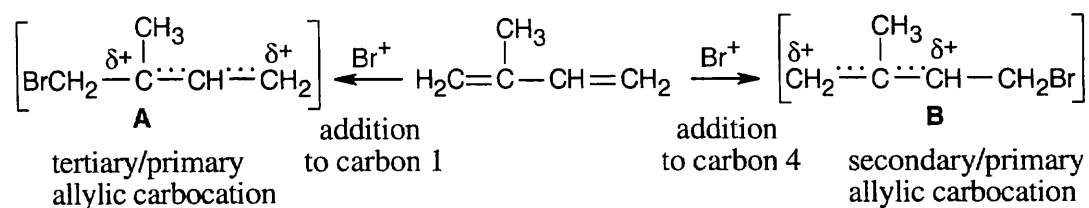


14.23

	$\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$ 3-Hexyne	$\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_3$ 2,4-Hexadiene	$\text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{CHCH}_3$ 2,3-Hexadiene
^1H NMR:	2 peaks (triplet, quartet) below 2.0 δ	3 peaks, two in region 4.5–6.5 δ	5 peaks, two in region 4.5–6.5 δ
^{13}C NMR:	3 peaks, 8–55 δ (2) 65–85 δ (1)	3 peaks, 8–30 δ (1) 100–150 δ (2)	6 peaks, 8–55 δ (3) 100–150 δ (2) ~200 δ (1)(<i>sp</i> carbon)
UV absorption?	no	yes	no

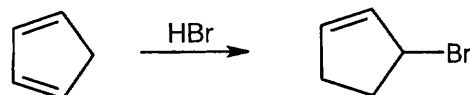
2,4-Hexadiene can easily be distinguished from the other two isomers because it is the only isomer that absorbs in the UV region. The other two isomers show significant differences in their ^1H and ^{13}C NMR spectra and can be identified by either technique.

14.24

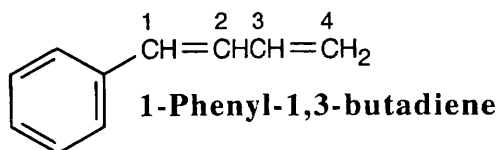


Tertiary/primary allylic carbocation **A** is more stable than secondary/primary allylic carbocation **B**. Since the products formed from the more stable intermediate predominate, 3,4-dibromo-3-methyl-1-butene is the major product of 1,2 addition of bromine to isoprene. In both cases, the product with the more substituted double bond (1,4 addition product) predominates.

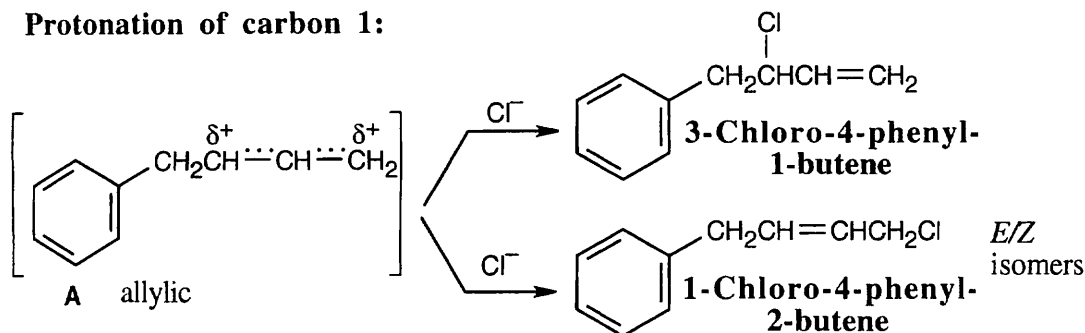
14.25 Any unsubstituted cyclic 1,3-diene cyclic diene gives the same product from 1,2- and 1,4 addition. For example:



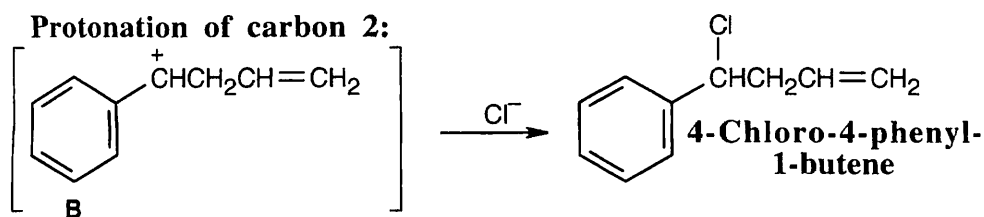
14.26



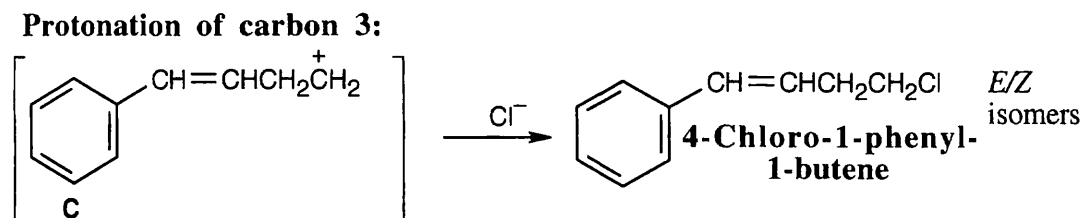
Protonation of carbon 1:



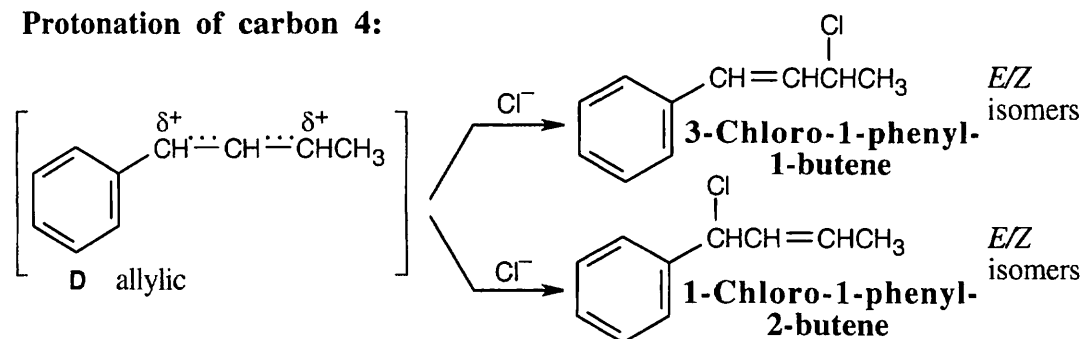
Protonation of carbon 2:



Protonation of carbon 3:



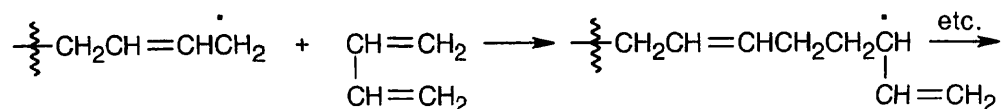
Protonation of carbon 4:



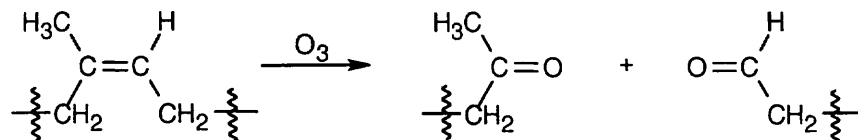
Carbocation **D** is most stable because it can use the π systems of both the benzene ring and the side chain to further delocalize positive charge. 3-Chloro-1-phenyl-1-butene is the major product because it results from cation **D** and because its double bond can be conjugated with the benzene ring to provide extra stability.

14.27 This conformation of 2,3-di-*tert*-butyl-1,3-butadiene, in which the bulky *tert*-butyl groups have a *cis* relationship, suffers from steric strain due to the bulky substituents. Instead, the molecule adopts the *s-trans* conformation, which relieves the strain but does not allow Diels–Alder reaction to take place.

14.28 A vinyl branch in a diene polymer is the result of an occasional 1,2 double bond addition to the polymer chain. Branching can also occur in cationic polymerization for the same reason.



14.29

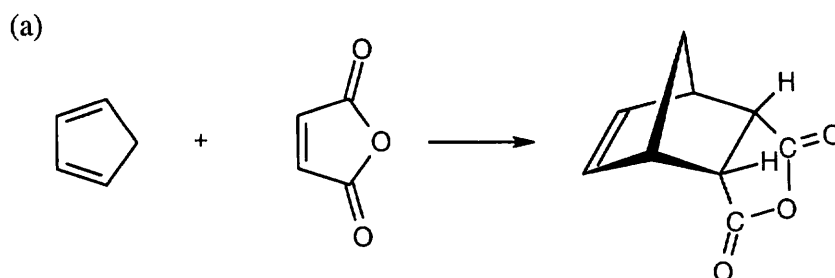


Ozone causes oxidative cleavage of the double bonds in rubber and breaks the polymer chain.

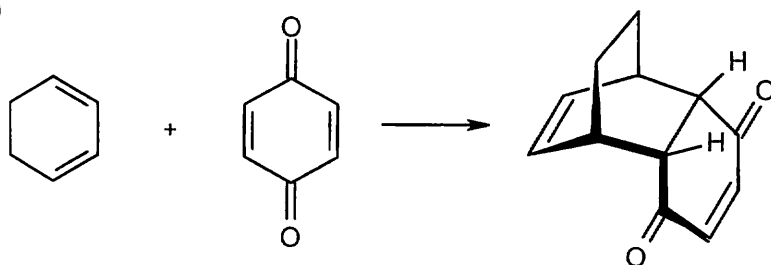
14.30 To absorb in the 200–400 nm range, an alkene must be conjugated. Since the double bonds of allene aren't conjugated, allene doesn't absorb light in the UV region.

14.31 Only compounds having alternating multiple bonds show $\pi \rightarrow \pi^*$ ultraviolet absorptions in the 200–400 nm range. Of the compounds shown, only pyridine (b) absorbs in this range.

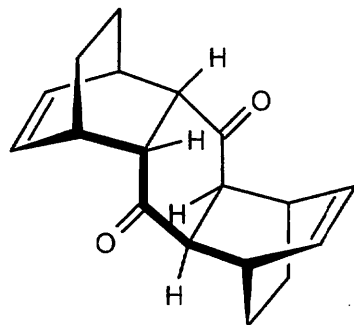
14.32



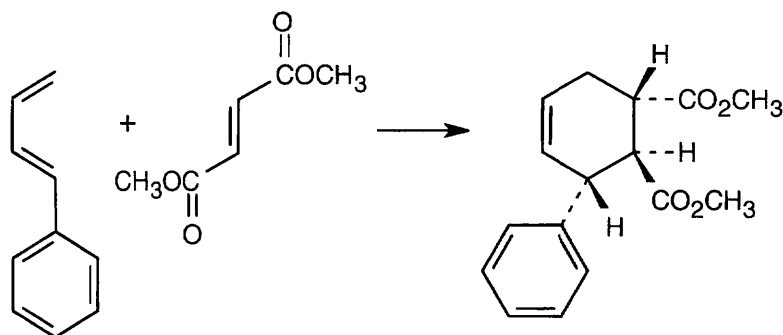
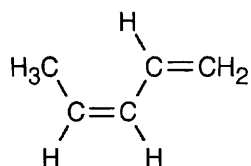
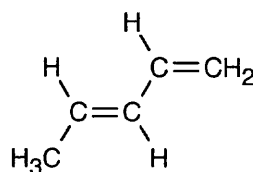
(b)



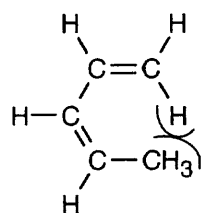
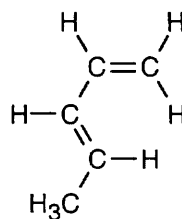
If two equivalents of cyclohexadiene are present for each equivalent of dienophile, you can also obtain a second product:



14.33 The diene rotates to the *s*-cis conformation. The *trans* relationship of the two ester groups in the dienophile is preserved in the product.

**14.34*****cis*-1,3-Pentadiene*****trans*-1,3-Pentadiene**

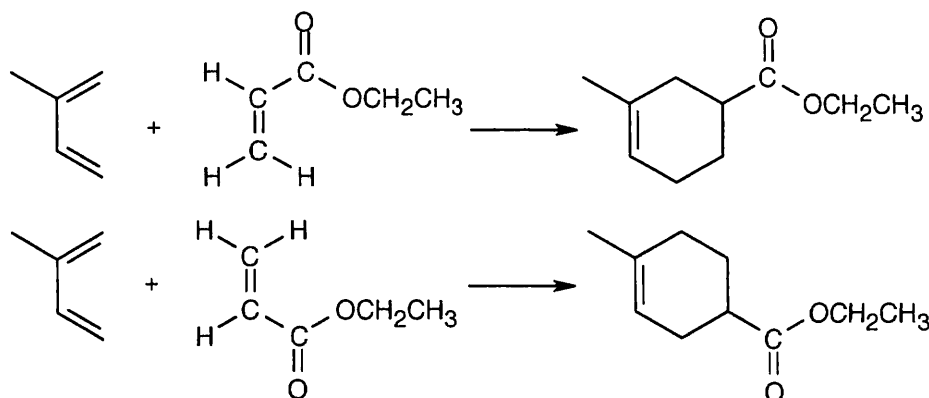
Both pentadienes are more stable in *s*-trans conformations. To undergo Diels-Alder reactions, however, they must rotate about the single bond between the double bonds to assume *s*-cis conformations.

*cis*-1,3-Pentadiene*trans*-1,3-Pentadiene

When *cis*-1,3-pentadiene rotates to the *s*-cis conformation, a steric interaction occurs between the methyl-group protons and a hydrogen on C1. Since it's more difficult for *cis*-1,3-pentadiene to assume the *s*-cis conformation, it is less reactive in the Diels–Alder reaction.

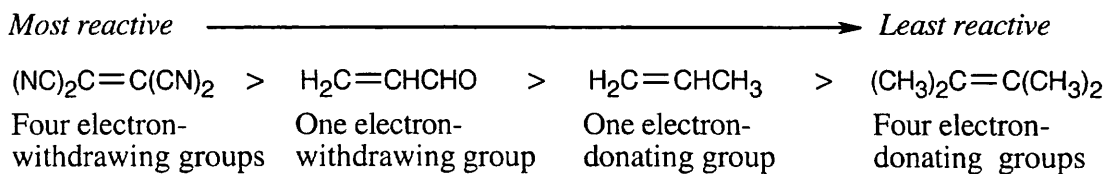
14.35 $\text{HC}\equiv\text{CC}\equiv\text{CH}$ can't be used as a Diels–Alder diene because it is linear. The end carbons are too far apart to be able to react with a dienophile in a cyclic transition state. Furthermore, the product of Diels–Alder addition would be impossibly strained, with two *sp*-hybridized carbons in a six-membered ring.

14.36



Two different orientations of the dienophile ester group are possible, and two different products can form.

14.37 The most reactive dienophiles contain electron-withdrawing groups.

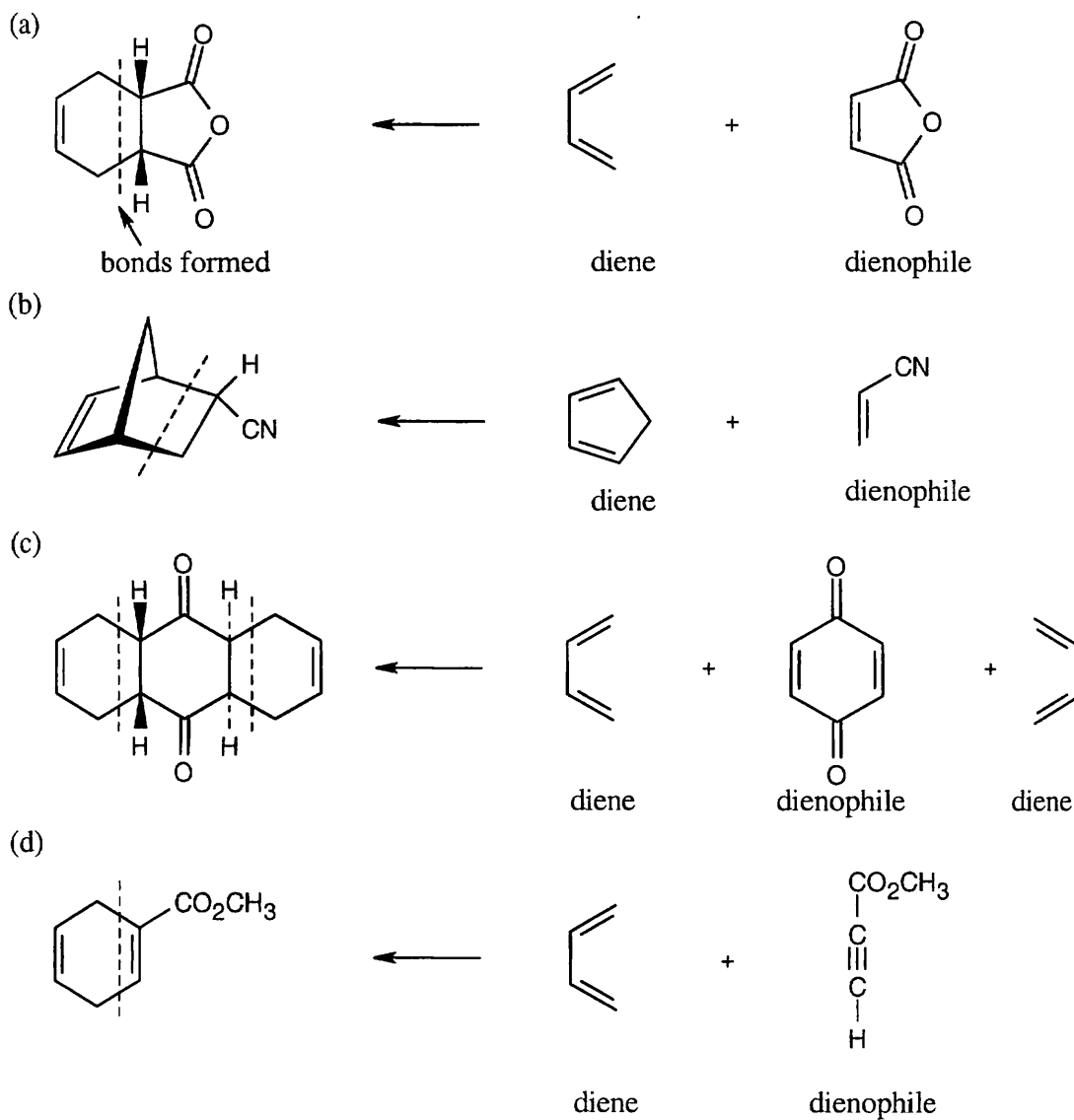


The methyl groups of 2,3-dimethyl-2-butene also decrease reactivity for steric reasons.

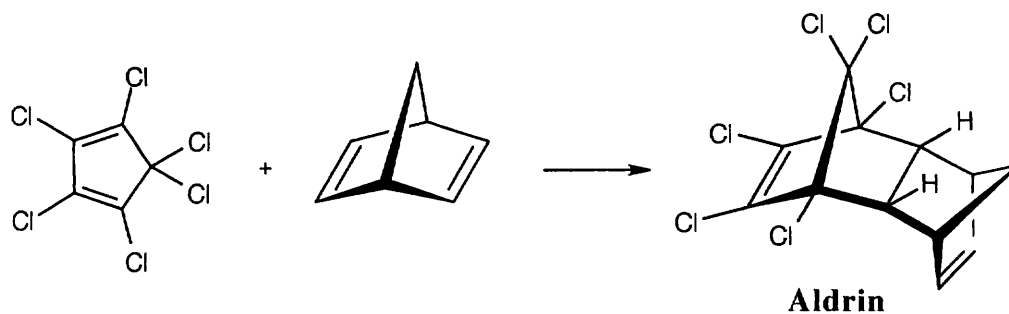
14.38 The difference in reactivity of the three cyclic dienes is due to steric factors. As the non-diene part of the molecule becomes larger, the carbon atoms at the end of the diene portion of the ring are forced farther apart. Overlap with the π system of the dienophile in the cyclic transition state is poorer, and reaction is slower.

14.39 Although an electron-withdrawing group increases the reactivity of a dienophile, it decreases the reactivity of a diene.

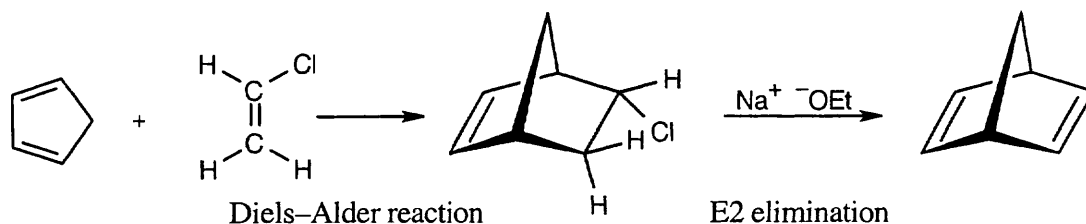
14.40 First, find the cyclohexene ring formed by the Diels–Alder reaction. After you locate the new bonds, you should then be able to identify the diene and the dienophile.



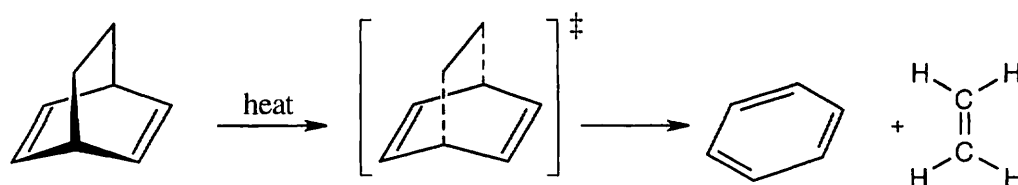
14.41



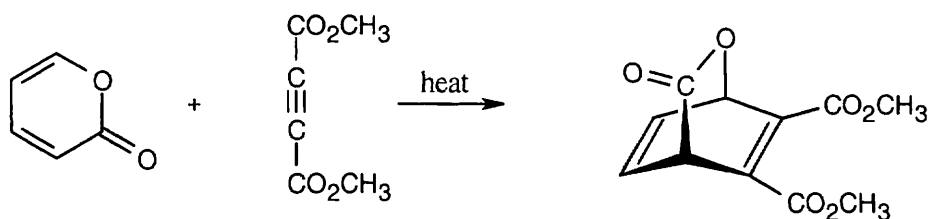
14.42



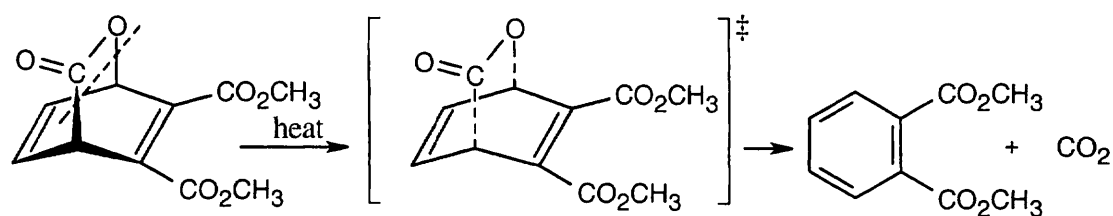
14.43 Diels-Alder reactions are reversible when the products are much more stable (of lower energy) than the reactants. In this case, the reactant is a nonconjugated diene, and the products are benzene (a stable, conjugated molecule) and ethylene.



14.44 A Diels-Alder reaction between α -pyrone (diene) and the alkyne dienophile yields the following product.

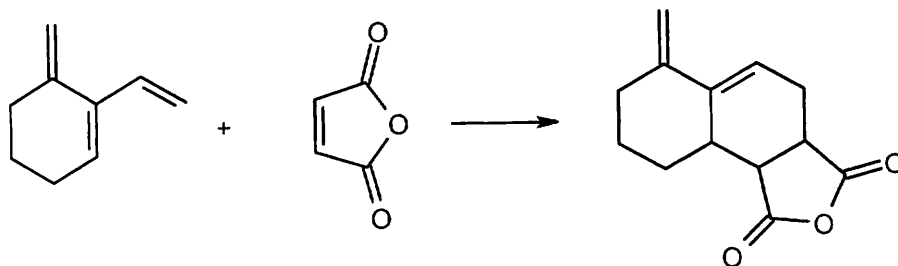


The double bonds in this product are not conjugated, and a more stable product can be formed by loss of CO_2 .

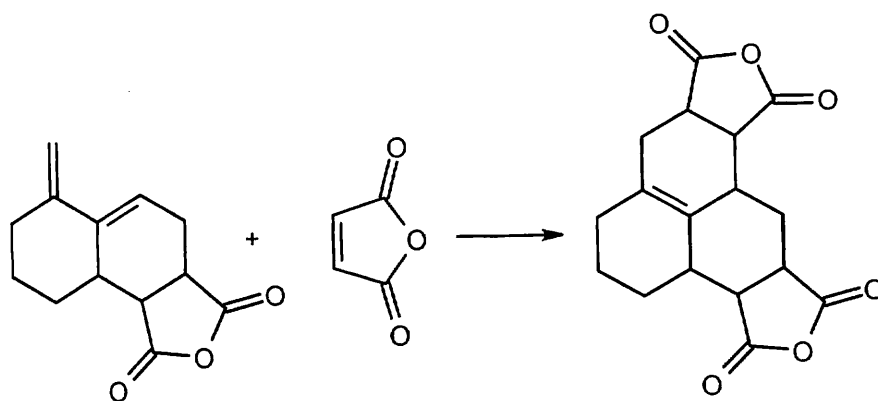


This process can occur in a manner similar to the reverse Diels-Alder reaction of the previous problem.

14.45 The first equivalent of maleic anhydride adds to the *s*-cis bond of the triene.



The new double bond has an *s*-cis relationship to the remaining double bond of the triene starting material. A second equivalent of maleic anhydride adds to the diene to form the product shown.

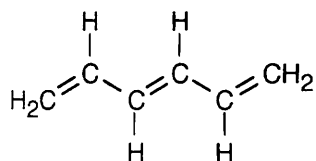


14.46 The value of λ_{\max} in the ultraviolet spectrum of dienes becomes larger with increasing alkyl substitution. Since energy is inversely related to λ_{\max} , the energy needed to produce ultraviolet absorption decreases with increasing substitution.

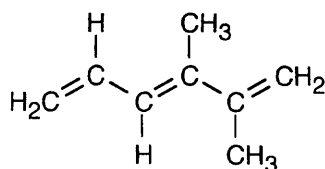
<i>Diene</i>	# of $-CH_3$ groups	λ_{\max} (nm)	$\lambda_{\max} - \lambda_{\max}$ (butadiene)
	0	217	0
	1	220	3
	1	223	6
	2	226	9
	2	227	10
	3	232	15
	4	240	23

Each alkyl substituent causes an increase in λ_{\max} of approximately 5 nm.

14.47

**1,3,5-Hexatriene**

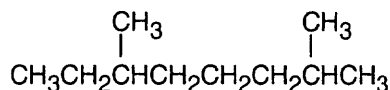
$$\lambda_{\text{max}} = 258 \text{ nm}$$

**2,3-Dimethyl-1,3,5-hexatriene**

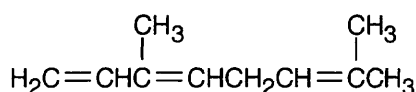
$$\lambda_{\text{max}} \approx 268 \text{ nm}$$

In Problem 14.46, we concluded that one alkyl group increases λ_{max} of a conjugated diene by approximately 5 nm. Since 2,3-dimethyl-1,3,5-hexatriene has two methyl substituents, its UV λ_{max} should be about 10 nm longer than the λ_{max} of 1,3,5-hexatriene.

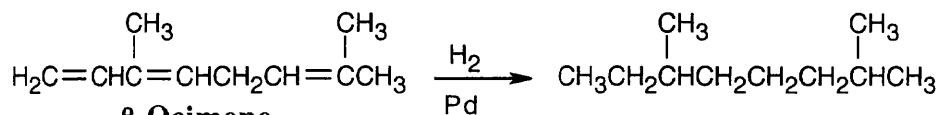
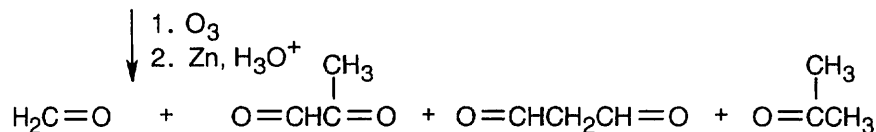
- 14.48** (a) β -Ocimene, $\text{C}_{10}\text{H}_{16}$, has three degrees of unsaturation. Catalytic hydrogenation yields a hydrocarbon of formula $\text{C}_{10}\text{H}_{22}$. β -Ocimene thus contains three double bonds and no rings.
 (b) The ultraviolet absorption at 232 nm indicates that β -ocimene is conjugated.
 (c) The carbon skeleton, as determined from hydrogenation, is:

**2,6-Dimethyloctane**

Ozonolysis data are used to determine the location of the double bonds. The acetone fragment, which comes from carbon atoms 1 and 2 of 2,6-dimethyloctane, fixes the position of one double bond. Formaldehyde results from ozonolysis of a double bond at the other end of β -ocimene. Placement of the other fragments to conform to the carbon skeleton yields the following structural formula for β -ocimene.

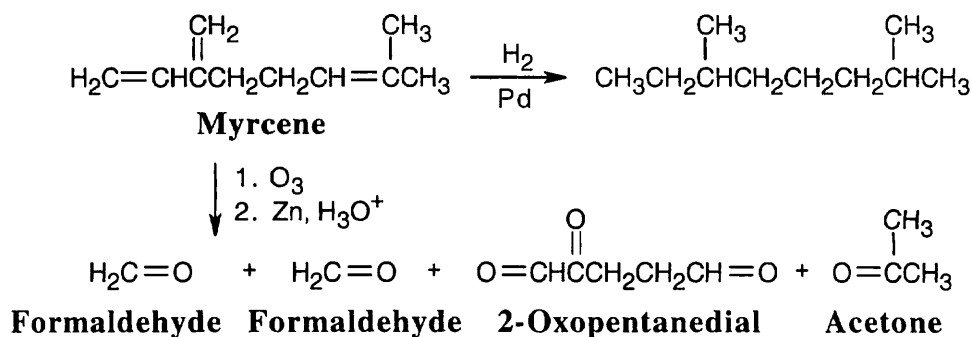
 **β -Ocimene**

(d)

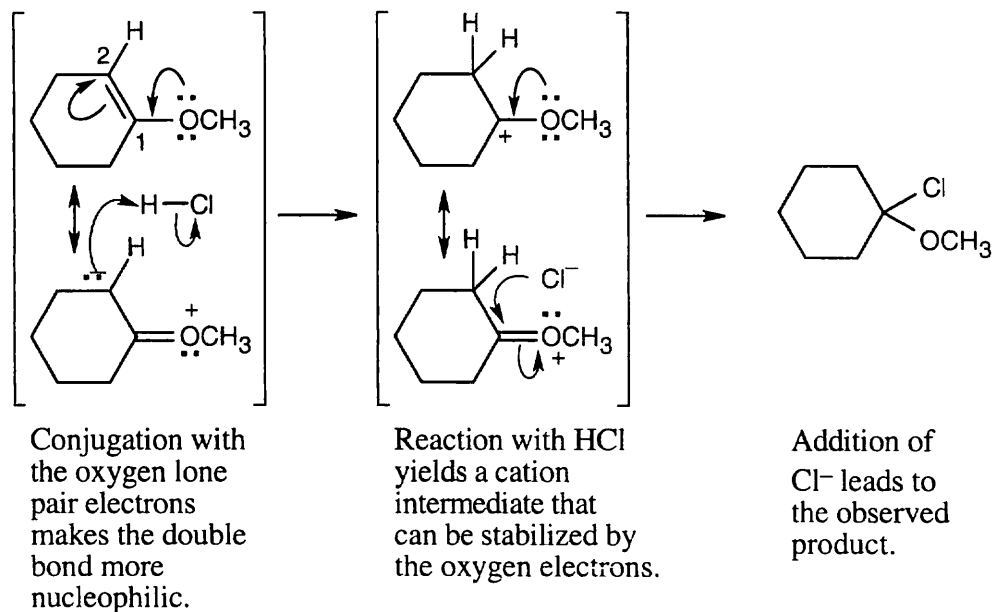
 **β -Ocimene****Formaldehyde Pyruvaldehyde Malonaldehyde Acetone**

14.49 Much of what was proven for β -ocimene is also true for myrcene, since both hydrocarbons have the same carbon skeleton and contain conjugated double bonds. The difference between the two isomers is in the placement of the double bonds.

The ozonolysis fragments from myrcene are 2-oxopentanedial (five carbon atoms), acetone (three carbon atoms), and two equivalents of formaldehyde (one carbon atom each). Putting these fragments together in a manner consistent with the data gives the following structural formula for myrcene:

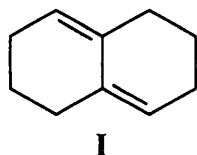


14.50

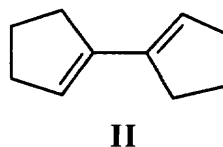


There are two reasons why the other regioisomer is not formed: (1) Carbon 1 is less nucleophilic than carbon 2; (2) The cation intermediate that would result from protonation at carbon 1 can't be stabilized by the oxygen electrons.

14.51 (a) Hydrocarbon **A** must have two double bonds and two rings, since the sole ozonolysis product contains all the carbons and a diketone-dialdehyde is formed.

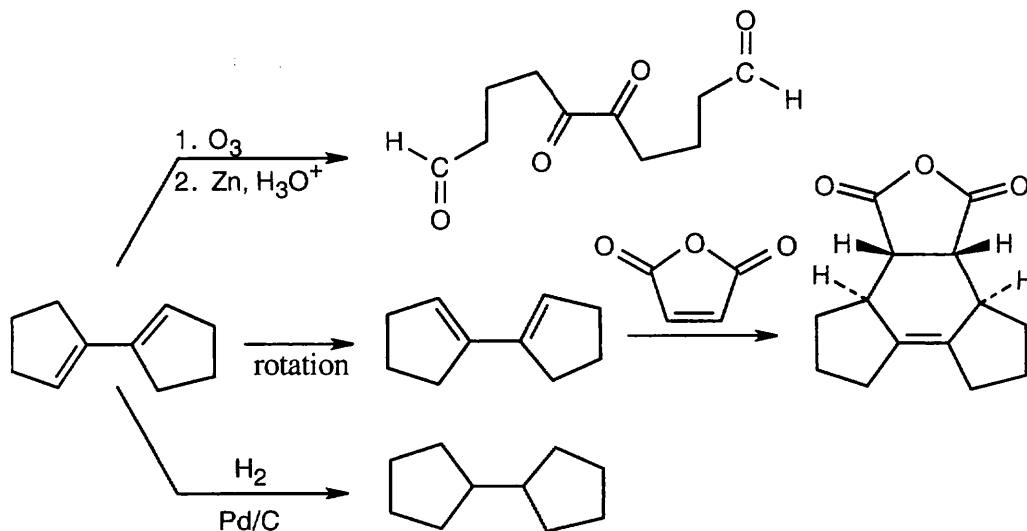


or

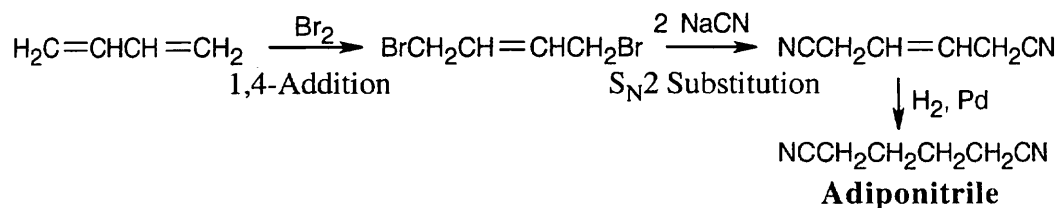


(b) Rotation about the central single bond of **II** allows the double bond to assume the *s*-cis conformation necessary for a Diels–Alder reaction. Rotation is not possible for **I**.

(c)



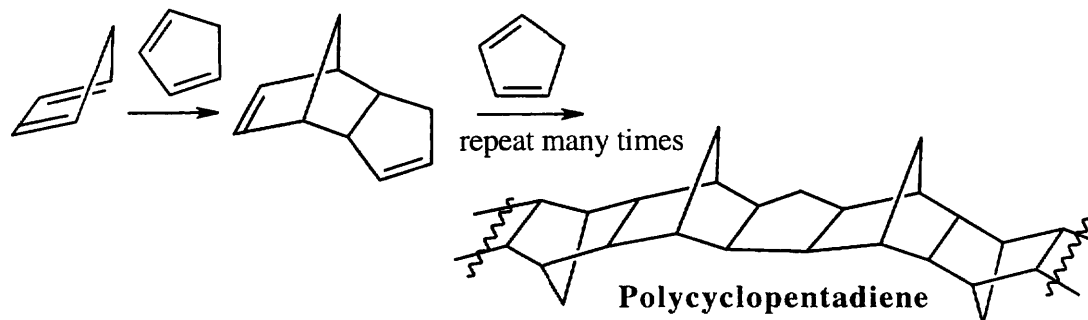
14.52



14.53

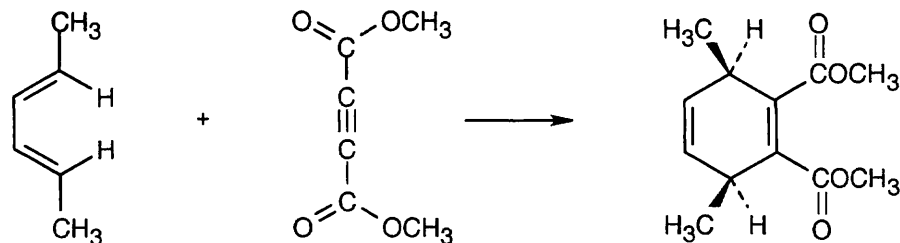
$$c = \frac{A}{\epsilon \times l} = \frac{0.065}{11,900 \text{ L/mol}\cdot\text{cm} \times 1.00 \text{ cm}} = \frac{6.5 \times 10^{-2}}{1.19 \times 10^4 \text{ L/mol}} = 5.5 \times 10^{-6} \text{ M}$$

14.54

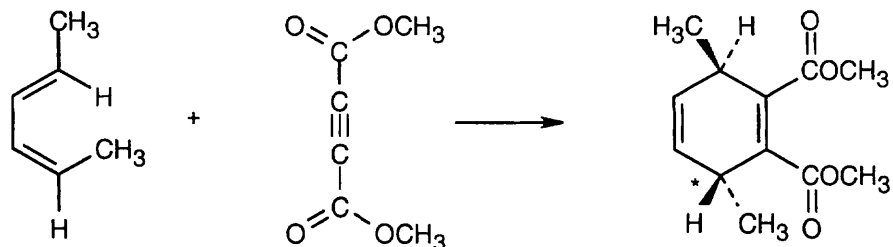


Polycyclopentadiene is the product of successive Diels–Alder additions of cyclopentadiene to a growing polymer chain. Strong heat causes depolymerization of the chain and reformation of cyclopentadiene monomer units.

14.55

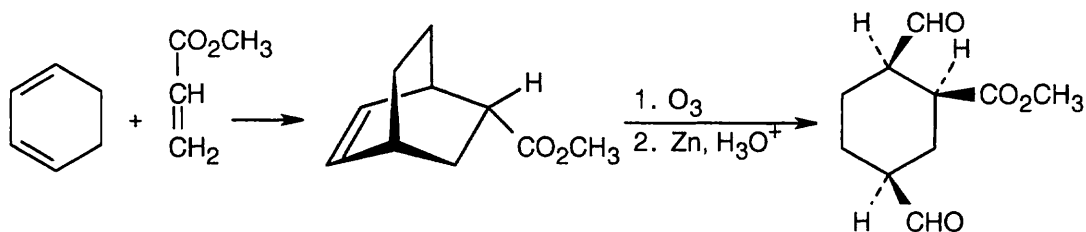


14.56



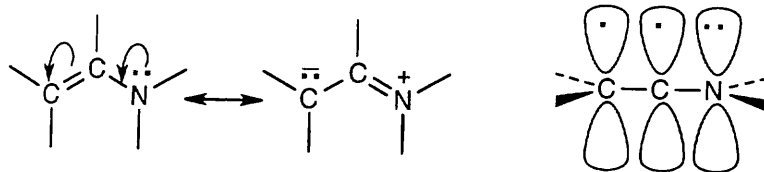
The stereochemistry of the product resulting from Diels-Alder reaction of the (2E,4Z) diene differs at the starred carbon from that of the (2E,4E) diene. Not only is the stereochemistry of the dienophile maintained during the Diels-Alder reaction, the stereochemistry of the diene is also maintained.

14.57 Although it is usually best to work backwards in a synthesis problem, it sometimes helps to work *both* forwards and backwards. In this problem, we know that the starting materials are a diene and a dienophile. This suggests that the synthesis involves a Diels-Alder reaction. The product is a dialdehyde in which the two aldehyde groups have a cis relationship, indicating that they are the products of ozonolysis of a bridgehead double bond. These two pieces of information allow us to propose the following synthesis:



The $-\text{CHO}$ groups are cis to the ester in the product.

- 14.58** The lone pair electrons from nitrogen can overlap with the double bond π electrons in a manner similar to the overlap of the π electrons of two conjugated double bonds. This electron contribution from nitrogen makes an enamine double bond electron-rich.



The orbital picture of an enamine shows a 4 p -electron system that resembles the system of a conjugated diene.

- 14.59** Double bonds can be conjugated not only with other multiple bonds but also with the lone-pair electrons of atoms such as oxygen and nitrogen. *p*-Toluidine has the same number of double bonds as benzene, yet its λ_{max} is 31 nm greater. The electron pair of the nitrogen atom can conjugate with the π electrons of the three double bonds of the ring, extending the π system and increasing λ_{max} .