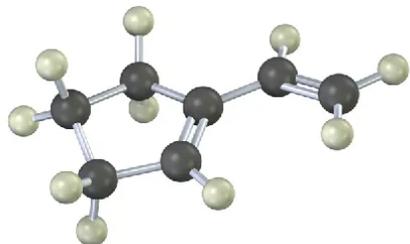


## 1.11: Additional Problems

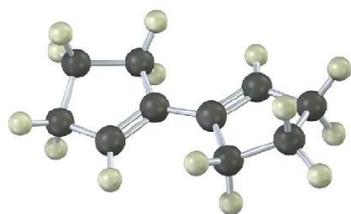
14 • Additional Problems

### Visualizing Chemistry

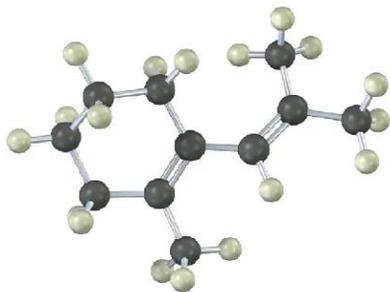
**PROBLEM 1-16** Show the structures of all possible adducts of the following diene with 1 equivalent of HCl:



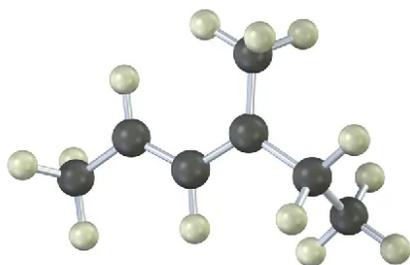
**PROBLEM 1-17** Show the product of the Diels–Alder reaction of the following diene with 3-buten-2-one,  $\text{H}_2\text{C}=\text{CHCOCH}_3$ . Make sure you show the full stereochemistry of the reaction product.



**PROBLEM 1-18** The following diene does not undergo Diels–Alder reactions. Explain.

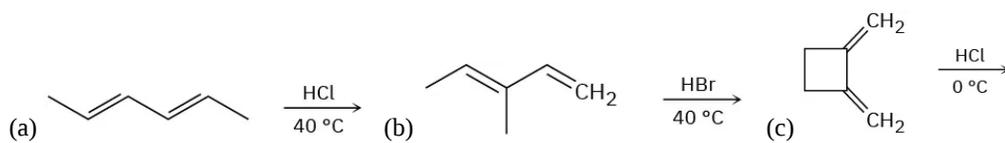


**PROBLEM 1-19** The following model is that of an allylic carbocation intermediate formed by protonation of a conjugated diene with HBr. Show the structure of the diene and the structures of the final reaction products.

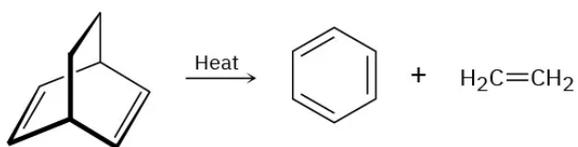


### Mechanism Problems

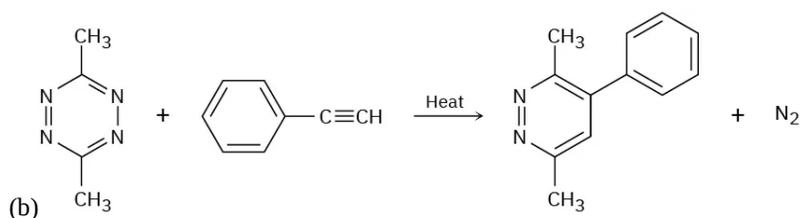
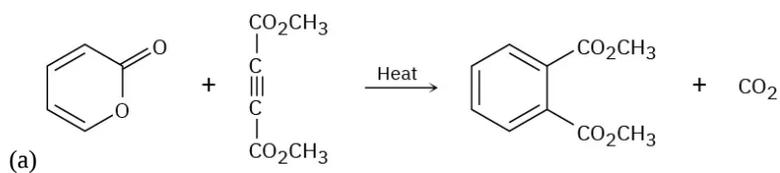
**PROBLEM 1-20** Predict the major product(s) from the addition of 1 equivalent of HX and show the mechanism for each of the following reactions.



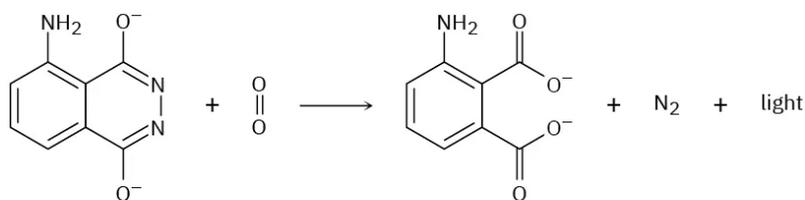
**PROBLEM 1-21** We've seen that the Diels–Alder cycloaddition reaction is a one-step, pericyclic process that occurs through a cyclic transition state. Propose a mechanism for the following reaction:



**PROBLEM 1-22** In light of your answer to Problem 21 propose mechanisms for the following reactions.

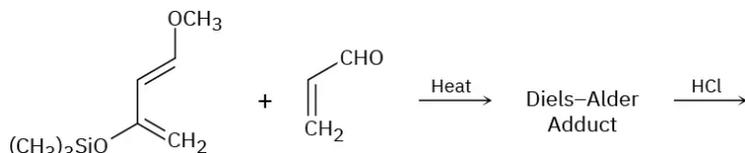


**PROBLEM 1-23** Luminol, which is used by forensic scientists to find blood, fluoresces as a result of Diels–Alder-like process. The dianion of luminol reacts with O<sub>2</sub> to form an unstable peroxide intermediate that then loses nitrogen to form a dicarboxylate and emit light. The process is similar to that in Problems 21 and 22. Propose a mechanism for this process.

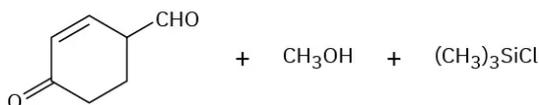


### Luminol dianion

**PROBLEM 1-24** A useful diene in the synthesis of many naturally occurring substances is known as Danishefsky's diene. It's useful because after the Diels–Alder reaction it can be converted into a product that can't be accessed by a typical Diels–Alder reaction. Show the Diels–Alder adduct and propose a mechanism that accounts for the final products.

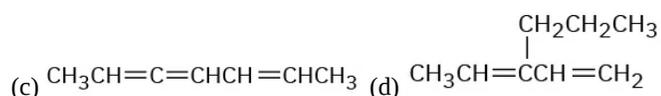
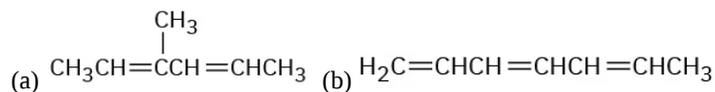


### Danishefsky's Diene



### Conjugated Dienes

**PROBLEM 1-25** Name the following compounds:



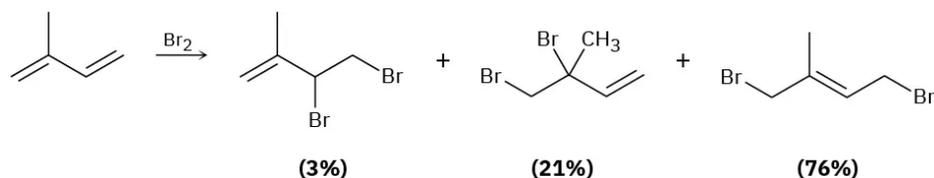
**PROBLEM 1-26** Draw and name the six possible diene isomers of formula  $\text{C}_5\text{H}_8$ . Which of the six are conjugated dienes?

**PROBLEM 1-27** What product(s) would you expect to obtain from the reaction of 1,3-cyclohexadiene with each of the following?

(a) 1 mol  $\text{Br}_2$  in  $\text{CH}_2\text{Cl}_2$  (b)  $\text{O}_3$  followed by Zn (c) 1 mol HCl in ether (d) 1 mol DCl in ether

(e) 3-Buten-2-one ( $\text{H}_2\text{C}=\text{CHCOCH}_3$ ) (f) Excess  $\text{OsO}_4$ , followed by  $\text{NaHSO}_3$

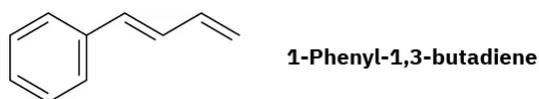
**PROBLEM 1-28** Electrophilic addition of  $\text{Br}_2$  to isoprene (2-methyl-1,3-butadiene) yields the following product mixture:



Of the 1,2-addition products, explain why 3,4-dibromo-3-methyl-1-butene (21%) predominates over 3,4-dibromo-2-methyl-1-butene (3%).

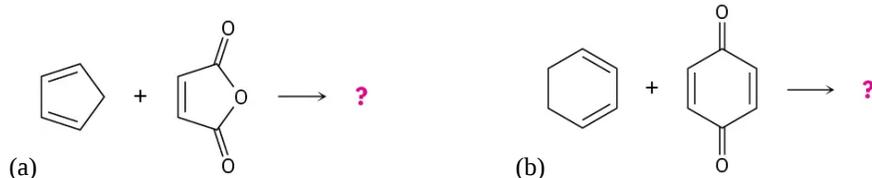
**PROBLEM 1-29** Propose a structure for a conjugated diene that gives the same product from both 1,2 and 1,4-addition of HBr.

**PROBLEM 1-30** Draw the possible products resulting from addition of 1 equivalent of HCl to 1-phenyl-1,3-butadiene. Which would you expect to predominate, and why?

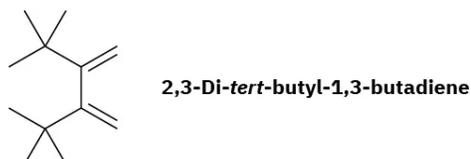


### Diels–Alder Reactions

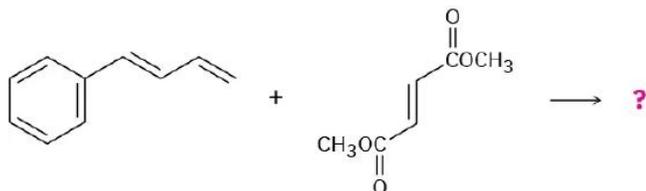
**PROBLEM 1-31** Predict the products of the following Diels–Alder reactions:



**PROBLEM 1-32** 2,3-Di-*tert*-butyl-1,3-butadiene does not undergo Diels–Alder reactions. Explain.



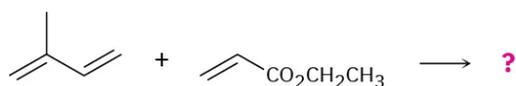
**PROBLEM 1-33** Show the structure, including stereochemistry, of the product from the following Diels–Alder reaction:



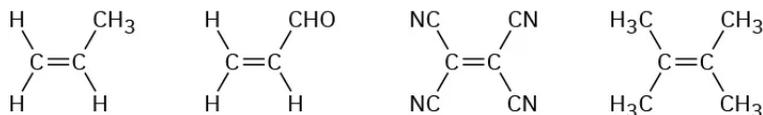
**PROBLEM 1-34** How can you account for the fact that *cis*-1,3-pentadiene is much less reactive than *trans*-1,3-pentadiene in the Diels–Alder reaction?

**PROBLEM 1-35** Would you expect a conjugated diyne such as 1,3-butadiyne to undergo Diels–Alder reaction with a dienophile? Explain.

**PROBLEM 1-36** Reaction of isoprene (2-methyl-1,3-butadiene) with ethyl propenoate gives a mixture of two Diels–Alder adducts. Show the structure of both, and explain why a mixture is formed.

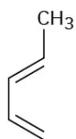


**PROBLEM 1-37** Rank the following dienophiles in order of their expected reactivity in the Diels–Alder reaction.

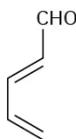


**PROBLEM 1-38** 1,3-Cyclopentadiene is very reactive in Diels–Alder cycloaddition reactions, but 1,3-cyclohexadiene is less reactive and 1,3-cycloheptadiene is nearly inert. Explain. (Molecular models are helpful.)

**PROBLEM 1-39** 1,3-Pentadiene is much more reactive in Diels–Alder reactions than 2,4-pentadienal. Why might this be?

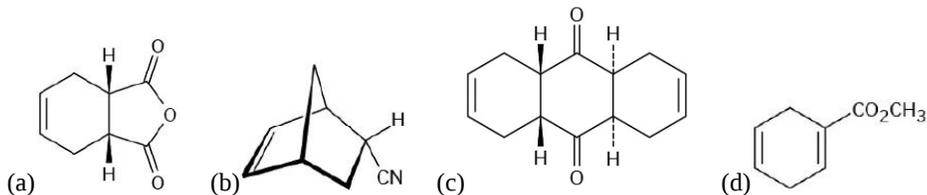


1,3-Pentadiene

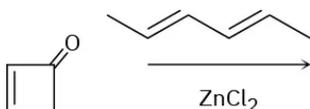


2,4-Pentadienal

**PROBLEM 1-40** How could you use Diels–Alder reactions to prepare the following products? Show the starting diene and dienophile in each case.



**PROBLEM 1-41** Show the product of the following reaction.



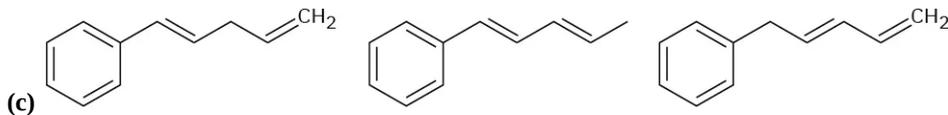
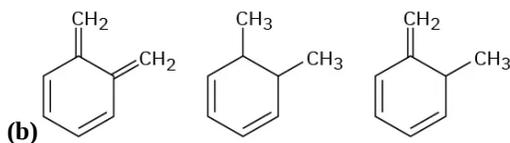
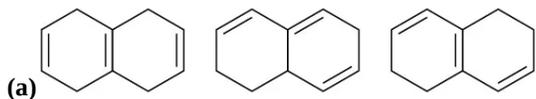
### Diene Polymers

**PROBLEM 1-42** Tires whose sidewalls are made of natural rubber tend to crack and weather rapidly in areas around cities where high levels of ozone and other industrial pollutants are found. Explain.

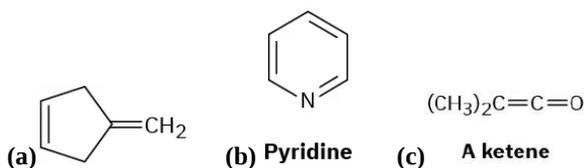
**PROBLEM 1-43** 1,3-Cyclopentadiene polymerizes slowly at room temperature to yield a polymer that has no double bonds except on the ends. On heating, the polymer breaks down to regenerate 1,3-cyclopentadiene. Propose a structure for the product.

### UV Spectroscopy

**PROBLEM 1-44** Arrange the molecules in each of the following sets according to where you would expect to find their wavelength of maximum absorption in UV spectroscopy, from shortest to longest wavelength.



**Problem 1-45** Which of the following compounds would you expect to have a  $\pi \rightarrow \pi^*$  UV absorption in the 200 to 400 nm range?



**Problem 1-46** Would you expect allene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ , to show a UV absorption in the 200 to 400 nm range? Explain.

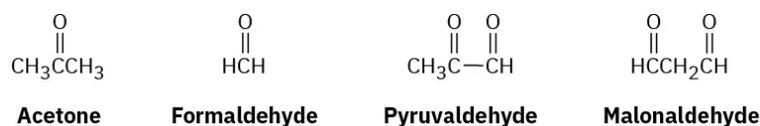
**Problem 1-47** The following ultraviolet absorption maxima have been measured:

Molecule	ultraviolet absorption maxima
1,3-Butadiene	217 nm
2-Methyl-1,3-butadiene	220 nm
1,3-Pentadiene	223 nm
2,3-Dimethyl-1,3-butadiene	226 nm
2,4-Hexadiene	227 nm
2,4-Dimethyl-1,3-pentadiene	232 nm
2,5-Dimethyl-2,4-hexadiene	240 nm

What conclusion can you draw about the effect of alkyl substitution on UV absorption maxima? Approximately what effect does each added alkyl group have?

**Problem 1-48** 1,3,5-Hexatriene has  $\lambda_{\text{max}} = 258 \text{ nm}$ . In light of your answer to Problem 1-47, approximately where would you expect 2,3-dimethyl-1,3,5-hexatriene to absorb?

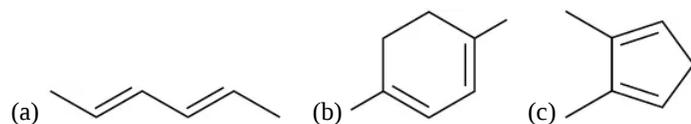
**Problem 1-49**  $\beta$ -Ocimene is a pleasant-smelling hydrocarbon found in the leaves of certain herbs. It has the molecular formula  $\text{C}_{10}\text{H}_{16}$  and a UV absorption maximum at 232 nm. On hydrogenation with a palladium catalyst, 2,6-dimethyloctane is obtained. Ozonolysis of  $\beta$ -ocimene, followed by treatment with zinc and acetic acid, produces the following four fragments:



- (a) How many double bonds does  $\beta$ -ocimene have?
- (b) Is  $\beta$ -ocimene conjugated or nonconjugated?
- (c) Propose a structure for  $\beta$ -ocimene.
- (d) Write the reactions, showing starting material and products.

### General Problems

**Problem 1-50** Draw the resonance forms that result when the following dienes are protonated. If the resonance forms differ in energy, identify the most stable one.

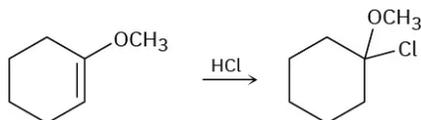


**Problem 1-51** Answer the following questions for 1,3,5-cycloheptatriene.

- (a) How many  $p$  atomic orbitals are in the conjugated system?
- (b) How many molecular orbitals describe the conjugated system?
- (c) How many molecular orbitals are bonding molecular orbitals?
- (d) How many molecular orbitals are anti-bonding molecular orbitals?
- (e) Which molecular orbitals are filled with electrons?
- (f) If this molecule were to absorb a photon of UV light an electron would move between which two molecular orbitals (be specific)?

**Problem 1-52** Treatment of 3,4-dibromohexane with strong base leads to loss of 2 equivalents of HBr and formation of a product with formula  $C_6H_{10}$ . Three products are possible. Name each of the three, and tell how you would use  $^1H$  and  $^{13}C$  NMR spectroscopy to help identify them. How would you use UV spectroscopy?

**Problem 1-53** Addition of HCl to 1-methoxycyclohexene yields 1-chloro-1-methoxycyclohexane as a sole product. Use resonance structures to explain why none of the other regioisomer is formed.

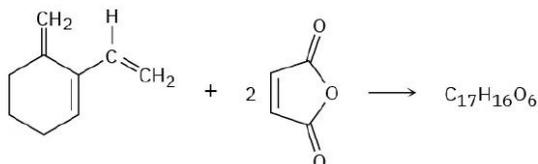


**Problem 1-54** Aldrin, a chlorinated insecticide now banned from use in most countries since 1990, can be made by Diels–Alder reaction of hexachloro-1,3-cyclopentadiene with norbornadiene. What is the structure of aldrin?



**Problem 1-55** Norbornadiene (Problem 54) can be prepared by reaction of chloroethylene with 1,3-cyclopentadiene, followed by treatment of the product with sodium ethoxide. Write the overall scheme, and identify the two kinds of reactions.

**Problem 1-56** The triene shown here reacts with 2 equivalents of maleic anhydride to yield a product with the formula  $C_{17}H_{16}O_6$ . Predict a structure for the product.

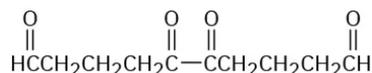


**Problem 1-57** Myrcene,  $C_{10}H_{16}$ , is found in oil of bay leaves and is isomeric with  $\beta$ -ocimene (Problem 49). It has an ultraviolet absorption at 226 nm and can be hydrogenated to yield 2,6-dimethyloctane. On ozonolysis followed by zinc/acetic acid treatment, myrcene yields formaldehyde, acetone, and 2-oxopentanal:



Propose a structure for myrcene, and write the reactions, showing starting material and products.

**Problem 1-58** Hydrocarbon **A**,  $C_{10}H_{14}$ , has a UV absorption at  $\lambda_{max} = 236$  nm and gives hydrocarbon **B**,  $C_{10}H_{18}$ , on hydrogenation. Ozonolysis of **A**, followed by zinc/acetic acid treatment, yields the following diketo dialdehyde:

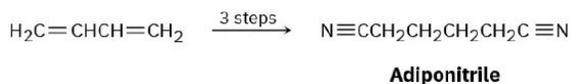


An illustration shows the structure of diketo dialdehyde. It shows two carbonyl groups single bonded to each other. Each carbonyl group is bonded to a chain of three methylene groups and then to an aldehyde group.

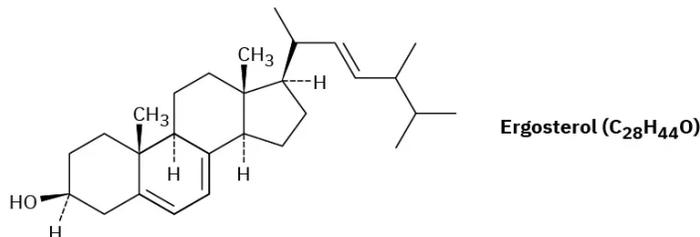
- (a) Propose two possible structures for **A**.
- (b) Hydrocarbon **A** reacts with maleic anhydride to yield a Diels–Alder adduct. Which of your structures for **A** is correct?

- (c) Write the reactions, showing the starting material and products.

**Problem 1-59** Adiponitrile, a starting material used in the manufacture of nylon, can be prepared in three steps from 1,3-butadiene. How would you carry out this synthesis?



**Problem 1-60** Ergosterol, a precursor of vitamin D, has  $\lambda_{\text{max}} = 282 \text{ nm}$  and molar absorptivity  $\epsilon = 11,900$ . What is the concentration of ergosterol in a solution whose absorbance  $A = 0.065$  with a sample pathlength  $l = 1.00 \text{ cm}$ ?

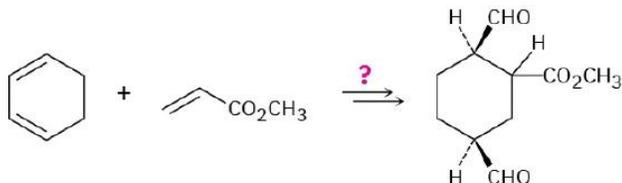


**Problem 1-61** Dimethyl butynedioate undergoes a Diels–Alder reaction with (2*E*,4*E*)-2,4-hexadiene. Show the structure and stereochemistry of the product.

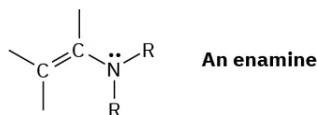


**Problem 1-62** Dimethyl butynedioate also undergoes a Diels–Alder reaction with (2*E*,4*Z*)-2,4-hexadiene, but the stereochemistry of the product is different from that of the (2*E*,4*E*) isomer (Problem 61). Explain.

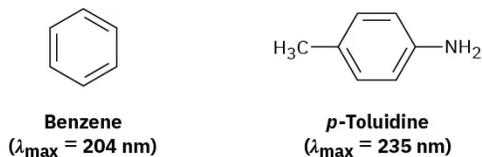
**Problem 1-63** How would you carry out the following synthesis (more than one step is required)? What stereochemical relationship between the  $-\text{CO}_2\text{CH}_3$  group attached to the cyclohexane ring and the  $-\text{CHO}$  groups would your synthesis produce?



**Problem 1-64** The double bond of an *enamine* (alkene + amine) is much more nucleophilic than a typical alkene double bond. Assuming that the nitrogen atom in an enamine is  $sp^2$ -hybridized, draw an orbital picture of an enamine, and explain why the double bond is electron-rich.



**Problem 1-65** Benzene has an ultraviolet absorption at  $\lambda_{\text{max}} = 204 \text{ nm}$ , and *para*-toluidine has  $\lambda_{\text{max}} = 235 \text{ nm}$ . How do you account for this difference?



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