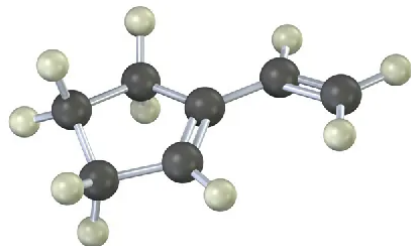


1.11: Additional Problems

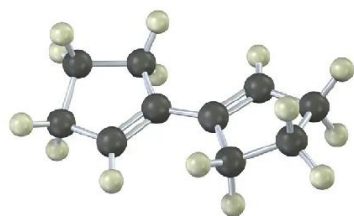
14 • Additional Problems

Visualizing Chemistry

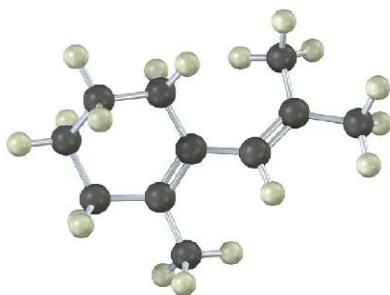
PROBLEM 1-16 Show the structures of all possible adducts of the following diene with 1 equivalent of HCl:



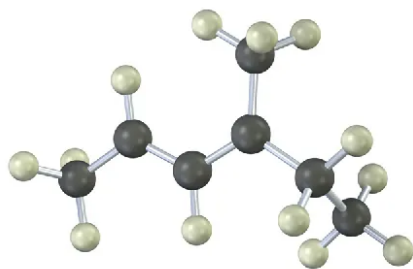
PROBLEM 1-17 Show the product of the Diels–Alder reaction of the following diene with 3-buten-2-one, $\text{H}_2\text{C}=\text{CHCOCH}_3$. Make sure you show the full stereochemistry of the reaction product.



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

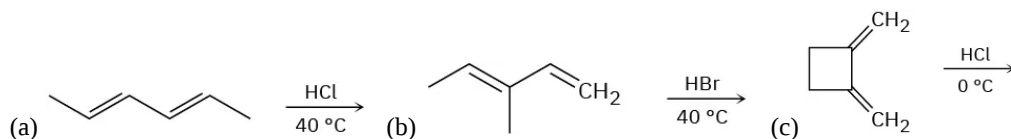


PROBLEM 1-19 The following model is that of an allylic carbocation intermediate formed by protonation of a conjugated diene with HBr. Show the structure of the diene and the structures of the final reaction products.

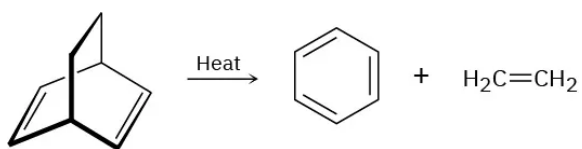


Mechanism Problems

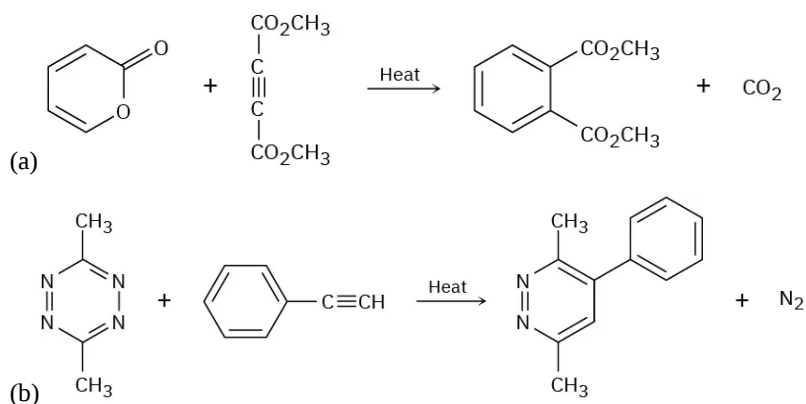
PROBLEM 1-20 Predict the major product(s) from the addition of 1 equivalent of HX and show the mechanism for each of the following reactions.



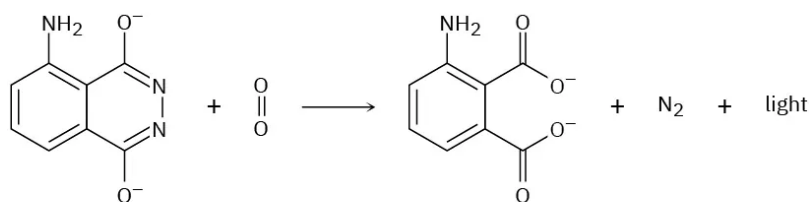
PROBLEM 1-21 We've seen that the Diels–Alder cycloaddition reaction is a one-step, pericyclic process that occurs through a cyclic transition state. Propose a mechanism for the following reaction:



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

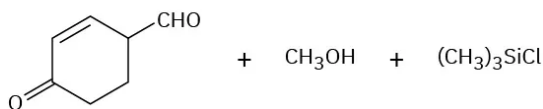
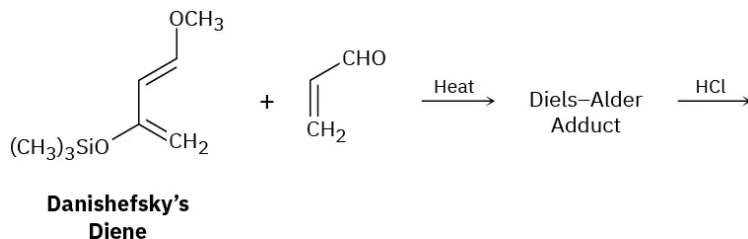


PROBLEM 1-23 Luminol, which is used by forensic scientists to find blood, fluoresces as a result of Diels–Alder-like process. The dianion of luminol reacts with O_2 to form an unstable peroxide intermediate that then loses nitrogen to form a dicarboxylate and emit light. The process is similar to that in Problems 21 and 22. Propose a mechanism for this process.



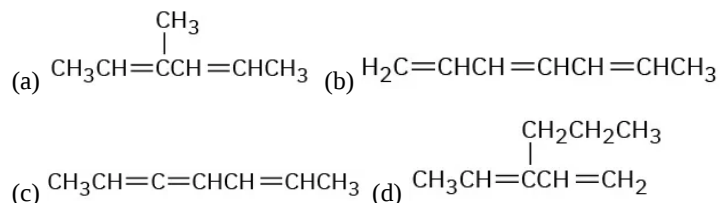
Luminol dianion

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.



Conjugated Dienes

PROBLEM 1-25 Name the following compounds:

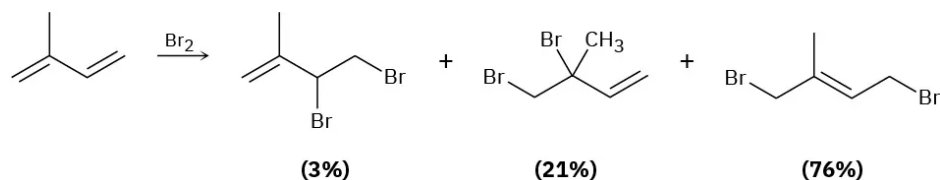


PROBLEM 1-26 Draw and name the six possible diene isomers of formula C_5H_8 . Which of the six are conjugated dienes?

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 Br_2 in CH_2Cl_2 (b) 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 OsO_4 , followed by NaHSO_3

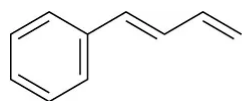
PROBLEM 1-28 Electrophilic addition of Br_2 to isoprene (2-methyl-1,3-butadiene) yields the following product mixture:



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.

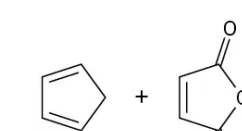
PROBLEM 1-30 Draw the possible products resulting from addition of 1 equivalent of HCl to 1-phenyl-1,3-butadiene. Which would you expect to predominate, and why?



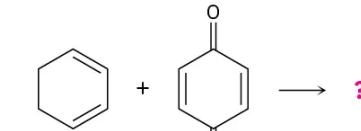
1-Phenyl-1,3-butadiene

Diels–Alder Reactions

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

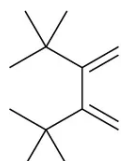


(a)



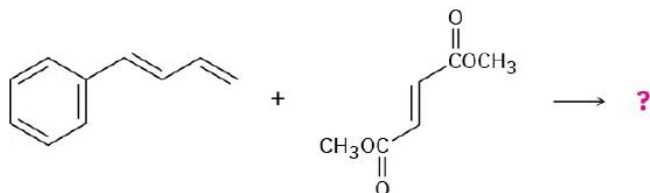
(b)

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



2,3-Di-*tert*-butyl-1,3-butadiene

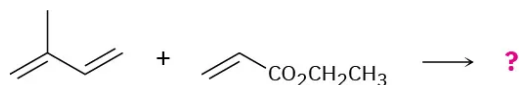
PROBLEM 1-33 Show the structure, including stereochemistry, of the product from the following Diels–Alder reaction:



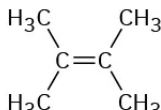
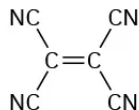
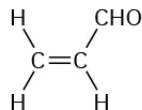
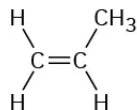
PROBLEM 1-34 How can you account for the fact that *cis*-1,3-pentadiene is much less reactive than *trans*-1,3-pentadiene in the Diels–Alder reaction?

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.

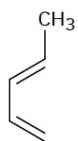


PROBLEM 1-37 Rank the following dienophiles in order of their expected reactivity in the Diels–Alder reaction.

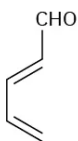


PROBLEM 1-38 1,3-Cyclopentadiene is very reactive in Diels–Alder cycloaddition reactions, but 1,3-cyclohexadiene is less reactive and 1,3-cycloheptadiene is nearly inert. Explain. (Molecular models are helpful.)

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

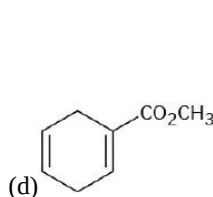
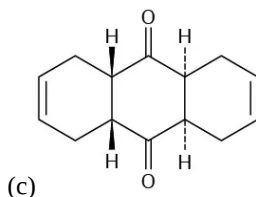
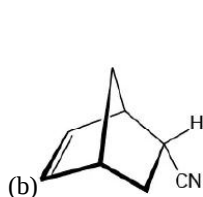
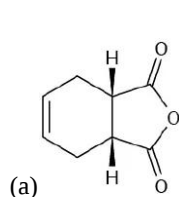


1,3-Pentadiene

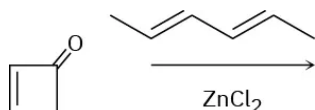


2,4-Pentadienal

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.



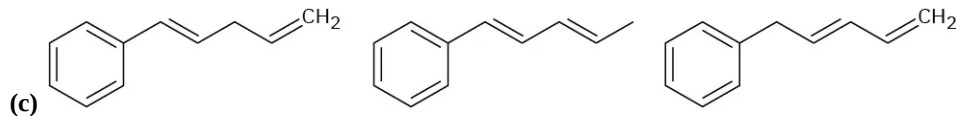
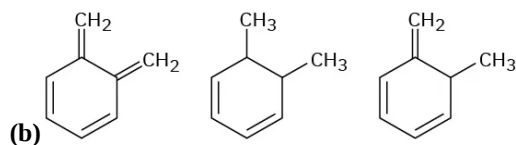
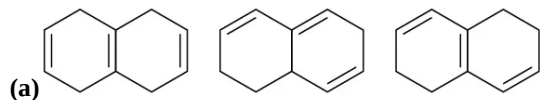
Diene Polymers

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.

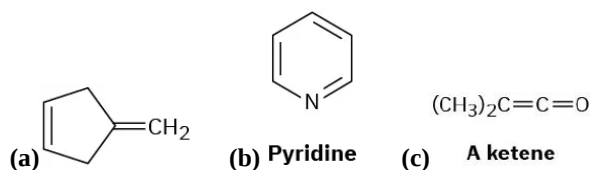
PROBLEM 1-43 1,3-Cyclopentadiene polymerizes slowly at room temperature to yield a polymer that has no double bonds except on the ends. On heating, the polymer breaks down to regenerate 1,3-cyclopentadiene. Propose a structure for the product.

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.

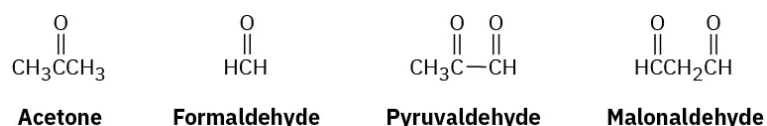
Problem 1-47 The following ultraviolet absorption maxima have been measured:

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 14-47, approximately where would you expect 2,3-dimethyl-1,3,5-hexatriene to absorb?

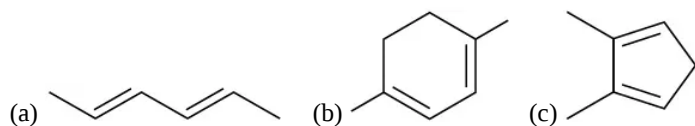
Problem 1-49 β -Ocimene is a pleasant-smelling hydrocarbon found in the leaves of certain herbs. It has the molecular formula $\text{C}_{10}\text{H}_{16}$ and a UV absorption maximum at 232 nm. On hydrogenation with a palladium catalyst, 2,6-dimethyloctane is obtained. Ozonolysis of β -ocimene, followed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



- (a) How many double bonds does β -ocimene have?
- (b) Is β -ocimene conjugated or nonconjugated?
- (c) Propose a structure for β -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.

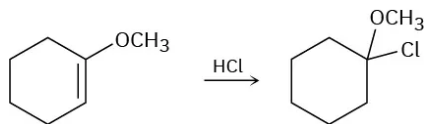


Problem 1-51 Answer the following questions for 1,3,5-cycloheptatriene.

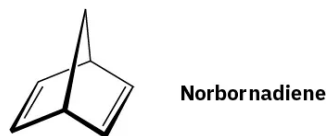
- (a) How many p atomic orbitals are in the conjugated system?
- (b) How many molecular orbitals describe the conjugated system?
- (c) How many molecular orbitals are bonding molecular orbitals?
- (d) How many molecular orbitals are anti-bonding molecular orbitals?
- (e) Which molecular orbitals are 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.

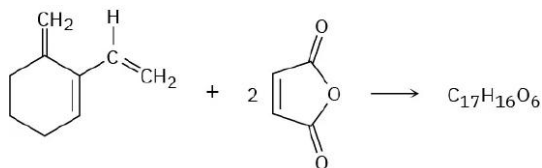


Problem 1-54 Aldrin, a chlorinated insecticide now banned from use in most countries since 1990, can be made by Diels–Alder reaction of hexachloro-1,3-cyclopentadiene with norbornadiene. What is the structure of aldrin?



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.

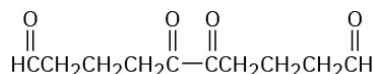


Problem 1-57 Myrcene, $C_{10}H_{16}$, is found in oil of bay leaves and is isomeric with β -ocimene (Problem 49). It has an ultraviolet absorption at 226 nm and can be hydrogenated to yield 2,6-dimethyloctane. On ozonolysis followed by zinc/acetic acid treatment, myrcene yields formaldehyde, acetone,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



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:

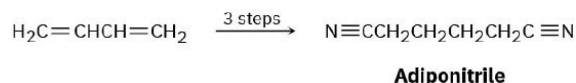


An illustration shows the structure of diketo dialdehyde. It shows two carbonyl groups single bonded to each other. Each carbonyl group is bonded to a chain of three methylene groups and then to an aldehyde group.

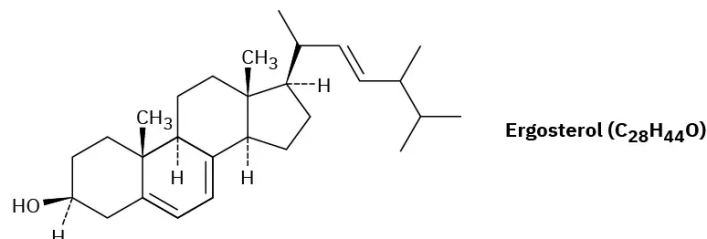
- (a) Propose two possible structures for **A**.
- (b) Hydrocarbon **A** reacts with maleic anhydride to yield a Diels–Alder adduct. Which of your structures for **A** is correct?

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

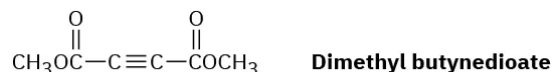
Problem 1-59 Adiponitrile, a starting material used in the manufacture of nylon, can be prepared in three steps from 1,3-butadiene. How would you carry out this synthesis?



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 $l = 1.00 \text{ cm}$?

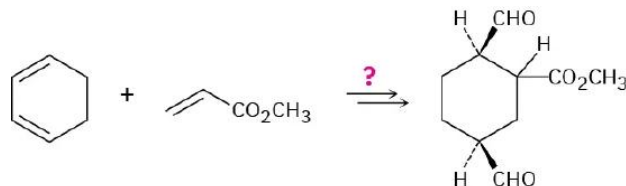


Problem 1-61 Dimethyl butynedioate undergoes a Diels–Alder reaction with (2*E*,4*E*)-2,4-hexadiene. Show the structure and stereochemistry of the product.

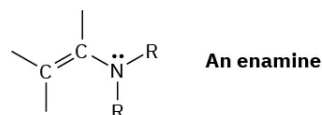


Problem 1-62 Dimethyl butynedioate also undergoes a Diels–Alder reaction with (2*E*,4*Z*)-2,4-hexadiene, but the stereochemistry of the product is different from that of the (2*E*,4*E*) isomer (Problem 61). Explain.

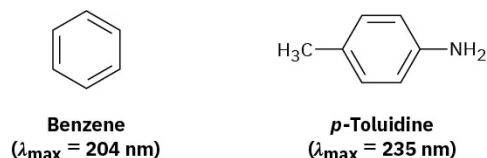
Problem 1-63 How would you carry out the following synthesis (more than one step is required)? What stereochemical relationship between the $-\text{CO}_2\text{CH}_3$ group attached to the cyclohexane ring and the $-\text{CHO}$ groups would your synthesis produce?



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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