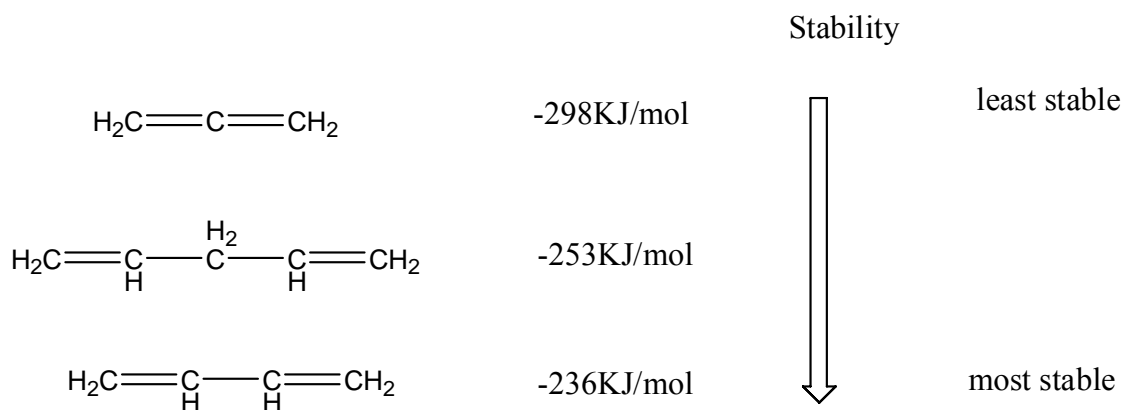


Chapter 14

14.1 Allene, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, has a heat of hydrogenation of -298KJ/mol (-71.3 kcal/mol). Rank a conjugated diene, a nonconjugated diene, and an allene in order of stability.

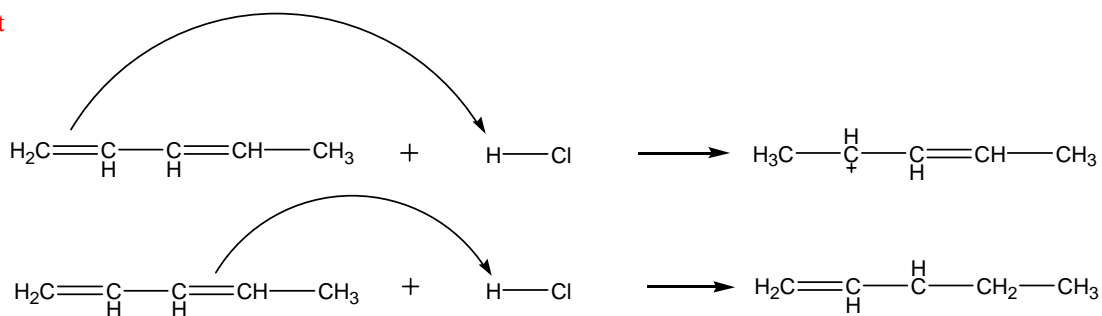
Solution:



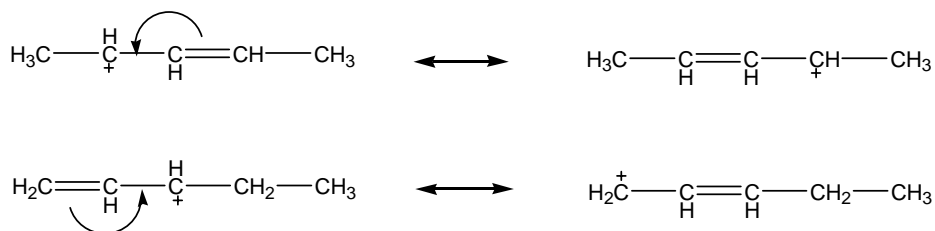
14.2 Give the structures of both 1,2 and 1,4 adducts resulting from reaction of 1 equivalent of HCl with 1,3-pentadiene.

Solution:

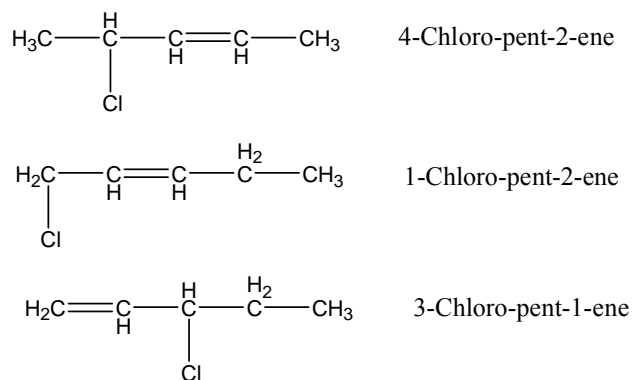
1st



2nd

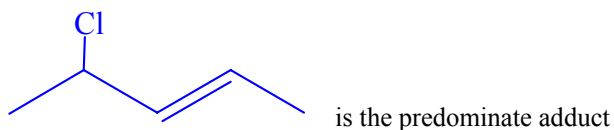


Therefore, the adducts are:



14.3 Look at the possible carbocation intermediates produced during addition of HCl to 1,3-pentadiene (Problem 14.2), and predict which 1,2 adduct predominates. Which 1,4 addition adduct predominates?

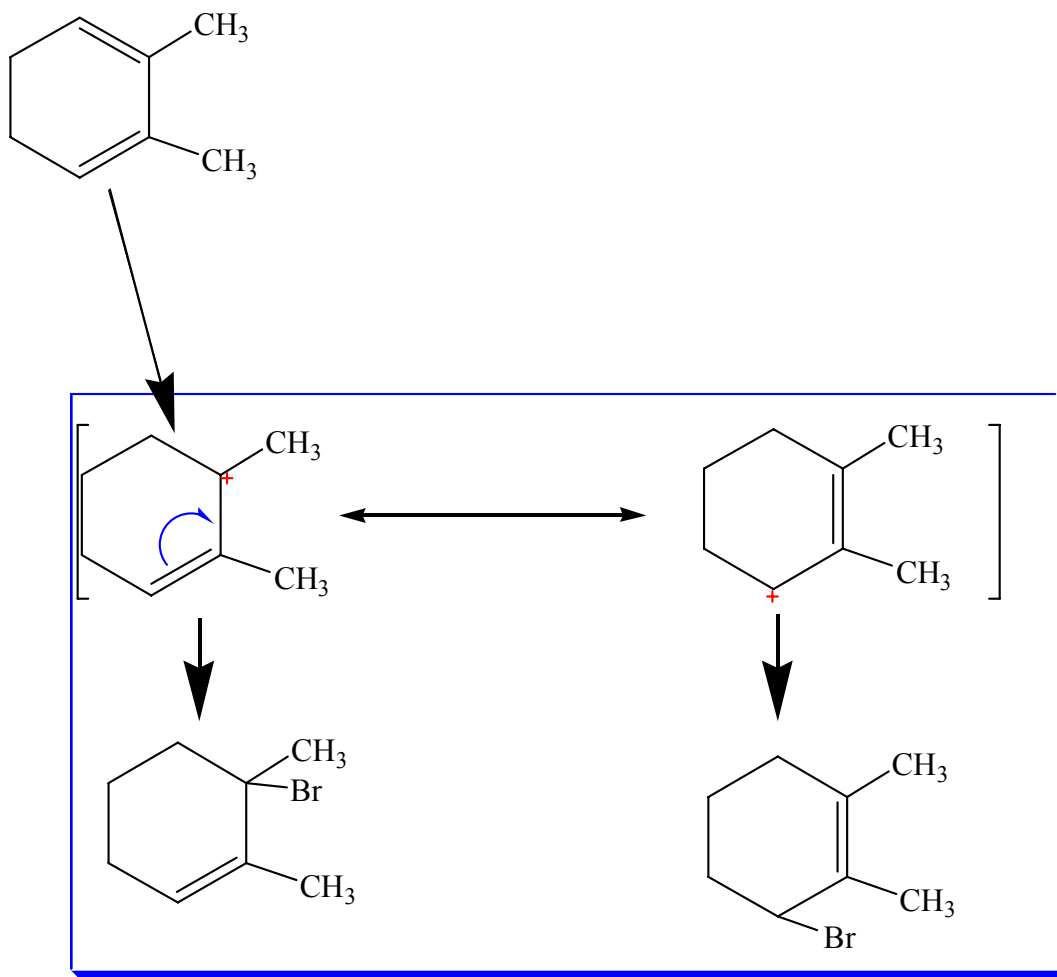
Solutions



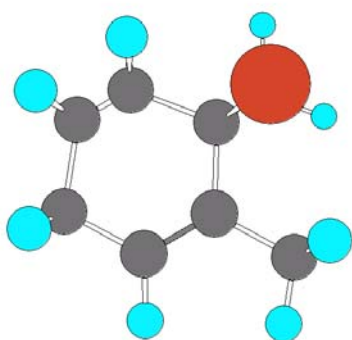
14.4 Give the structure of both 1,2 and 1,4 adduct resulting from reaction of 1 equivalent of HBr with the following substance?

Solutions:

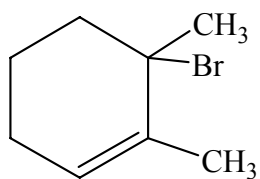
The reaction carries out as follows:

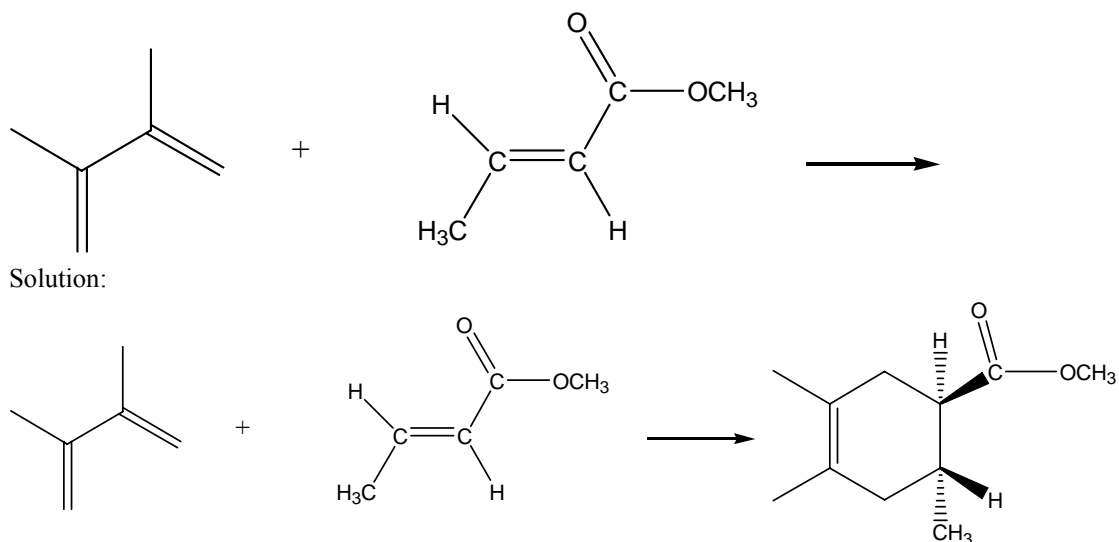


Red stands for Br atom, green stands for hydrogen atoms and black stands for carbon atoms.

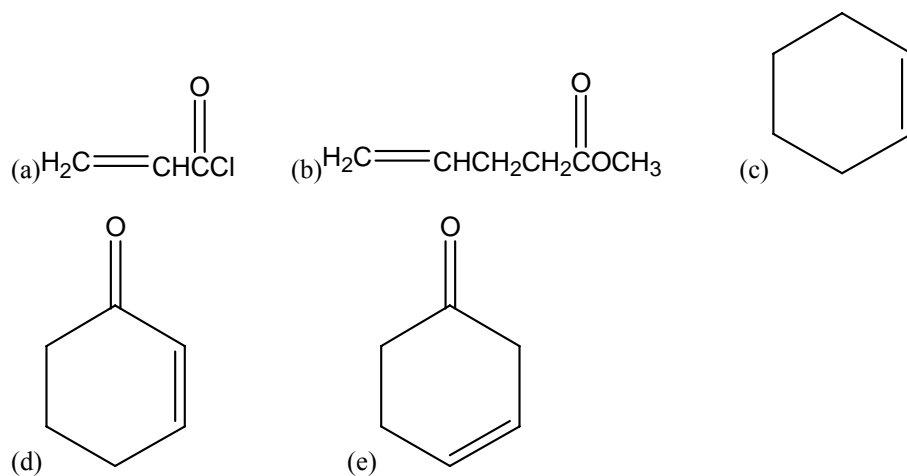


is the structure of





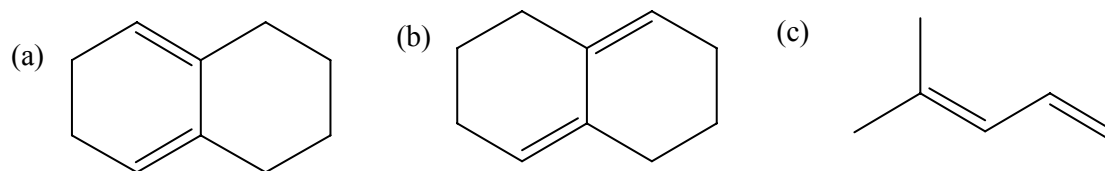
14.8 Which of the following alkenes would you expect to be good Diels-Alder dienophiles?



Solution:

(a),(d)

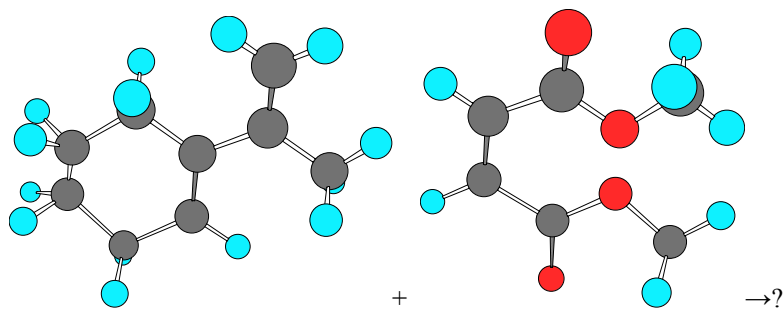
14.9 Which of the following dienes have an s-cis conformation, and which have an s-trans conformation? Of the s-trans dienes, which can readily rotate to s-cis?



Solution:

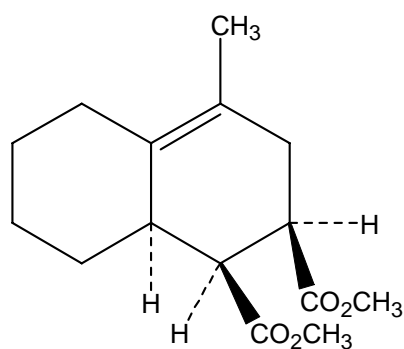
(a) has an s-cis conformation, (b) and (c) have an s-trans conformation, and (c) rotate to s-cis.

14.10 Predict the product of the following Diels-Alder reaction:

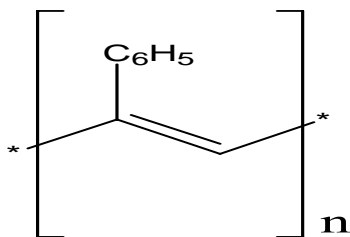


Solution:

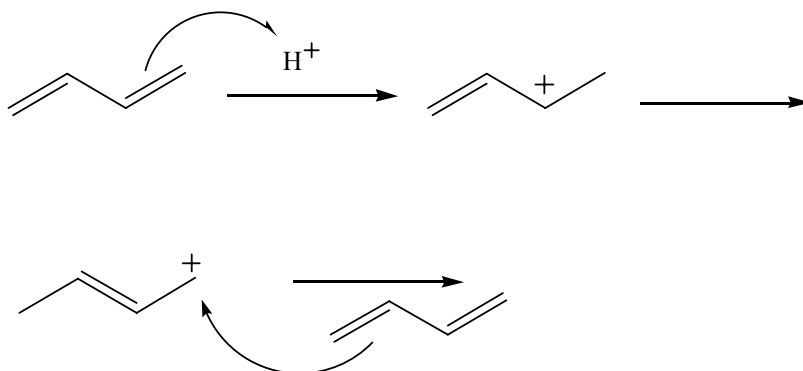
The product is:



14.11 Draw a segment of the polymer that might be prepared from 2-phenyl-1, 3-butadiene.



14.12 Show the mechanism of the acid-catalyzed polymerization of 1, 3-butadiene.



The process goes on and product polymers.

14.13 Calculate the energy range of electromagnetic radiation in the UV region of the spectrum from 200 to 400 nm. Recall the equation.

$$E = N_A hc / \lambda = (1.20 \times 10^4 \text{ kJ/mol}) / \lambda \text{ (m)}$$

Solution: $E_1 = 1.20 \times 10^4 / 200 \text{ (nm)} = 600 \text{ kJ}$

$$E = 1.20 \times 10^{-4} / 400(\text{nm}) = 300 \text{kJ}$$

The energy range of UV is 300~600kJ/mol

14.14 How does the energy you calculated in Problem 14.13 for UV radiation compare with the values calculated previously for IR and NMR spectroscopy?

Solution: The energy range of IR is 4.8~48kJ/mol;

NMR required about 8.0×10^{-5} kJ/mol.

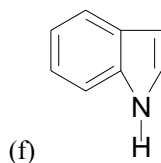
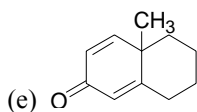
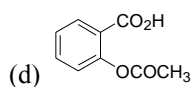
So the energy for UV is greater than IR and NMR.

14.15 A knowledge of molar absorptivities is particularly important in biochemistry where UV spectroscopy can provide an extremely sensitive method of analysis. For example, imagine that you wanted to determine the concentration of vitamin A in a sample. If pure vitamin A has $\lambda_{\text{max}} = 325$ (ε = 50,000), what is the vitamin A concentration in a sample whose absorbance at 325 nm is A = 0.735 in a cell with a path length of 1.00 cm?

Solution: $C = A / (\epsilon \cdot l) = 1.47 \times 10^{-5}$ mol/L

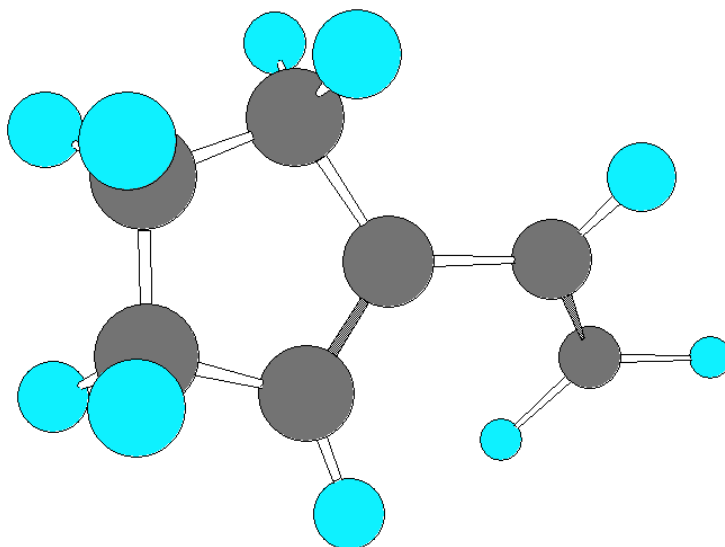
14.16 Which of the following compounds would you expect to show ultraviolet absorption in the 200 to 400 nm range?

(a) 1,4-cyclohexadiene (b) 1,3-cyclohexadiene (c) $\text{H}_2\text{C}=\text{C}(\text{H})-\text{C}\equiv\text{N}$



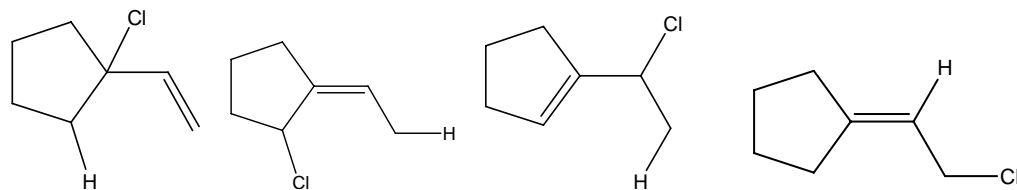
Solution: b, c, d, e, f

14.17 Write the structure of all possible adducts of the following diene with 1 equivalent of HCl.

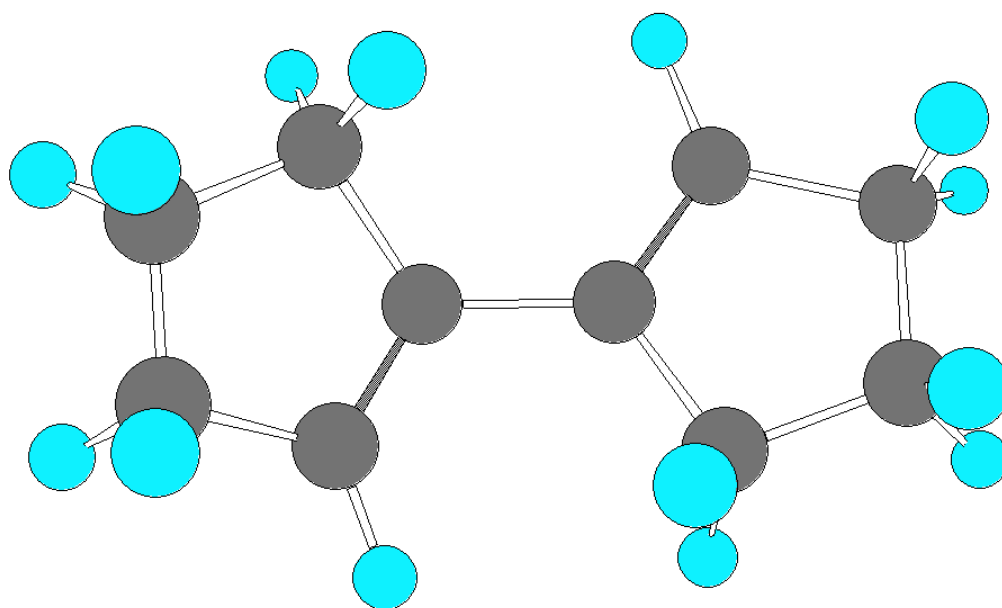


Solution:

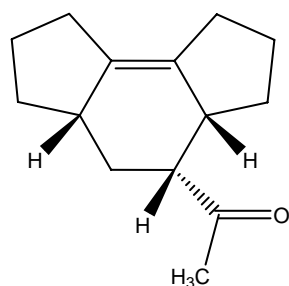
All possible adducts as follow:



14.18 Write 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.

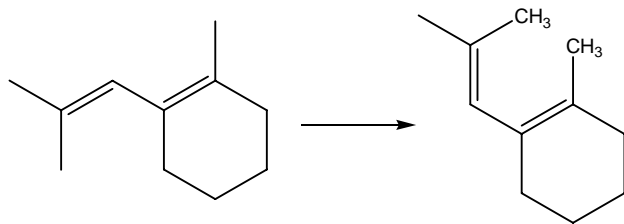


Solution:

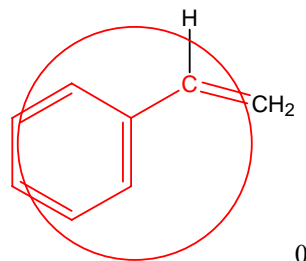
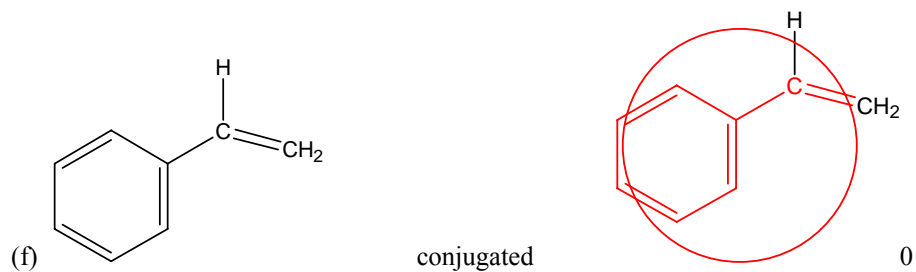
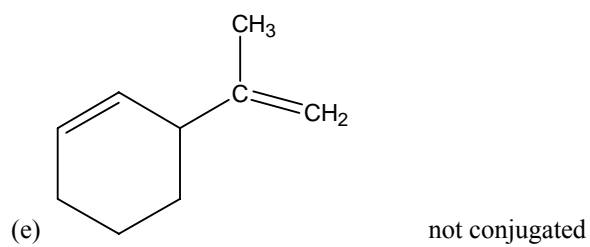
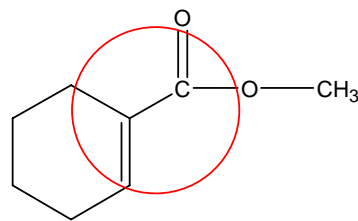
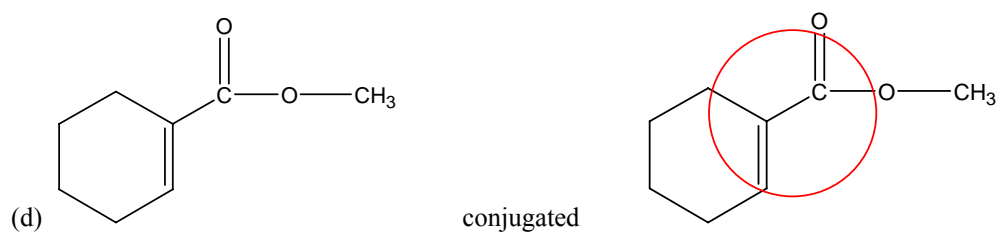
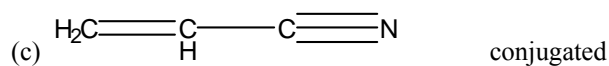
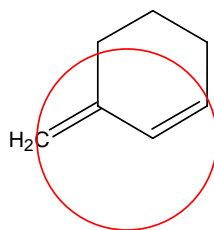
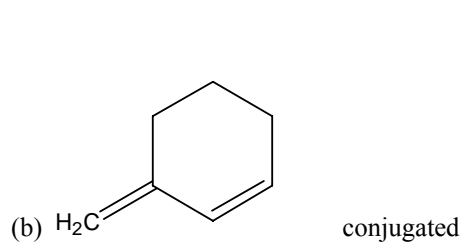
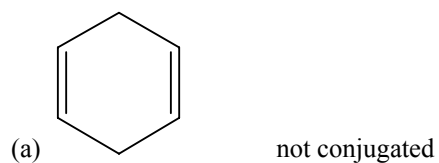


14.19 The following diene does not undergo Diels-Alder reactions. Explain.

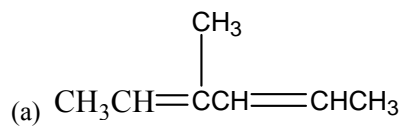
Solution: Because the ends of the diene partner are too far apart and steric strain between the two methyl group prevents the molecule from adopting s-cis geometry.

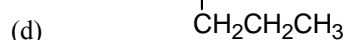
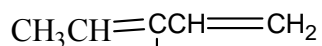
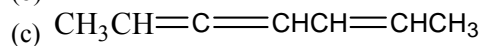
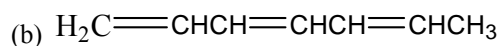


14.20 Which of the following molecules are conjugated? Circle the conjugated part in each.



14.21 Give IUPAC names for the following compounds:





Solution:

(a) 3-methyl-2,4-hexadiene

(b) 1,3,5-heptatriene

(c) 2,3,5-heptatriene

(d) 3-propyl-1,3-pentadiene

14.22 What product(s) would you expect from 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

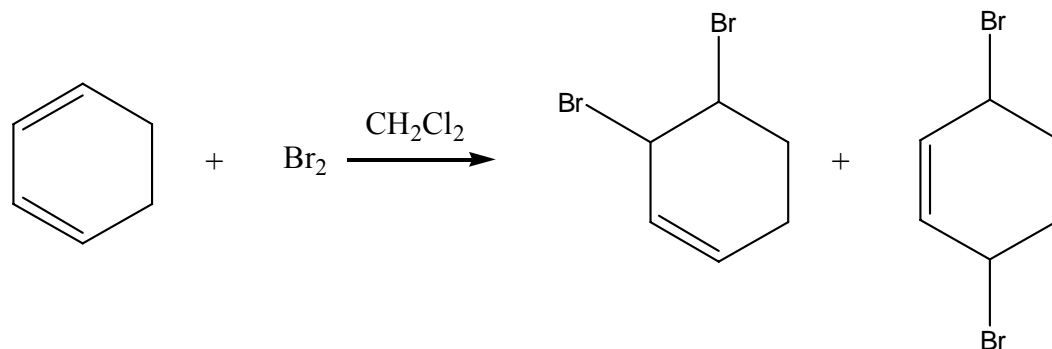
(d) 1 mol DCl in ether

(e) 3-Buten-2-one ($\text{H}_2\text{C}=\text{CHCOCH}_3$)

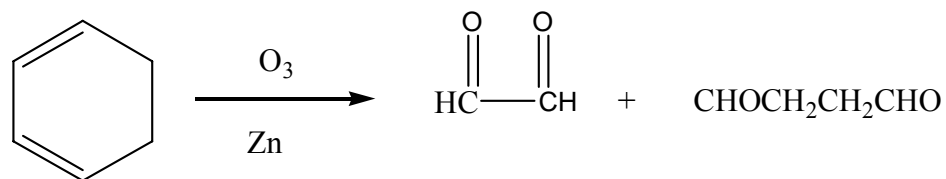
(f) Excess OsO_4 , followed by NaHSO_3

Solution:

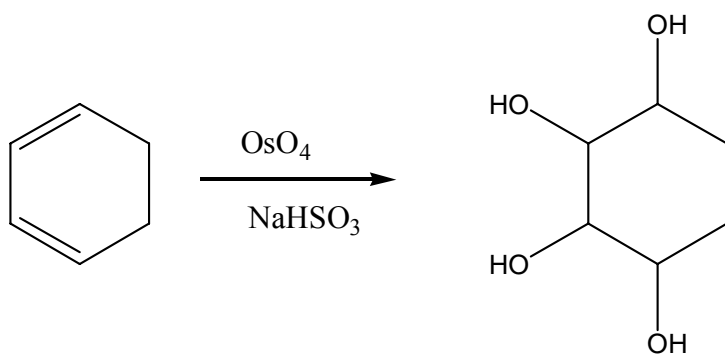
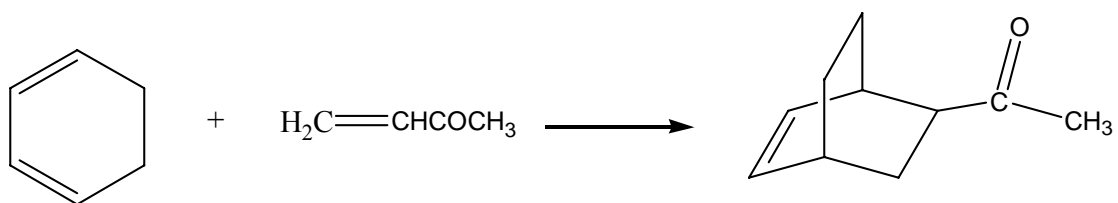
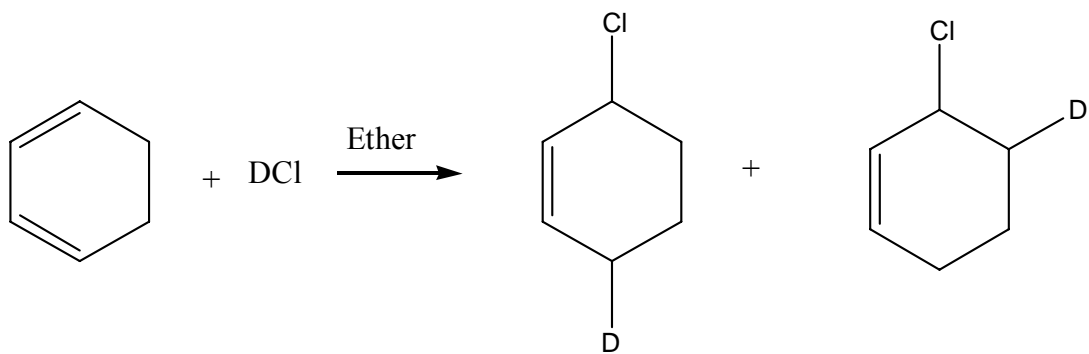
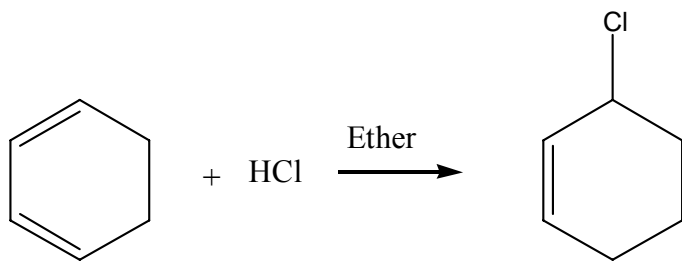
(a)



(b)

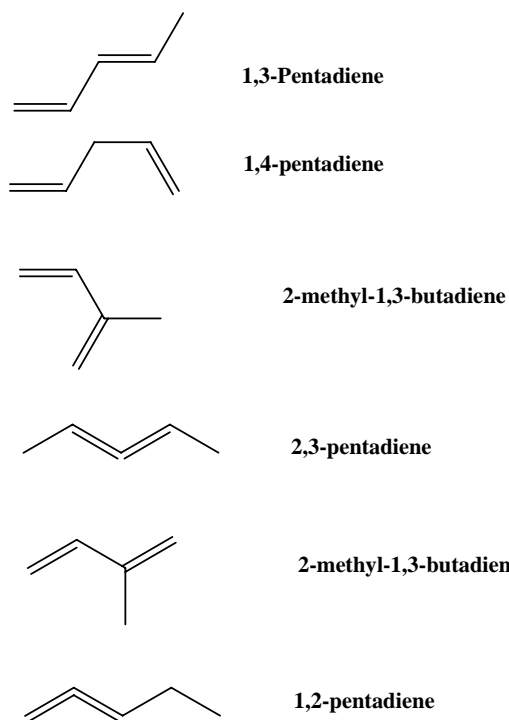


(c)



14.23 Draw and name the six possible diene isomers of formula C_5H_8 . Which of the six are conjugated dienes?

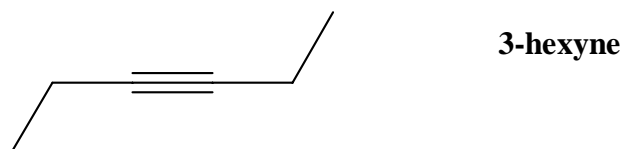
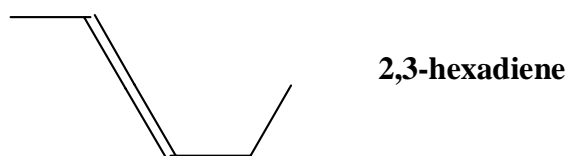
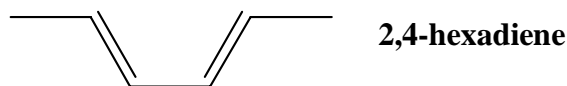
Solution:



14.24. 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 ^{13}C NMR spectroscopy to help identify them. How would you use UV spectroscopy?

Solution:

The three products:



The way to identify:

1. Use of ^{13}C NMR Spectroscopy:

2,4-Hexadiene has 1 sp^3 carbon resonance in the 20 to 50 δ range and 2 sp^2 -carbon resonances in the 100 to 150 δ range.

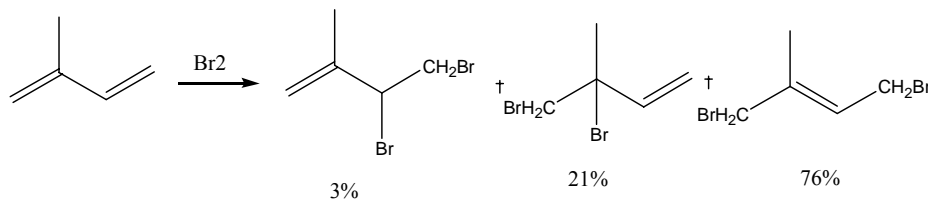
2,3-hexadiene has 3 sp^3 -carbon resonances in the 20 to 50 δ range and 3 sp^2 -carbon resonances in the 100 to 150 δ range.

3-hexyne has 2 sp^3 -carbon resonances in the 20 to 50 δ range and one signal between 65-85 ppm assigned to sp hybridized carbon.

2. Use of UV spectroscopy:

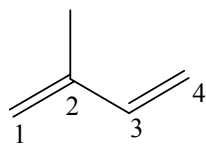
2,3-hexadiene has a shorter λ_{max} than 2,4-hexadiene and 3-hexyne hasn't absorption.

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



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

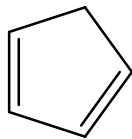
Solution:



For the methyl group is an electron pushing group. So the density of electron on C1 and C2 are bigger than the electron density on C3 and C4. So, as an electrophile, the Br_2 is more likely to add to C1 and C2.

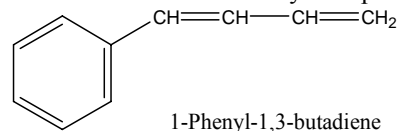
14.26 Propose a structure for a conjugated diene that gives the same product from both 1,2 and 1,4 addition of HBr.

Solution:

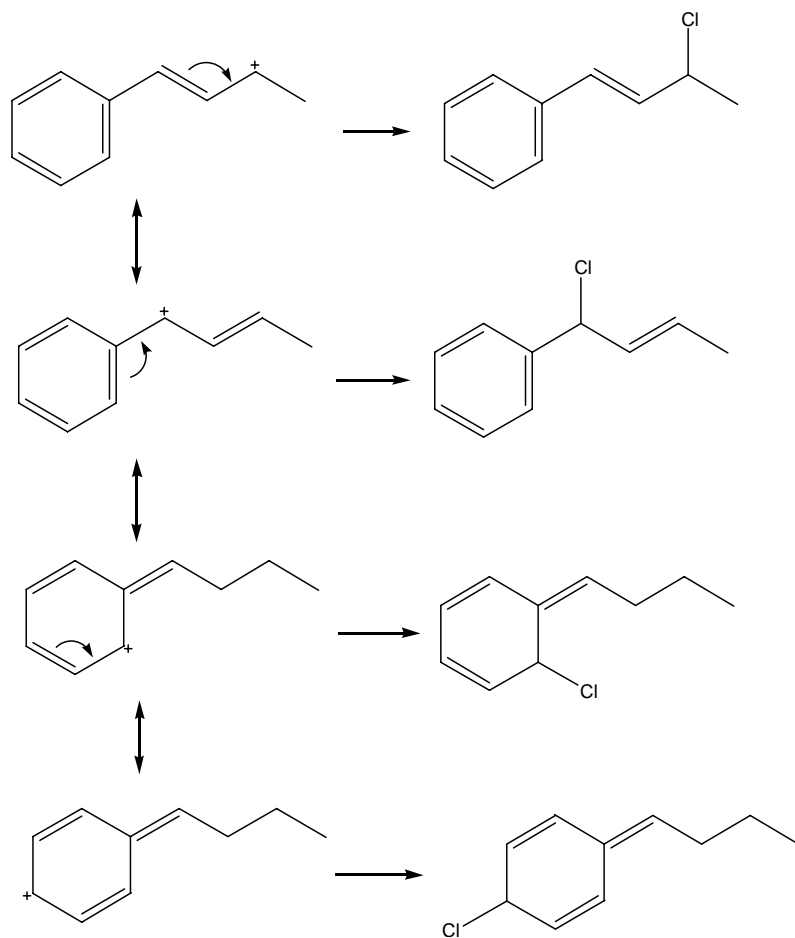


can be the conjugated diene that gives the same product.

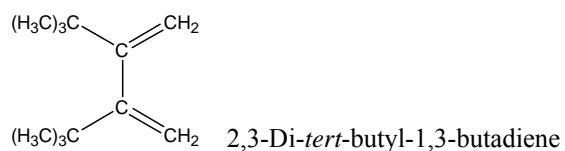
14.27 Draw the possible products resulting from addition of 1 equivalent of HCl to 1-phenyl-1,3-butadiene. Which would you expect to predominate, and why?



Solution:

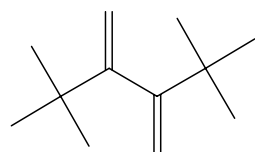


10.28 2,3-Di-*tert*-butyl-1,3-butadiene does not undergo Diels-Alder reactions. Explain.



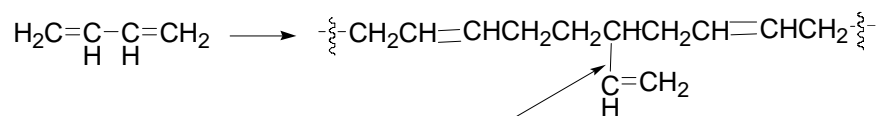
Solution:

Because of the bulk of the *tert*-butyl, the C-C bond has the *s*-trans relationship.



This structure forbids the Diels-Alder reactions.

14.29 Diene polymers contain occasional vinyl branches along the chain. How do you think these branches might arise?



A vinyl branch

Solution: The presence of a vinyl branch is because of the occurring of 1,2-addition.

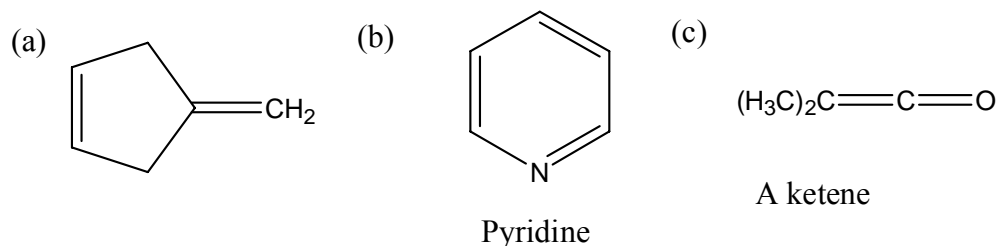
14.30 Tires whose sidewalls are made of natural rubber tend to crack and weather rapidly in areas around cities where high levels of ozone and other industrial pollutants are found. Explain.

Solution: Because natural rubber is the polymer of isoprene containing carbon double bonds, which can be oxidized by ozone, causing the polymer to be decomposed, as a result tires tend to crack and weather rapidly in areas where high levels of ozone are found.

14.31 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.

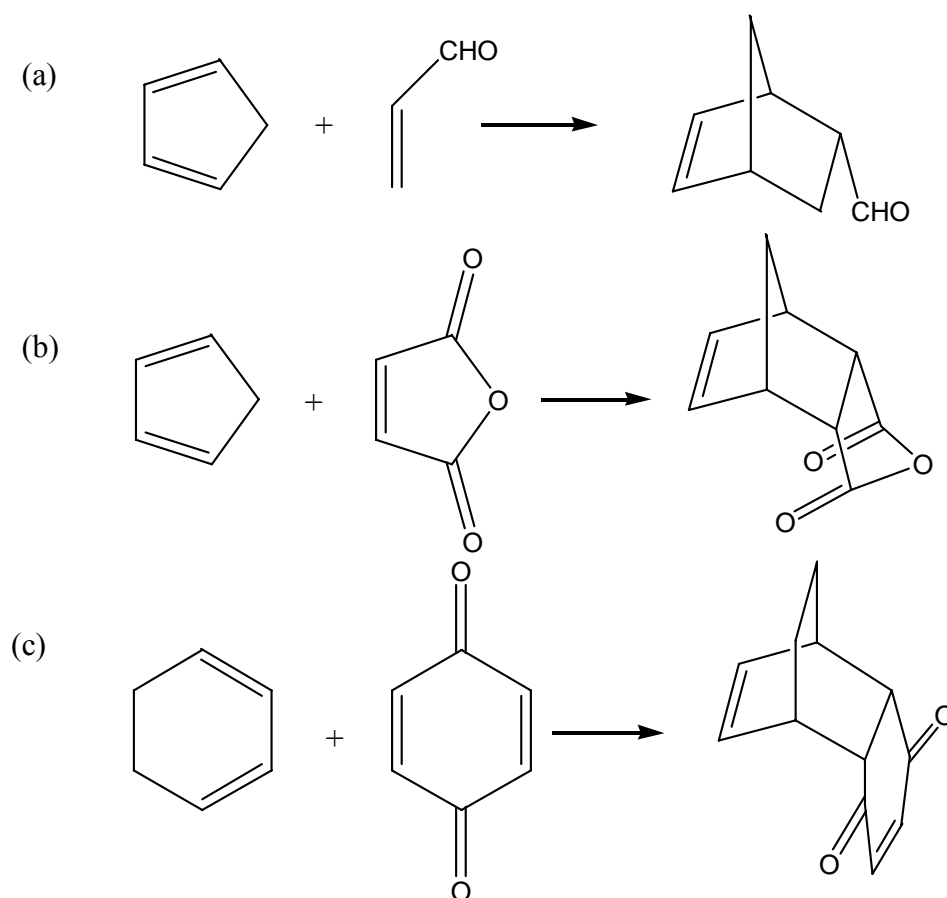
Solution: No I wouldn't expect it. Because the molecular is not conjugated π electron system.

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

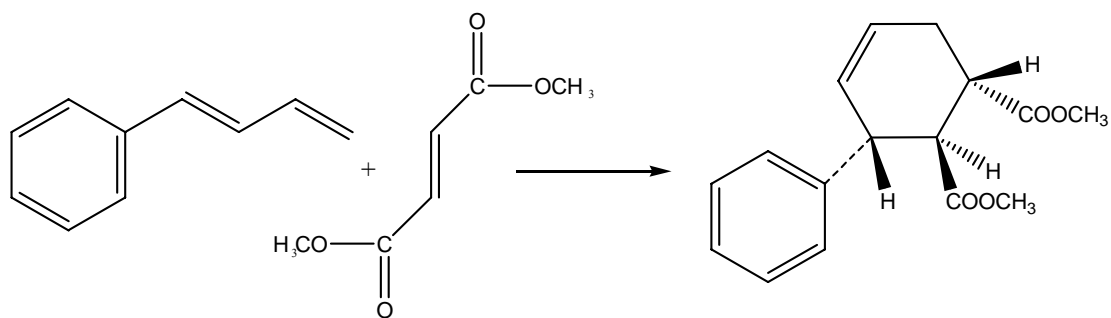


Solution: (b)

14.33 Predict the products of the following Diels-Alder reactions:

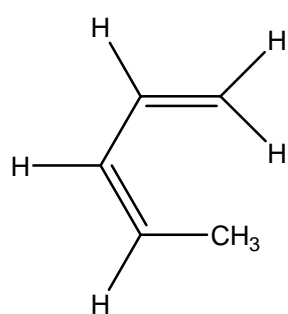


14.34 Show the structure, including stereochemistry, of the product from the following Diels-Alder Reaction

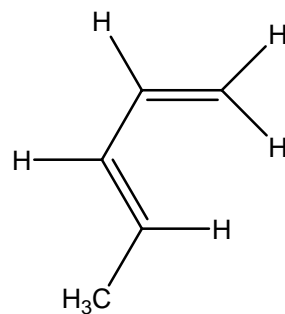


14.35 How can you account for the fact that cis-1,3-pentadiene is much less reactive than trans-1,3-pentadiene in the Diels-Alder reaction?

Solution: 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 D-A reaction.



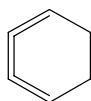
cis-1,3-pentadiene



trans-1,3-pentadiene

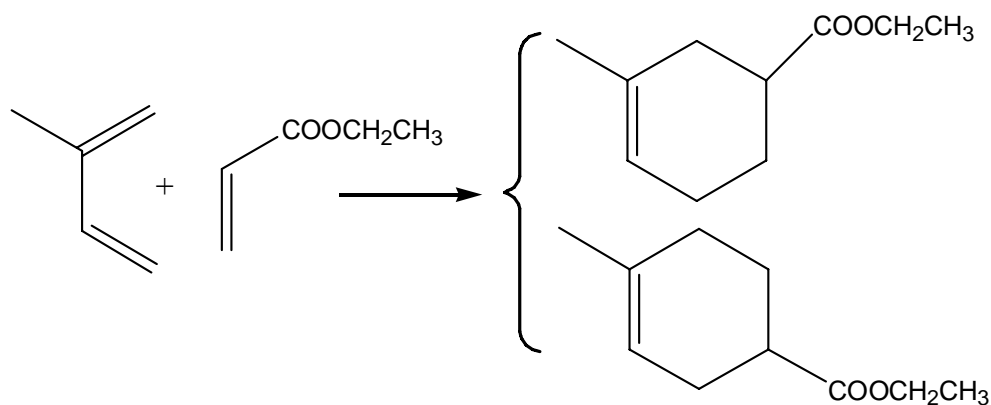
14.36 Would you expect a conjugated diyne such as 1,3-butadiyne to undergo Diels-Alder reaction with a dienophile? Explain.

Solution: it is hard to take place this reaction. First, the diyne is linear structure, the two ends are too far apart just like trans-1,3-butadiene. Second, suppose it can react, the product will be



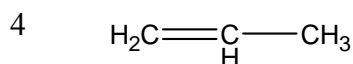
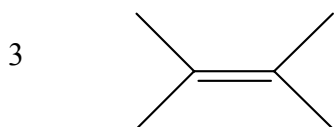
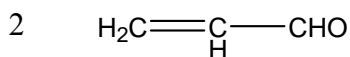
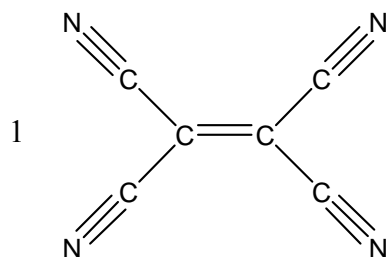
, they are so reactive that they are hardly exist.

14.37 Reaction of isoprene (2-methyl-1,3-butadiene) with ethyl propenoate gives a mixture of two Diels-Alder adducts. Show the structures of each, and explain why a mixture is formed.



For isoprene both the 1,4 carbons are partial negative, and for ethyl propenoate the terminal carbon connected with double bond are partial positive. So we get two products.

14.38 Rank the following dienophile in order of their expected reactivity in the Diels-Alder reaction. Explain.

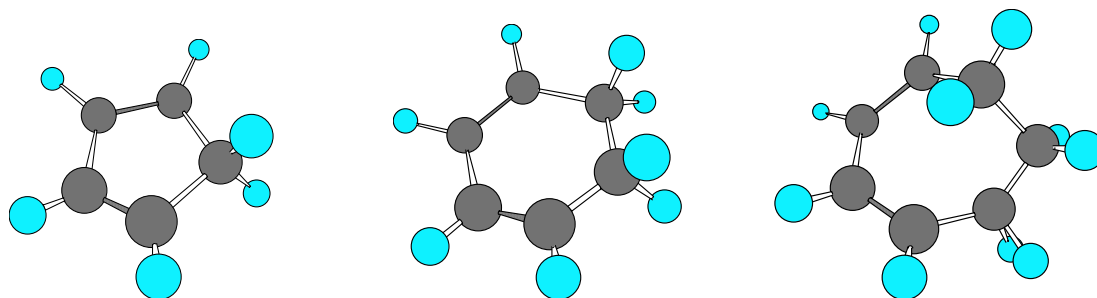


Reactivity $1 > 2 > 4 > 3$. The Diels-Alder cycloaddition reaction occurs most rapidly and in highest yield if the dienophile has an electron withdrawing substituent group. So the dienophile with the stronger electron withdrawing will be more reactive.

14.39 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)

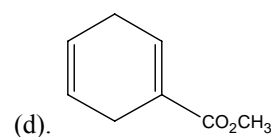
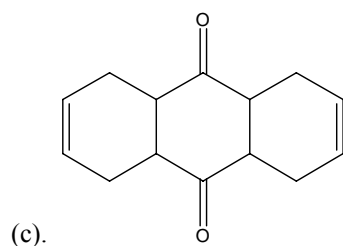
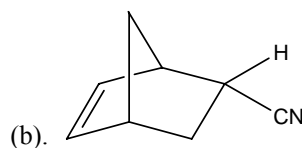
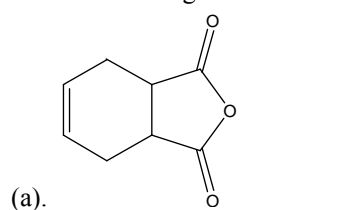
Solution:

The structures of the three cyclo diene are showed as follow:

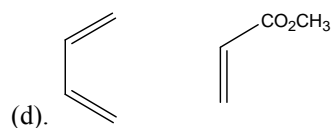
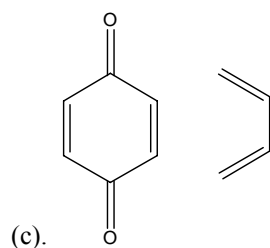
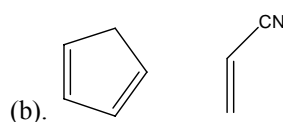
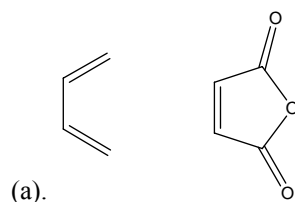


In the reaction process, the dienophile need to overcome the repulsion of steric strain, as we know that the more methylene groups the cyclohexadiene has, the more steric strain it contains. So the reactivity of cyclohexadiene is in the given order.

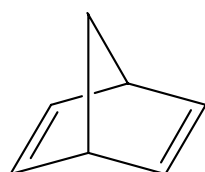
14.40 How would you use Dies-Alder cycloaddition reactions to prepare the following product? Show the starting diene and dienophile in each case.



Solution:

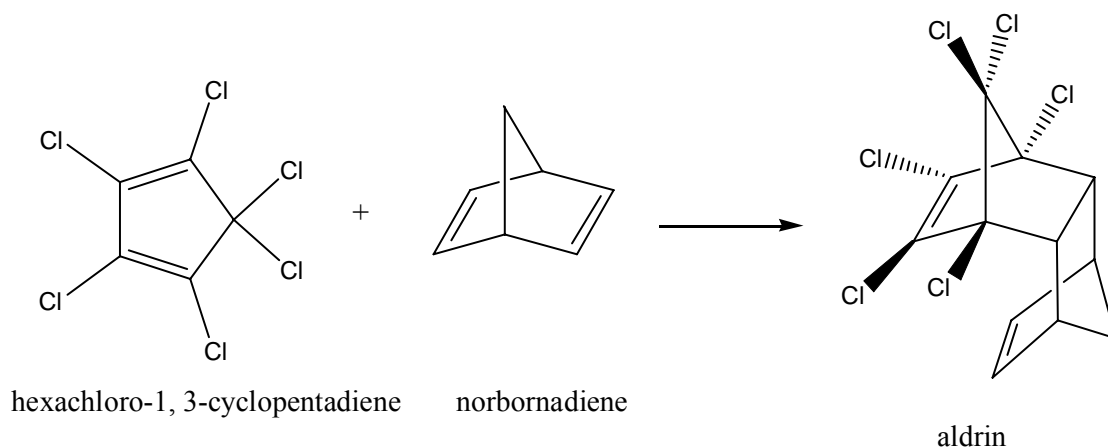


14.41 Aldrin, a chlorinated insecticide now banned for use in the United States, can be made by Diels-Alder reaction of hexachloro-1, 3-cyclopentadiene with norbornadiene. What is the structure of aldrin?



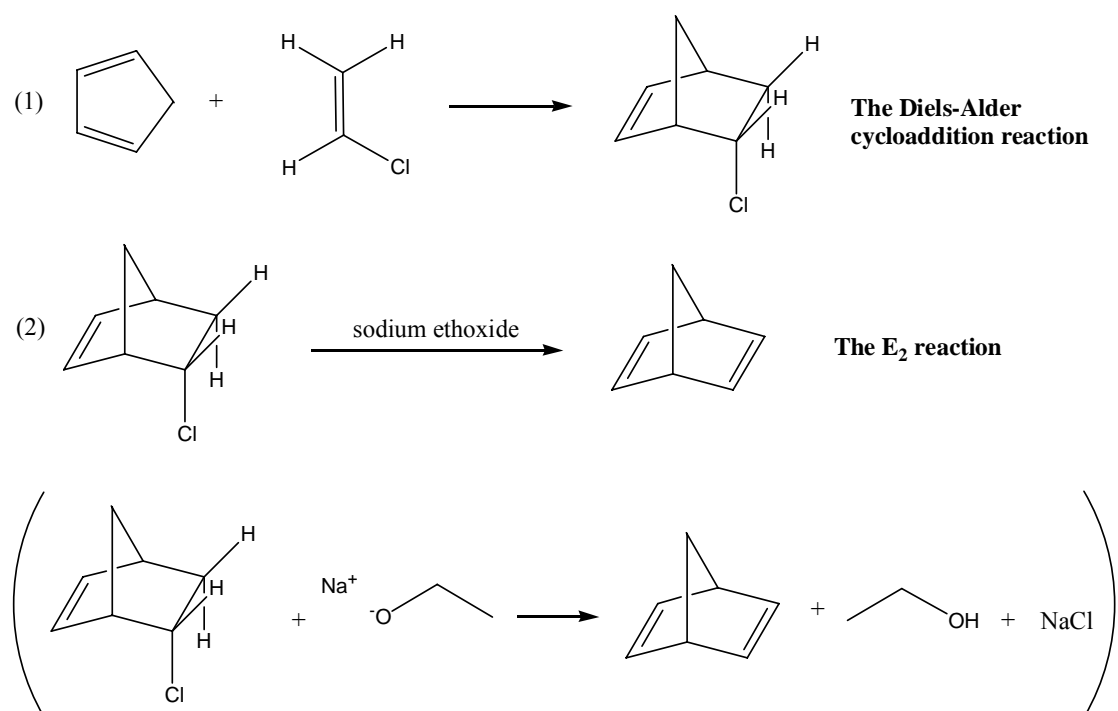
Norbornadiene

Solution:

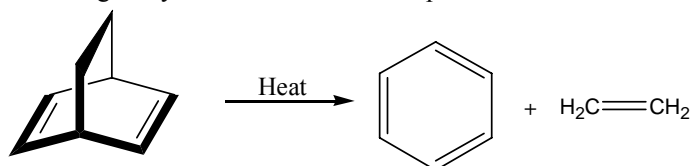


14.42 Norbornadiene (Problem 14.41) can be prepared by reaction of chloroethylene with cyclopentadiene, followed by treatment of the product with sodium ethoxide. Write out the overall scheme, and identify the two kinds of reactions.

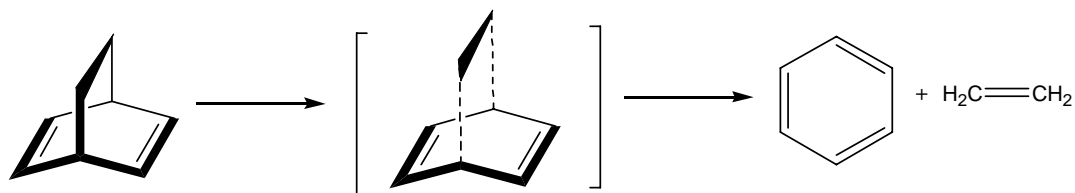
Solution:



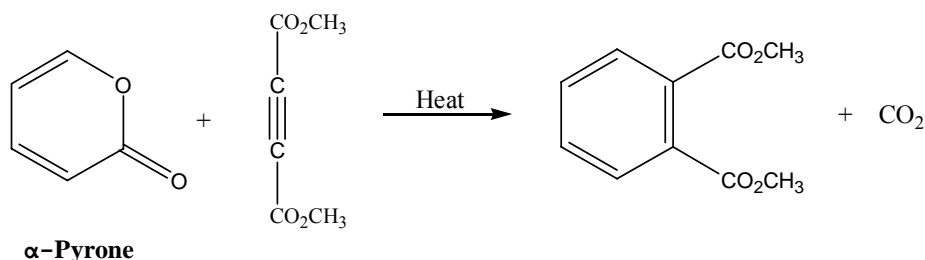
14.43 We've seen that the Diels-Alder cycloaddition reaction is a one-step, pericyclic process that occurs through a cyclic transition state. Propose a mechanism for the following reaction:



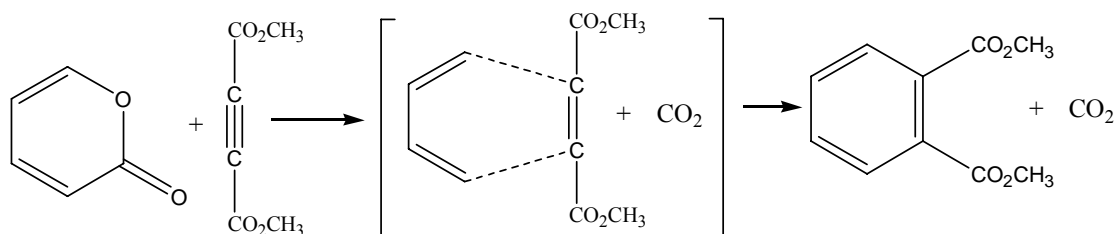
Solution:



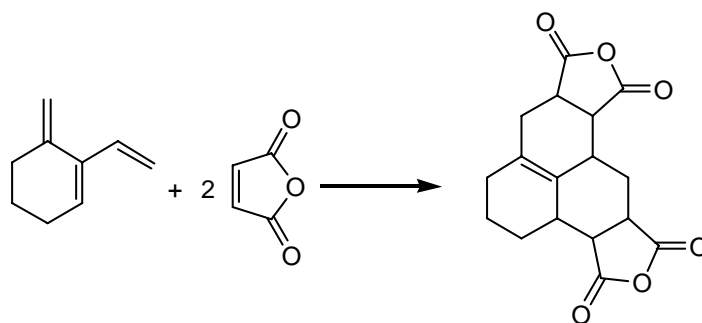
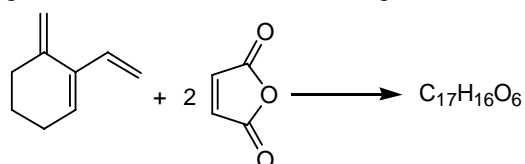
14.44 Propose a mechanism to explain the following reaction (see Problem 14.43):



Solution:



14.45 The triene shown below reacts with two equivalents of maleic anhydride to yield $C_{17}H_{16}O_6$ as product. Predict a structure for the product.



Solution:

14.46 The following ultraviolet absorption maxima have measured:

	$\lambda_{\text{max}}(\text{nm})$
1,3-Butadiene	217
2-Methyl-1,3-butadiene	220
1,3-pentadiene	223
2,3-Dimethyl-1,3-butadiene	226
2,4-Hexadiene	227
2,4-Dimethyl-1,3-pentadiene	232
2,5-Dimethyl-2,4-hexadiene	240

What conclusion can you draw about the effect of alkyl substitution on UV absorption maxima?

Approximately what effect does each added alkyl group have?

Solution: 1) When alkyl substitution is added to dienes, the UV absorption wavelength maxima will be longer.

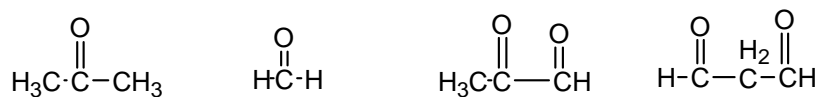
2) The alkyl group added to the edge of the dienes make the wavelength maxima increase more than the alkyl group added to the middle of the dienes.

The more alkyl group added to dienes, the longer the wave length maxima will be.

14.47 1,3,5-Hexatriene has $\lambda_{\text{max}}=258\text{nm}$. In light of your answer to Problem 14.46, approximately where would you expect 2, 3-dimethyl-1, 3, 5-hexatriene to absorb? Explain.

Solution: According to the figures of Problem 14.46: 1,3-Butadiene has $\lambda_{\text{max}}=217\text{nm}$, while 2,3-Dimethyl-1,3-butadiene has $\lambda_{\text{max}}=226\text{nm}$, so I would expect 2, 3-dimethyl-1,3,5-hexatriene to absorb at $\lambda_{\text{max}}=267\text{nm}$.

14.48 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 exhibits a UV absorption maximum at 232 nm. On hydrogenation with a palladium catalyst, 2,6-dimethyl-octane is obtained. Ozonolysis of β -Ocimene, followed by treatment with zinc and acetic acid, produces four fragments: acetone, formaldehyde, pyruvaldehyde, and malonaldehyde:

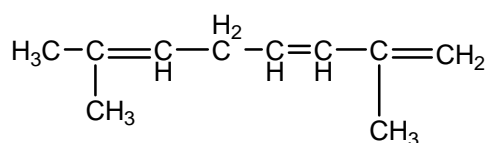


Acetone Formaldehyde Pyruvaldehyde Malonaldehyde

- How many double bonds does β -Ocimene have?
- Is β -Ocimene conjugated or nonconjugated?
- Propose a structure for β -Ocimene.
- Formulate the reactions, showing starting material and products.

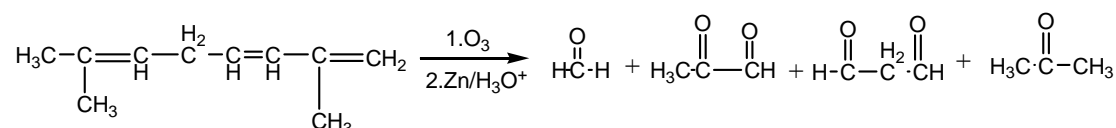
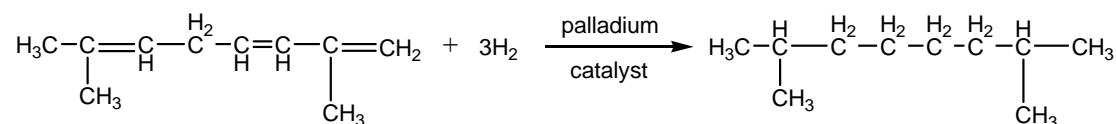
Solution: (a) β -Ocimene has three double bonds.

(b) β -Ocimene is conjugated.

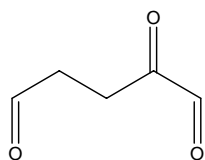


(c)

(d)

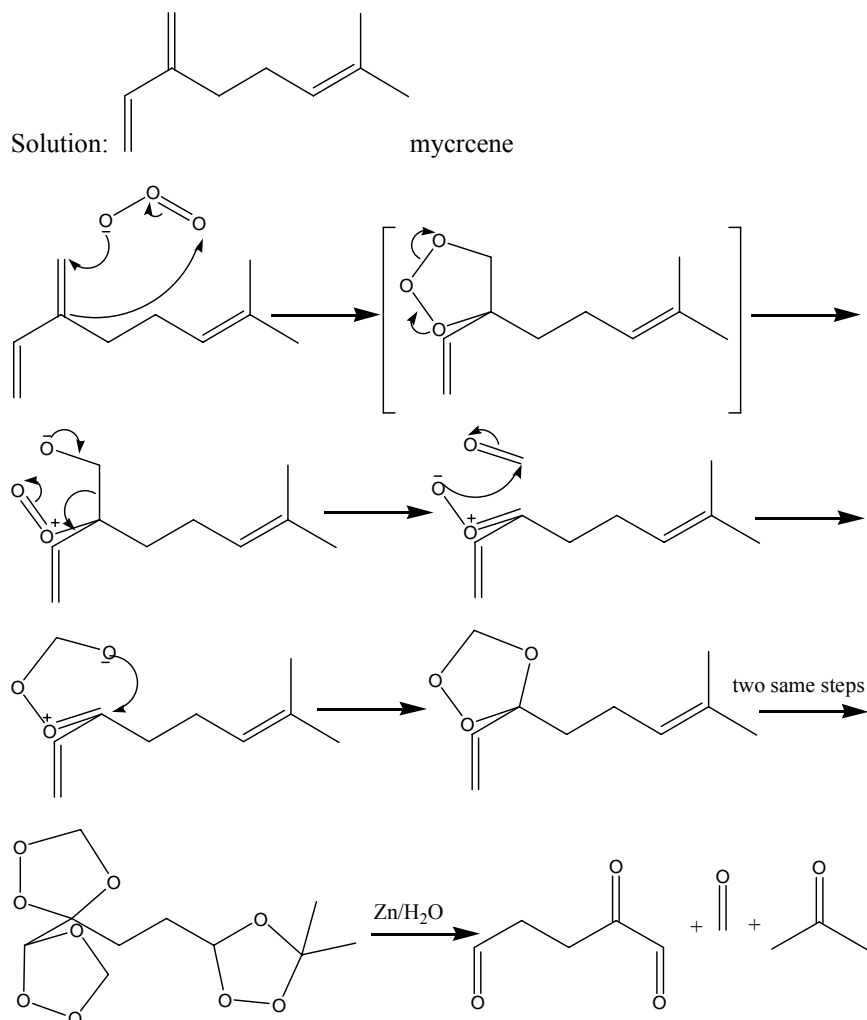


14.49 Myrcene, $\text{C}_{10}\text{H}_{16}$, is found in oil of bay leaves and is isomeric with β -ocimene (see Problem 14.48). It shows an ultraviolet absorption at 226 nm and can be catalytically hydrogenated to yield 2,6-dimethyloctane. On ozonolysis followed by zinc/acetic acid treatment, myrcene yields

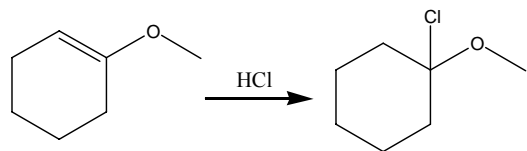


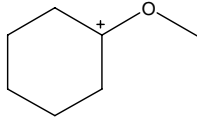
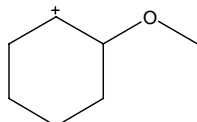
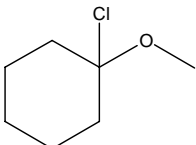
formaldehyde, acetone, and 2-oxopentanedial: 2-oxopentanedial

Propose a structure for myrcene, and formulate the reaction, showing starting material and products.

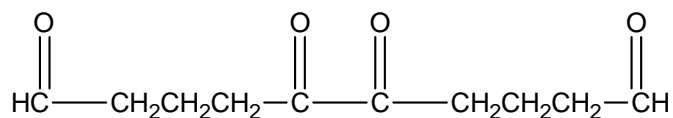


14.50 Addition of HCl to 1-methoxycyclohexene yields 1-chloro-1-methoxycyclohexane as the sole product. Why is none of the other regioisomer formed?

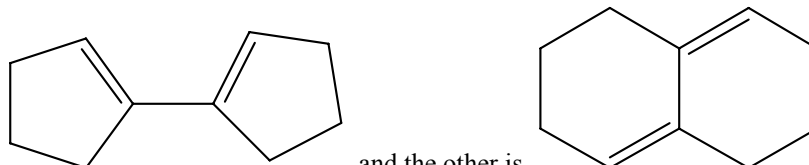


Solution: Because the interaction intermediate  is more stable than the other one: , so there is only one product , and no other regioisomer formed.

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



(a) Propose two possible structures for A.

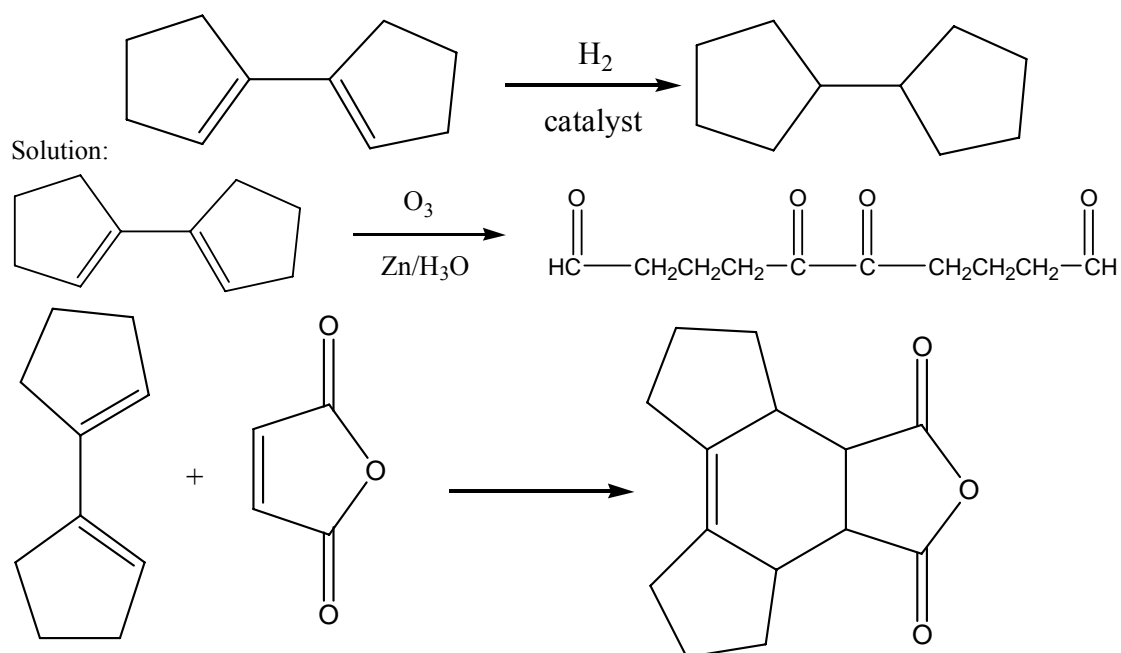


Solution: One is and the other is

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

Solution: The left one is correct.

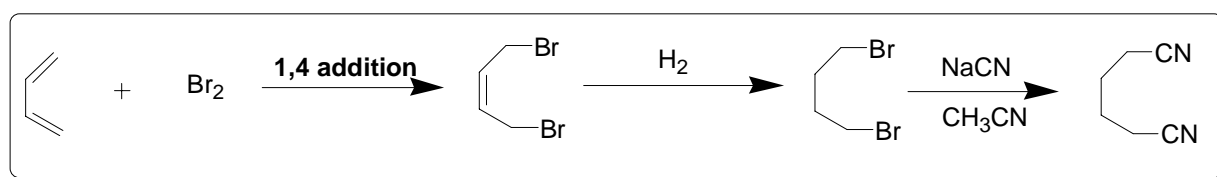
(c) Formulate the reactions showing starting material and products.



14.52 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?



Solution:



14.53 Ergosterol, ($C_{28}H_{44}O$), $\lambda_{\max}=282\text{nm}$ and molar absorption $\epsilon=11,900$. What is the concentration of it in a solution whose absorbance $A=0.065$ with a sample $l=1.00\text{cm}$.

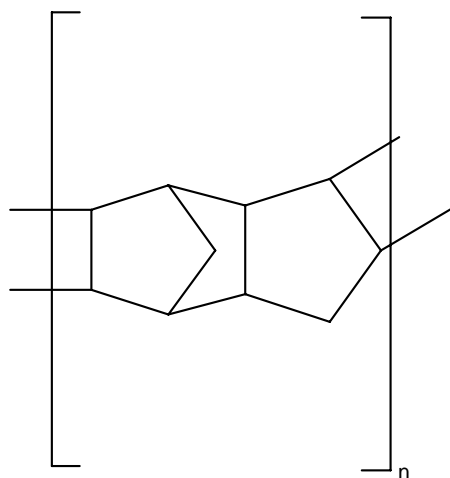
Solution:

$$\epsilon=A/C \times l$$

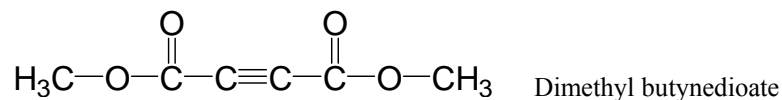
$$\text{so } C=A/\epsilon \times l=5.462.$$

14.54 Cyclopentadiene polymerizes slowly at room temperature to yield a polymer that has no double bonds. On heating, the polymer breaks down to regenerate cyclopentadiene. Propose a structure for the product.

Solution:

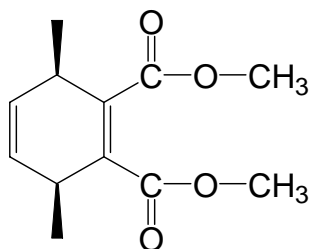


14.55 Dimethyl butynedioate undergoes a Diels-Alder reaction with (2E, 4E)-hexadiene. Show the structure and stereochemistry of the product.



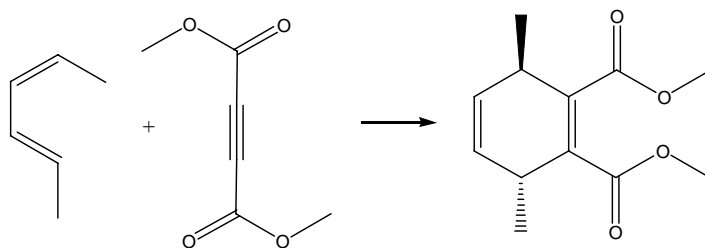
Solution:

The product of Dimethyl butynedioate undergoes a Diels-Alder reaction with (2E, 4E)-hexadiene.

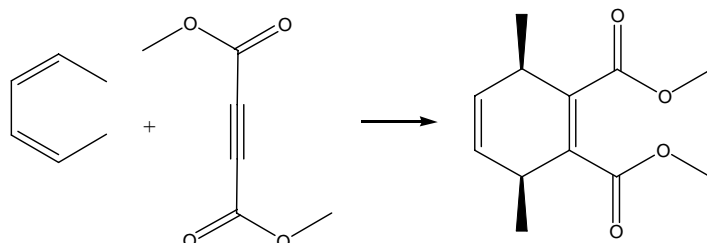


14.56 Dimethyl butynedioate also undergoes a Diels-Alder reaction with (2E, 4Z)-hexadiene, but the stereochemistry of the product is different from that of the (2E, 4E) isomer. Explain.

Solution: The reaction with (2E, 4Z)-hexadiene can be written as follows:



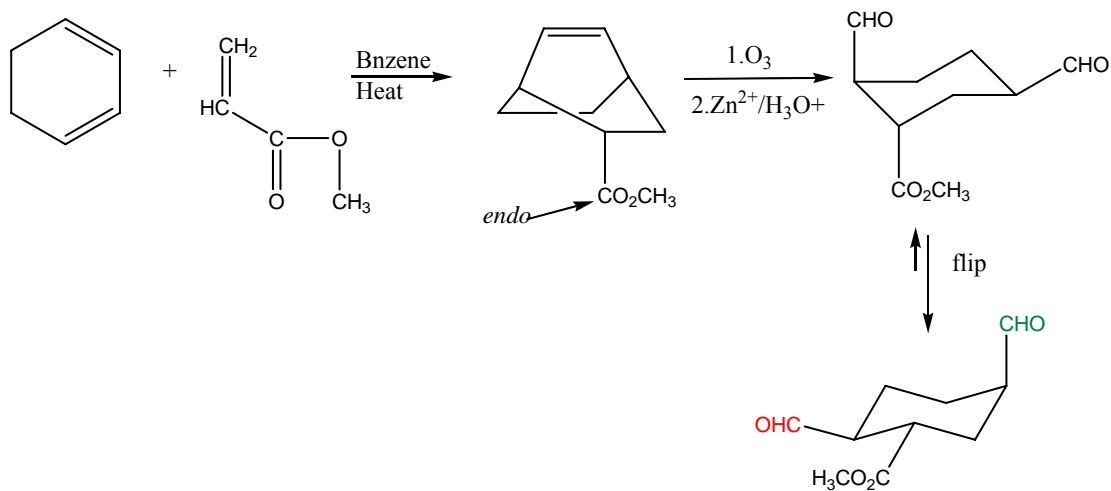
and with the (2E,4E) isomer can be written as follows:



Because their *s*-Cis conformations are different, the products are different.

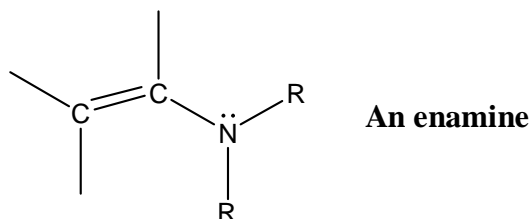
14.57 How would you carry out the following synthesis (more than one step is required)? What stereochemical relationship between the CO₂CH₃ group attached to the cyclohexane ring and the CHO groups would your synthesis produce?

Solution:

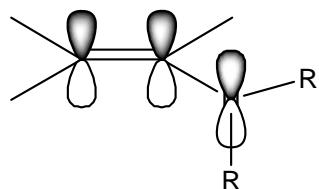


Obviously the group CO₂CH₃ and the red CHO are cis, however, CO₂CH₃ and green CHO are trans.

14.58 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 sp²-hybridized, draw an orbital picture of an enamine, and explain why the double bond is electron-rich.

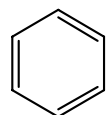


Solution:

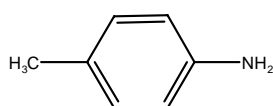


the carbon atom and nitrogen atom are all sp^2 -hybridized, so the p orbitals will form a π_3^4 conjugated system, the electrons are delocalized, it will surely lower the system's energy and make the electron cloud between the carbon-carbon more rich, so it looks as if the double bond of an enamine (alkene+amine) is much more nucleophilic than a typical alkene double bond.

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

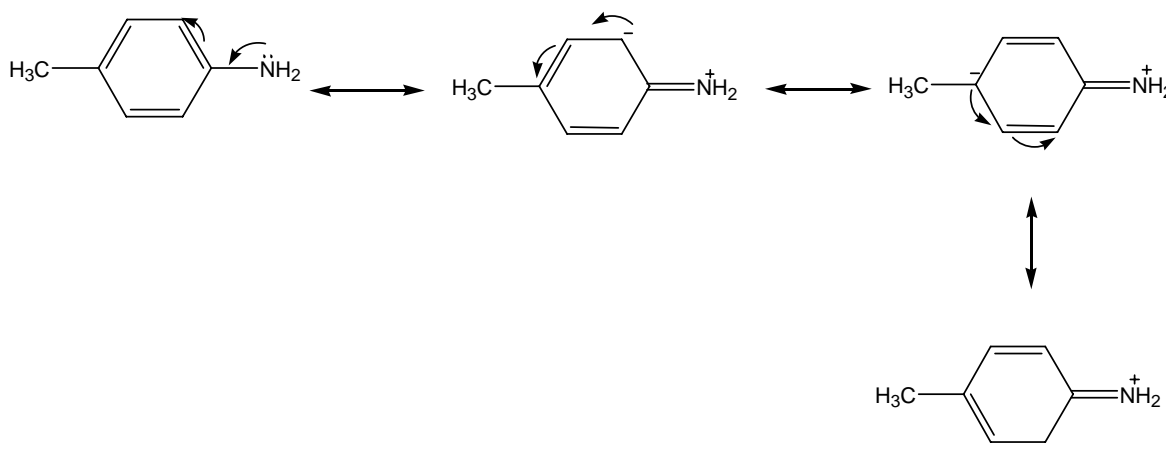


Benzene



para-toluidine

Solution:

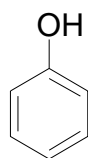


Because CH_3 — and NH_2 — are electro-donating groups, and

The NH_2 — group enlarges the conjugation system, so its ultraviolet absorption becomes larger than benzene.

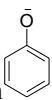
14.60 Phenol, a weak acid with $\text{p}K_a=10.0$, has a UV absorption at $\lambda_{\max}=210\text{nm}$ in the ethanol solution.

When dilute NaOH is added, the absorption increases to $\lambda_{\max}=235\text{nm}$. Explain.



Phenol

Solution:

When NaOH is added, it reacts with phenol to yield phenol anion . And the conjugation of O-C in phenol anion is stronger than it in phenol, so the λ_{max} becomes a little longer.