

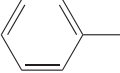
CHAPTER 8

Delocalized Electrons: Their Effect on Stability, pK_a , and the Products of a Reaction • Aromaticity and Electronic Effects: An Introduction to the Reactions of Benzene

Important Terms

1,2-addition (direct addition)	addition to the 1- and 2-positions of a conjugated system.
1,4-addition (conjugate addition)	addition to the 1- and 4-positions of a conjugated system.
aliphatic compound	an organic compound that does not contain an aromatic ring.
allene	a compound with two adjacent double bonds.
allylic carbon	a carbon adjacent to an sp^2 carbon of a carbon–carbon double bond.
allylic cation	a compound with a positive charge on an allylic carbon.
antiaromatic compound	a cyclic and planar compound with an uninterrupted cloud of π electrons containing an even number of pairs of π electrons.
antibonding molecular orbital	the molecular orbital formed when out-of-phase orbitals interact.
antisymmetric molecular orbital	a molecular orbital that does not have a plane of symmetry but would have one if half of the MO is turned upside down.
aromatic compound	a cyclic and planar compound with an uninterrupted cloud of π electrons containing an odd number of pairs of π electrons.
benzylic carbon	a carbon, joined to other atoms by single bonds, that is bonded to a benzene ring.
benzylic cation	a compound with a positive charge on a benzylic carbon.
bonding molecular orbital	the molecular orbital formed when in-phase orbitals overlap.
bridged bicyclic compound	a bicyclic compound in which the rings share two nonadjacent carbons.
common intermediate	an intermediate that reaction pathways have in common.
concerted reaction	a reaction in which all the bond-making and breaking processes occur in a single step.
conjugate addition	addition to the 1- and 4-positions of a conjugated system.
conjugated diene	a compound with two conjugated double bonds.

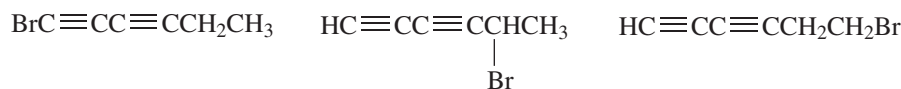
conjugated double bonds	double bonds separated by one single bond.
contributing resonance structure	a structure with localized electrons that approximates the true structure of a compound with delocalized electrons.
cumulated double bonds	double bonds that are adjacent to one another.
cycloaddition reaction	a reaction in which two π electron-containing reactants combine to form a single cyclic product.
[4 + 2] cycloaddition reaction	a cycloaddition reaction in which six π electrons participate in the transition state with four π electrons coming from one reactant and two π electrons coming from the other reactant.
delocalization energy (resonance energy)	the extra stability associated with a compound as a result of having delocalized electrons.
delocalized electrons	electrons that result from a p orbital overlapping the p orbitals of two adjacent atoms; therefore, delocalized electrons are shared by three or more atoms.
Diels–Alder reaction	a [4+2] cycloaddition reaction.
diene	a hydrocarbon with two double bonds.
dienophile	an alkene that reacts with a diene in a Diels–Alder reaction.
direct addition (1,2-addition)	addition to the 1- and 2-positions of a conjugated system.
donation of electrons by resonance	donation of electrons through π bonds.
electron delocalization	the sharing of electrons by more than two atoms.
endo	a substituent is endo if it and the bridge are on opposite sides of a bicyclic compound.
equilibrium control	thermodynamic control.
exo	a substituent is exo if it and the bridge are on the same side of a bicyclic compound.
fused rings	rings that share two adjacent carbons.
highest occupied molecular orbital (HOMO)	the highest-energy molecular orbital that contains electrons.
heteroatom	an atom other than carbon.
heterocyclic compound (heterocycle)	a cyclic compound in which one or more of the atoms of the ring is a heteroatom.

Hückel's rule or the $4n + 2$ rule	a rule that gives the number of π electrons a compound must have in its π cloud to be aromatic.
isolated double bonds	double bonds separated from one another by more than one single bond.
kinetic control	when a reaction is under kinetic control, the relative amounts of the products depend on the rates at which they are formed.
kinetic product	the product that is formed the fastest.
linear combination of molecular orbitals (LCAO)	the combination of atomic orbitals to produce molecular orbitals.
localized electrons	electrons that are restricted to a particular locality.
lowest unoccupied molecular orbital (LUMO)	the lowest-energy molecular orbital that does not contain electrons.
pericyclic reaction	a reaction that takes place in one step as a result of a cyclic reorganization of electrons.
phenyl group	 $\text{C}_6\text{H}_5\text{—}$
polyene	a compound that has several double bonds.
polymer	a large molecule made by linking many small molecules together.
polymerization	the process of linking many small molecules to form a polymer.
proximity effect	an effect caused by one species being close to another.
resonance	electron delocalization.
resonance contributor (resonance structure)	a structure with localized electrons that approximates the true structure of a compound with delocalized electrons.
resonance electron donation	donation of electrons through π bonds.
resonance electron withdrawal	withdrawal of electrons through π bonds.
resonance energy (delocalization energy) (resonance stabilization energy)	the extra stability a compound possesses as a result of having delocalized electrons.

resonance hybrid	the actual structure of a compound with delocalized electrons; it is represented by two or more resonance contributors with localized electrons.
<i>s</i>-cis-conformation	the conformation in which two double bonds of a conjugated diene are on the same side of a connecting single bond.
separated charges	a positive and a negative charge that can be neutralized by the movement of electrons.
<i>s</i>-trans-conformation	the conformation in which two double bonds of a conjugated diene are on opposite sides of a connecting single bond.
symmetric molecular orbital	an orbital with a plane of symmetry so that one half is the mirror image of the other half.
thermodynamic control	when a reaction is under thermodynamic control, the relative amounts of the products depend on their stabilities.
thermodynamic product	the most stable product.
withdrawal of electrons by resonance	withdrawal of electrons through π bonds.

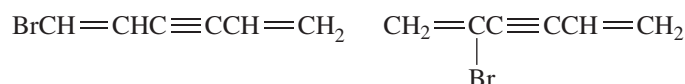
Solutions to Problems

1. a. 1. If stereoisomers are not included, three different monosubstituted compounds are possible.



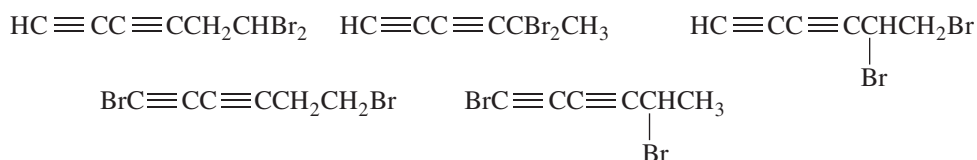
If stereoisomers are included, four different monosubstituted compounds are possible, because the second listed compound has an asymmetric center so that it can have both the *R* and *S* configuration.

2. If stereoisomers are not included, two different monosubstituted compounds are possible.

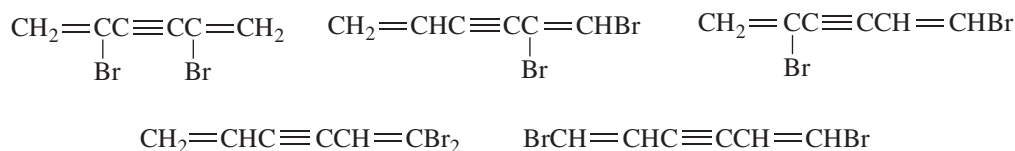


If stereoisomers are included, three different monosubstituted compounds are possible, because the first listed compound has a double bond that can have cis-trans isomers.

- b. 1. If stereoisomers are not included, five different disubstituted compounds are possible.

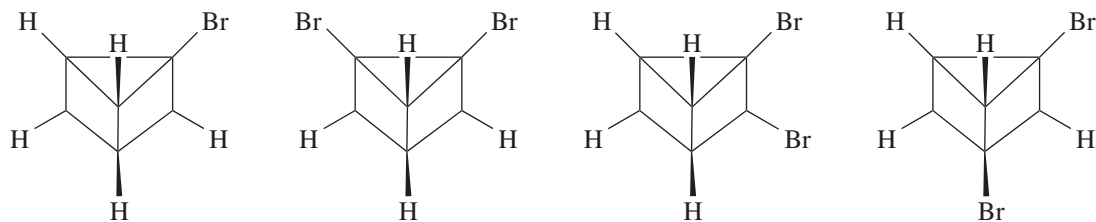


2. If stereoisomers are not included, five different disubstituted compounds are possible.

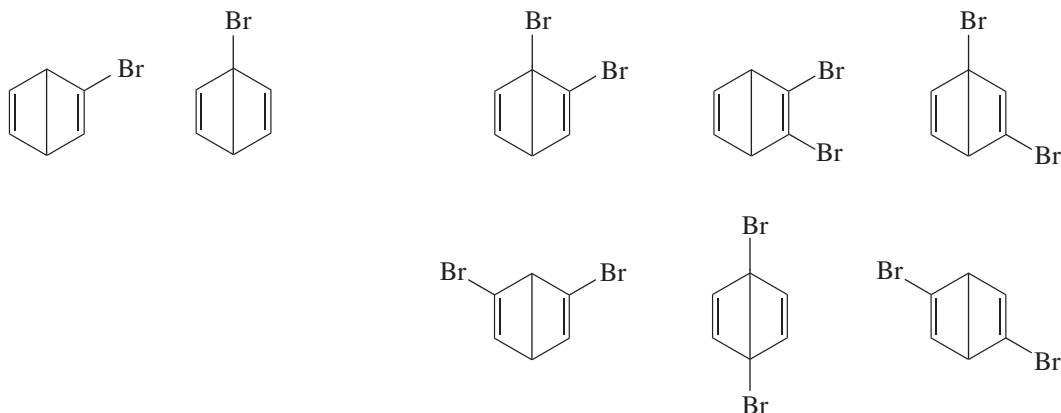


- c. 1. If stereoisomers are included, seven different disubstituted compounds are possible, because two of the compounds have asymmetric centers so each can have either the *R* or *S* configuration.
2. If stereoisomers are included, nine different disubstituted compounds are possible, because the second and third compounds can have cis-trans isomers and the fifth compound can have cis-cis, trans-trans, and cis-trans isomers. (Note that cis-trans is the same as trans-cis.)

2. Ladenburg benzene is a better proposal. It would form one monosubstituted compound and three disubstituted compounds, in accordance with what early chemists knew about the structure of benzene.

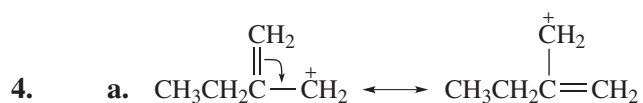
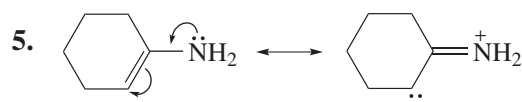
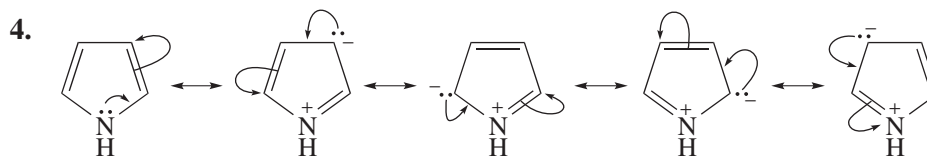
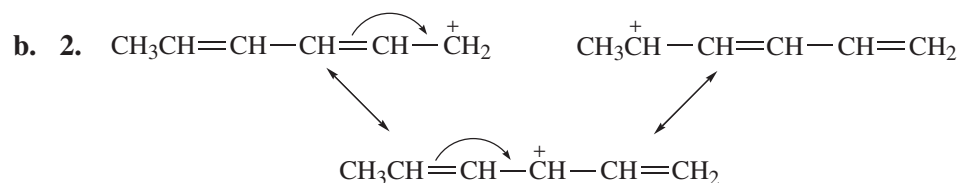


Dewar benzene is not in accordance with what early chemists knew about the structure of benzene, because it would form two monosubstituted compounds and six disubstituted compounds and it would undergo electrophilic addition reactions.



3. a. **2, 4, and 5** have delocalized electrons.

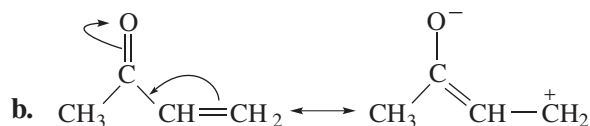
1, 3, 6, and 7 do not have delocalized electrons, because electrons cannot be moved to an sp^3 carbon.



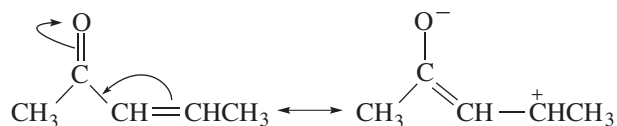
Less stable, because the positive charge is shared by two primary allylic carbons.



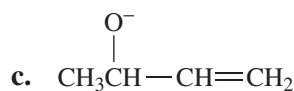
More stable, because the positive charge is shared by a primary allylic and a secondary allylic carbon.



Less stable, because the positive charge is on a primary allylic carbon.



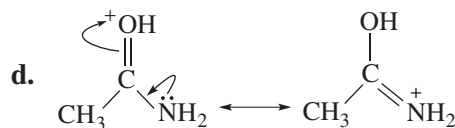
More stable, because the positive charge is on a secondary allylic carbon.



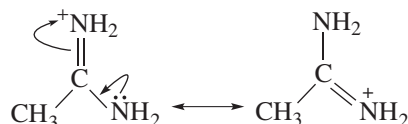
Less stable, because the negative charge is not delocalized.



More stable, because the negative charge is delocalized.



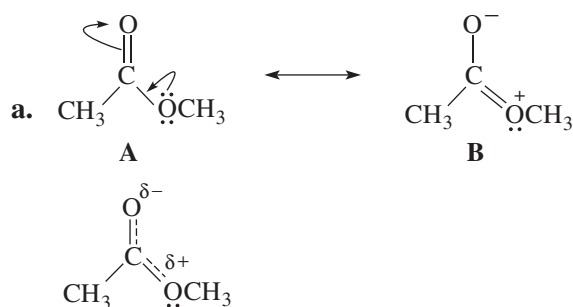
Less stable, because the positive charge is shared by an O and an N.



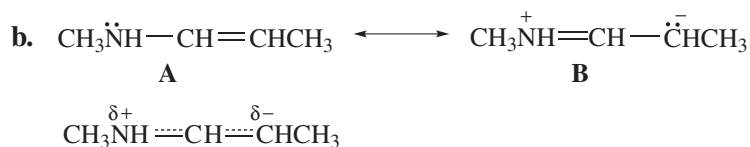
More stable, because the positive charge is shared by two nitrogens. Nitrogen is less electronegative than oxygen, so nitrogen is more comfortable with a positive charge.

5. Solved in the text.

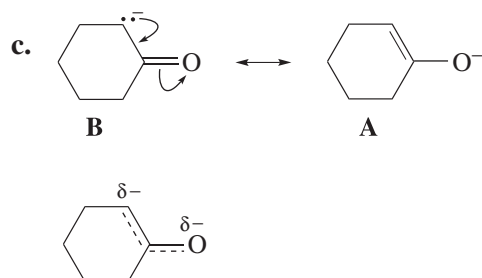
6. The resonance contributor that makes the greatest contribution to the hybrid is labeled **A**. **B** contributes less to the hybrid than **A**, and **C** contributes less to the hybrid than **B**.



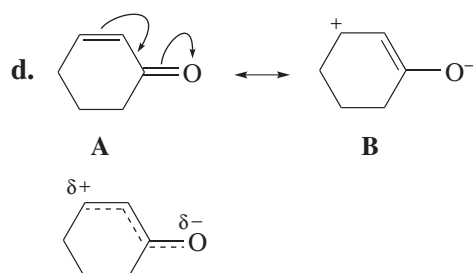
A is more stable than **B** because **B** has separated charges and has a positive charge on an oxygen.



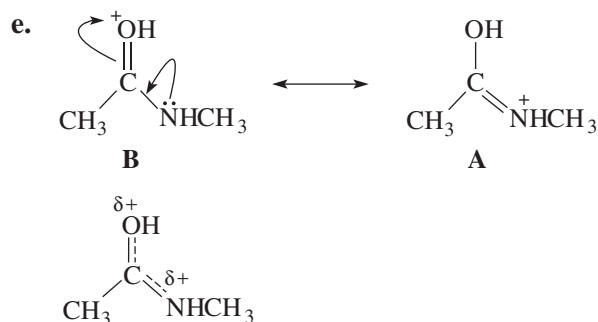
A is more stable than **B** because **B** has separated charges and a positive charge on a nitrogen.



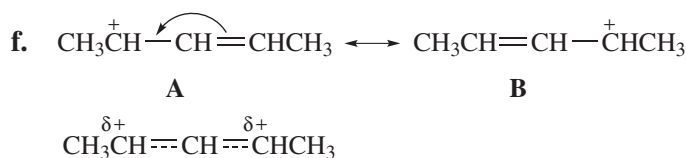
A is more stable than **B** because the negative charge in **A** is on an oxygen, whereas the negative in **B** is on carbon, which is less electronegative than oxygen.



A is more stable than **B** because **A** does not have separated charges and **B** has an atom with an incomplete octet.

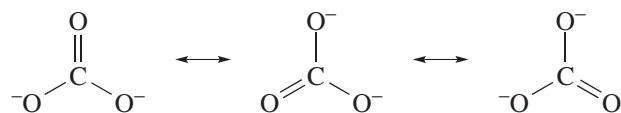


A is more stable than **B** because the positive charge in **A** is on a less electronegative atom. (N is less electronegative than O.)

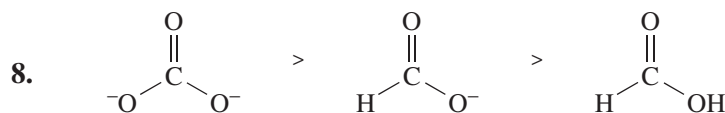


A and **B** are equally stable.

7. a. All the carbon–oxygen bonds in the carbonate ion are the same length, because each carbon–oxygen bond is represented in one resonance contributor by a double bond and in two resonance contributors by a single bond.



- b. Because the two negative charges are shared equally by three oxygens, each oxygen has two-thirds of a negative charge.

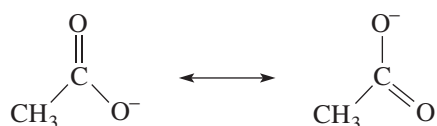


The dianion has the greatest delocalization energy; it has three relatively stable resonance contributors. (See the answer to Problem 7.)

The monoanion is the next most stable; it has two relatively stable resonance contributors.

The neutral species has the smallest delocalization energy; it has one relatively stable resonance contributor and one that has separated charges.

9. The carboxylate ion has the greater delocalization energy because it has two equivalent relatively stable resonance contributors.



In contrast, the diene has three resonance contributors but only one is relatively stable (see the top of page 330 in the text).

10. The compound on the left has the greater delocalization energy because the lone-pair electrons on oxygen are delocalized, whereas the lone-pair electrons on oxygen in the compound on the right are not delocalized.

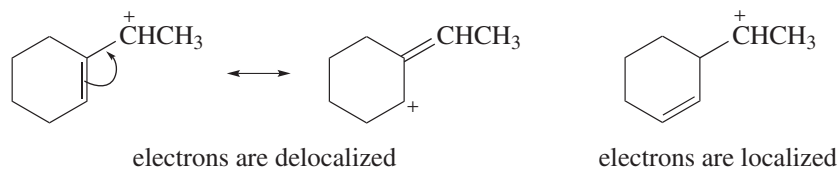


11. The smaller the heat of hydrogenation (the positive value of ΔH°), the more stable the compound. Therefore, the relative stabilities of the dienes are

conjugated diene > isolated diene > cumulated diene

12. $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}=\text{C}(\text{CH}_3)_2 > \text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_3 > \text{CH}_3\text{CH}=\text{CHCH}=\text{CH}_2 > \text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2$
 2,5-dimethyl-2,4-hexadiene 2,4-hexadiene 1,3-pentadiene 1,4-pentadiene

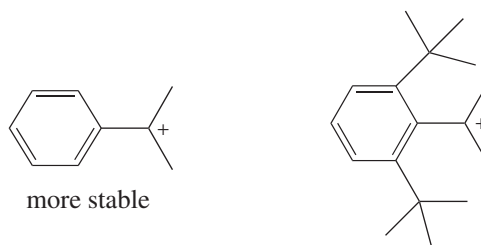
13. a. The compound with delocalized electrons is more stable than the compound in which all the electrons are localized.



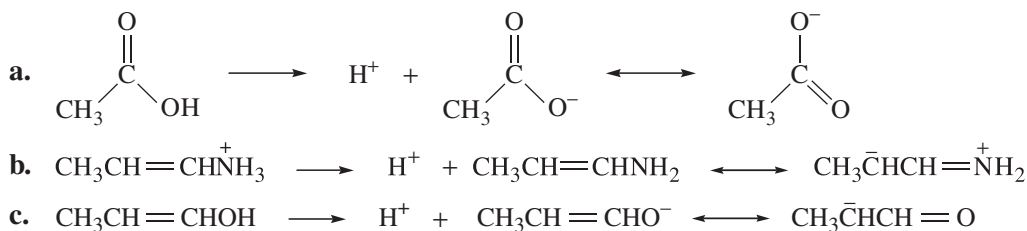
- b. Because nitrogen is less electronegative than oxygen, it shares the positive charge better.



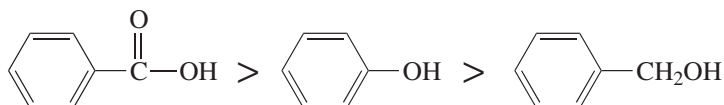
- c. In order for electron delocalization to occur, the atoms that share the π electrons must be in the same plane so that their p orbitals can overlap. The two bulky *tert*-butyl groups do not allow enough room for the group with the positively charged carbon to be in the same plane as the benzene ring. Therefore, the carbocation cannot be stabilized by electron delocalization because the p orbital of the positively charged carbon cannot overlap the p orbitals of the benzene ring since they are not in the same plane.



14. The ψ_3 molecular orbital of 1,3-butadiene has three nodes (two vertical and one horizontal).
The ψ_4 molecular orbital of 1,3-butadiene has four nodes (three vertical and one horizontal).
15. a. ψ_1 and ψ_2 are bonding molecular orbitals, and ψ_3 and ψ_4 are antibonding molecular orbitals.
b. ψ_1 and ψ_3 are symmetric molecular orbitals, and ψ_2 and ψ_4 are antisymmetric molecular orbitals.
c. ψ_2 is the HOMO and ψ_3 is the LUMO in the ground state.
d. ψ_3 is the HOMO and ψ_4 is the LUMO in the excited state.
e. If the HOMO is symmetric, the LUMO is antisymmetric and vice versa.
16. Benzene is more stable than 1,3,5-hexatriene because the MO of benzene has six bonding interactions, whereas the MO of 1,3,5-hexatriene has only five bonding interactions.
17. In each case, the compound shown is the stronger acid because the negative charge that results when it loses a proton can be delocalized. Electron delocalization stabilizes the base, and the more stable the base, the more acidic its conjugate acid. Electron delocalization is not possible for the other compound in each pair.



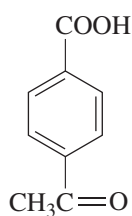
18. a. Ethylamine is a stronger base because when the lone pair on the nitrogen in aniline is protonated, it can no longer be delocalized into the benzene ring. Therefore, aniline is less apt to share its electrons with a proton.
 b. Ethoxide ion is a stronger base because a negatively charged oxygen is a stronger base than a neutral nitrogen.
 c. Ethoxide ion is a stronger base because when the phenolate ion is protonated, the pair of electrons that is protonated can no longer be delocalized into the benzene ring. Therefore, the phenolate ion is less apt to share its electrons with a proton.
 d. Phenolate ion is the stronger base because its conjugate acid is a weaker acid than the conjugate acid of acetate ion.
19. The carboxylic acid is the most acidic because its conjugate base has greater delocalization energy than does the conjugate base of phenol. The alcohol is the least acidic because, unlike the negative charge on the conjugate base of phenol, the negative charge on the conjugate base of the alcohol cannot be delocalized.



20. a. donates electrons by resonance and withdraws electrons inductively
 b. donates electrons by hyperconjugation
 c. withdraws electrons by resonance and withdraws electrons inductively
 d. donates electrons by resonance and withdraws electrons inductively
 e. donates electrons by resonance and withdraws electrons inductively
 f. withdraws electrons inductively

21. a. ClCH_2COOH

c.



e.

HCOOH

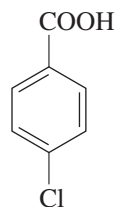
A hydrogen is electron-withdrawing compared to a methyl group, because a methyl group can donate electrons by hyperconjugation.

- b. $\text{O}_2\text{NCH}_2\text{COOH}$

The closer the electron-withdrawing substituent is to the COOH group, the stronger the acid.

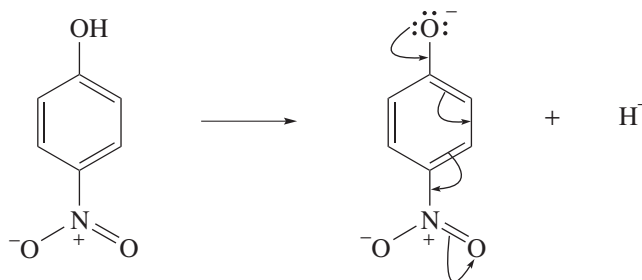
- d. $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$

- f.

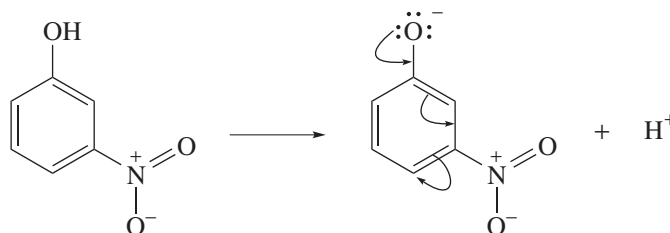


22. Solved in the text.

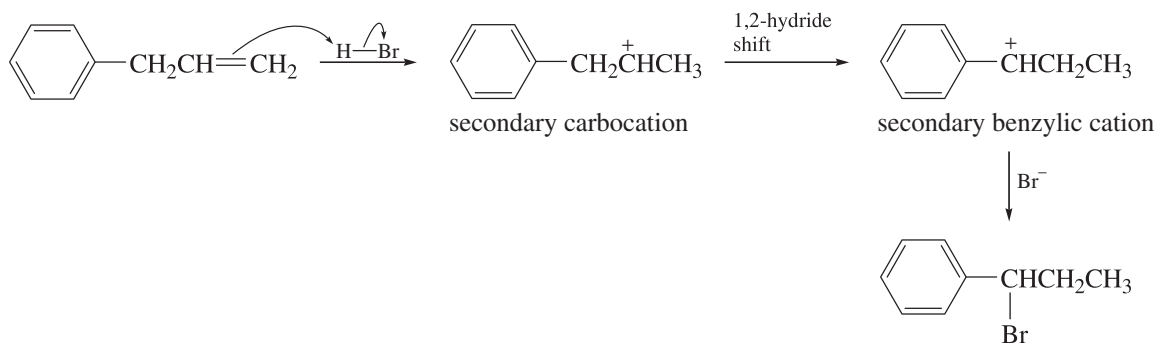
23. When *para*-nitrophenol loses a proton, the negative charge in the conjugate base can be delocalized onto the nitro substituent. Therefore, the *para*-nitro substituent decreases the pK_a both by resonance electron withdrawal and by inductive electron withdrawal.



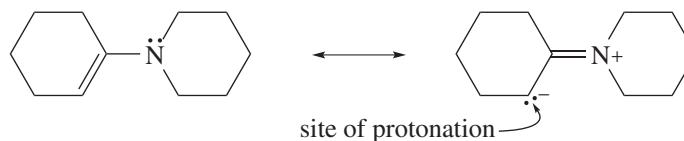
When *meta*-nitrophenol loses a proton, the negative charge in the conjugate base cannot be delocalized onto the nitro substituent. Therefore, the *meta*-nitro substituent can decrease the pK_a only by inductive electron withdrawal. Therefore, the *para* isomer has a lower pK_a .



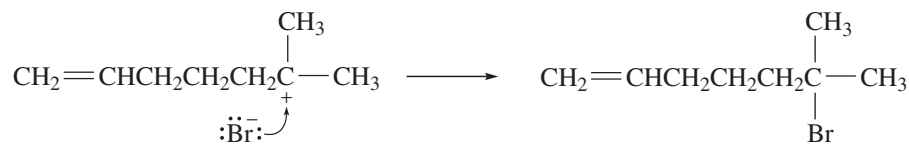
24. Recall that if a more stable carbocation can be formed as a result of carbocation rearrangement, rearrangement will occur.



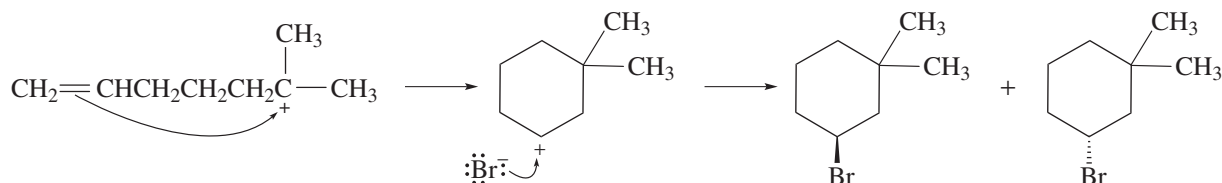
25. Solved in the text.
26. The resonance contributors show that one of the atoms has a partial negative charge. Therefore, that is the atom that is more apt to be protonated.



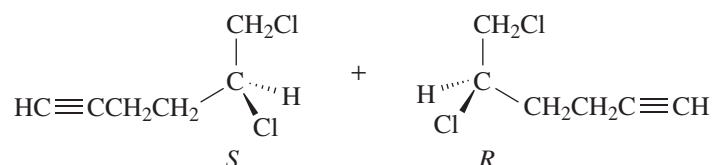
27. a. The more reactive double bond is the one that forms a tertiary carbocation.



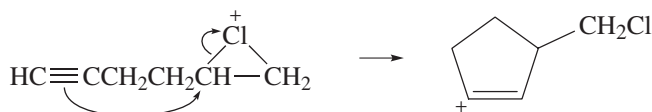
Instead of Br^- being the nucleophile that adds to the tertiary carbon, the π bond can be the nucleophile. In that case, a stable six-membered ring is formed. (See the Problem-Solving Strategy on page 257 of the text.) This is expected to be a minor product because, unlike the above reaction of the carbocation with Br^- , bond breaking is required to form the product.



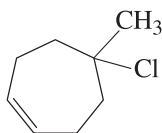
- b. The double bond is more reactive than the triple bond. The reaction forms a new asymmetric center, so a pair of enantiomers is formed.



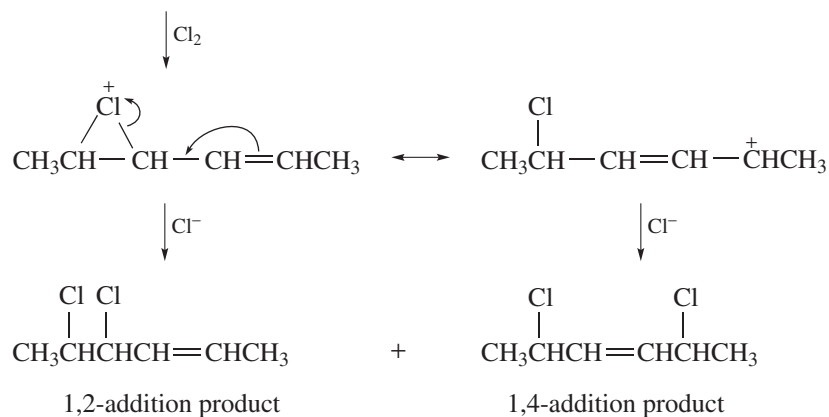
It is unlikely that the triple bond will act as a nucleophile, because it would have to form an unstable vinylic cation intermediate.

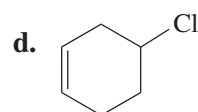
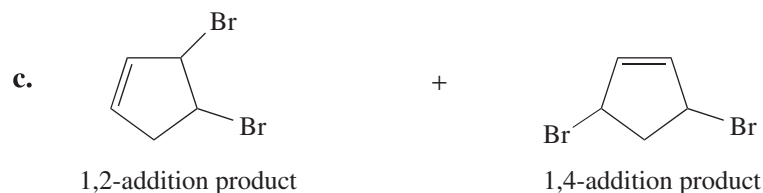
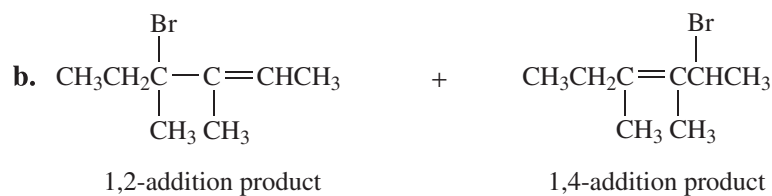


- c. The more reactive double bond is the one that forms a tertiary carbocation.

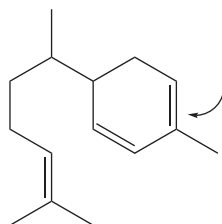


28. a. $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CHCH}_3$





29. The indicated double bond is the most reactive in an electrophilic addition reaction with HBr because addition of an electrophile to this double bond forms the most stable carbocation (a tertiary allylic cation).



30. first reaction:
- $$\begin{array}{c} \text{CH}_2-\overset{*}{\text{CH}}-\text{CH}=\text{CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$$

This compound has an asymmetric center, so both the *R* and *S* stereoisomers will be obtained. (Note that *E* and *Z* stereoisomers are not possible for the double bond.)

$$\begin{array}{c} \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \\ | \quad \quad | \\ \text{Cl} \quad \quad \text{Cl} \end{array}$$

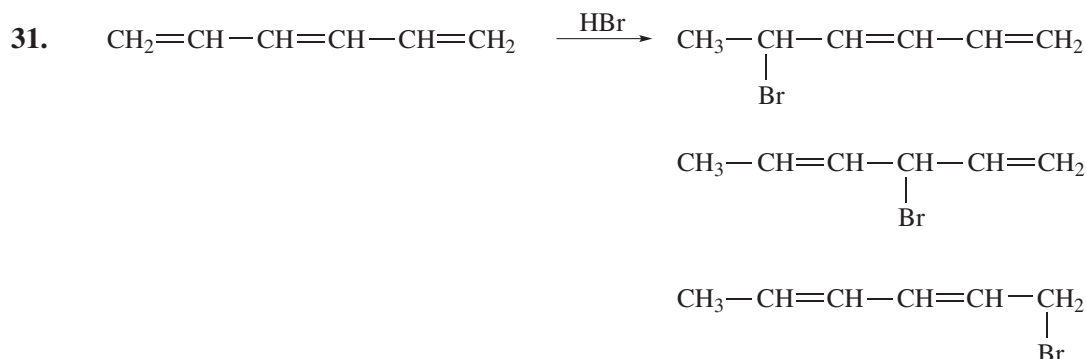
This compound has a double bond, so both the *E* and *Z* stereoisomers will be obtained.

- second reaction:
- $$\begin{array}{c} \text{CH}_3-\overset{*}{\text{CH}}-\text{CH}=\text{CH}_2 \\ | \\ \text{Br} \end{array}$$

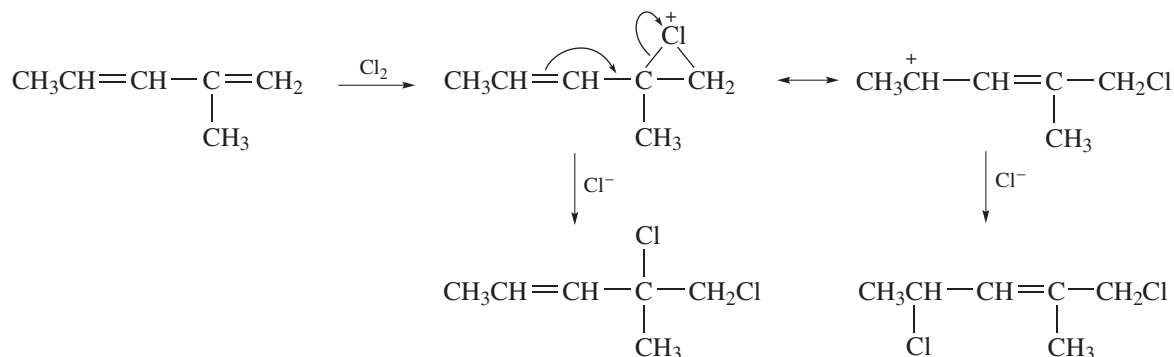
This compound has an asymmetric center, so both the *R* and *S* stereoisomers will be obtained. (Note that *E* and *Z* stereoisomers are not possible for the double bond.)

$$\begin{array}{c} \text{CH}_3\text{CH}=\text{CH}-\text{CH}_2 \\ | \\ \text{Br} \end{array}$$

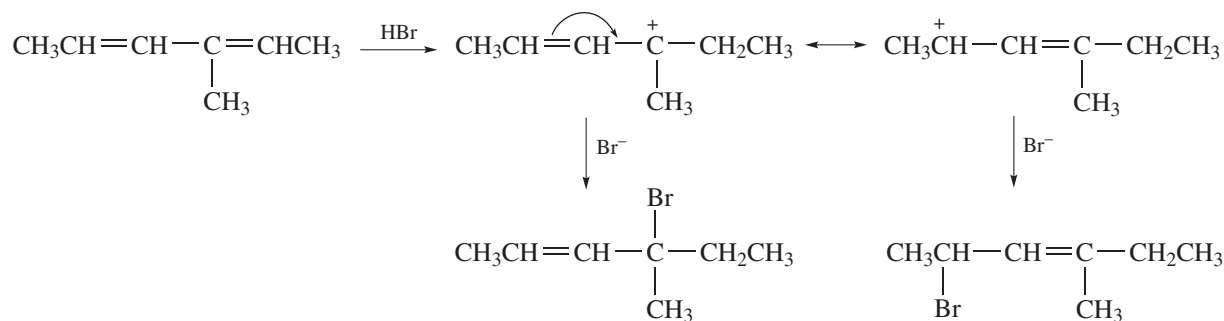
This compound has a double bond, so both the *E* and *Z* stereoisomers will be obtained.



32. a. The chlorine adds so that the positive charge in the resonance contributor is on a secondary allylic carbon. (If the chlorine had added to the other double bond, the positive charge would be on a primary allylic carbon.)

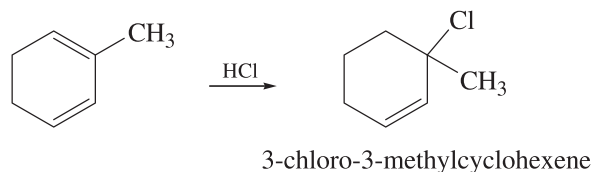


- b. The proton adds so that the positive charge in the carbocation is shared by a tertiary allylic and a secondary allylic carbon. (If the proton had added to the other double bond, the positive charge would be shared by two secondary allylic carbons.)

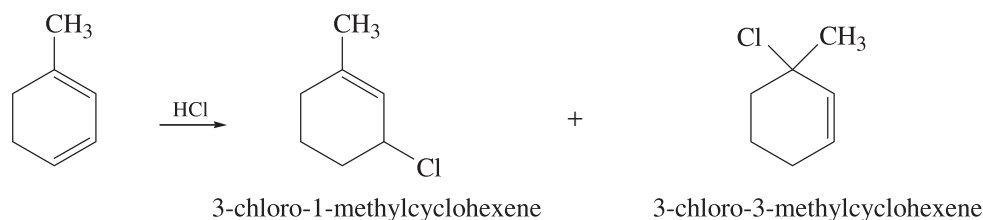


33. a. Addition at C-1 forms the more stable carbocation because the positive charge is shared by two secondary allylic carbons. If the deuterium had added to C-4, the positive charge would be shared by a secondary allylic and a primary allylic carbon.
- b. DCl was used to cause the 1,2- and 1,4-products to be different. If HCl had been used, the 1,2- and 1,4-products would be the same.

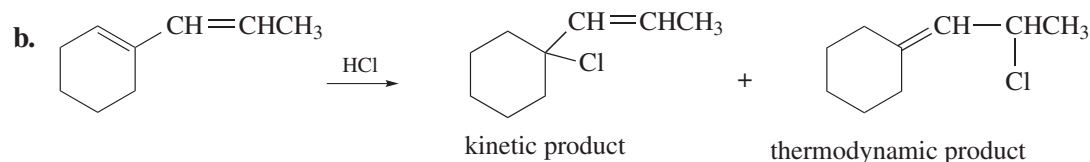
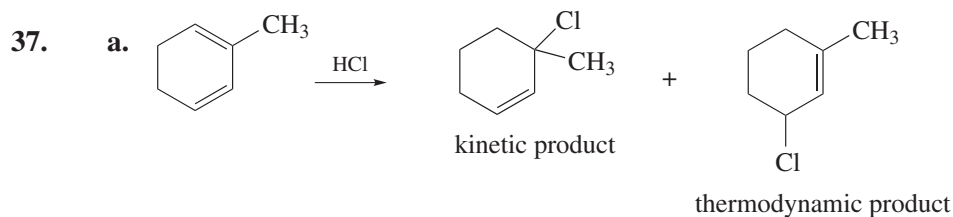
34. She should follow her friend's advice. If she uses 2-methyl-1,3-cyclohexadiene, the fastest formed product will be 3-chloro-3-methylcyclohexene, both if the proximity effect controls which product is formed faster *and* if the more stable transition state controls which product is formed faster, because this product is formed through a transition state in which the positive charge is primarily on a tertiary allylic carbon. Therefore, the experiment will not be able to establish which of the two effects controls which product is formed faster.



If she follows her friend's advice and uses 1-methyl-1,3-cyclohexadiene, the faster-formed product will be 3-chloro-1-methylcyclohexene only if the proximity effect controls which product is formed faster. The product will be 3-chloro-3-methylcyclohexene if the more stable transition state controls which product is formed faster, because only this product is formed through a transition state in which the positive charge is primarily on a tertiary allylic carbon.



35. a. The rate-determining step is formation of the carbocation.
 b. The product-determining step is reaction of the carbocation with the nucleophile.
36. Solved in the text.



Notice that the 1,2-product is always the kinetic product.
 The thermodynamic product is the product with the most highly substituted double bond.

38.



kinetic product

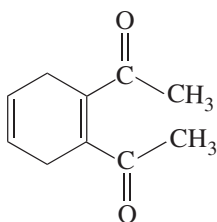
thermodynamic product

The first compound is the kinetic product because it is the 1,2-product.

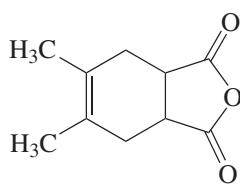
The first compound is the thermodynamic product because it is more stable since the double bond is conjugated with the benzene ring.

39.

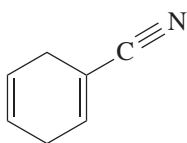
a.



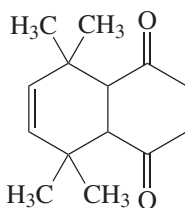
c.



b.

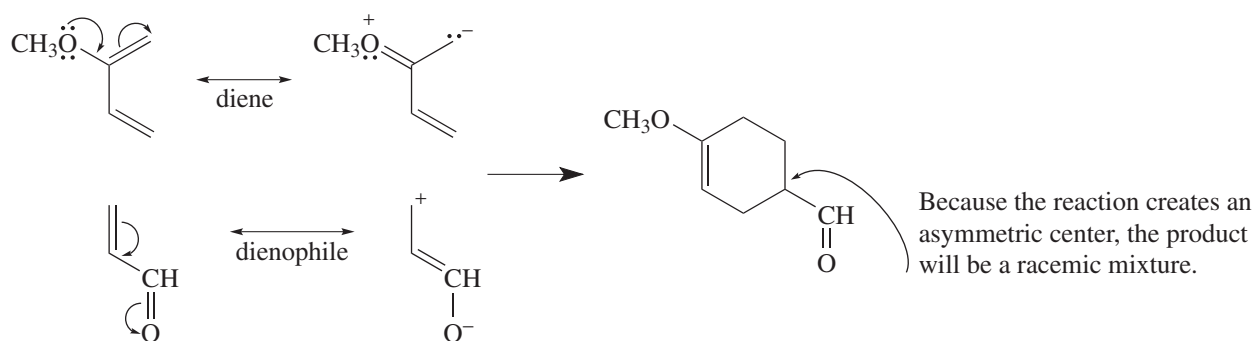


d.

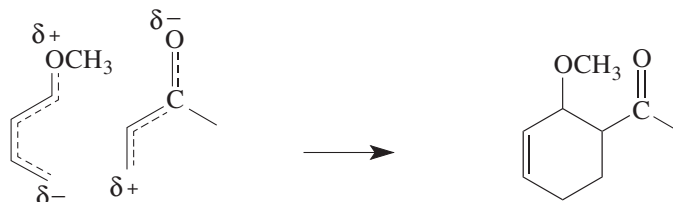


40.

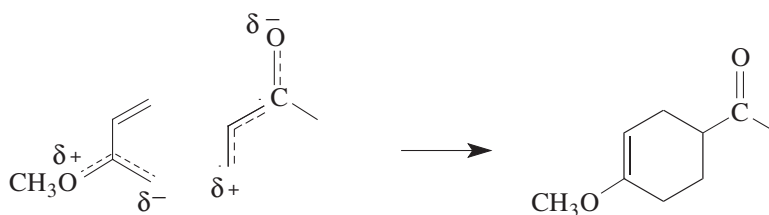
First draw the resonance contributors to determine where the charges are on the reactants. The major product is obtained by joining the negatively charged carbon of the diene with the positively charged carbon of the dienophile.



41. The resonance contributors show that if the electron-donating substituent is at the end of the conjugated system, it and the electron-withdrawing substituent of the dienophile will be adjacent to one another in the major product of the Diels–Alder reaction.



If the electron-donating substituent is not at the end of the conjugated system, it and the electron-withdrawing substituent of the dienophile will be opposite each other in the major product of the Diels–Alder reaction.



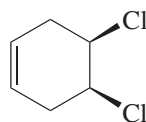
42. a. b.

43. A and C will not react, because they are both locked in an *s*-trans conformation.
D and E will react, because they are both locked in an *s*-cis conformation.
B and F will react, because they can rotate into an *s*-cis conformation.

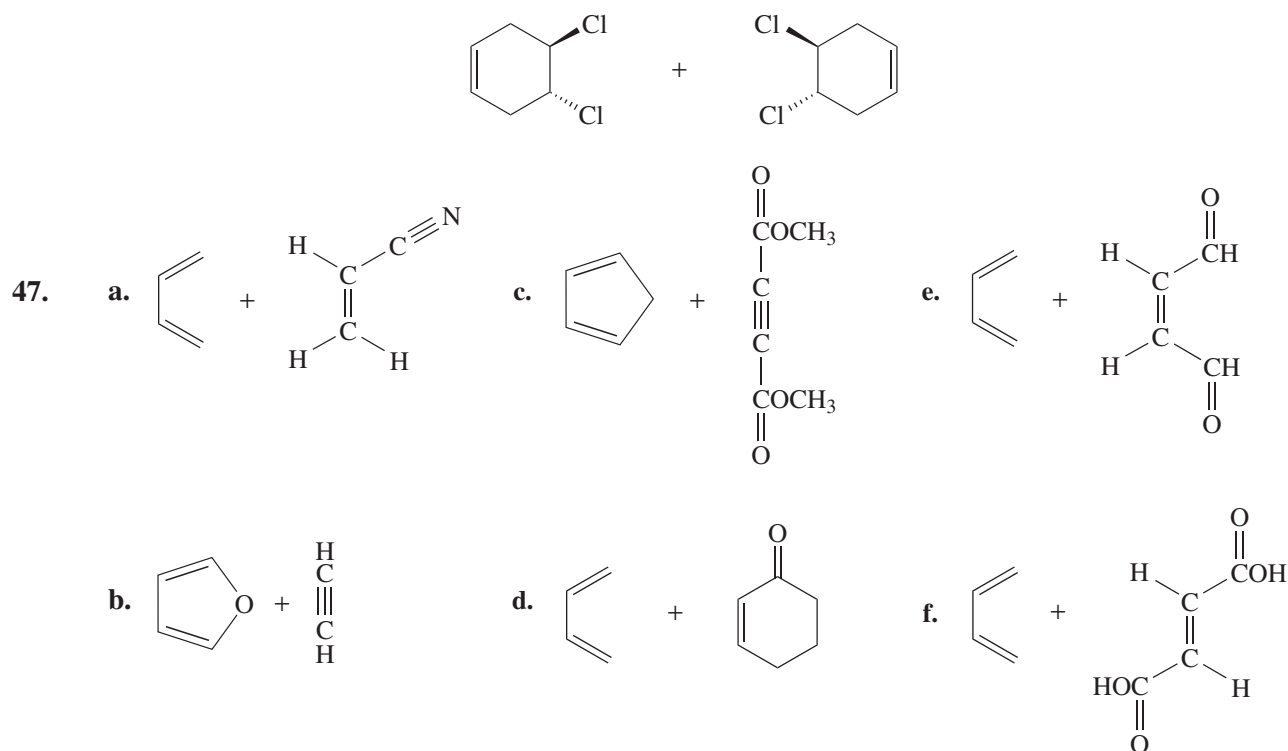
44. a. b.

45. Solved in the text.

46. a. It is not optically active, because it is a meso compound.
(It has two asymmetric centers and a plane of symmetry.)



- b. It is not optically active, because it is a racemic mixture.
(Identical amounts of the enantiomers will be obtained.)




48. None are aromatic.

c is not aromatic, because it has two pairs of π electrons.

a, b, d, and e are not aromatic, because each compound has two pairs of π electrons and every atom in the ring does not have a p orbital.

f is not aromatic, because it is not cyclic.

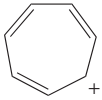
49. a. In the case of 9 pairs of π electrons, there are 18 electrons. Therefore, $4n + 2 = 18$ where $n = 4$.
b. Because it has an odd number of pairs of π electrons, it will be aromatic if it is cyclic and planar and if every atom in the ring has a p orbital.

50. a.  +

This is the only one that is aromatic; it is cyclic, it is planar, every ring atom has a p orbital, and it has one pair of π electrons.

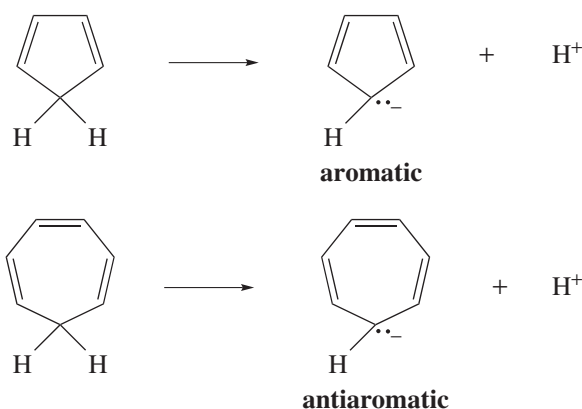
The first compound is not aromatic, because one of the atoms is sp^3 hybridized and, therefore, does not have a p orbital.

The third compound is not aromatic, because it has two pairs of π electrons.

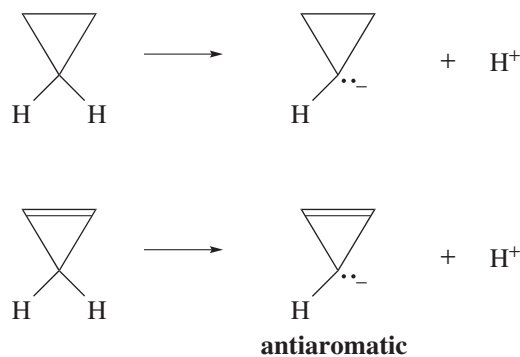
- b.  This is the only one that is aromatic; it is cyclic, it is planar, every ring atom has a p orbital, and it has three pairs of π electrons.
- The first compound is not aromatic, because one of the atoms is sp^3 hybridized and, therefore, does not have a p orbital.
- The third compound is not aromatic, because it has four pairs of π electrons.

51. Solved in the text.

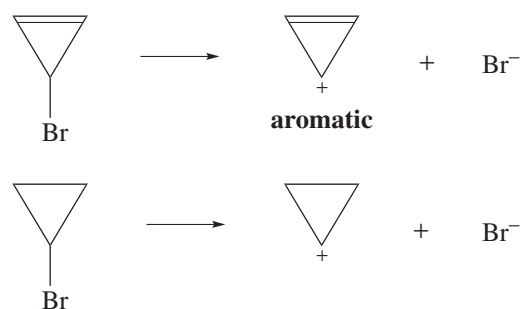
52. a. Cyclopentadiene has a lower pK_a value. That is, it is a stronger acid. When cyclopentadiene loses a proton, a relatively stable aromatic compound is formed. When cycloheptatriene loses a proton, an unstable antiaromatic compound is formed (Section 8.19). Recall that the more stable the base, the stronger its conjugate acid.



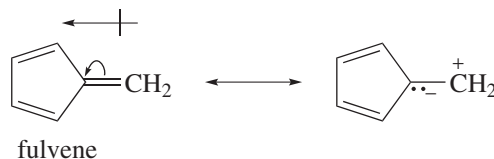
- b. Cyclopropane has a lower pK_a value because a very unstable antiaromatic compound is formed when cyclopropene loses a proton.



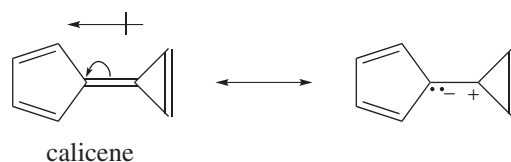
53. 3-Bromocyclopropene is more soluble in water because it is more apt to ionize since an aromatic compound is formed when its carbon–bromine bond breaks.



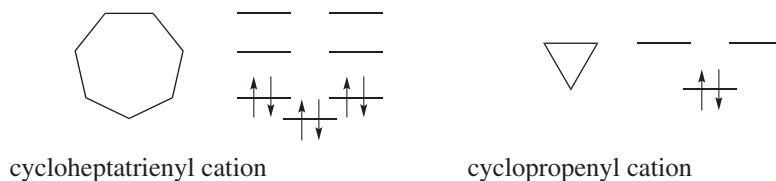
54. a. In fulvene, the electrons in the exocyclic double bond (a double bond attached to a ring) move toward the five-membered ring, because that results in a resonance contributor that is aromatic. Moving the electrons in the other direction would result in a resonance contributor with an antiaromatic ring.



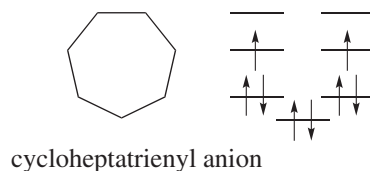
- b. In calicene, the electrons in the double bond between the two rings move toward the five-membered ring, because that results in a resonance contributor with two aromatic rings.



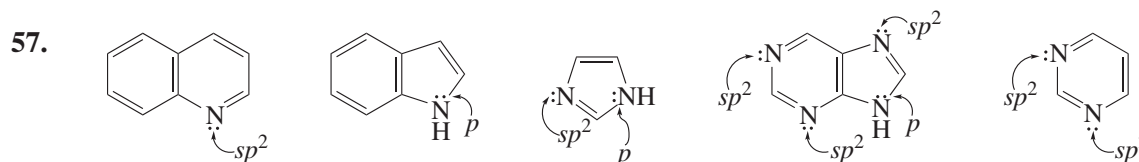
55. The Frost circles show that species with completely filled bonding MOs and with electrons in no other orbitals are aromatic (for example, the cycloheptatrienyl cation and the cyclopropenyl cation).



The species with unpaired electrons in degenerate MOs is antiaromatic (the cycloheptatrienyl anion).



56. a. $\text{CH}_3\text{CH}_2\ddot{\text{N}}\text{H}_2$ sp^3 b. $\text{Cyclohexyl}-\text{CH}=\ddot{\text{N}}\text{CH}_2\text{CH}_3$ sp^2 c. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N:}$ sp



58. Solved in the text.

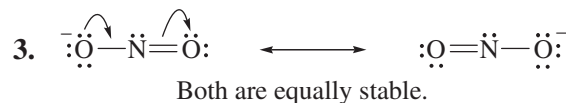
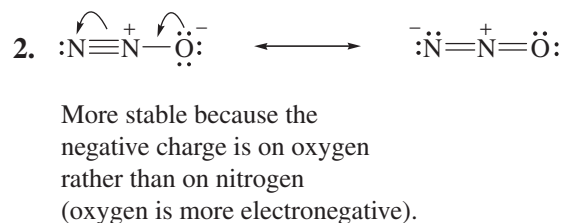
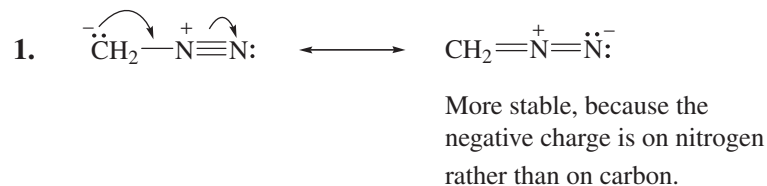
59. The lone-pair electrons on both nitrogens in the second compound are sp^2 electrons; therefore, they are not part of the π cloud and can be protonated without destroying the compound's aromaticity.

The lone-pair electrons on the nitrogen in the first compound are π electrons and are part of the π cloud. If these π electrons are protonated, they will no longer be part of the π cloud (they cannot be delocalized) and the compounds will not be aromatic.

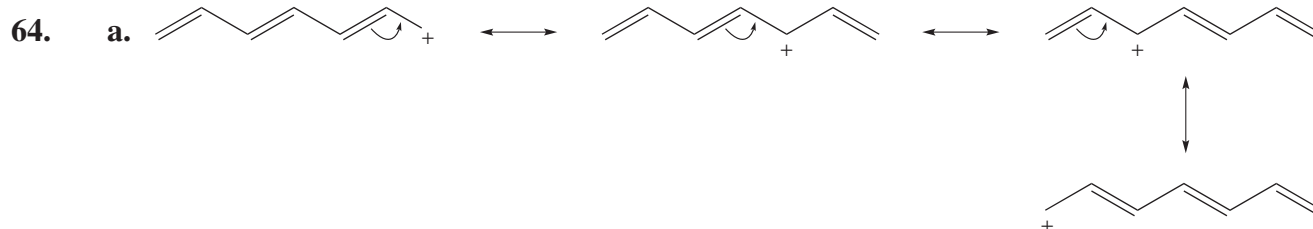
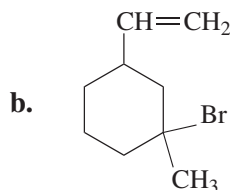
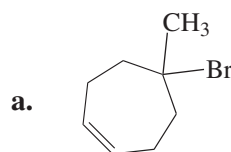
60. a. The nitrogen atom (the atom at the bottom of the epm) in pyrrole has a partial positive charge because it donates electrons by resonance into the ring.
- b. The nitrogen atom (the atom at the bottom of the epm) in pyridine cannot donate electrons by resonance; it withdraws electrons from the ring inductively because it is the most electronegative atom in the molecule. Thus, this nitrogen is electron-rich.
- c. The relatively electronegative nitrogen atom in pyridine withdraws electrons from the ring.

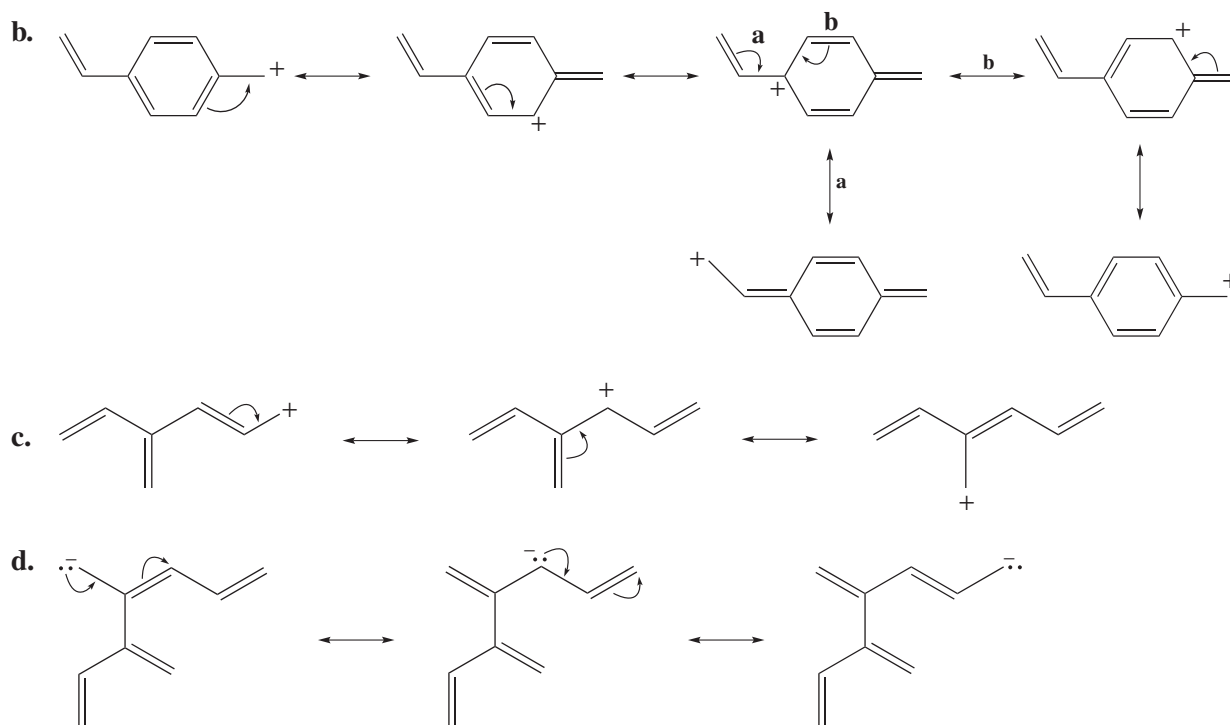
61. A, B, C, E, F, L, M, N, O

62. a and b.

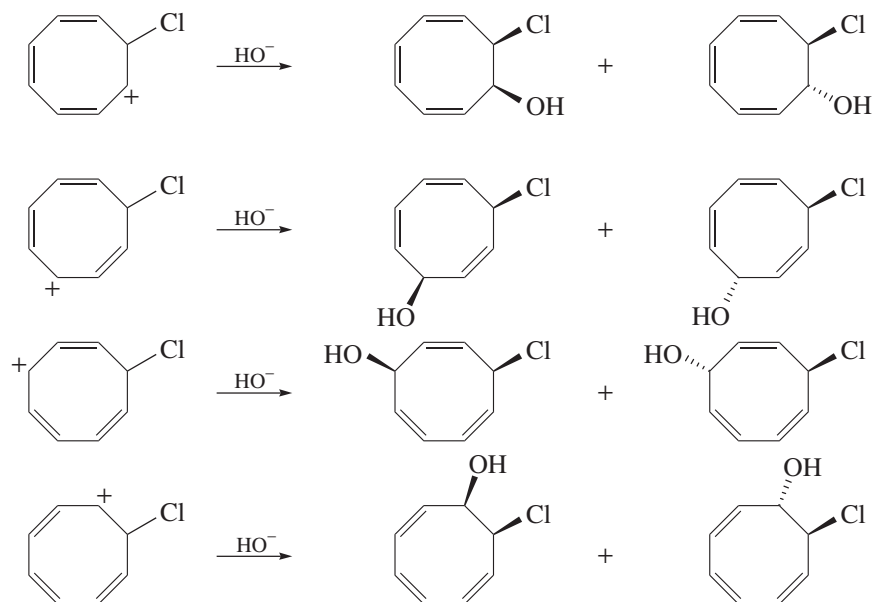


63. In each case, the proton adds to the sp^2 carbon that results in formation of a tertiary carbocation.





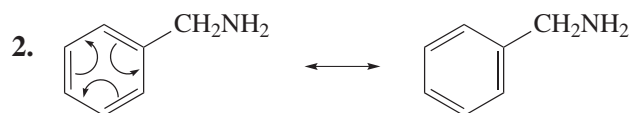
- 65.** Draw the resonance contributors. Then have the Cl pointing up in all the products, with the OH pointing up in one product and down in the other. Notice that the products in row 4 are the mirror images of the products in row 1 and that the products in row 3 are the mirror images of the products in row 2. (The same products would be obtained if the Cl pointed down in all the products with the OH pointing up in one structure and down in the other.)



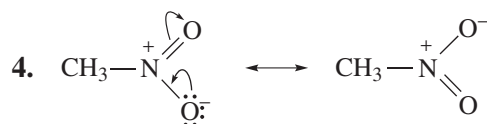
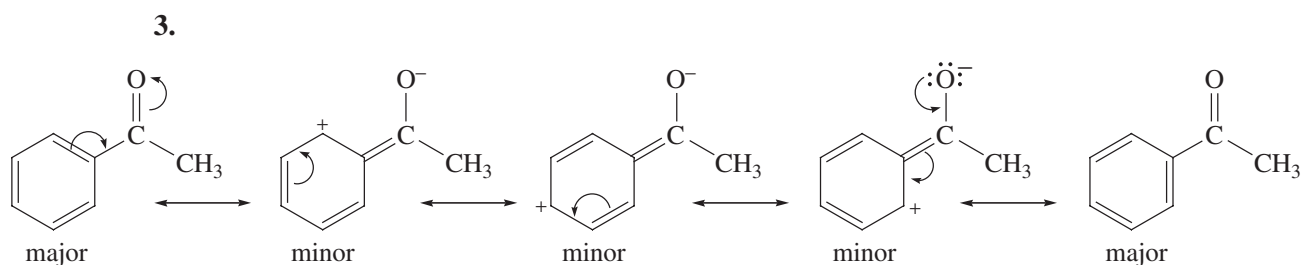
66. a. different compounds d. resonance contributors
 b. different compounds e. different compounds
 c. resonance contributors

Notice that in the structures that are different compounds, both atoms and electrons have changed their locations. In the structures that are resonance contributors, only the electrons have moved.

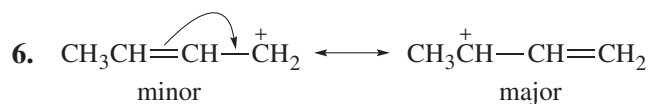
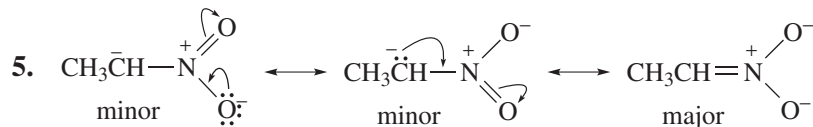
- 67.**
- a.** There are six linear dienes with molecular formula C_6H_{10} .
- b.** Two are conjugated dienes.
- c.** Two are isolated dienes.
- d.** Two are cumulated dienes.
- $CH_2=CHCH=CHCH_2CH_3$
 $CH_3CH=CHCH=CHCH_3$
- $CH_2=CHCH_2CH=CHCH_3$
 $CH_2=CHCH_2CH_2CH=CH_2$
- $CH_2=C=CHCH_2CH_2CH_3$
 $CH_3CH=C=CHCH_2CH_3$

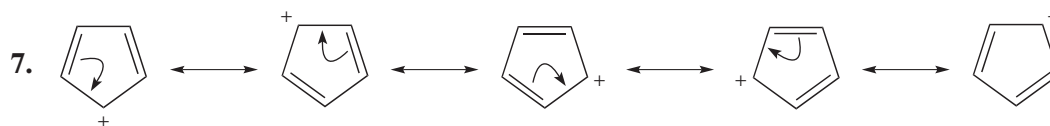


The two resonance contributors have the same stability and, therefore, contribute equally to the resonance hybrid.

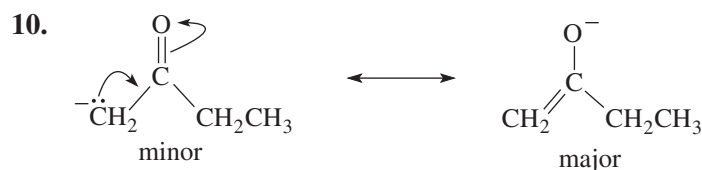
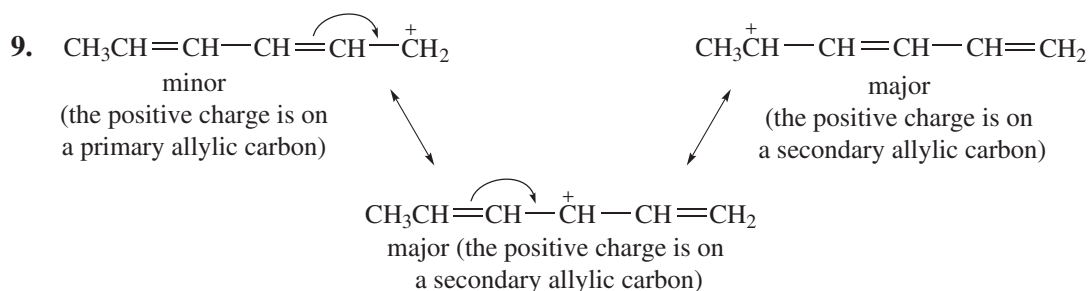
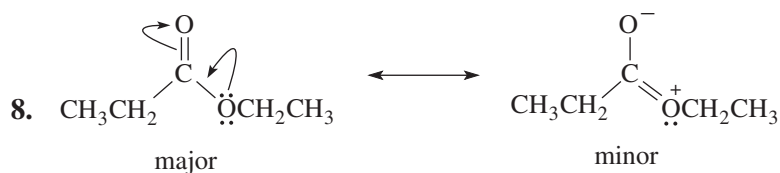


The two resonance contributors have the same stability and, therefore, contribute equally to the hybrid.

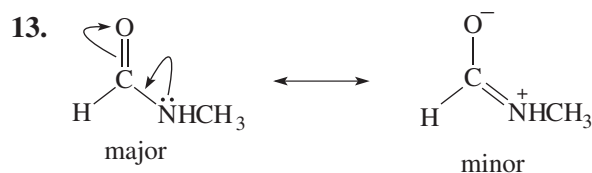
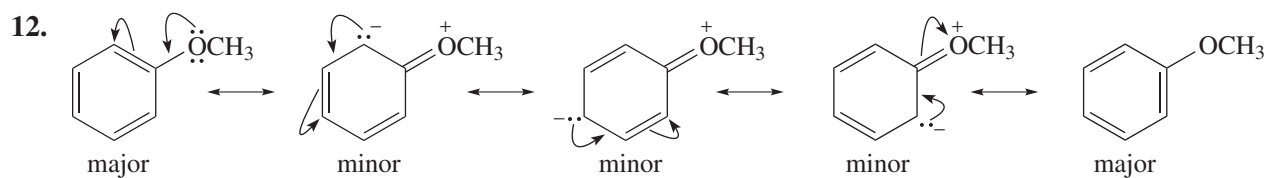
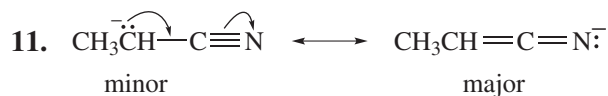


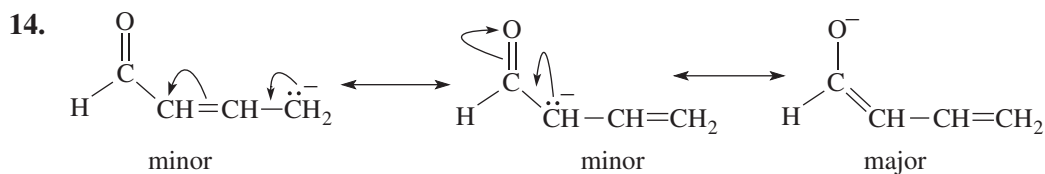


The five contributors are equally stable and, therefore, contribute equally to the resonance hybrid.



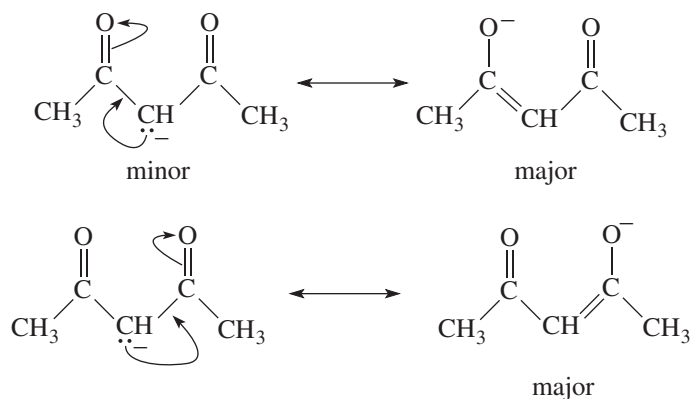
The major contributor has a negative charge on oxygen, which is more stable than a contributor with a negative charge on carbon.



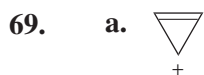


The major contributor has a negative charge on oxygen, which is more stable than a contributor with a negative charge on carbon.

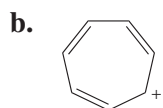
15. Notice that the electrons on the center carbon can be delocalized onto both of the carbonyl oxygens.



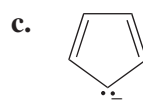
- b. **2, 4, and 7** have resonance contributors that all contribute equally to the hybrid.



It is aromatic.



It is aromatic.

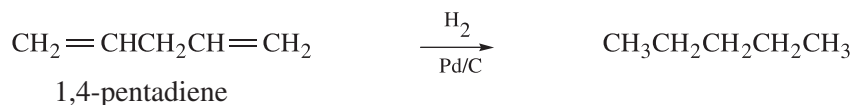
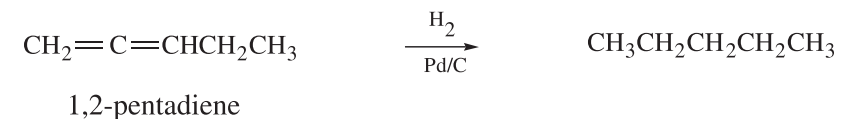


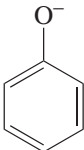
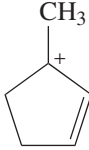
It is aromatic.

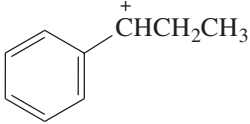


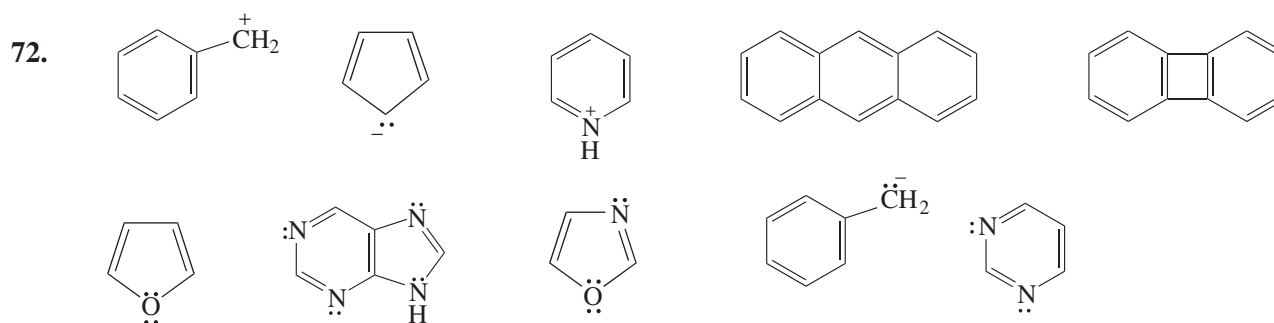
It is not antiaromatic.

70. Both compounds form the same product when they are hydrogenated, so the difference in the heats of hydrogenation depend only on the difference in the stabilities of the reactants. Because 1,2-pentadiene has cumulated double bonds and 1,4-pentadiene has isolated double bonds, 1,2-pentadiene is less stable and, therefore, has a greater heat of hydrogenation (a more negative ΔH°).

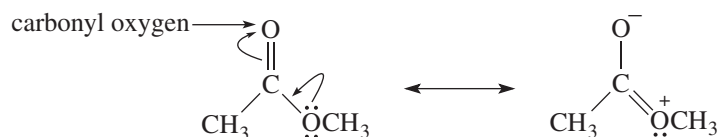


71. a. $\text{CH}_3\text{CH}^+\text{CH}=\text{CH}_2$
This makes the greater contribution because the positive charge is on a secondary allylic carbon.
- b.  This makes the greater contribution because the negative charge is on an oxygen.
- c.  This makes the greater contribution because the positive charge is on a tertiary allylic carbon.

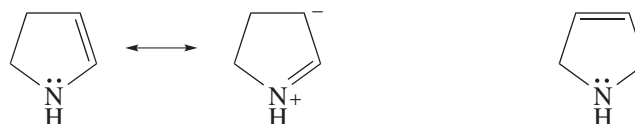
- d.  This makes the greater contribution because a secondary benzylic cation is more stable than a secondary alkyl cation.



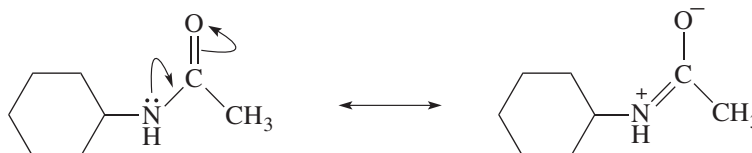
73. a. The resonance contributors show that the carbonyl oxygen has the greater electron density.



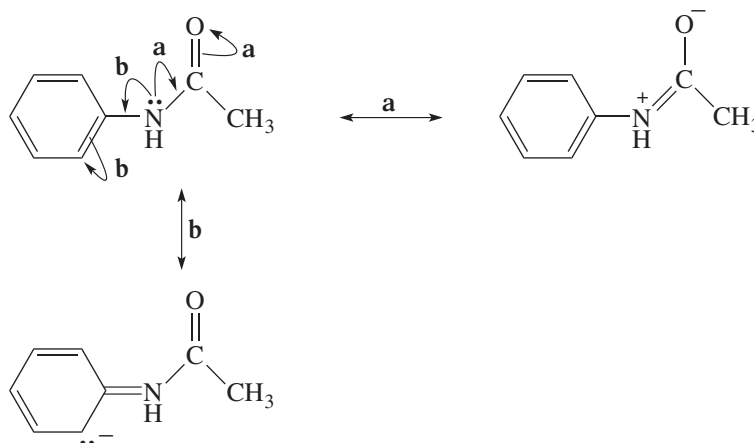
- b. The compound on the right has the greater electron density on its nitrogen, because the compound on the left has a resonance contributor with a positive charge on the nitrogen as a result of electron delocalization.



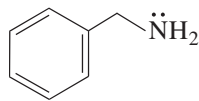
- c. The compound with the cyclohexane ring has the greater electron density on its oxygen, because the lone pair on the nitrogen can be delocalized only onto the oxygen.



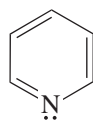
There is less delocalization onto oxygen by the lone pair in the compound with the benzene ring (path **a**) because the lone pair can also be delocalized away from the oxygen into the benzene ring (path **b**).



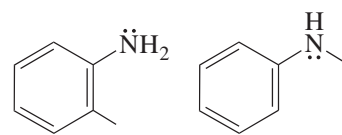
74. Remember that an sp^2 nitrogen is more electronegative than an sp^3 nitrogen, and the more electronegative the atom to which a hydrogen is attached, the stronger the acid. The stronger the acid, the weaker its conjugate base.



This is the strongest base because the lone pair is localized and the nitrogen is sp^3 hybridized.

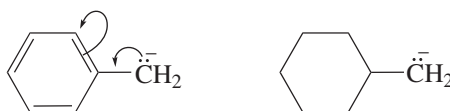


The lone pair is localized and the nitrogen is sp^2 hybridized, which is not as strong a base as an sp^3 hybridized nitrogen.

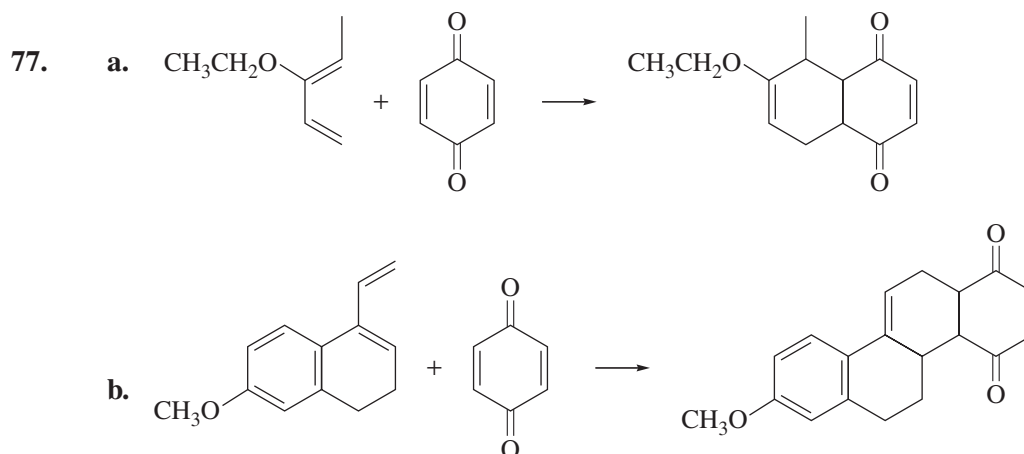


These are weak bases because the lone-pair electrons are delocalized.

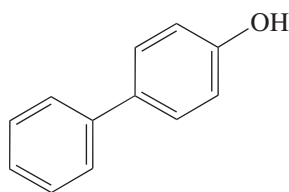
75. The methyl group on benzene can lose a proton easier than the methyl group on cyclohexane because the electrons left behind on the carbon in the former can be delocalized into the benzene ring. In contrast, the electrons left behind in the other compound cannot be delocalized.



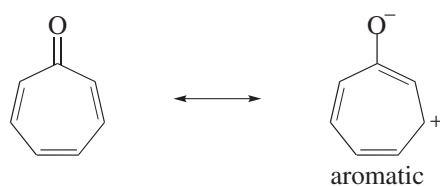
76. The triphenylmethyl carbocation is stable because the positive charge is shared by 10 carbons (the central carbon and three carbons of each of the three benzene rings) as a result of electron delocalization.



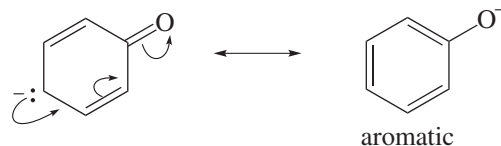
78. a. The structure shown below is the stronger acid because it has the weaker conjugate base. When this compound loses a proton, the electrons left behind can be delocalized onto six different carbons. The electrons left behind on the conjugate base of the other compound can be delocalized onto only three different carbons; they cannot be delocalized into the second benzene ring.



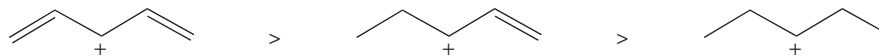
- b. 1. The first compound has the greater electron density on its oxygen because the resonance contributor with a negative charge on oxygen is particularly stable since it is aromatic.

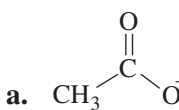
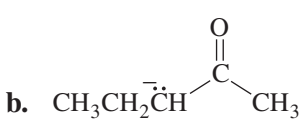
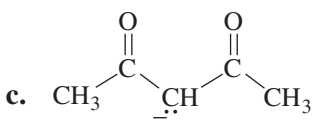
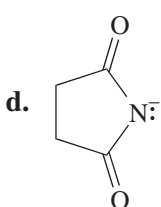


2. The first compound has the greater electron density on its oxygen because the resonance contributor with a negative charge on oxygen is particularly stable since it is aromatic.

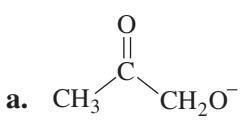
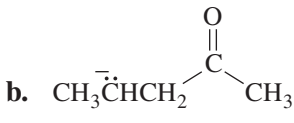
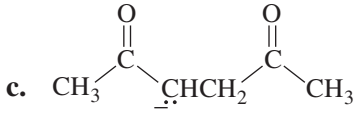
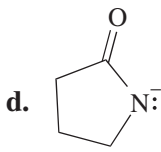


79. The first carbocation is the most stable because its positive charge can be shared by two other carbons; the positive charge on the next carbocation can be shared by one other carbon; the positive charge on the cation on the right cannot be shared by other carbons.

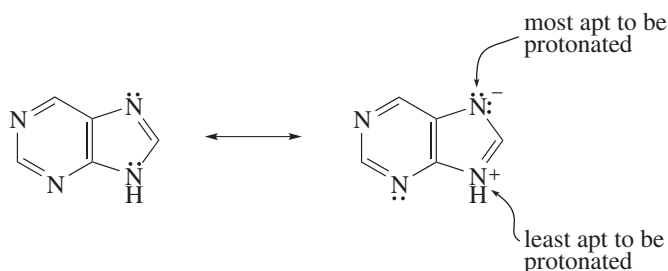


80. a.  The negative charge is shared by two oxygens.
- b.  The negative charge is shared by a carbon and an oxygen.
- c.  The negative charge is shared by a carbon and two oxygens.
- d.  The negative charge is shared by a nitrogen and two oxygens.

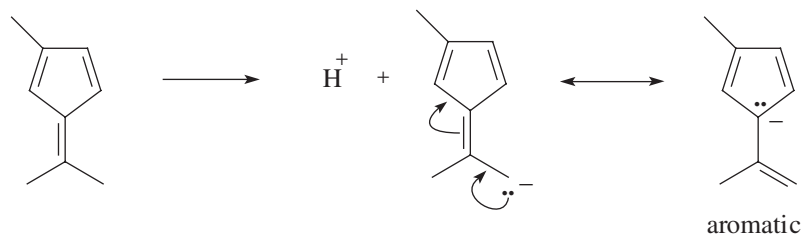
81. The stronger base is the less stable base of each pair in Problem 80.

- a.  Less stable because the negative charge cannot be delocalized.
- b.  Less stable because the negative charge cannot be delocalized.
- c.  Less stable because the negative charge can be delocalized onto only one oxygen.
- d.  Less stable because the negative charge can be delocalized onto only one oxygen.

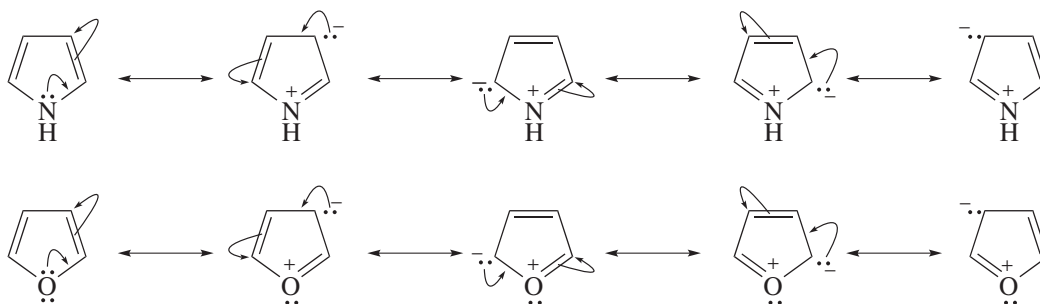
82. The resonance contributor shown here indicates which nitrogen is most apt to be protonated (the one with the greatest negative charge) and which nitrogen is least apt to be protonated (the one with the greatest positive charge).



83. The following compound is the strongest acid, because it is the only one that forms a conjugate base that is aromatic. Recall that the more stable (weaker) the base, the stronger is its conjugate acid.



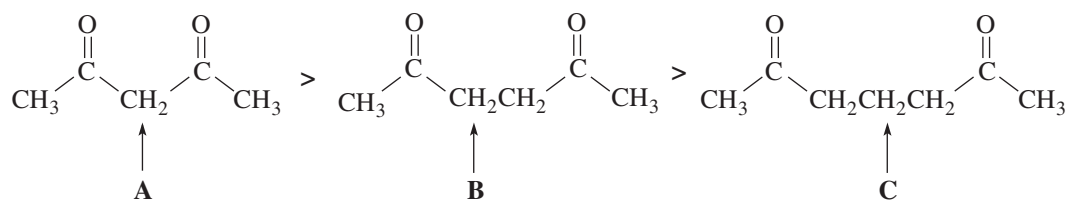
84. The resonance contributors of pyrrole are more stable because the positive charge is on nitrogen. In furan, the positive charge is on oxygen, which, being more electronegative, is less stable with a positive charge.



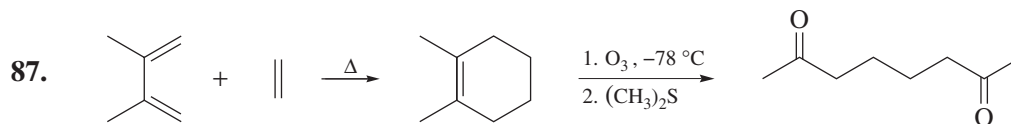
85. A is the most acidic because the electrons left behind when the proton is removed can be delocalized onto two oxygens.

B is the next most acidic because the electrons left behind when the proton is removed can be delocalized onto one oxygen.

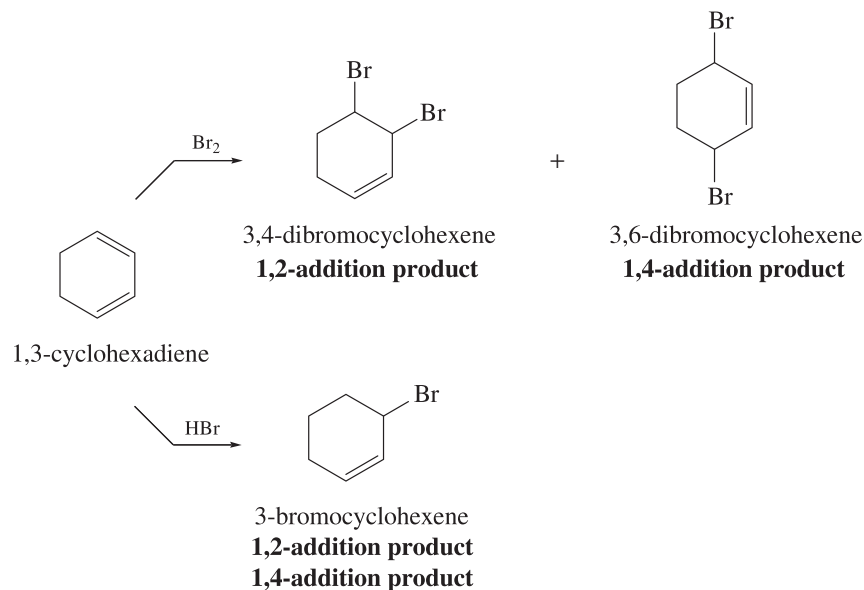
C is the least acidic because the electrons left behind when the proton is removed cannot be delocalized.



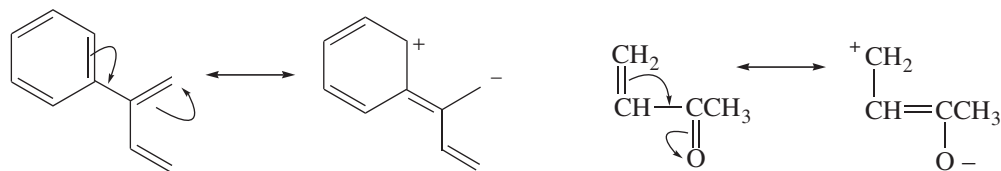
86. a. It has eight molecular orbitals.
 b. ψ_1 , ψ_2 , ψ_3 , and ψ_4 are bonding molecular orbitals; ψ_5 , ψ_6 , ψ_7 , and ψ_8 are antibonding molecular orbitals.
 c. ψ_1 , ψ_3 , ψ_5 , and ψ_7 are symmetric molecular orbitals; ψ_2 , ψ_4 , ψ_6 , and ψ_8 are antisymmetric molecular orbitals.
 d. ψ_4 is the HOMO and ψ_5 is the LUMO in the ground state.
 e. ψ_5 is the HOMO and ψ_6 is the LUMO in the excited state.
 f. If the HOMO is symmetric, the LUMO is antisymmetric and vice versa.
 g. It has seven nodes between the nuclei. It also has one node that passes through the nuclei.



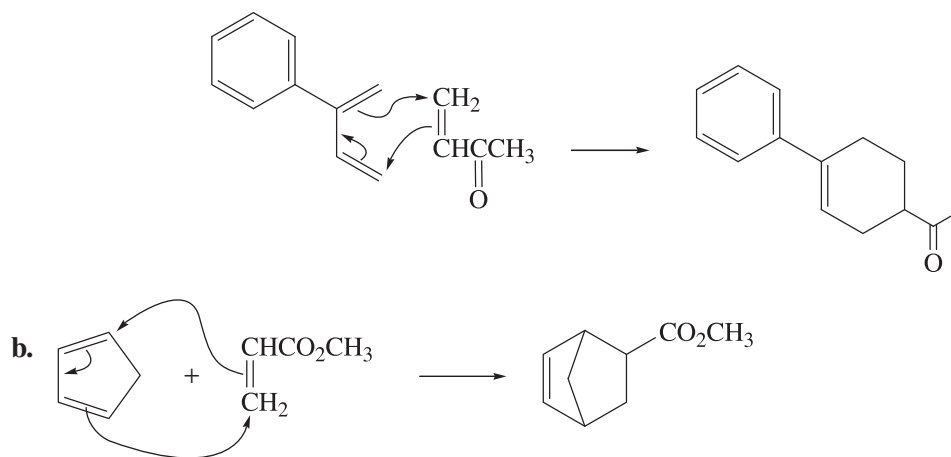
88. The reaction of 1,3-cyclohexadiene with Br_2 forms 3,4-dibromocyclohexene as the 1,2-addition product and 3,6-dibromocyclohexene as the 1,4-addition product. The reaction of 1,3-cyclohexadiene with HBr forms only 3-bromocyclohexene, so it is both the 1,2-addition product and the 1,4-addition product.

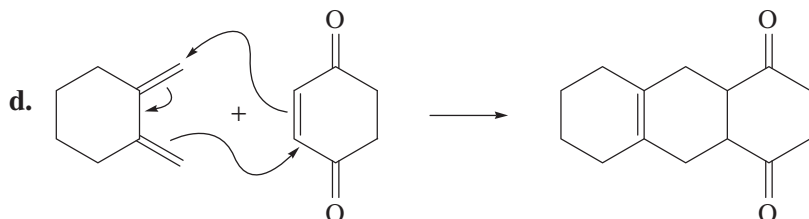
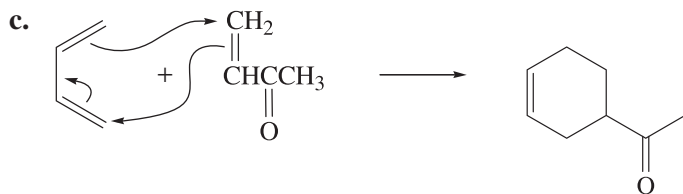


89. a. Only part **a** involves the reaction of two unsymmetrically substituted reactants. Therefore, only for part **a** do we need to look at the charge distribution in the reactants to determine the major product of the reaction.

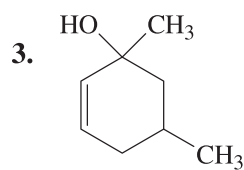
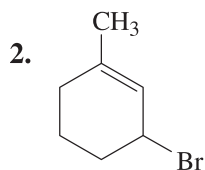
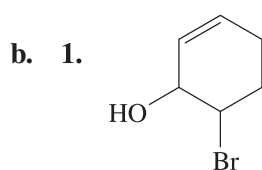
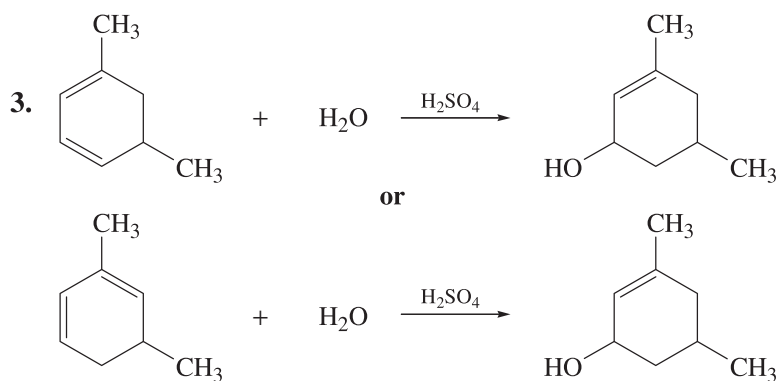
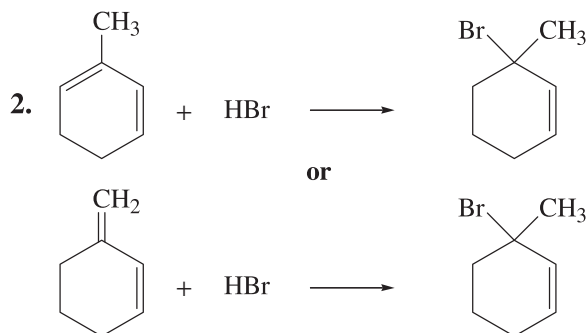
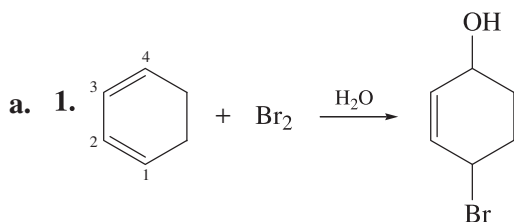


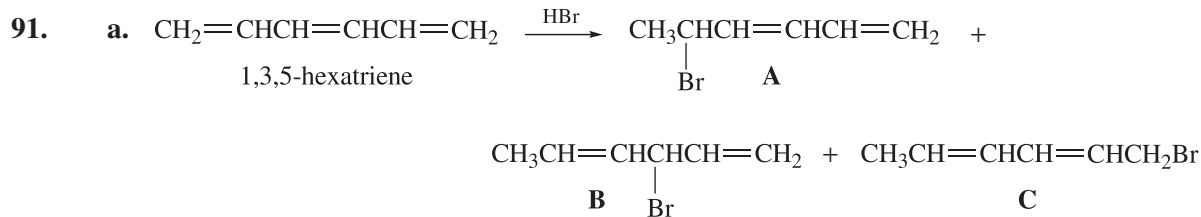
We now need to join the negative end of the diene and the positive end of the dienophile.





90. Numbering the carbons in the conjugated system will help you determine the 1,2- and 1,4-addition products.



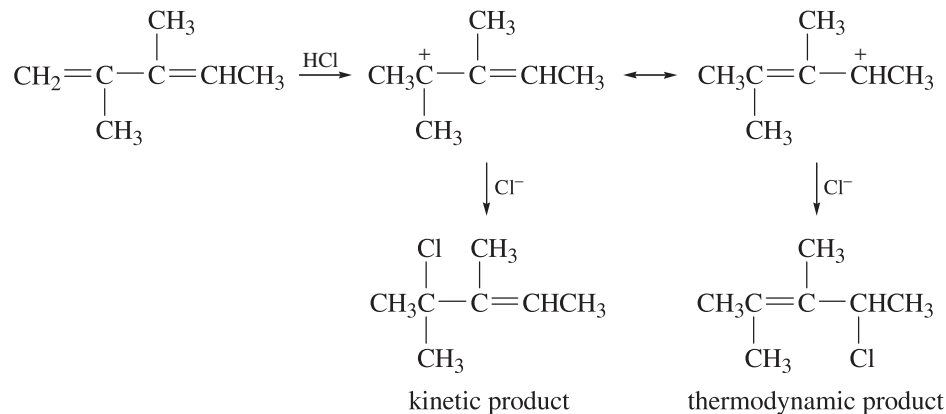


- b. **A** will predominate if the reaction is under kinetic control because it is the 1,2-product and, therefore, is the product formed most rapidly as a result of the proximity effect. Notice that **A** will be the 1,2-product regardless of which end of the conjugated system reacts with the electrophile.
- c. **C** will predominate if the reaction is under thermodynamic control because it is the most stable diene. (It is the most substituted conjugated diene.)

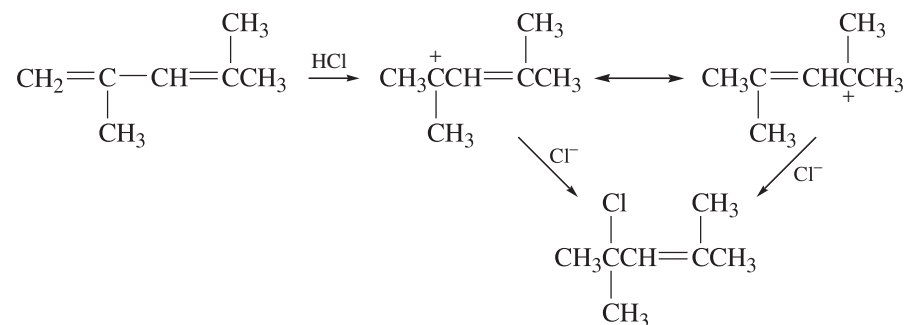
92. The diene is the nucleophile, and the dienophile is the electrophile in a Diels–Alder reaction.

- a. An electron-donating substituent in the diene will increase the rate of the reaction, because electron donation increases its nucleophilicity.
- b. An electron-donating substituent in the dienophile will decrease the rate of the reaction, because electron donation decreases its electrophilicity.
- c. An electron-withdrawing substituent in the diene will decrease the rate of the reaction, because electron withdrawal decreases its nucleophilicity.

93. a. Addition of an electrophile to C-1 forms a carbocation with two resonance contributors, a *tertiary allylic cation* and a *secondary allylic cation*. Addition of an electrophile to C-4 forms a carbocation with two resonance contributors, a *tertiary allylic cation* and a *primary allylic cation*. Therefore, addition to C-1 results in formation of the more stable carbocation intermediate, and the more stable intermediate leads to the major products.

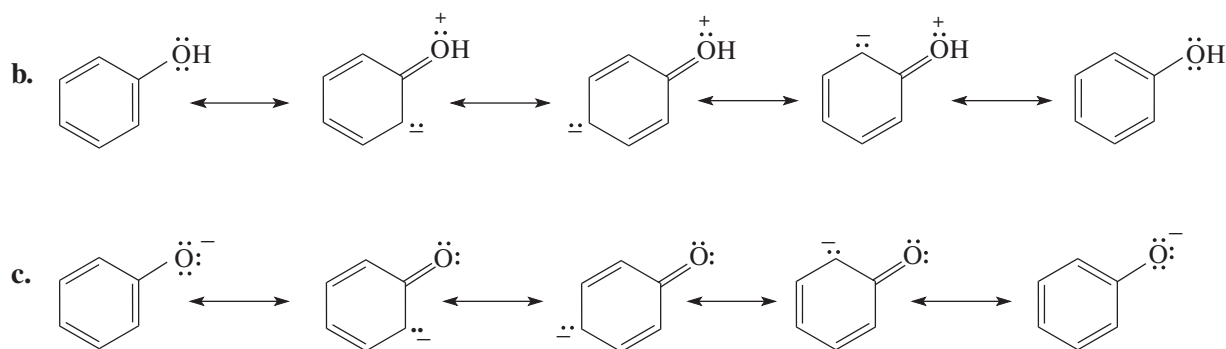
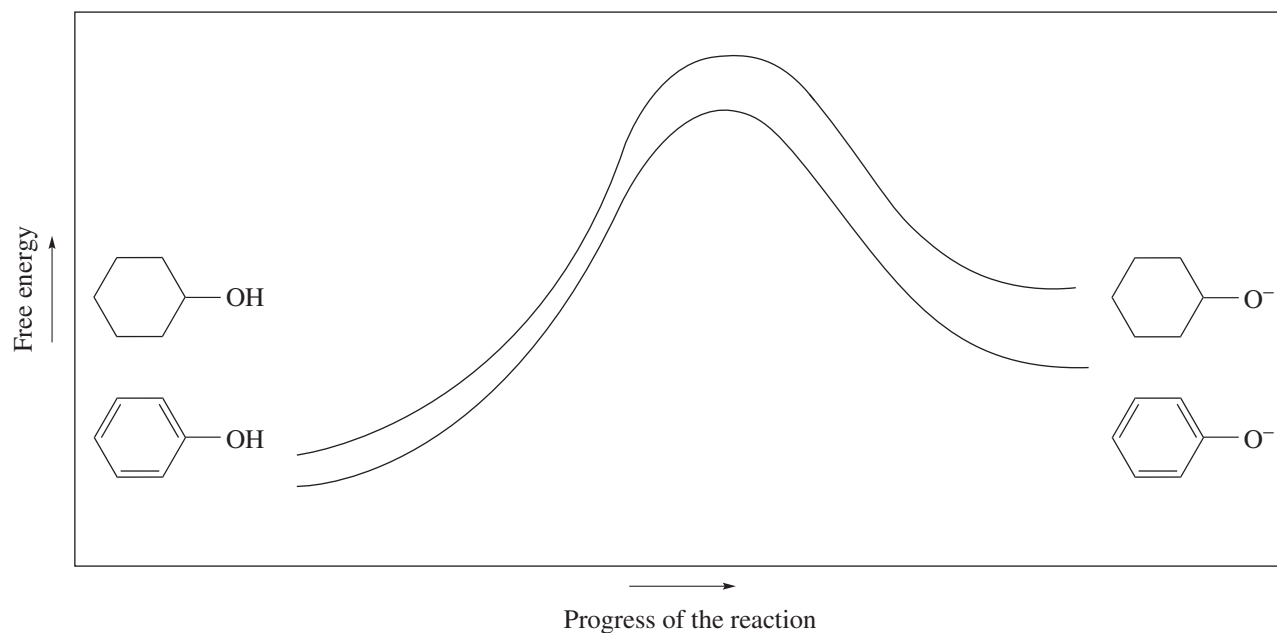


- b. Addition of an electrophile to C-1 forms a carbocation with two resonance contributors; both are *tertiary allylic* cations. Addition of an electrophile to C-4 forms a carbocation with two resonance contributors, a *secondary allylic* cation and a *primary allylic* cation. Therefore, addition to C-1 results in formation of the more stable carbocation. Only one product is formed, because the carbocation is symmetrical.



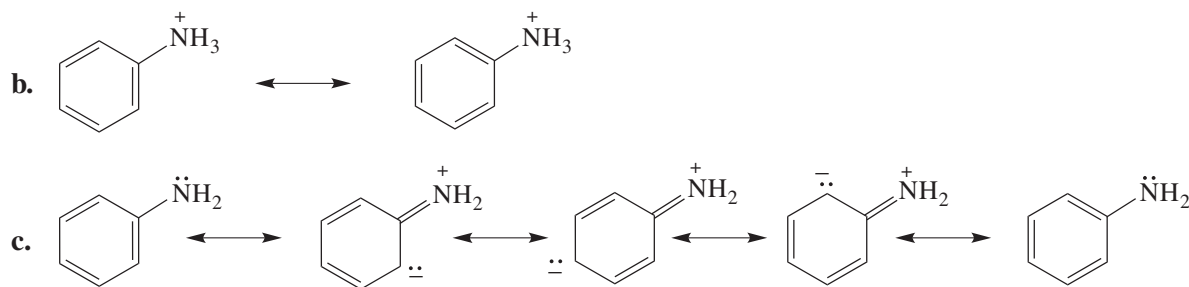
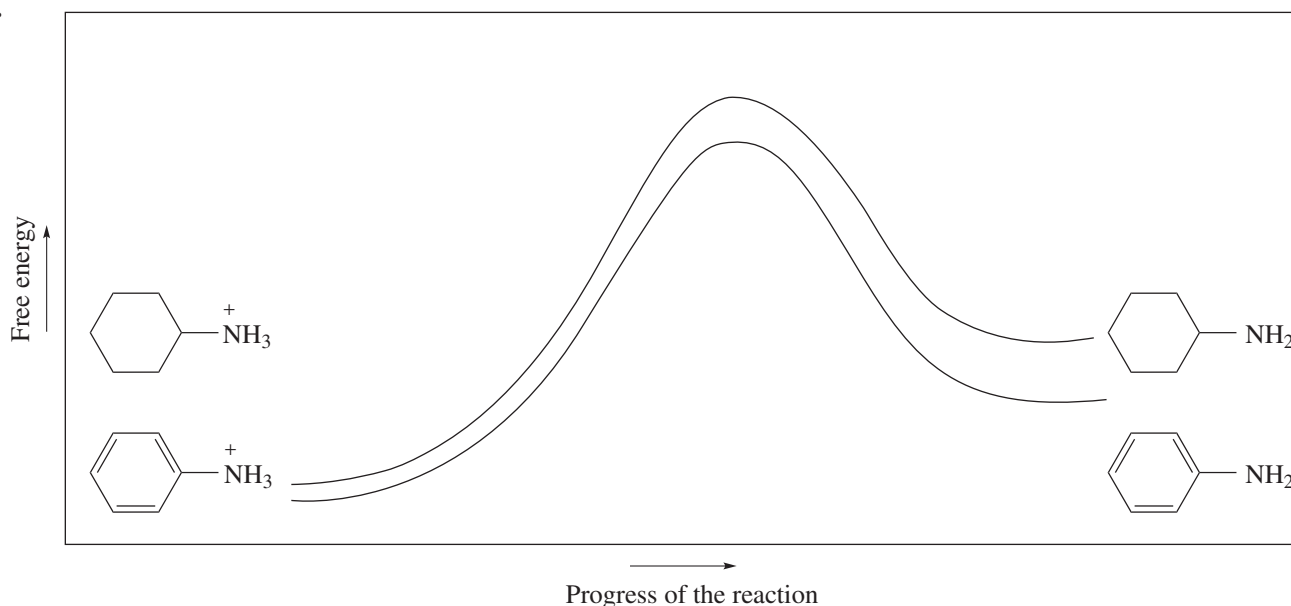
This is the only product because the carbocation is symmetrical.

94. a and d.



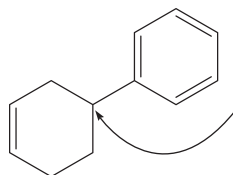
- d. The 2nd, 3rd, and 4th resonance contributors in **c** are more stable than those resonance contributors in **b**, because in **b**, a positive charge is on the most electronegative atom (the oxygen) and there is charge separation. Therefore, the phenolate ion has greater electron delocalization than phenol. Thus, as shown in the energy diagram, the difference in energy between the phenolate ion and the cyclohexoxide ion is greater than the difference in energy between phenol and cyclohexanol.
- e. Because of greater electron delocalization in the phenolate ion compared to that in phenol, phenol has a larger K_a than cyclohexanol.
- f. Because it has a larger K_a (a lower pK_a), phenol is a stronger acid.

95.



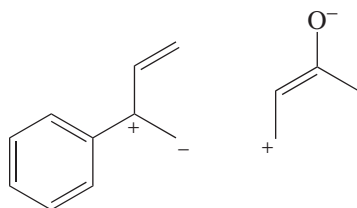
- d. Aniline has greater electron delocalization than the anilinium ion. Therefore, in the energy diagram, the difference in energy between aniline and cyclohexylamine is greater than the difference in energy between the anilinium ion and the cyclohexylammonium ion.
- e. Because of greater electron delocalization in aniline compared to that in the anilinium ion, the anilinium ion has a larger K_a than the cyclohexylammonium ion.
- f. Because it has a larger K_a (a lower pK_a), the anilinium ion is a stronger acid than the cyclohexylammonium ion. Therefore, cyclohexylamine is a stronger base than aniline. (The stronger the acid, the weaker its conjugate base.)

96. a.

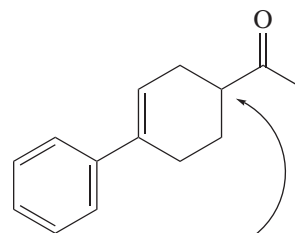


Because the reaction creates an asymmetric center in the product, the product will be a racemic mixture.

b.

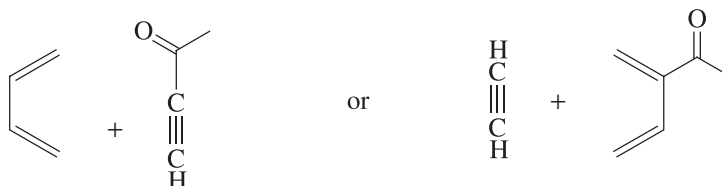


Even though both reactants are unsymmetrically substituted, they will be aligned primarily as shown, because of the relatively stable tertiary benzylic cation resonance contributor and delocalization of the π electrons of the dienophile onto the oxygen.



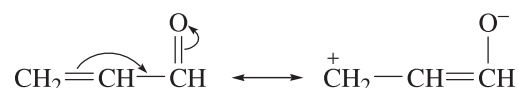
Because the reaction creates an asymmetric center, the product will be a racemic mixture.

97. The first pair is the preferred set of reagents because it has the more nucleophilic diene and the more electrophilic dienophile.

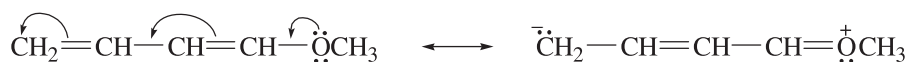


98. A Diels–Alder reaction is a reaction between a nucleophilic diene and an electrophilic dienophile.

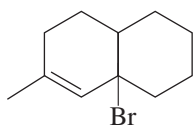
a. The compound shown below is more reactive in both **1** and **2**, because electron delocalization increases the electrophilicity of the dienophile.



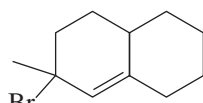
b. The compound shown below is more reactive, because electron delocalization increases the nucleophilicity of the diene.



99. a.

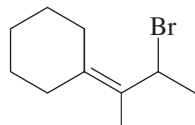


1,2-product
kinetic product

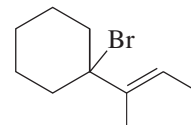


1,4-product

b.



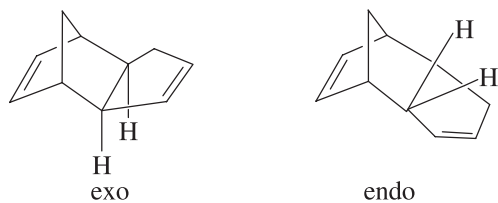
1,2-product
kinetic product
thermodynamic product



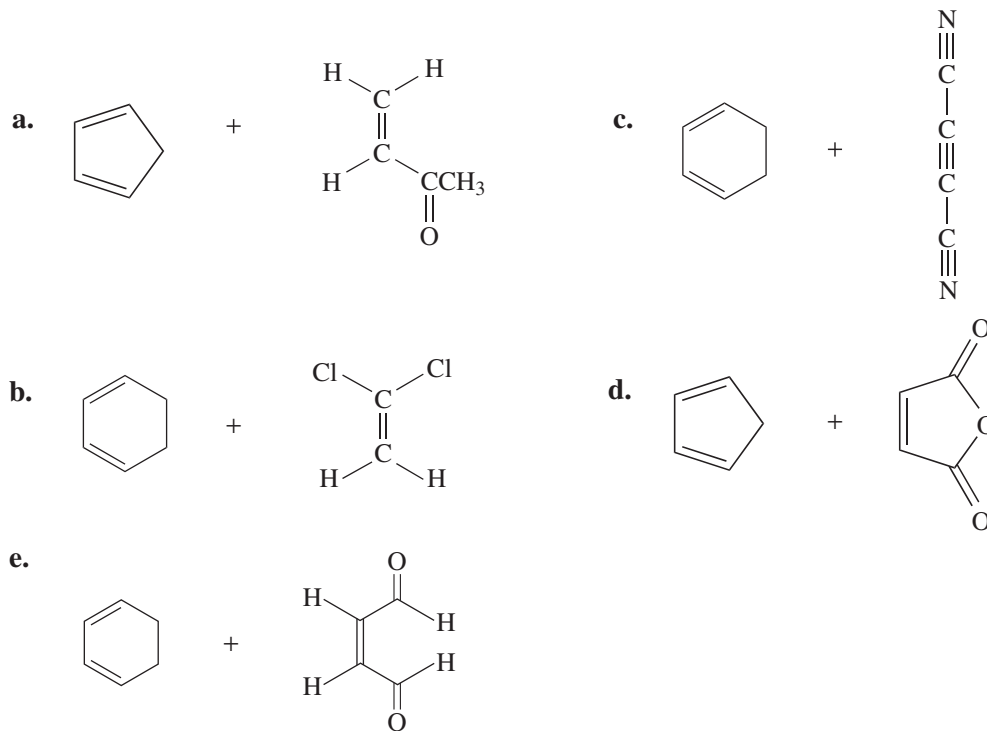
1,4-product

Both have the same stability, so neither exclusively is the thermodynamic product. When the reaction is under thermodynamic control, approximately equal amounts of the two products will be obtained.

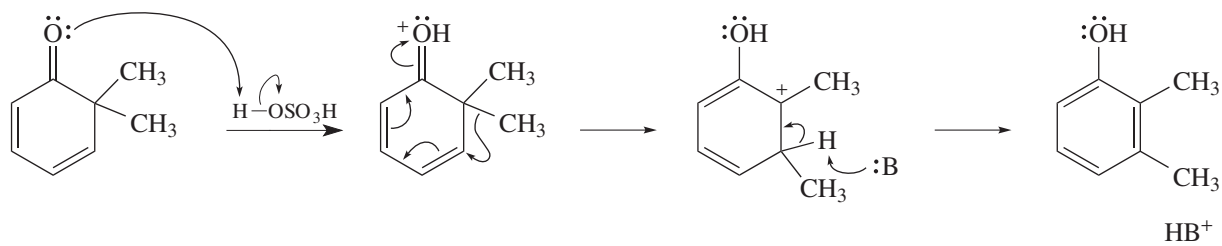
100.



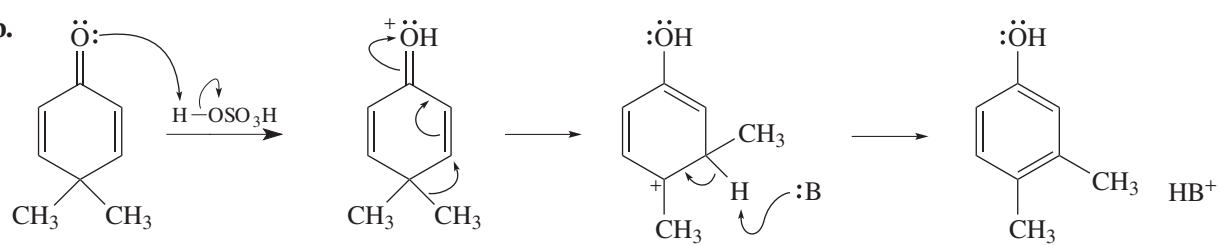
101.



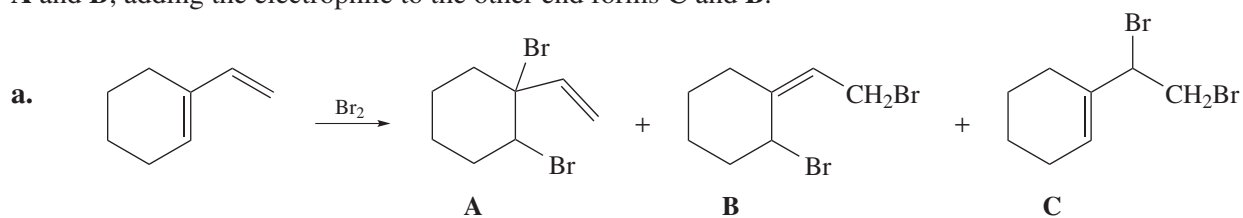
102. a.



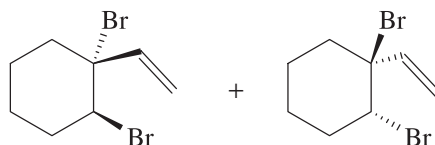
b.



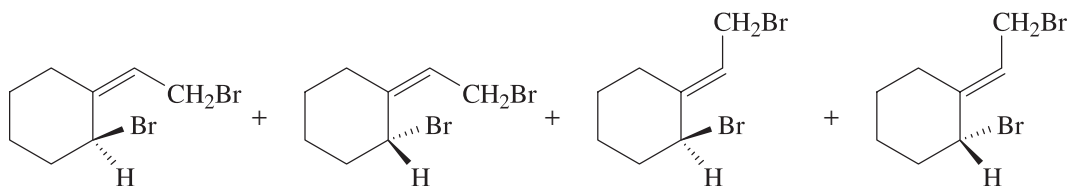
103. The electrophile can add to either end of the conjugated system. Adding the electrophile to one end forms **A** and **B**; adding the electrophile to the other end forms **C** and **B**.



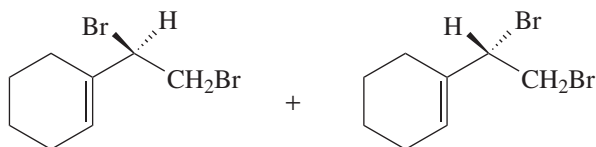
- b. **A** has two asymmetric centers, but only two stereoisomers are obtained because only anti addition of Br_2 can occur.



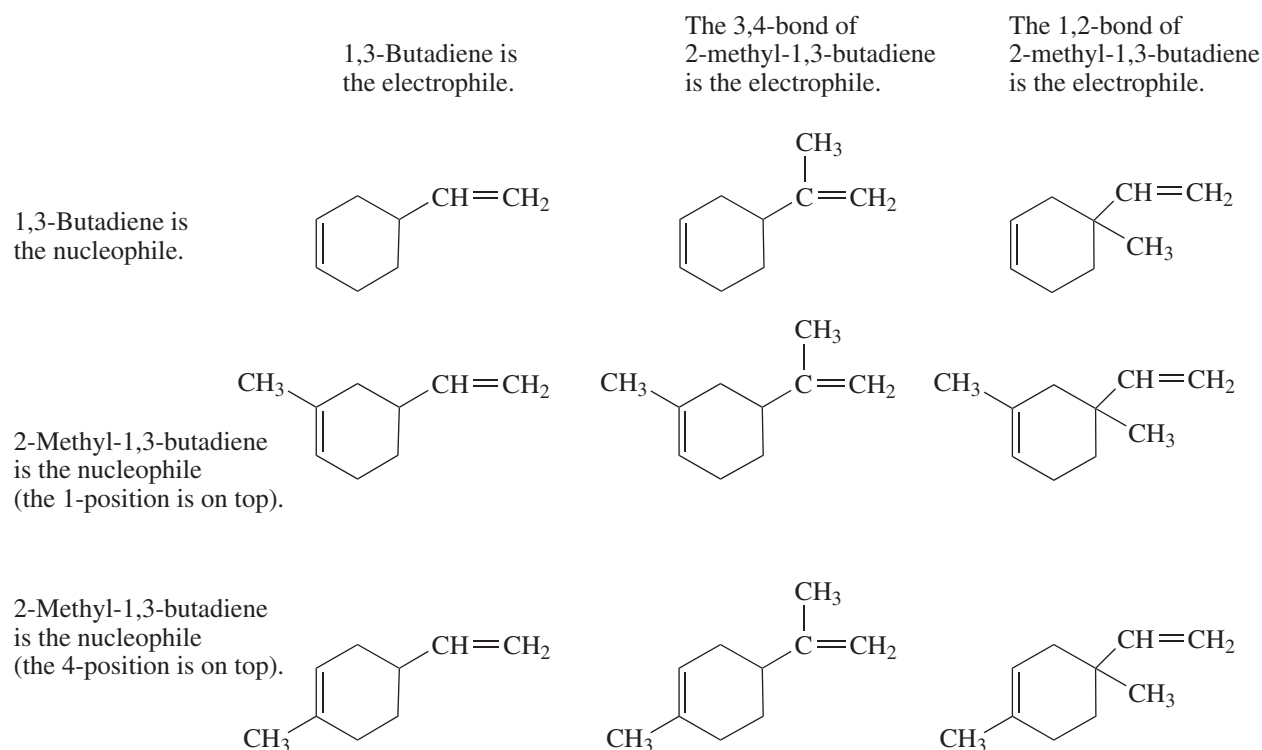
B has four stereoisomers because it has an asymmetric center and a double bond that can be in either the *E* or *Z* configuration.



C has two stereoisomers because it has one asymmetric center.



104. Nine of the compounds are shown below. Because each has one asymmetric center, each can have either the *R* or *S* configuration. Therefore, 18 different products can be obtained.



105. 2-Methyl-1,3-pentadiene (with conjugated double bonds) is more stable than 2-methyl-1,4-pentadiene (with isolated double bonds). The rate-limiting step of the reaction is formation of the carbocation intermediate. 2-Methyl-1,3-pentadiene forms a more stable carbocation intermediate than does 2-methyl-1,4-pentadiene.

Because the more stable reactant forms the more stable carbocation intermediate, the relative free energies of activation for the rate-limiting steps of the two reactions depend on whether the difference in the stabilities of the reactants is greater or less than the difference in the stabilities of the transition states leading to formation of the carbocation intermediates (which depend on the difference in stabilities of the carbocation intermediates).

There is a significant difference in the stabilities of the carbocation intermediates because one is stabilized by electron delocalization and one is not. The transition states look more like the carbocation intermediates than like the alkenes.

Therefore, the difference in the stabilities of the reactants is less than the difference in the stabilities of the transition states, so the rate of reaction of HBr with 2-methyl-1,3-pentadiene is the faster reaction. (If the difference in the stabilities of the reactants had been greater than the difference in the stabilities of the transition states, the rate of reaction of HBr with 2-methyl-1,4-pentadiene would have been the faster reaction.)



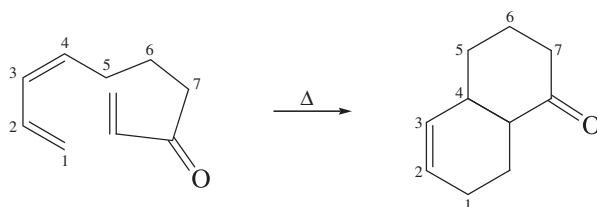
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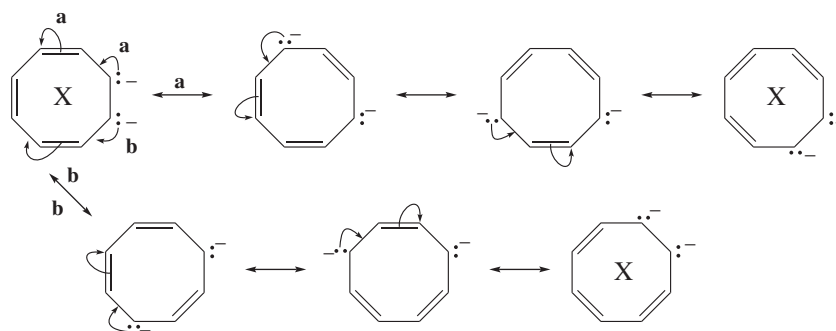
109. a. Unless the reaction is being carried out under kinetic control, the amount of product obtained is not dependent on the rate at which the product is formed, so the relative amounts of products obtained will not tell you which product was formed faster.
- b. In a thermodynamically controlled reaction, the product distribution depends on the relative stabilities of the products because the products come to equilibrium. Therefore, if the distribution of products does not reflect the relative stabilities of the products, the reaction must have been kinetically controlled.

110.



First line up the conjugated diene and the double bond of the dienophile in a way that prepares them to undergo the Diels–Alder reaction. Once they are lined up correctly, you can rearrange the electrons to determine the product of the reaction.

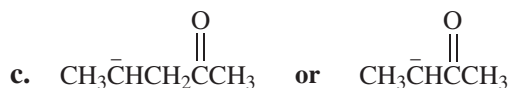
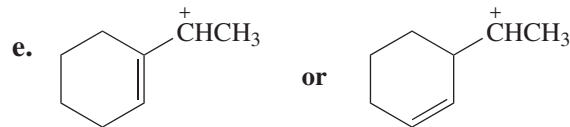
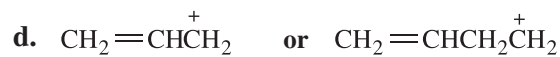
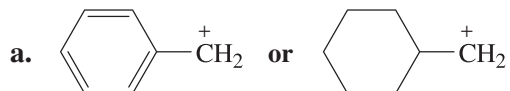
111. a. The three resonance contributors marked with an X are the least stable because in these contributors, the two negative charges are on adjacent carbons.
- b. Because these contributors are the least stable, they make the smallest contribution to the hybrid.



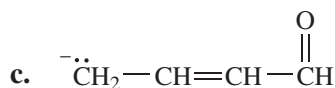
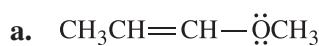
112. We have classified cyclobutadiene as antiaromatic. However, the recent observation that cyclobutadiene is rectangular and the observation that there are two different 1,2-dideuterio-1,3-cyclobutadienes both indicate that the π electrons are localized rather than delocalized. Localization of the π electrons prevents the compound from being antiaromatic. Apparently, the extreme instability associated with being antiaromatic causes cyclobutadiene to be rectangular.

Chapter 8 Practice Test

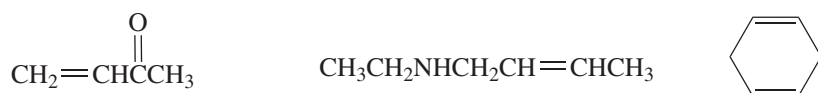
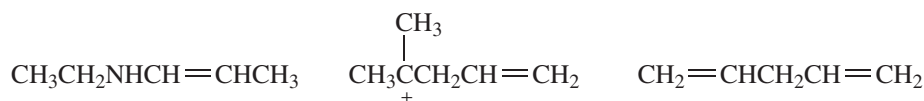
1. Indicate the more stable species in each pair:



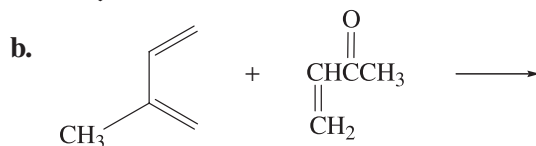
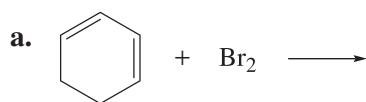
2. Draw resonance contributors for each of the following:



3. Which compounds do not have delocalized electrons?



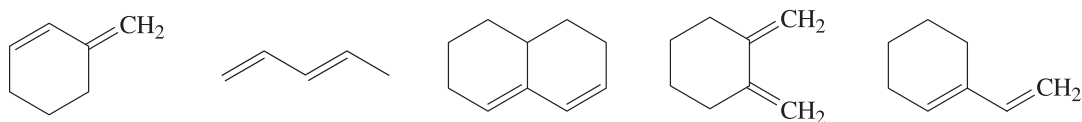
4. What are the products of the following reactions?



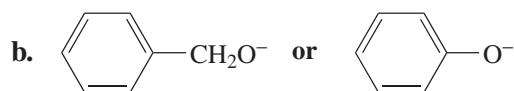
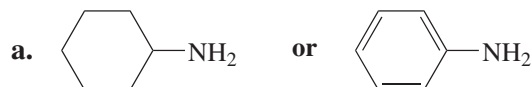
5. Which of the following pairs are resonance contributors?



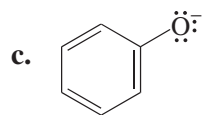
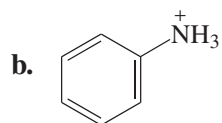
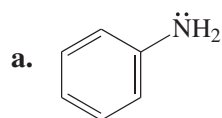
6. Which of the following dienes can be used in a Diels–Alder reaction?



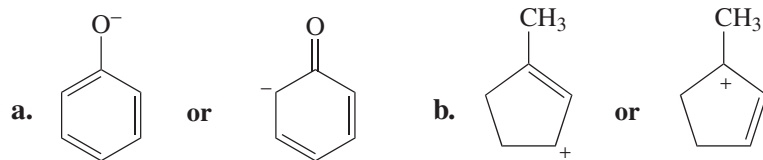
7. Which is a stronger base?



8. Draw resonance contributors for each of the following:



9. Which resonance contributor makes a greater contribution to the resonance hybrid?

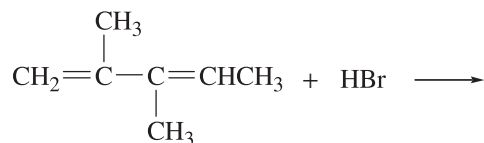


10. Indicate whether each of the following statements is true or false.

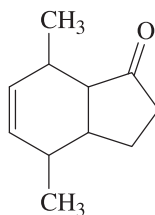
- | | | |
|---|---|---|
| a. A compound with four conjugated double bonds has four molecular orbitals. | T | F |
| b. ψ_1 and ψ_2 are symmetric molecular orbitals. | T | F |
| c. If ψ_3 is the HOMO in the ground state, ψ_4 will be the HOMO in the excited state. | T | F |
| d. If ψ_3 is the LUMO, ψ_4 will be the HOMO. | T | F |
| e. If the ground-state HOMO is symmetric, the ground-state LUMO will be antisymmetric. | T | F |

- f. A single bond formed by an sp^2-sp^2 overlap is longer than a single bond formed by an sp^2-sp^3 overlap. T F
- g. The thermodynamically controlled product is the major product obtained when the reaction is carried out under mild conditions. T F
- h. 1,3-Hexadiene is more stable than 1,4-hexadiene. T F

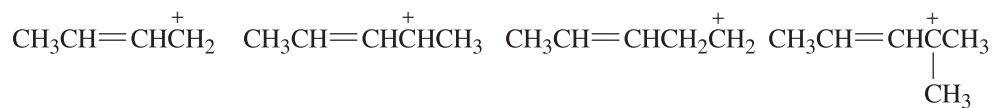
11. Draw the four products that will be obtained from the following reaction. Ignore stereoisomers.



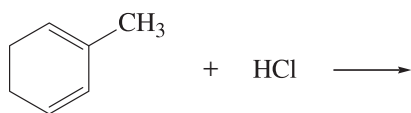
12. What reactants are necessary for the synthesis of the following compound via a Diels–Alder reaction?



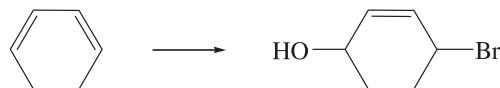
13. Rank the following carbocations from most stable to least stable:



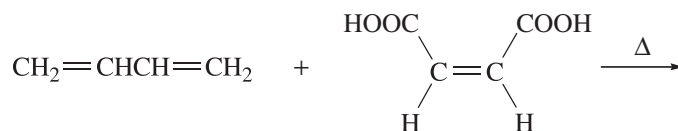
14. a. Draw the predominant 1,2- and 1,4-products of the following reaction.
b. Which is the product of thermodynamic control?



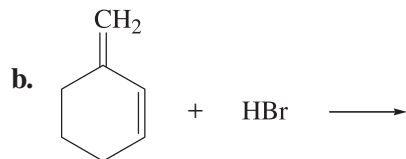
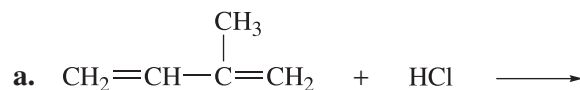
15. What reagents can be used to convert the given starting material into the given product?



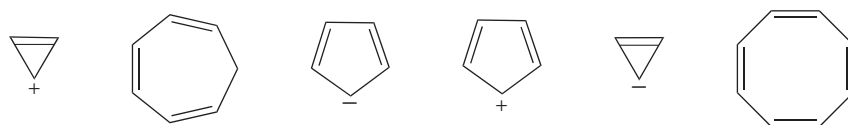
16. Draw the product of the following reaction, showing its configuration:



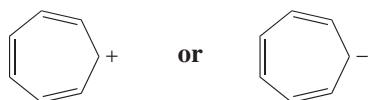
17. For each of the following reactions, give the major 1,2- and 1,4-products. Label the product of kinetic control and the product of thermodynamic control.



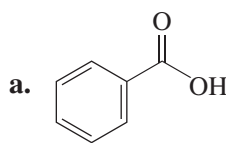
18. Which are aromatic compounds?



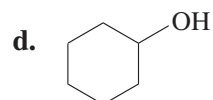
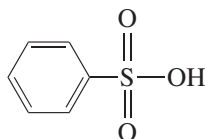
19. Which compound has the greater delocalization energy?



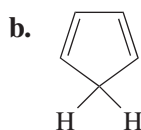
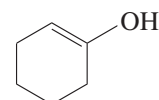
20. Which is a stronger acid?



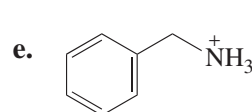
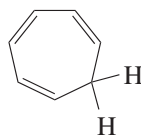
or



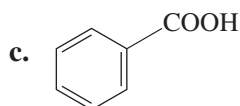
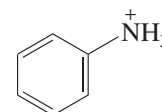
or



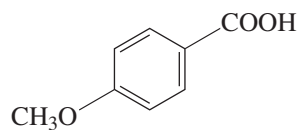
or



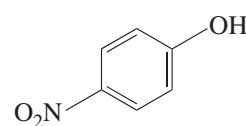
or



or



f.



or

