Solutions to Problems

1. a. 1. If stereoisomers are not included, 3 different monosubstituted compounds can be formed.

$BrC{\equiv}CC{\equiv}CCH_2CH_3$ $\quad HC{\equiv}CC{\equiv}CCHCH_3$ (with Br on CH) $\quad HC{\equiv}CC{\equiv}CCH_2CH_2Br$

If stereoisomers are included, 4 different monosubstituted compounds can be formed because the second listed compound has an asymmetric center.

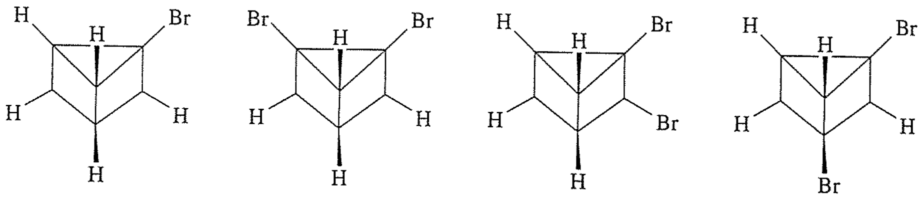
2. If stereoisomers are not included, 2 different monosubstituted compounds can be formed.

$BrCH{=}CHC{\equiv}CCH{=}CH_2$ $\quad CH_2{=}CC{\equiv}CCH{=}CH_2$ (with Br on C-2)

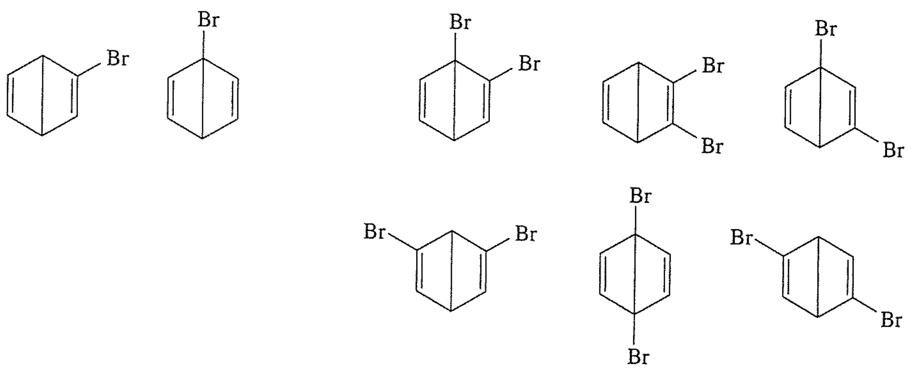
If stereoisomers are included, 3 different monosubstituted compounds can be formed because the first compound has a double bond that can have cis–trans isomers.

b. 1. 5 2. 5 c. 1. 7 2. 10

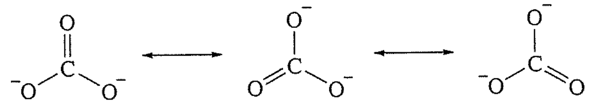
2. Ladenburg benzene is a better proposal. It would form 1 monosubstituted compound, 3 disubstituted compounds, and would not add Br_2, all in accordance with what early chemists knew about the structure of benzene.



Dewar benzene is not in accordance with what early chemists knew about the structure of benzene, because it would form 2 monosubstituted compounds, 6 disubstituted compounds, and it would add Br_2.



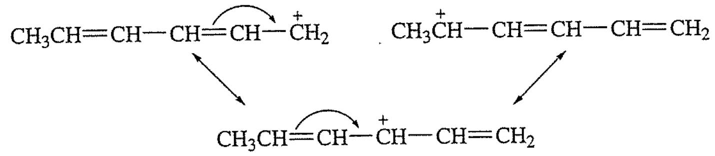
3. a. All the carbon-oxygen bonds in the carbonate ion should be the same length because each carbon-oxygen bond is represented in one resonance contributor with a double bond and in two resonance contributors with single bonds.



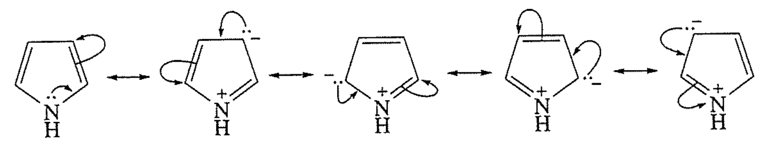
b. Because the two negative charges are shared equally by three oxygens, each oxygen should have two thirds of a negative charge.

4. a. 2, 4, and 7

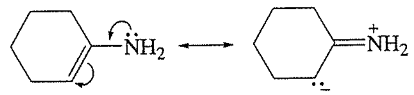
2.



4.



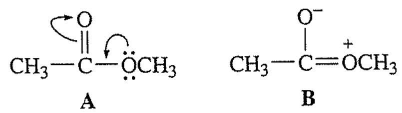
7.



5. 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**".

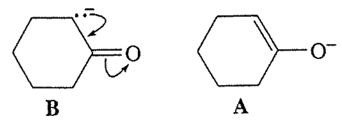
a. Solved in the text.

b.



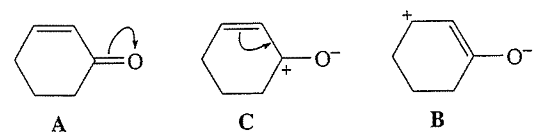
A is more stable than B because, unlike B, A does not have separated charges.

c.



A is more stable than B because the negative charge in A is on an O, while that is B is on a less electronegative C.

d.



B is more stable than C because the electronegative oxygen atom is closer to the postive charge in C.
C is so unstable that it can be neglected.

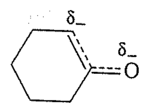
e. $CH_3—C(=\overset{+}{O}H)—\ddot{N}HCH_3$ **B** $CH_3—C(OH)=\overset{+}{N}HCH_3$ **A**

A is more stable than B because the positive charge in A is on a less electronegative atom.

f. $CH_3\overset{+}{C}H—CH=CHCH_3$ $CH_3CH=CH—\overset{+}{C}HCH_3$

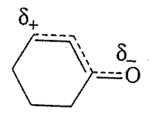
equally stable

6\. a. $CH_3\overset{\delta+}{C}{=}CH{=}\overset{\delta+}{C}HCH_3$ (with CH_3 on C-2)

c. 

e. $CH_3—\overset{\delta+}{C}(\overset{\delta+}{O}H){=}\overset{\delta+}{N}HCH_3$

b. $CH_3—\overset{\delta+}{C}(=\overset{\delta-}{O}){=}\overset{\delta+}{O}CH_3$

d. 

f. $CH_3\overset{\delta+}{C}H{=}CH{=}\overset{\delta+}{C}HCH_3$

7\. a. $CH_3CH_2C(=CH_2)—\overset{+}{C}H_2 \longleftrightarrow CH_3CH_2C(\overset{+}{C}H_2)=CH_2$

$CH_3CH_2CH=CH—\overset{+}{C}H_2 \longleftrightarrow CH_3CH_2\overset{+}{C}H—CH=CH_2$

more stable because the positive charge is shared by a primary and a secondary carbon

b. $CH_3C(=O)—CH=CH_2 \longleftrightarrow CH_3C(O^-)=CH—\overset{+}{C}H_2$

$CH_3C(=O)—CH=CHCH_3 \longleftrightarrow CH_3C(O^-)=CH—\overset{+}{C}HCH_3$

more stable because the positive charge is on a secondary carbon

c. $CH_3CH(O^-)—CH=CH_2$

$CH_3C(\ddot{O}:^-)=CHCH_3 \longleftrightarrow CH_3C(=O)—\overset{-}{C}HCH_3$

more stable because only in this compound is the negative charge delocalized

d. $CH_3—C(=\overset{+}{N}H_2)—\ddot{N}H_2 \longleftrightarrow CH_3—C(NH_2)=\overset{+}{N}H_2$

more stable because the positive charge is on a N rather than on a more electronegative O

$CH_3—C(=\overset{+}{O}H)—\ddot{N}H_2 \longleftrightarrow CH_3—C(OH)=\overset{+}{N}H_2$

8\. The second species has the greatest delocalization energy; it has three resonance contributors and none of them have separated charges. (See the answer to Problem 3.)
The first species has two resonance contributors and none of them have separated charges.
The third species has two resonance contributors, one of which has separated charges.

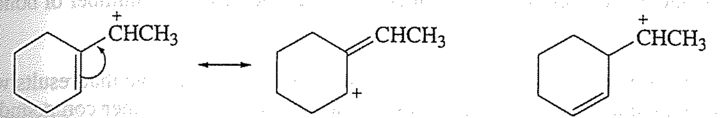
9\. The smaller the heat of hydrogenation (the absolute value of $\Delta H°$), the more stable the compound. Therefore, the relative stabilities of the dienes are:

conjugated diene > isolated diene > cumulated diene

10\. $CH_2=CHCH_2CH=CH_2$ < $CH_3CH=CHCH=CH_2$ < $CH_3CH=CHCH=CHCH_3$ < $CH_3C(CH_3)=CHCH=C(CH_3)CH_3$

1,4-pentadiene; 1,3-pentadiene; 2,4-hexadiene; 2,5-dimethyl-2,4-hexadiene

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



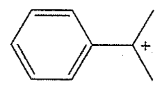
electrons are delocalized — electrons are localized

b. Because nitrogen is less electronegative than oxygen, it is better able to share the positive charge.

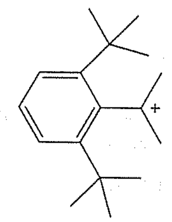
$CH_3\ddot{O}—\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{O}=CH_2$ $CH_3\ddot{N}H—\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{N}H=CH_2$

more stable

c. In order for electron delocalization to occur, the atoms that share the electrons must be in the same plane. The two *tert*-butyl groups prevent the positively charged carbon and the benzene ring from being in the same plane. Therefore, the carbocation cannot be stabilized by electron delocalization.



more stable



12\. The ψ_3 molecular orbital of 1,3-butadiene has 3 nodes (two vertical and one horizontal).
The ψ_4 molecular orbital of 1,3-butadiene has 4 nodes (three vertical and one horizontal).

13\. 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.

14. a. ψ_1, ψ_2, and ψ_3 are bonding molecular orbitals, and ψ_4, ψ_5, and ψ_6 are antibonding molecular orbitals.

b. ψ_1, ψ_3, and ψ_5 are symmetric molecular orbitals, and ψ_2, ψ_4, and ψ_6 are antisymmetric molecular orbitals.

c. ψ_3 is the HOMO and ψ_4 is the LUMO in the ground state.

d. ψ_4 is the HOMO and ψ_5 is the LUMO in the excited state.

e. If the HOMO is symmetric, the LUMO is antisymmetric and vice versa.

15. a. The ψ_1 molecular orbital of 1,3-butadiene has 3 bonding interactions and the ψ_2 molecular orbital has 2 bonding interactions.

b. The ψ_1 molecular orbital of 1,3,5,7-octatetraene has 7 bonding interactions and the ψ_2 molecular orbital has 6 bonding interactions.
Notice that the ψ_1 molecular orbital has one bonding interaction between each of the overlapping *p* orbitals. Notice also that as the energy of the molecular orbital increases, the number of bonding interactions decreases.

16. 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 is not possible for the other compound in each pair.

a. $CH_3CH{=}CHOH \longrightarrow H^+ + CH_3CH{=}CHO^- \longleftrightarrow CH_3\bar{C}HCH{=}O$

b. $CH_3C({=}O){-}OH \longrightarrow H^+ + CH_3C({=}O){-}O^- \longleftrightarrow CH_3C({-}O^-){=}O$

c. $CH_3CH{=}CHOH \longrightarrow H^+ + CH_3CH{=}CHO^- \longleftrightarrow CH_3\bar{C}HCH{=}O$

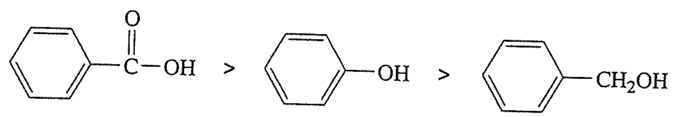
d. $CH_3CH{=}CH\overset{+}{N}H_3 \longrightarrow H^+ + CH_3CH{=}CHNH_2 \longleftrightarrow CH_3\bar{C}HCH{=}\overset{+}{N}H_2$

17. 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.

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.

18. The carboxylic acid is the most acidic because its conjugate base has greater resonance stabilization than does the conjugate base of phenol. The alcohol is the least stable because, unlike the negative change on the conjugate base of phenol, the negative change on its oxygen atom cannot be delocalized.

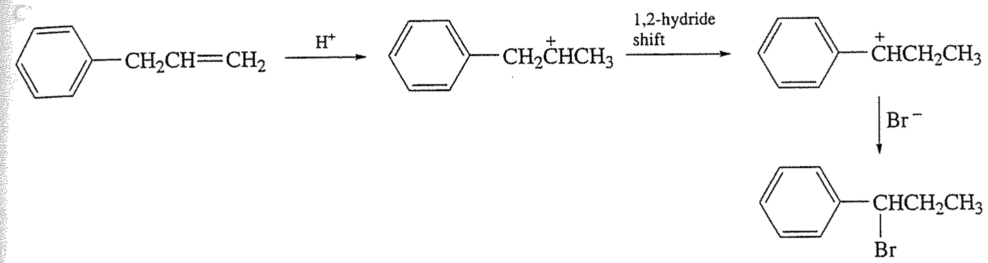


19. Solved in the text.

20. Electron withdrawal will make it a stronger acid (because it will make the conjugate base weaker). Electron donation will make it a weaker acid (because it will make the conjugate base stronger).

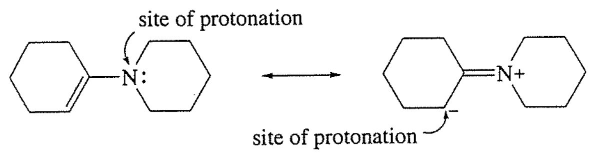
The pK_a values show that the methoxy substituted acid is a weaker acid (it has a larger pK_a value). Therefore, we know that resonance electron donation is a more important effect than inductive electron withdrawal.

21.



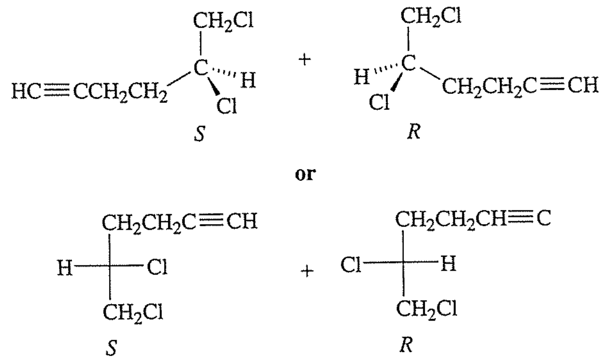
22. a. Solved in the text.

b. The contributing resonance structures show that there are two sites that could be protonated.

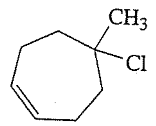


23. a. $CH_2{=}CHCH_2CH_2CH_2C(CH_3)(Br)CH_3$ The more reactive double bond is the one that forms a tertiary carbocation.

b.

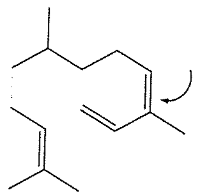


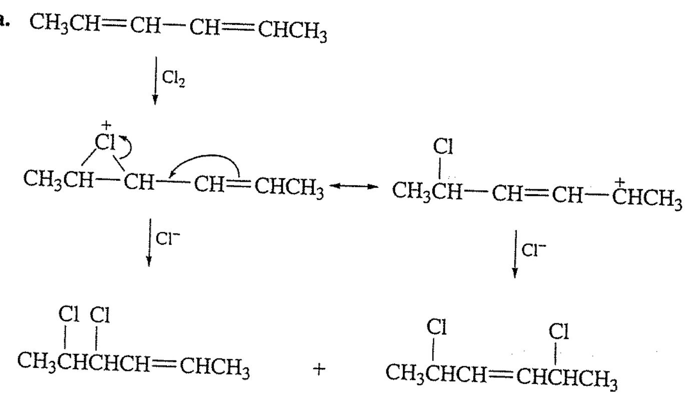
The double bond is more reactive than the triple bond. The reaction forms a new asymmetric center so a pair of enantiomers is formed.

c. 

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

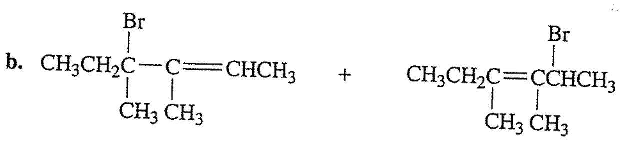
24. The indicated double bond is the most reactive in an electrophilic addition reaction because addition of an electrophile to this double bond forms the most stable carbocation (a tertiary allylic carbocation).



25. a. 

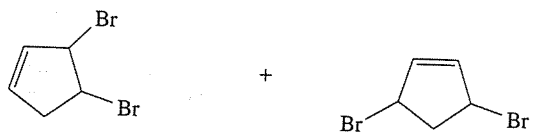
1,2- addition product

1,4- addition product

b. 

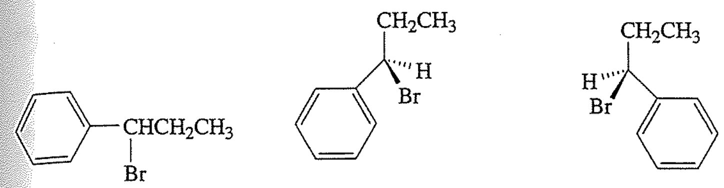
1, 2-addition product

1, 4-addition product

c. 

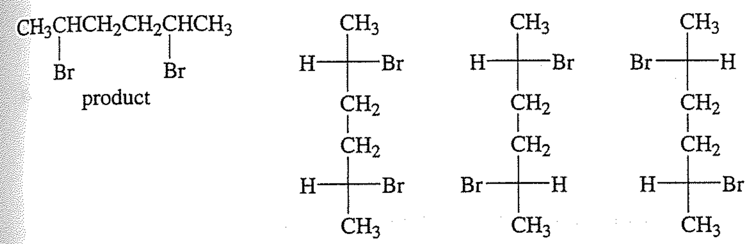
1, 2-addition product

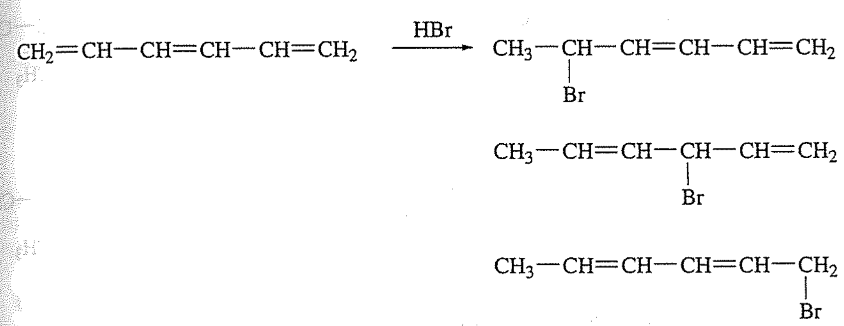
1, 4-addition product

26. 

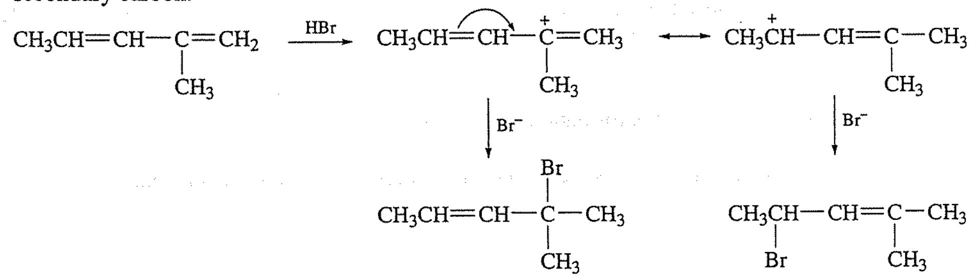
product

stereoisomers of the product

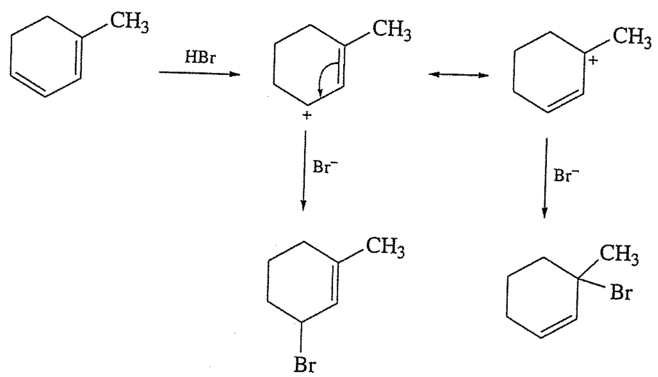


27. 

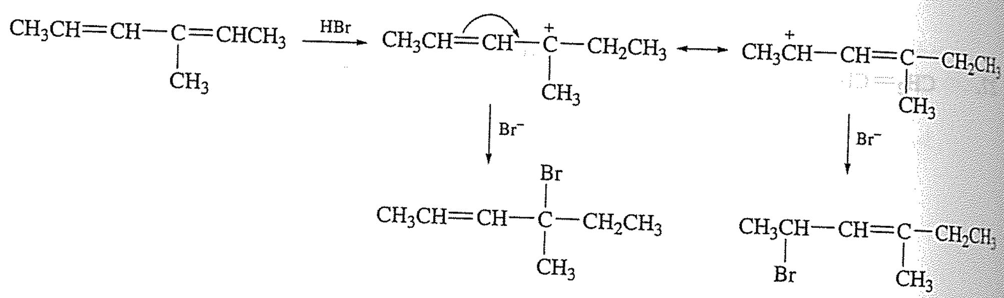
28. a. The proton adds so that the positive charge in the carbocation is shared by a tertiary and a secondary carbon.



b. The proton adds so that the positive charge in the carbocation is shared by a tertiary and a secondary carbon.



c. The proton adds so that the positive charge in the carbocation is shared by a tertiary and a secondary carbon.



29. **a.** Addition at C-1 forms the more stable carbocation, because the positive charge is shared by two secondary allylic carbons. If it had added to C-4, the positive charge would have been shared by a secondary and a primary carbocation.

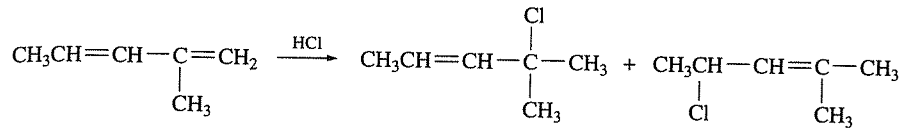
b. DCl was used to cause the 1,2- and 1,4-products to be different. If HCl had been used the 1,2-and 1,4-products would have been the same.

30. **a.** The rate-determining step is formation of the carbocation

b. The product-determining step is reaction of the carbocation with the nucleophile.

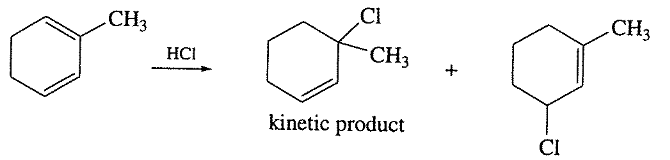
31. **a.** Solved in the text.

b.



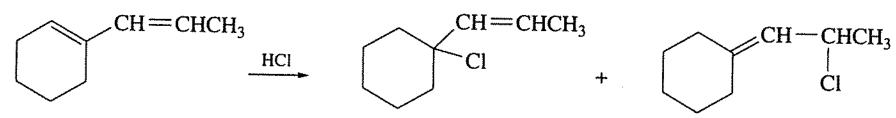
kinetic product thermodynamic product

c.



kinetic product thermodynamic product

d.

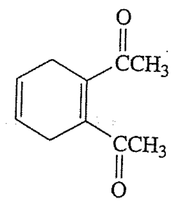


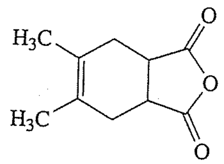
kinetic product thermodynamic product

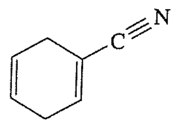
Notice that the 1,2-product is always the kinetic product.
The thermodynamic product is the product with the most substituted double bond

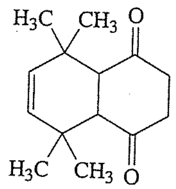
32. In order for a Diels-Alder reaction to occer, the overlapping orbitals of the reactants must have the same color (the same symmetry). In other words, they must both be symmetric or both be antisymmetric. In a [2+2] cycloaddition reaction at room temperature (in the ground state electronic configuration), the HOMO of one of the reactants will be symmetric and the LUMO of the other will be antisymmetric (see Figure 7.11 on p. 328 of the text). Thus, they will not have the same symmetry and the reaction will not occur.

In contrast, a [2+2] cycloaddition reaction does occur under photochemical conditions. Under photochemical conditions one of the alkenes will be in an excited state. Therefore, its HOMO will be antisymmetric and will be able to overlap with the antisymmetric LUMO of the other alkene.

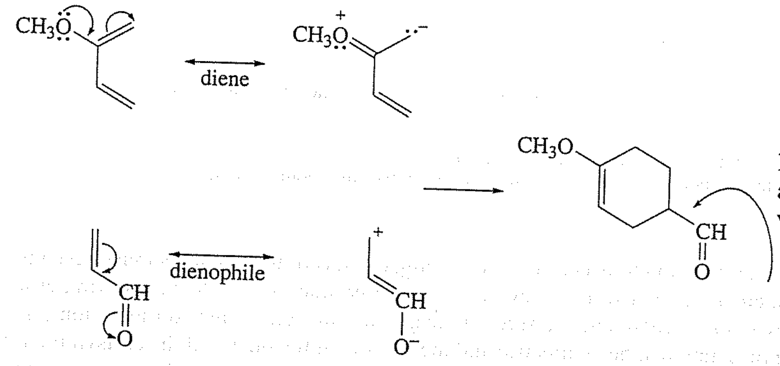
33. a. 

c. 

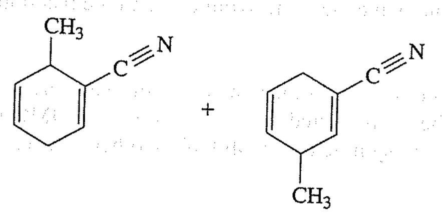
b. 

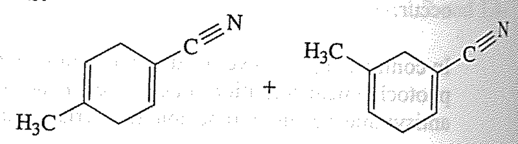
d. 

34. 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.



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

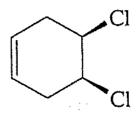
35. a. 

b. 

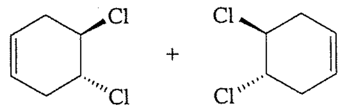
36. **a** and **d** will not react, because they are both locked in an *s*-trans conformation.
c and **e** will react, because they are both locked in an *s*-cis conformation.
b and **f** will react, because they can rotate into an *s*-cis conformation.

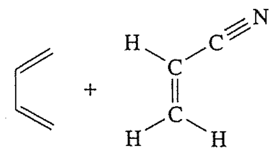
37. Solved in the text.

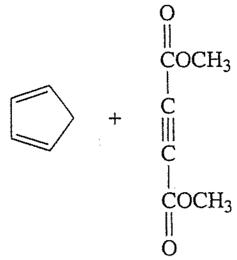
38. **a.** It is not optically active because it is a meso compound.
(It has 2 asymmetric centers and a plane of symmetry.)

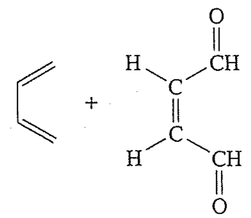


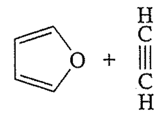
b. It is not optically active because it is a racemic mixture.
(Identical amounts of the enantiomers will be obtained.)

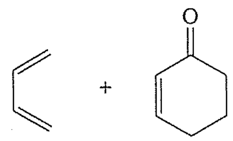


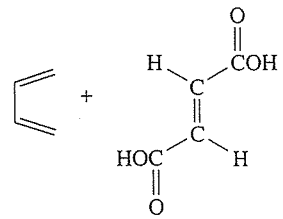
39. a. 

c. 

e. 

b. 

d. 

f. 

40. **a, b, d, e, i, l, m, n**

41. **a.** and **b.**

1. $\ddot{C}H_2^{-}-\overset{+}{N}\equiv N: \longleftrightarrow CH_2=\overset{+}{N}=\ddot{N}:^{-}$

More stable, because the negative charge is on nitrogen rather than on carbon.

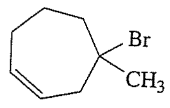
2. $:N\equiv\overset{+}{N}-\ddot{O}:^{-} \longleftrightarrow {}^{-}\ddot{N}=\overset{+}{N}=\ddot{O}:$

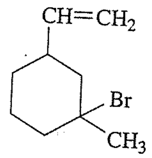
More stable, because the negative charge is on oxygen rather than on nitrogen.

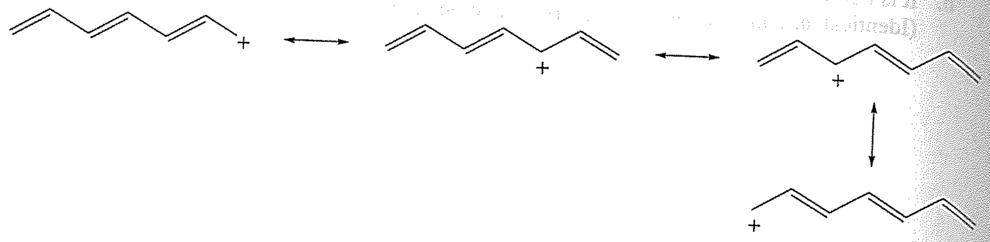
3. ${}^{-}:\ddot{O}-\ddot{N}=\ddot{O}: \longleftrightarrow :\ddot{O}=\ddot{N}-\ddot{O}:^{-}$

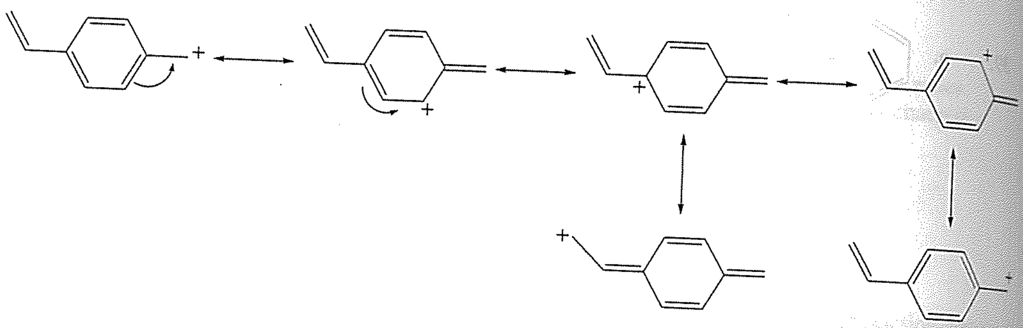
Both are equally stable.

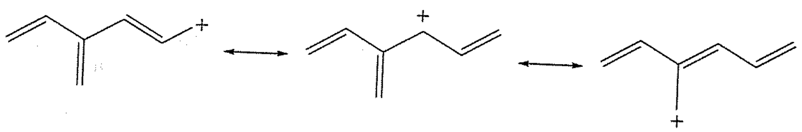
Additional resonance structures could be drawn for each of these three species, but they are relatively unstable because each has an incomplete octet.

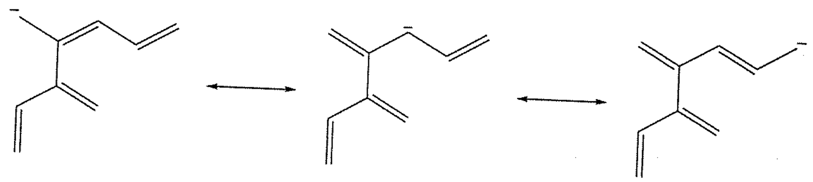
42. **a.** 

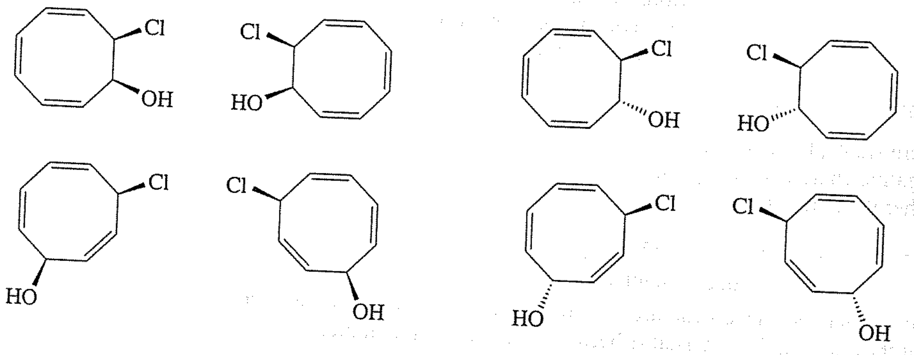
b. 

43. **a.** 

b. 

c. 

d. 

44. 

45. **a.** different compounds
b. different compounds
c. resonance contributors
d. resonance contributors
e. different compounds

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

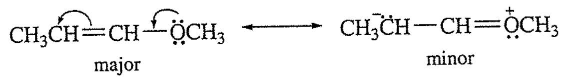
46. **a.** There are six linear dienes with molecular formula C_6H_{10}.

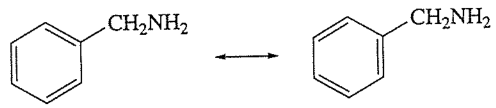
b. Two are conjugated dienes.
$CH_2{=}CHCH{=}CHCH_2CH_3$
$CH_3CH{=}CHCH{=}CHCH_3$

c. Two are isolated dienes.
$CH_2{=}CHCH_2CH{=}CHCH_3$
$CH_2{=}CHCH_2CH_2CH{=}CH_2$

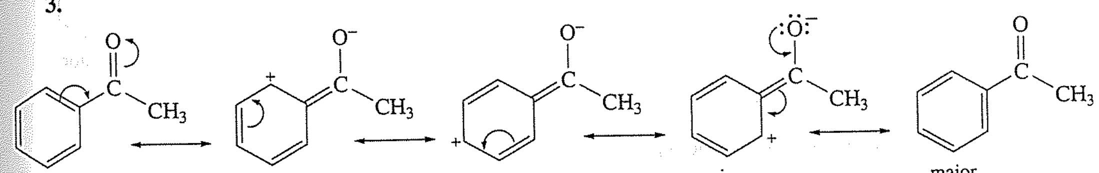
There are also two cumulated dienes.
$CH_2{=}C{=}CHCH_2CH_2CH_3$
$CH_3CH{=}C{=}CHCH_2CH_3$

47. **a.**

1. 

2. 

the two resonance contributors have the same stability

3. 

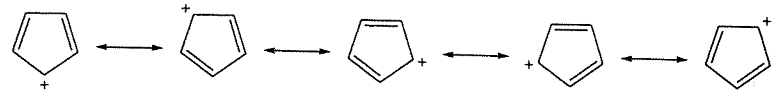
major minor minor minor major

4. $CH_3-\overset{+}{N}(=O)-O^- \longleftrightarrow CH_3-\overset{+}{N}(-O^-)=O$

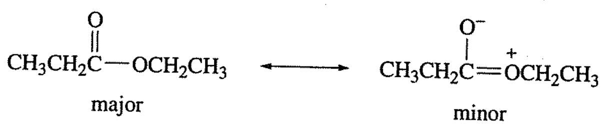
the two resonance contributors have the same stability

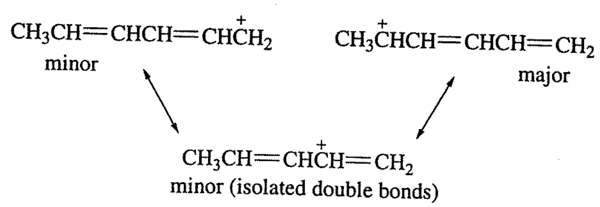
5. $CH_3\bar{C}H-\overset{+}{N}(=O)-O^-$ (minor) $\longleftrightarrow$ $CH_3\bar{C}H-\overset{+}{N}(-O^-)=O$ (minor) $\longleftrightarrow$ $CH_3CH{=}\overset{+}{N}(-O^-)-O^-$ (major)

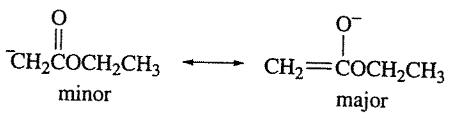
6. $CH_3CH{=}CH\overset{+}{C}H_2$ (minor) $\rightleftharpoons$ $CH_3\overset{+}{C}HCH{=}CH_2$ (major)

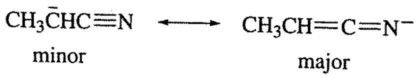
7. 

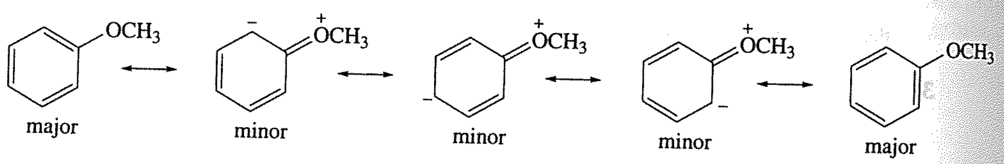
The five contributors are equally stable

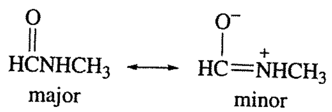
8. 

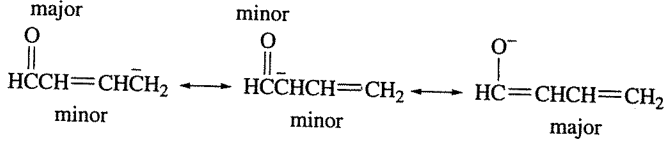
9. 

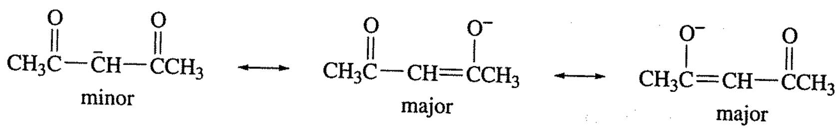
10. 

11. 

12. 

13. 

14. 

15. 

b. **2, 4** and **7**

48. Both compounds form the same product when they are hydrogenated, so the difference in heats of hydrogenation will 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, will have a greater heat of hydrogenation (a more negative $\Delta H°$).

$$CH_2{=}C{=}CHCH_2CH_3 \xrightarrow[Pd/C]{H_2} CH_3CH_2CH_2CH_2CH_3$$

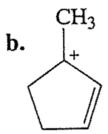
1,2-pentadiene

$$CH_2{=}CHCH_2CH{=}CH_2 \xrightarrow[Pd/C]{H_2} CH_3CH_2CH_2CH_2CH_3$$

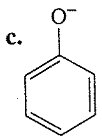
1,4-pentadiene

49. **a.** $CH_3\overset{+}{C}HCH{=}CH_2$

This makes the greater contribution because the positive charge is on a secondary carbon.

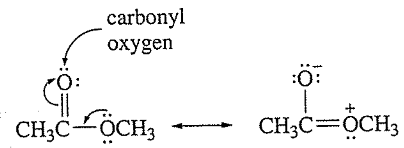
b. 

This makes the greater contribution because the positive charge is on a tertiary carbon.

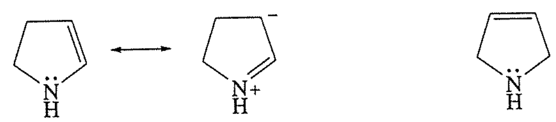
c. 

This makes the greater contribution because the negative charge is on an oxygen.

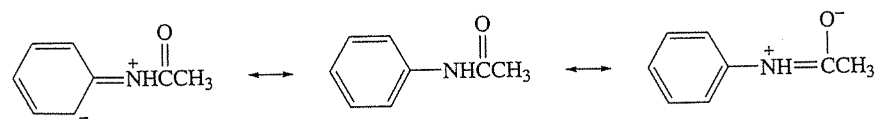
50. **a.** The resonance contributors show that the carbonyl oxygen has the greater electron density.



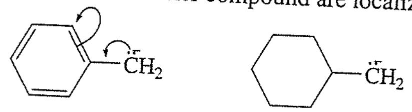
b. The compound on the right has the greater electron density on its nitrogen because the compound on the left has a resonance contributor with a positive charge on the nitrogen.



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

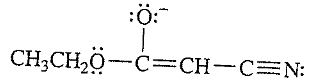


51. The methyl group on benzene can lose a proton easier than the methyl group on cyclohexane because the electrons left behind on the carbon in the former can be delocalized into the benzene ring. In contrast, the electrons left behind in the other compound are localized on the carbon.

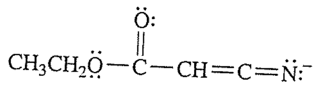


52. The carbocation is stable because the positive charge is shared by 10 carbon atoms (the central carbon and 3 carbons of each of the 3 benzene rings).

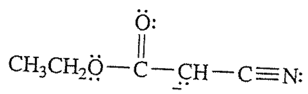
53.



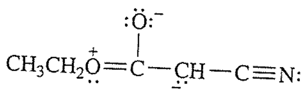
#1 most stable because the negative charge is on oxygen



#2 because the negative charge is on nitrogen

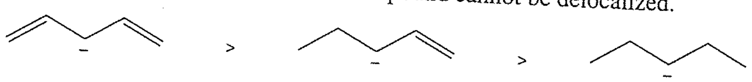


#3 because the negative charge is on carbon



#4 the least stable because the negative charge is on carbon and it has separated charges

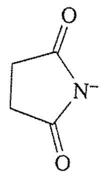
54. The more the electrons that are left behind when the proton is removed can be delocalized, the greater the stability of the base. The more stable the base, the more acidic its conjugate acid. The negative charge on the base in the first compound can be delocalized onto two other carbons; the negative charge on the base in the second compound can be delocalized onto one other carbon; the negative charge on the base in the last compound cannot be delocalized.



55.
a. $CH_3\overset{O}{\overset{\|}{C}}O^-$ — the negative charge is shared by 2 oxygens

b. $CH_3\overset{O}{\overset{\|}{C}}\underset{-}{C}H\overset{O}{\overset{\|}{C}}CH_3$ — the negative charge is shared by a carbon and 2 oxygens

c. $CH_3CH_2\underset{-}{C}H\overset{O}{\overset{\|}{C}}CH_3$ — the negative charge is shared by a carbon and an oxygen

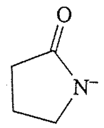
d.  the negative charge is shared by a nitrogen and 2 oxygens

56. The stronger base is the less stable base of each pair in Problem 55.

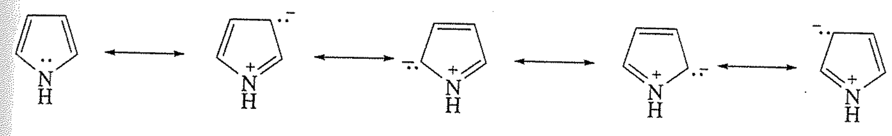
a. $H\overset{O}{\overset{\|}{C}}CH_2O^-$ — Less stable because the negative charge cannot be delocalized.

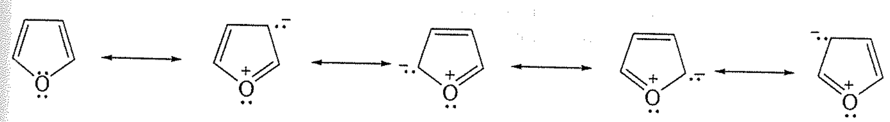
b. $CH_3\overset{O}{\overset{\|}{C}}\underset{-}{C}HCH_2\overset{O}{\overset{\|}{C}}CH_3$ — Less stable because the negative charge can be delocalized onto only one carbonyl oxygen.

c. $CH_3\bar{C}HCH_2\overset{O}{\overset{\|}{C}}CH_3$ — Less stable because the negative charge cannot be delocalized.

d.  Less stable because the negative charge can be delocalized onto only one carbonyl oxygen.

57. 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.





58. **A** is the most acidic because the electrons left behind when the proton is removed can be delocalized onto two oxygen atoms. **B** is the next most acidic because the electrons left behind when the proton is removed can be delocalized onto one oxygen atom. **C** is the least acidic because the electrons left behind when the proton is removed cannot be delocalized.

$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$ (A) > $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$ (B) > $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$ (C)

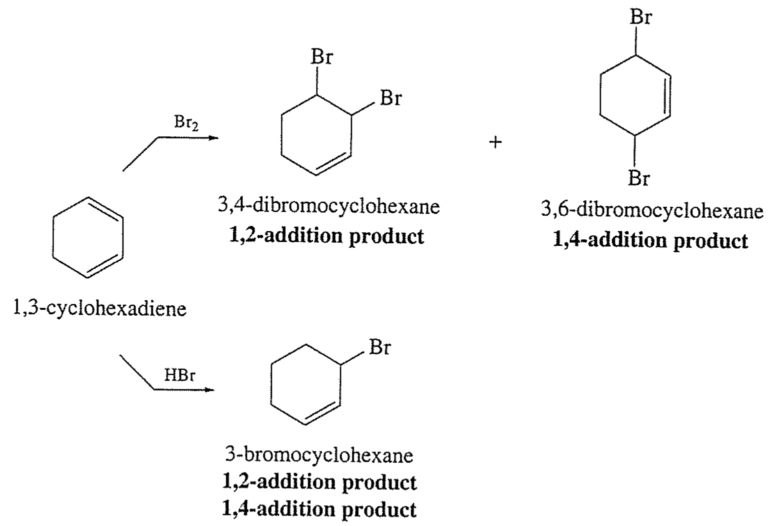
59.
a. It has 8 molecular orbitals.
b. ψ_1, ψ_2, ψ_3, and ψ_4 are bonding molecular orbitals; ψ_5, ψ_6, ψ_7, and ψ_8 are antibonding molecular orbitals.
c. ψ_1, ψ_3, ψ_5 and ψ_7 are symmetric molecular orbitals; ψ_2, ψ_4, ψ_6, and ψ_8 are antisymmetric molecular orbitals.
d. ψ_4 is the HOMO and ψ_5 is the LUMO in the ground state.

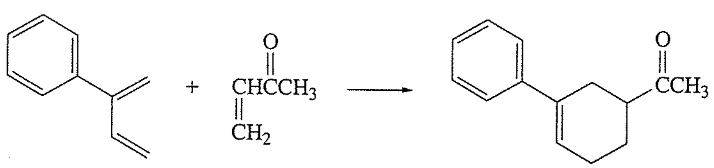
e. ψ_5 is the HOMO and ψ_6 is the LUMO in the excited state.

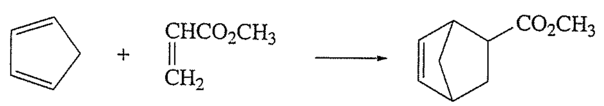
f. The HOMO is symmetric, the LUMO is antisymmetric and vice versa.

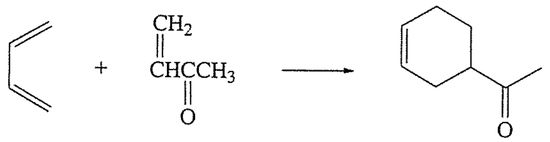
g. It has 7 nodes between the nuclei. It also has one node that passes through the nuclei.

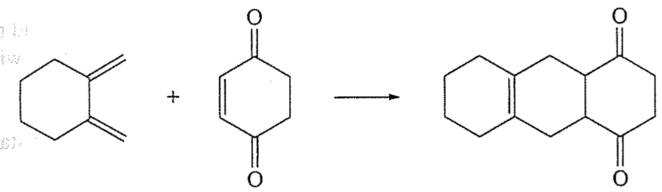
60. The reaction of 1,3-cyclohexadiene with Br_2 forms 3,4-dibromocyclohexene as the 1,2-addition product and 3,6-dibromocyclohexene as the 1,4-addition product. (Recall that in naming the compounds, the double bond is at the 1,2-position.) The reaction of 1,3-cyclohexadiene with HBr forms 3-bromocyclohexene as both the 1,2-addition product and the 1,4-addition product.

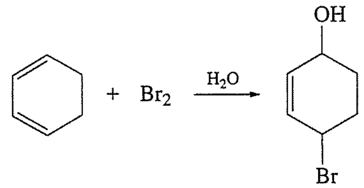


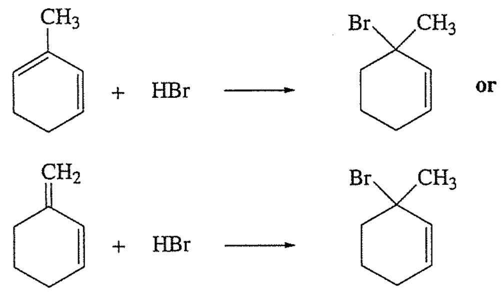
61. a. 

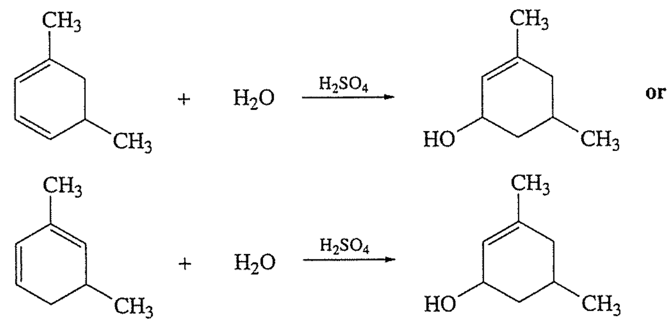
b. 

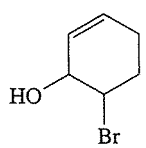
c. 

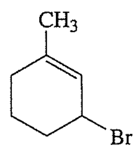
d. 

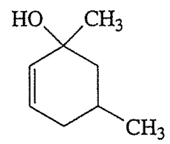
62. a. 1. 

2. 

3. 

b. 1. 

2. 

3. 

63. a. $CH_2{=}CHCH{=}CHCH{=}CH_2 \xrightarrow{HBr} CH_3CHCH{=}CHCH{=}CH_2$ (Br on C-2) **A** +

1,3,5-hexatriene

$CH_3CH{=}CHCHCH{=}CH_2$ (Br on C-4) **B** + $CH_3CH{=}CHCH{=}CHCH_2Br$ **C**

b. A will predominate if the reaction is under kinetic control because it is the 1,2-product and therefore will be the product formed most rapidly as a result of the proximity effect. In addition, A will be the 1,2-product regardless of which end of the conjugate 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.)

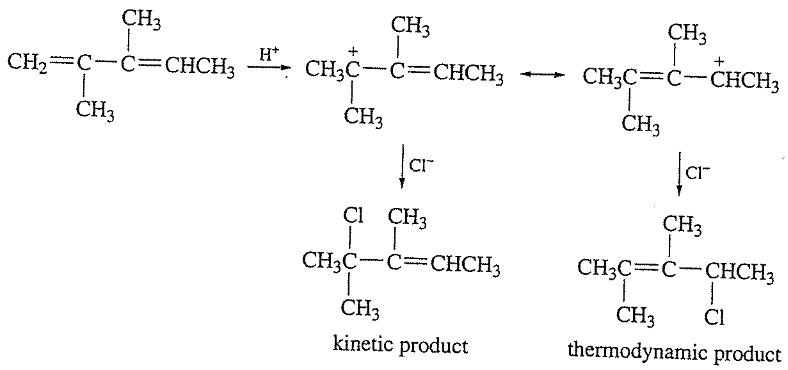
64. The diene is the nucleophile, and the dienophile is the electrophile in a Diels-Alder reaction.

a. An electron-donating substituent in the diene would increase the rate of the reaction, because electron donation would increase its nucleophilicity.

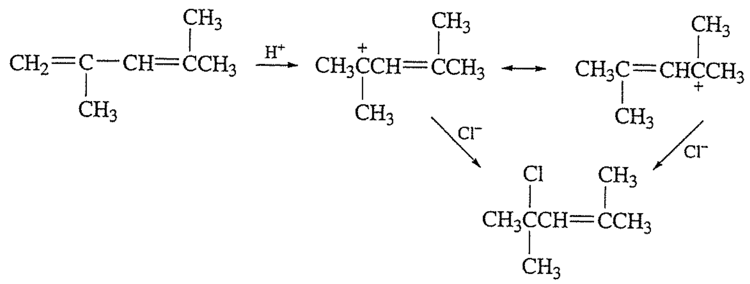
b. An electron-donating substituent in the dienophile would decrease the rate of the reaction, because electron donation would decrease its electrophilicity.

c. An electron-withdrawing substituent in the diene would decrease the rate of the reaction, because electron withdrawal would decrease its nucleophilicity.

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

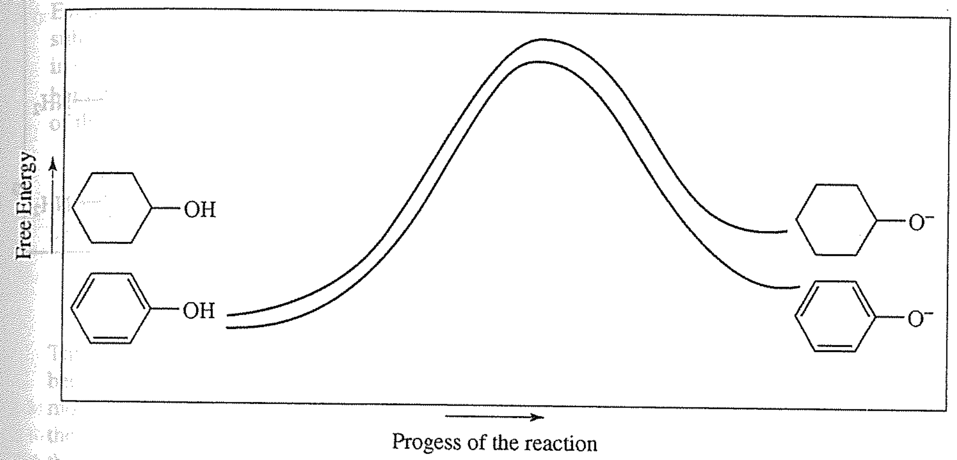


b. Addition of an electrophile to C-1 forms a carbocation with two resonance contributors; both are *tertiary allylic* carbocations.
Addition of an electrophile to C-4 forms a carbocation with two resonance contributors, a *secondary allylic* carbocation and a *primary allylic* carbocation.
Therefore,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

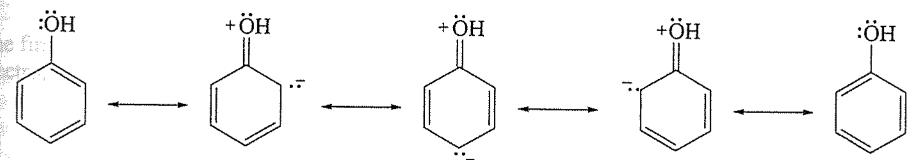


This is the only product because the carbocation is symmetrical.

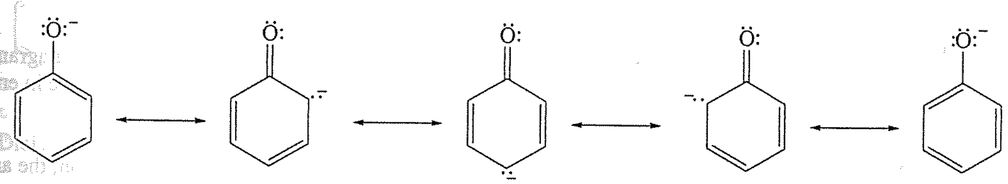
66. **a.** and **d.**



b.



c.



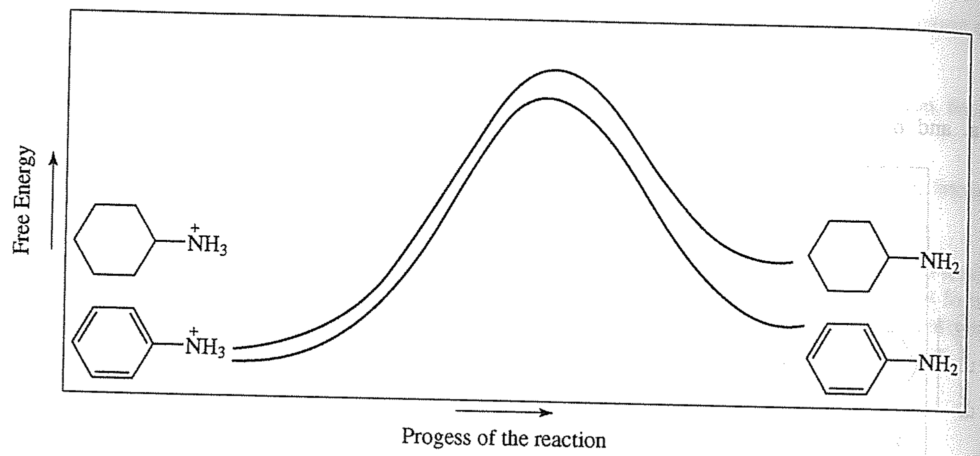
d. The resonance contributors in "c" are more stable than the resonance contributors in "b" because in "b" a positive charge is on the most electronegative atom (the oxygen).
Therefore, the phenolate ion has greater resonance stabilization than phenol.

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.

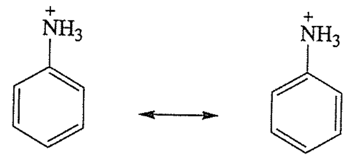
e. Because of the greater resonance stabilization of the phenolate ion compared to phenol, phenol has a larger K_a than cyclohexanol.

f. Because it has a larger K_a (a lower pK_a), phenol is a stronger acid.

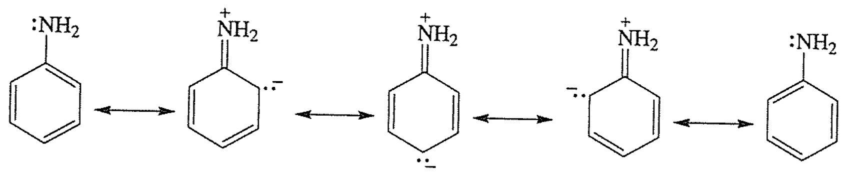
67.



b.



c.

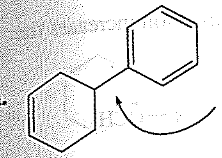


d. Aniline has greater resonance stabilization than the anilinium ion. Thus in the energy diagram, the difference in energy between aniline and cyclohexylamine is greater than the difference in energy between the anilinium ion and the cyclohexylammonium ion.

e. Because of the greater resonance stabilization of aniline compared to the anilinium ion, the anilinium ion has a larger K_a than the cyclohexylammonium ion.

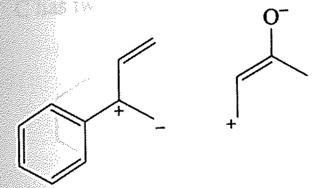
f. Because it has a larger K_a (a lower pK_a), the anilinium ion is a stronger acid than the cyclohexylammonium ion. Therefore, cyclohexylamine is a stronger base than aniline. (The stronger the acid, the weaker its conjugate base.)

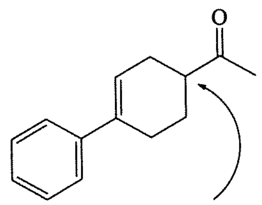
68. **a.**



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

b.

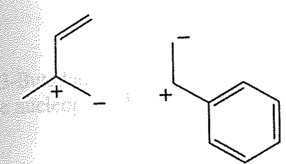


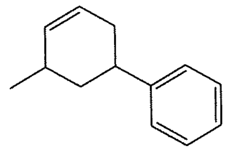


Even though both reacts are unsymmetrically substituted, the reactants will be aligned primarily in one way, because of the relatively stable tertiary benzylic cation and delocalization of the π electrons of the dieneophile onto the oxygen.

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

c.

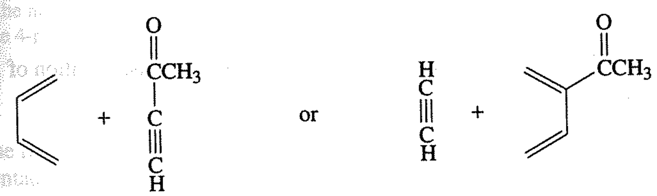




The products will be aligned primarily as shown because in the diene, a tertiary allylic carbocation is more stable than a secondary allylic carbocation. In the dienophile, a primary carbanion is more stable than a primary carbocation would be.

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

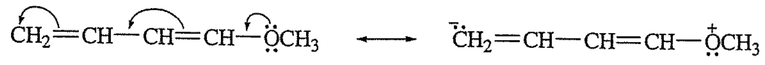
69. The first pair is the preferred set of reagents because it has the more nucleophilic diene and the more electrophilic dienophile.



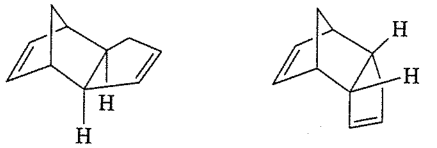
70. A Diels-Alder reaction is a reaction between a nucleophilic diene and an electrophilic dienophile.

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.

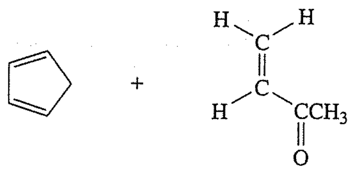


71.

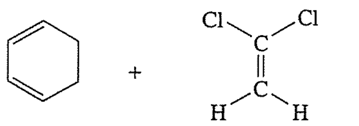


exo endo

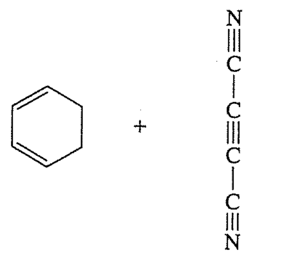
72. **a.**



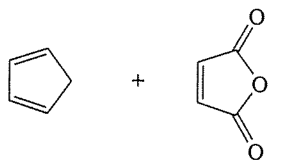
b.



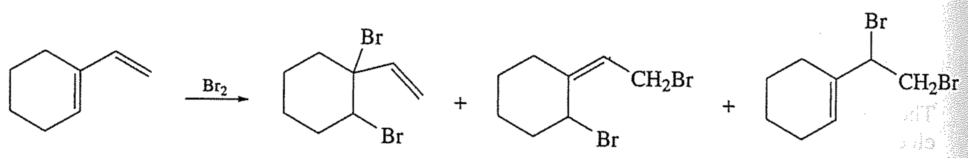
c.



d.

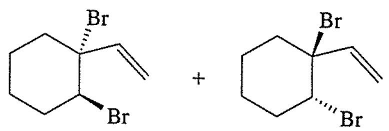


73. **a.**

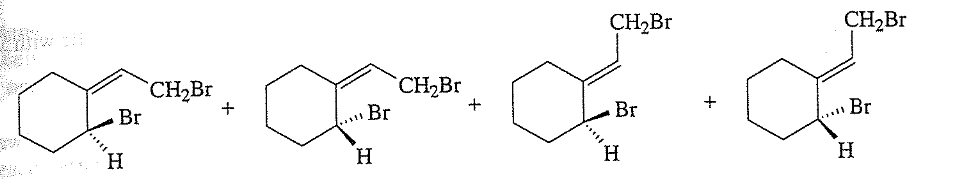


A B C

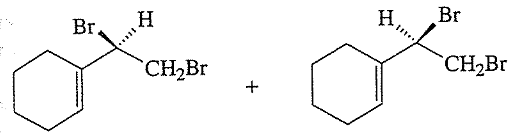
b. A has two asymmetric centers but only two stereoisomers are obtained because addition of Br_2 can occur only in an anti fashion.



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



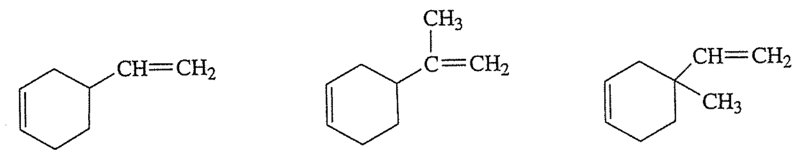
C has two stereoisomers because it has one asymmetric center



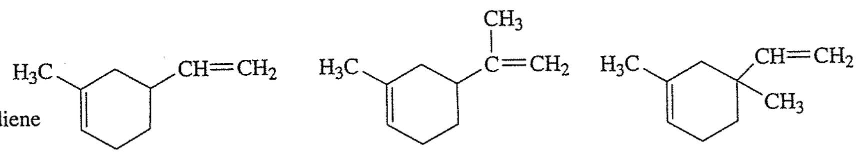
74. Nine of the compounds are shown below. Since each has one asymmetric center, each can have either the *R* or the *S* configuration. Therefore, 18 different products can be obtained.

	1,3-Butadiene is the electrophile.	The 3,4-bond of 2-methyl-1,3-butadiene is the electrophile.	The 1,2-bond of 2-methyl-1,3-butadiene is the electrophile.

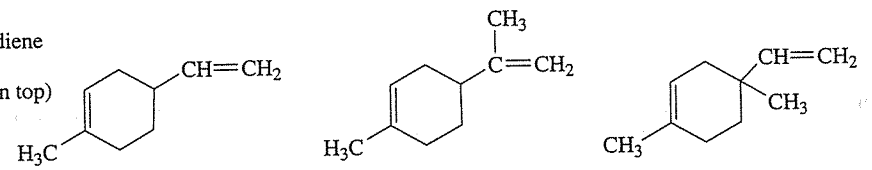
1,3-Butadiene is the nucleophile.



2-Methyl-1,3-butadiene is the nucleophile. (the 1-position is on top)

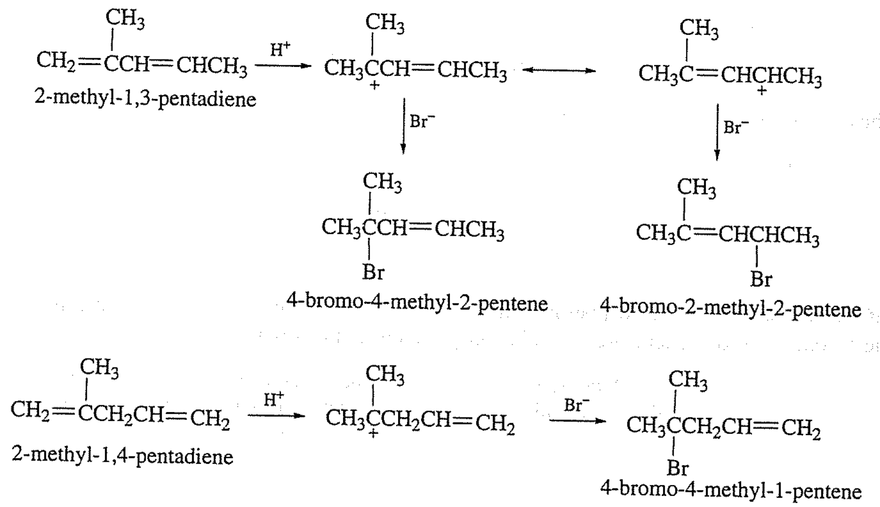


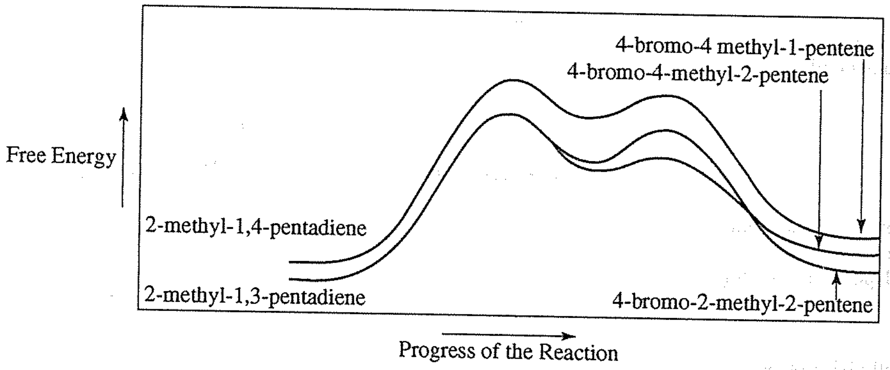
2-Methyl-1,3-butadiene is the nucleophile. (the 4-position is on top)



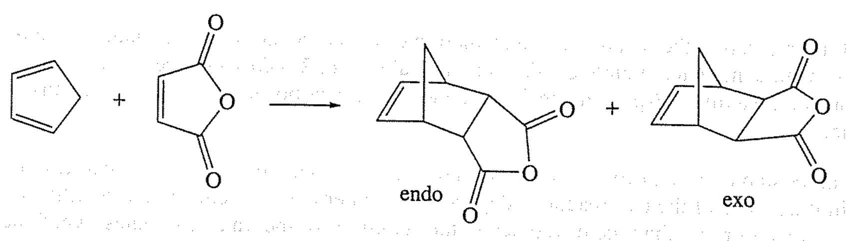
75. The rate-limiting step of the reaction is the formation of the carbocation intermediate. 2-Methyl-1,3-pentadiene (with conjugated double bonds) is more stable than 2-methyl-1,4-pentadiene (with isolated double bonds). 2-Methyl-1,3-pentadiene forms a more stable carbocation than does 2-methyl-1,4-pentadiene.

Since the more stable reactant forms the more stable carbocation, the relative free energies of activation of 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 (which depend on the difference in stabilities of the carbocations). Because the difference in the stabilities of the reactants is less than the difference in the stabilities of the transition states, 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.)





76. His recrystallization was not successful. Because maleic anhydride is a dienophile, it reacts with cyclopentadiene in a Diels-Alder reaction.



77. High temperatures are required in order to break the bonds formed by the overlapping in-phase orbitals. The Diels-Alder product will not reform at high temperatures, because a [4+2] cycloaddition will not occur unless both of the reactants are in their ground states.

78. We saw in Problem 76 that maleic anhydride reacts with cyclopentadiene. The function of maleic acid in this reaction is to remove the cyclopentadiene, since removal of a product drives the equilibrium toward products. (See Le Châtelier's principle on page 144 of the text.)

79. The bridgehead carbon cannot have the 120° bond angle required for the sp^2 hybridized carbon of a double bond. With a 120° bond angle, the compound would be too strained to exist.

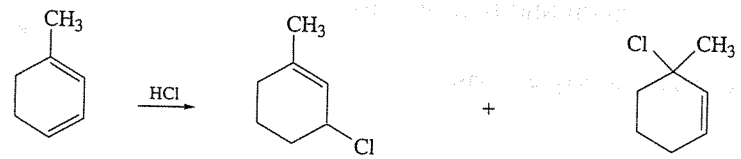
80. **a.** Unless the reaction is being carried out under kinetic control, the amount of product obtained is not dependent on the rate at which the product is formed, so the relative amounts of products obtained will not tell you which product was formed faster.

b. In a thermodynamically controlled reaction, the product distribution depends on the realative stabilites of the products since the products come to equilibrium. Thus if the distribution of products that is obtained does not reflect the relative stabilities of the products, the reaction must have been kinetically controlled.

81. He should follow his friend's advice. If he uses 2-methyl-1-3,cyclohexadiene, the product that is formed faster 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 on primarily on a tertiary carbon. Thus the experiment will not be able to differentiate between the two.

3-chloro-3-methylcyclohexene

If he follows his friend's advice and uses 1-methyl-1-3,cyclohexadiene, the product that is formed faster 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 this is the product that is formed through a transition state in which the positive charge on primarily on a tertiary carbon.



3-chloro-1-methylcyclohexene 3-chloro-3-methylcyclohexene