

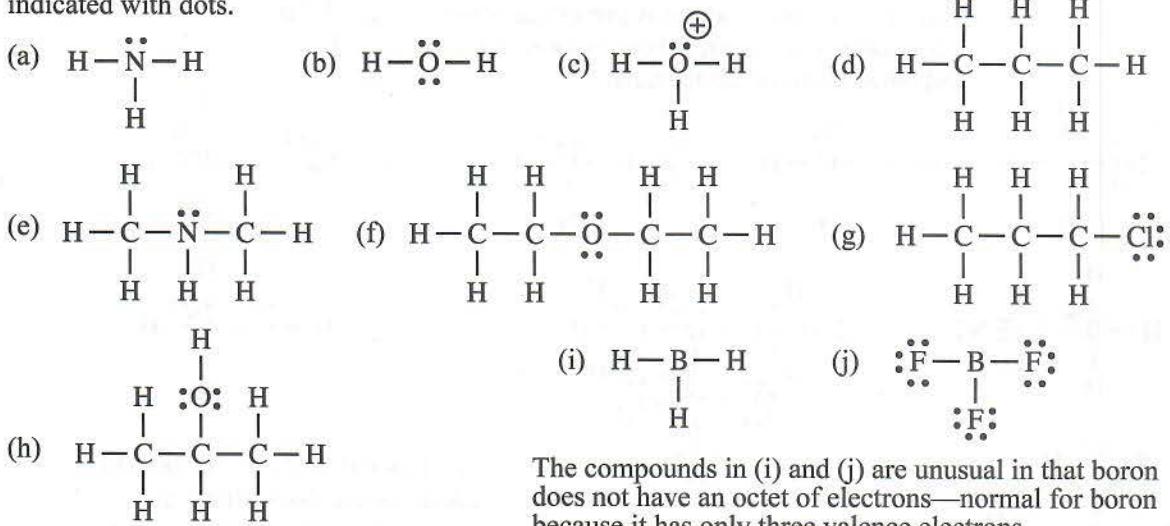
## CHAPTER 1—STRUCTURE AND BONDING

1-1

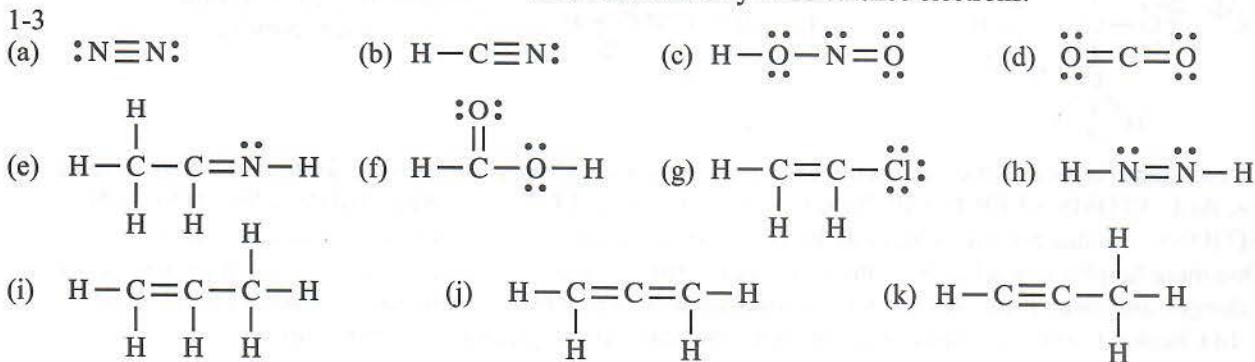
(a) Nitrogen has atomic number 7, so all nitrogen atoms have 7 protons. The mass number is the total number of neutrons and protons; therefore,  $^{13}\text{N}$  has 6 neutrons,  $^{14}\text{N}$  has 7 neutrons,  $^{15}\text{N}$  has 8 neutrons,  $^{16}\text{N}$  has 9 neutrons, and  $^{17}\text{N}$  has 10 neutrons.

(b)	Na	$1s^2 2s^2 2p^6 3s^1$	P	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
	Mg	$1s^2 2s^2 2p^6 3s^2$	S	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
	Al	$1s^2 2s^2 2p^6 3s^2 3p_x^1$	Cl	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
	Si	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$	Ar	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$

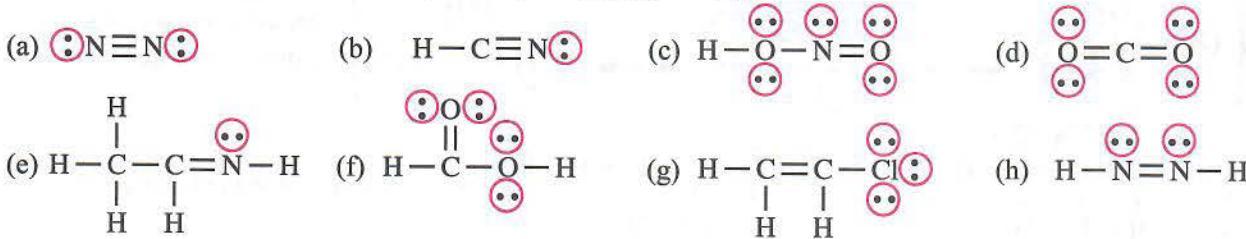
1-2 Lines between atom symbols represent covalent bonds between those atoms. Nonbonding electrons are indicated with dots.



The compounds in (i) and (j) are unusual in that boron does not have an octet of electrons—normal for boron because it has only three valence electrons.



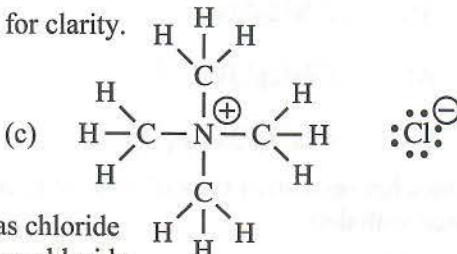
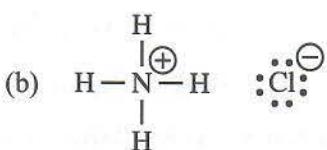
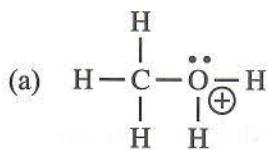
1-4 There are no unshared electron pairs in parts (i), (j), and (k).



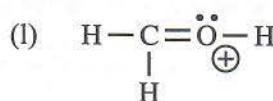
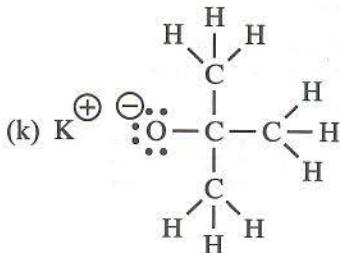
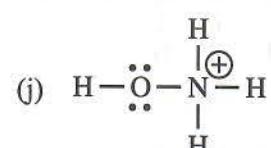
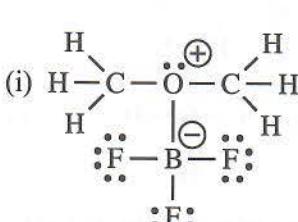
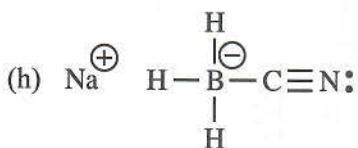
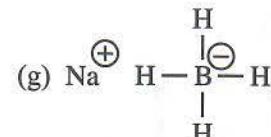
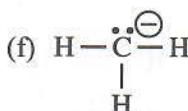
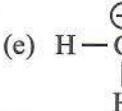
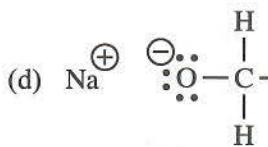
1-5 The symbols " $\delta^+$ " and " $\delta^-$ " indicate bond polarity by showing partial charge. (In the arrow symbolism, the arrow should point to the partial negative charge.)

- |          |         |         |         |          |
|----------|---------|---------|---------|----------|
| (a) C—Cl | (b) C—O | (c) C—N | (d) C—S | (e) C—B  |
| (f) N—Cl | (g) N—O | (h) N—S | (i) N—B | (j) B—Cl |

1-6 Non-zero formal charges are shown beside the atoms, circled for clarity.



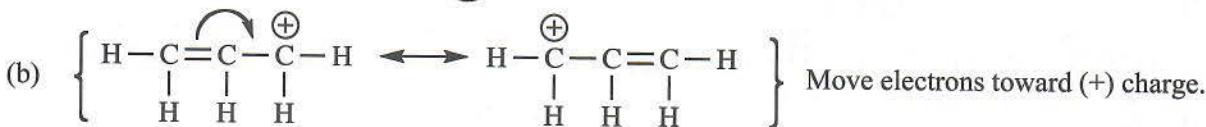
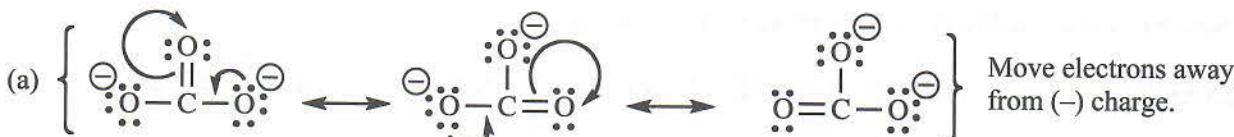
In (b) and (c), the chlorine is present as chloride ion. There is no covalent bond between chloride and other atoms in the formula.



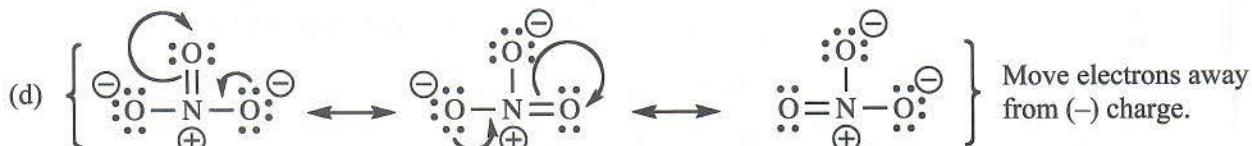
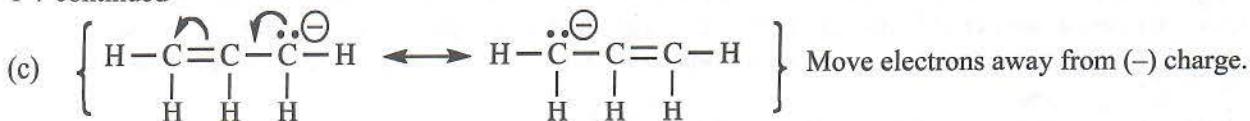
As shown in (d), (g), (h), and (k), alkali metals like sodium and potassium form only ionic bonds, never covalent bonds.

1-7 Resonance forms in which all atoms have full octets are the most significant contributors. In resonance forms, ALL ATOMS KEEP THEIR POSITIONS—ONLY ELECTRONS ARE SHOWN IN DIFFERENT POSITIONS. (In this Solutions Manual, braces {} are commonly used to denote resonance forms.)

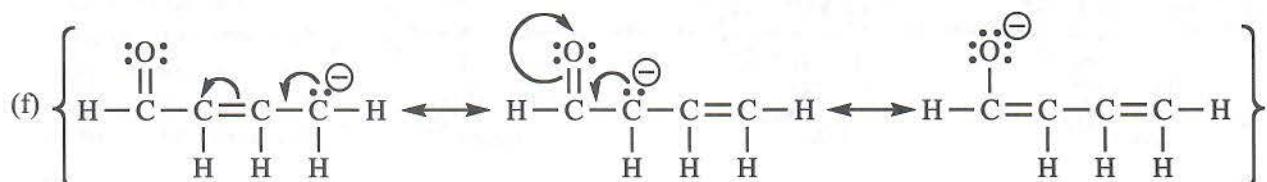
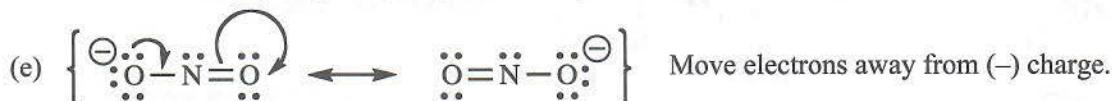
One more helpful hint when drawing resonance forms of structures with charges: *move electrons toward (+) charges and away from (-) charges*. Arrows show how to alter one structure to make it into the next one. In Chapter 1, arrows in resonance forms are the same as the green arrows in the text.



1-7 continued

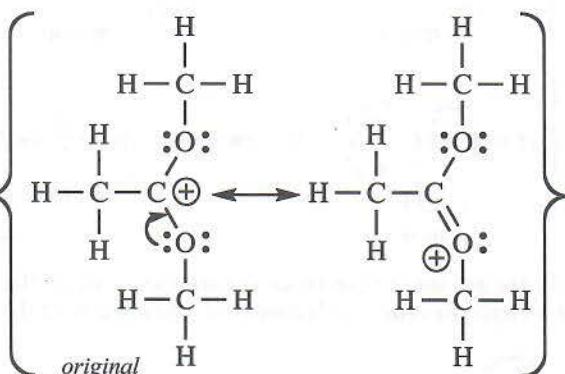
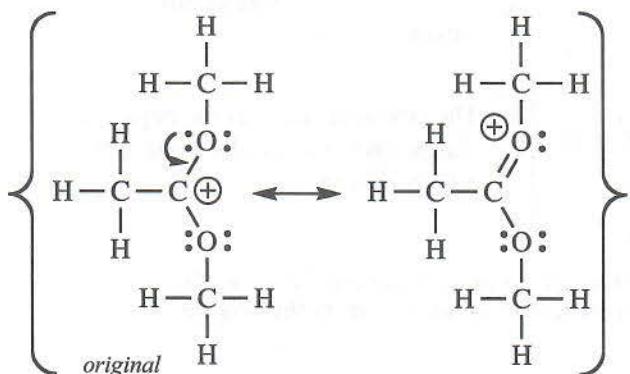


Look how similar part (d) is to part (a) above. They are "isoelectronic", meaning the same number of electrons.



Move electrons away from (-) charge.

(g) There are three resonance forms shown here; the structure given in the problem ("original") is shown twice because the electrons can be delocalized in two different directions; each of the other structures is derived from the original.

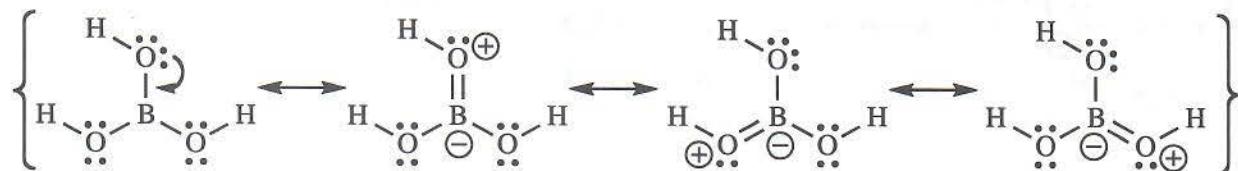


Move electrons toward (+) charge.

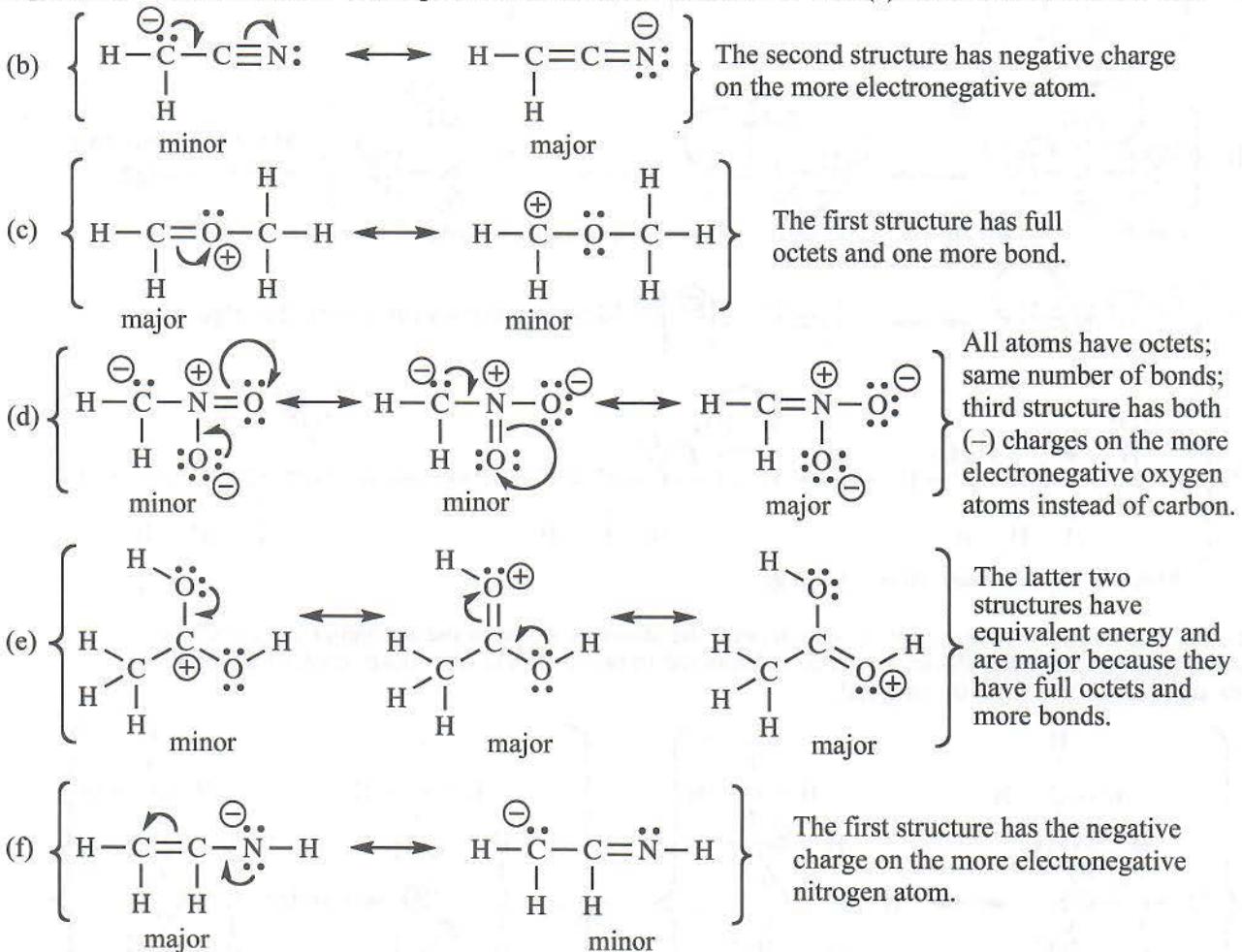
Move electrons toward (+) charge.

(h) In similar fashion to part (g), the three other resonance forms are derived from the first. In this solution, however, for simplicity, only the first structure has the arrow showing how the first structure can be made into the second. It should be apparent to you to see how to make the first structure into the third and fourth. Alternatively, you can transform the second into the third directly by using two arrows.

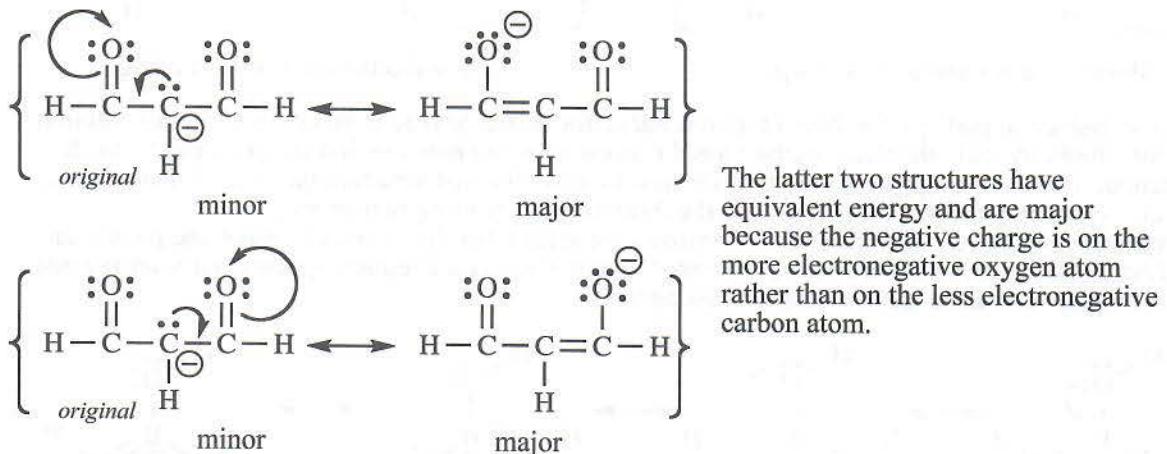
It is very important to keep in mind that these arrows are simply helpful devices to make one picture into another. *They do not mean that electrons are moving!* There is one real chemical species that is an average of all the individual resonance forms which are just pictures.



1-8 Major resonance contributors would have the lowest energy. The most important factors are: maximize full octets; maximize number of bonds; put negative charge on electronegative atoms; minimize charge separation— see the Problem-Solving Hint above Solved Problem 1-2. Part (a) has been solved in the text.



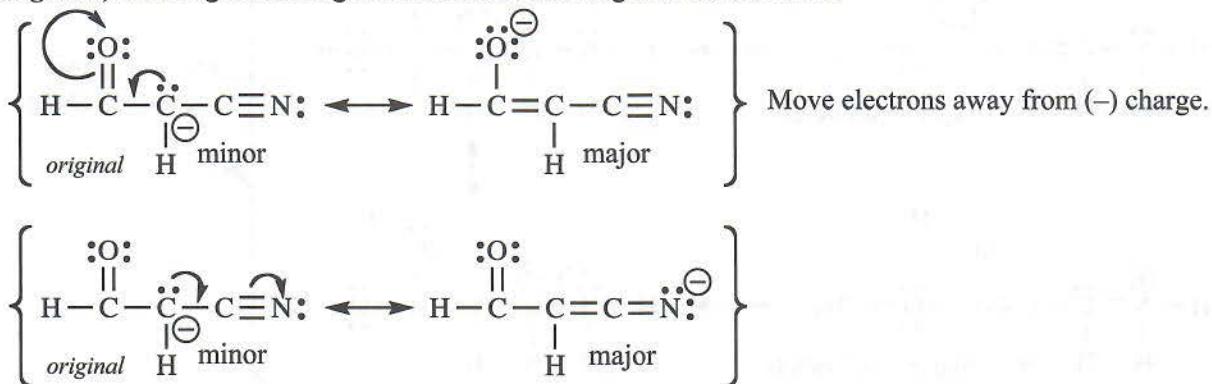
(g) There are three resonance forms shown here; the structure given in the problem ("original") is shown twice in order to demonstrate how each of the other structures is derived from the original.



1-8 continued

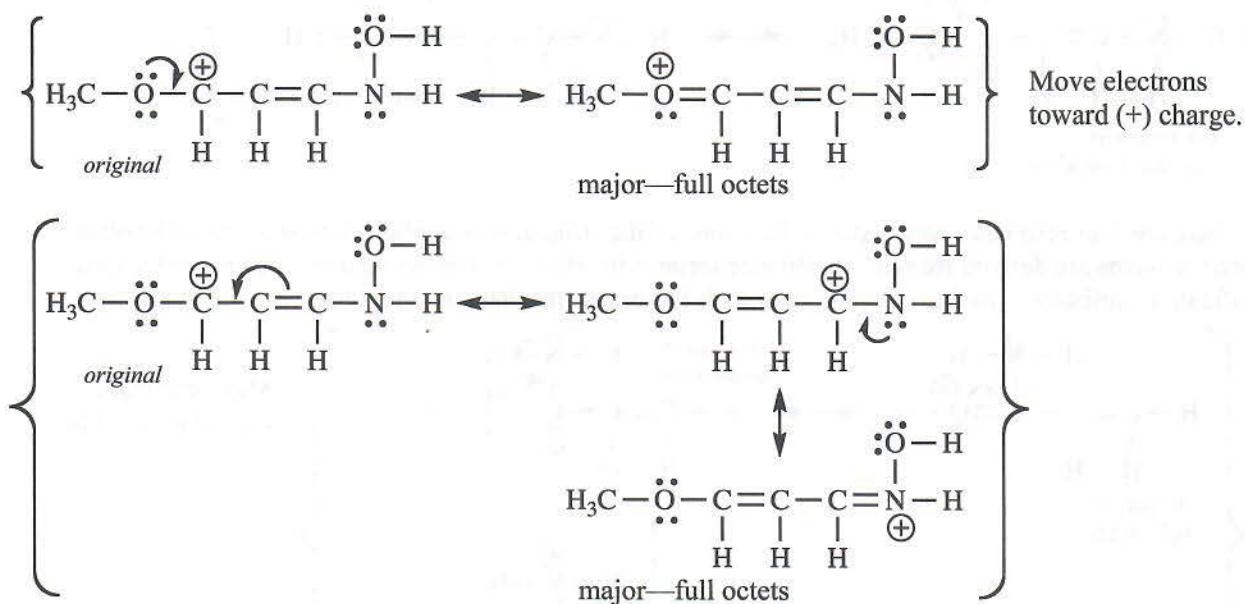
(h) There are three resonance forms shown here; the structure given in the problem ("original") is shown twice in order to demonstrate how each of the other structures is derived from the original.

All three resonance forms have full octets and the same number of bonds. The second structure is the most significant contributor because the negative charge is on the oxygen (most electronegative); the third structure with negative charge on nitrogen is next; the least significant contributor is the first structure ("original") with negative charge on the least electronegative carbon atom.



1-9

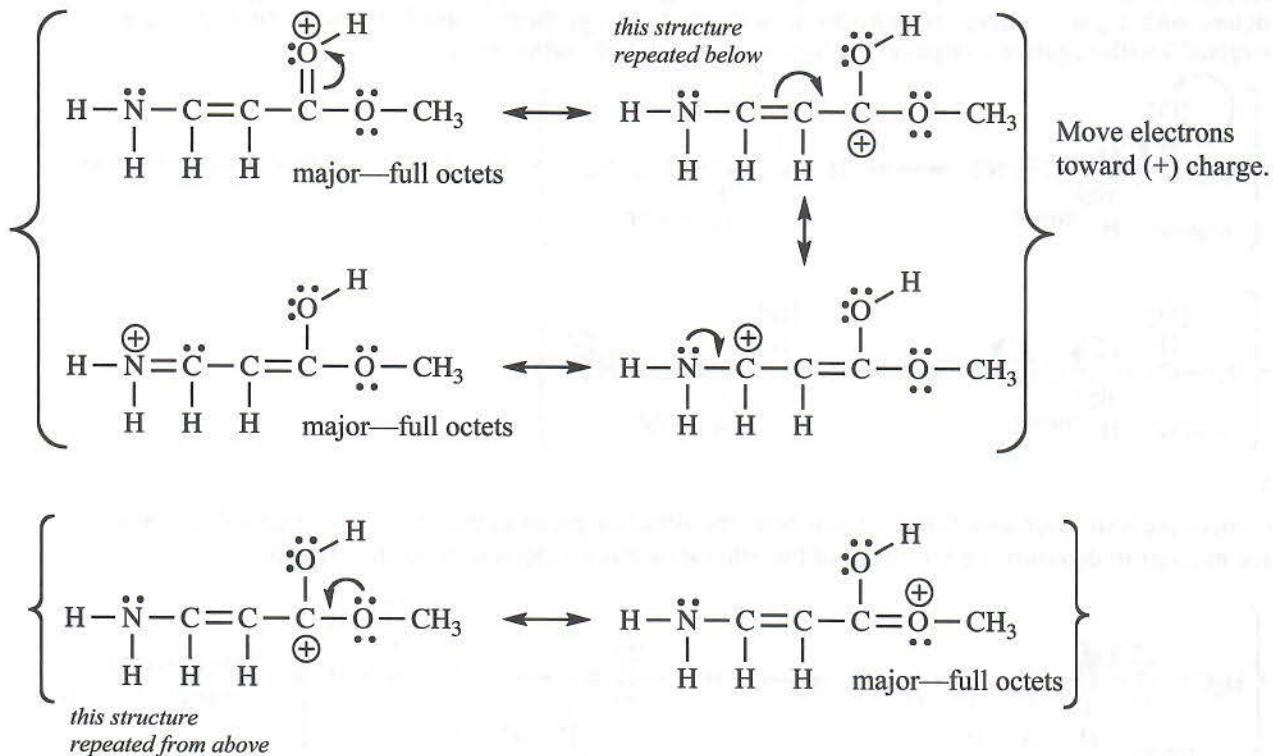
(a) There are four resonance forms shown here; the structure given in the problem ("original") is shown twice in order to demonstrate how each of the other structures is derived from the original.



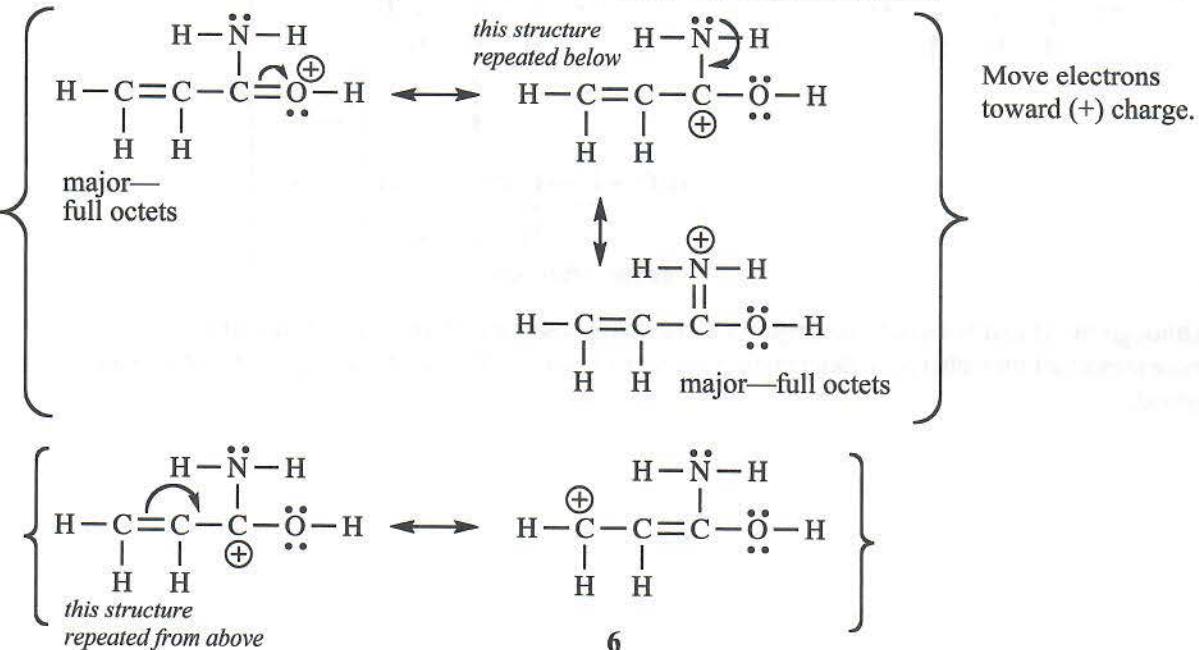
Although the O and N have (+) charges in these major resonance forms, their full octets are more important than charge in determining the significance of their contribution to the resonance hybrid.

1-9 continued

(b) There are five resonance forms shown here; one of the structures is duplicated to show how the other resonance forms are derived from it. Resonance forms with all atoms having their full octets are the most significant contributors. In this case, the ones with full octets also have more bonds.

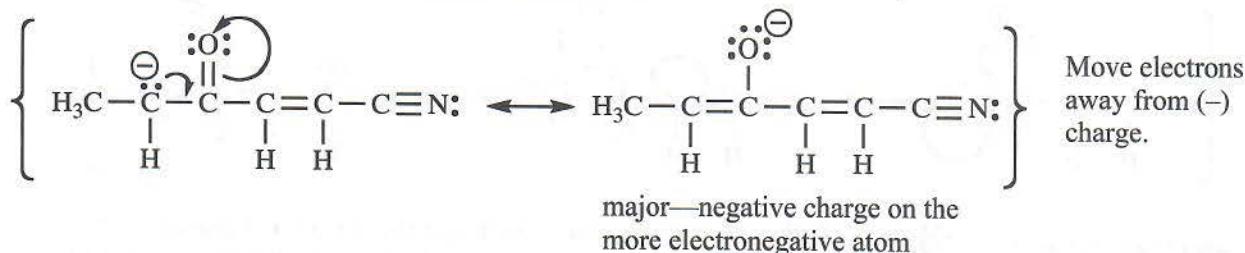


(c) There are four resonance forms shown here; one of the structures is duplicated to show how the other resonance forms are derived from it. Resonance forms with all atoms having their full octets are the most significant contributors. In this case, the ones with full octets also have more bonds.

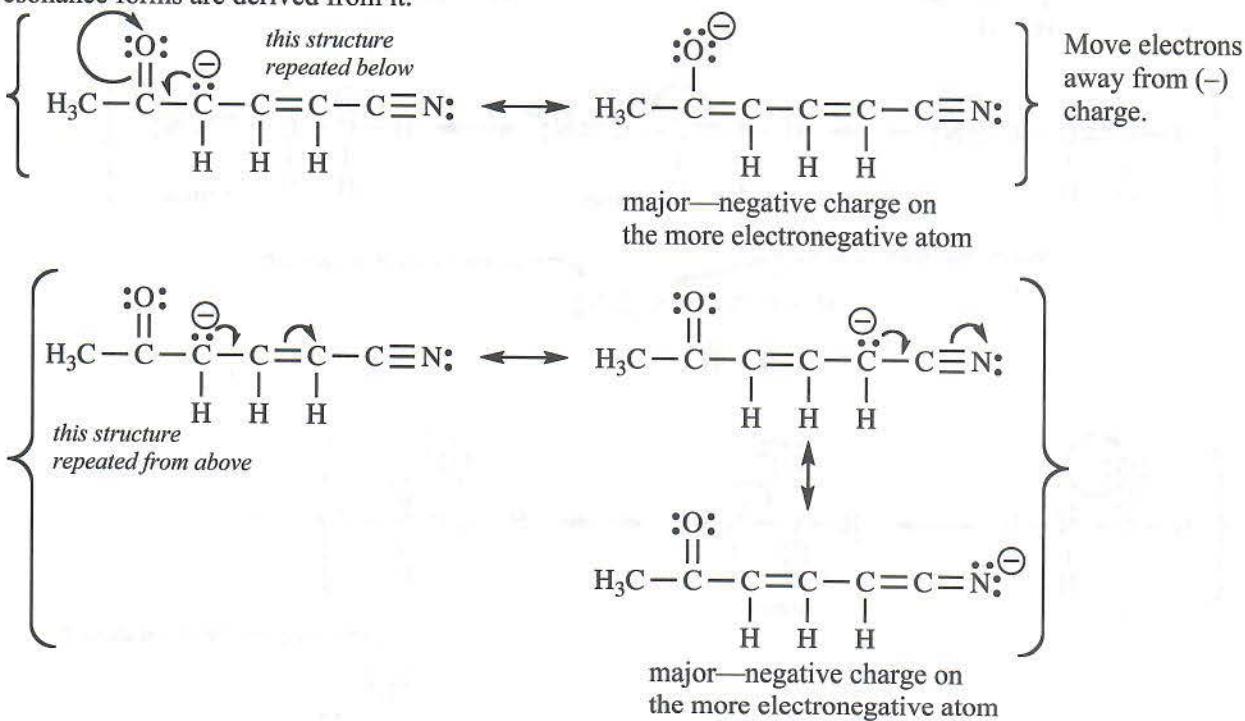


1-9 continued

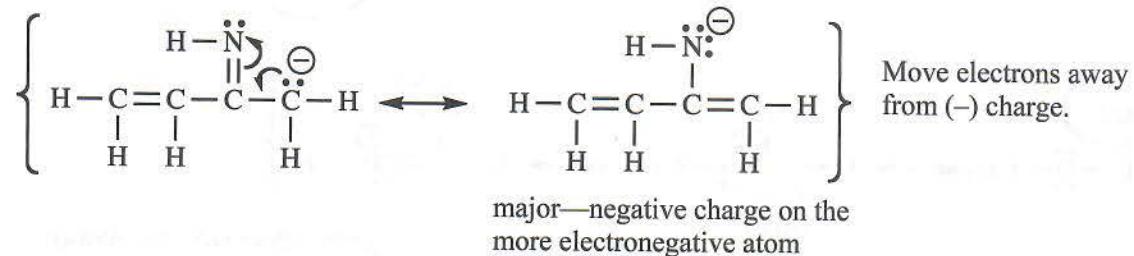
- (d) The lone pair of electrons on C cannot be delocalized to the C=C or the triple bond.



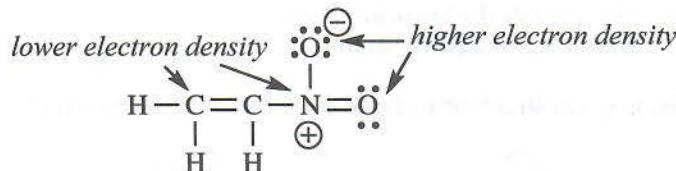
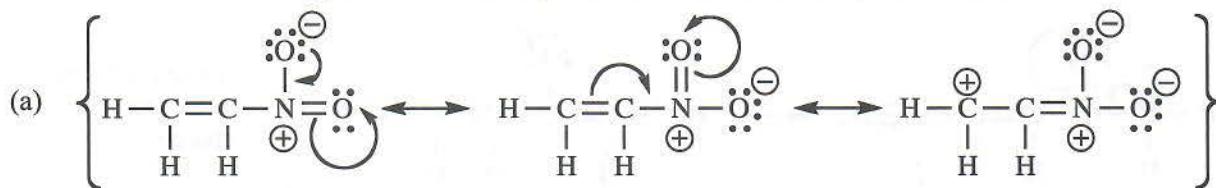
- (e) There are four resonance forms shown here; the original structure is duplicated to show how the other resonance forms are derived from it.



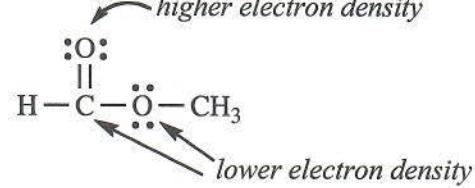
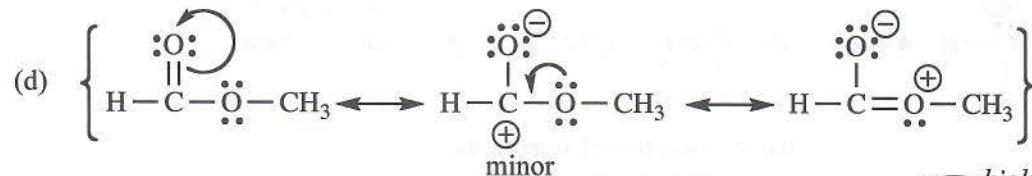
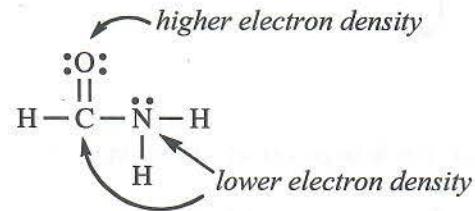
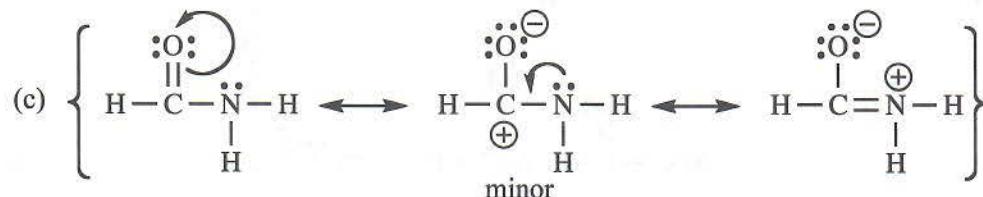
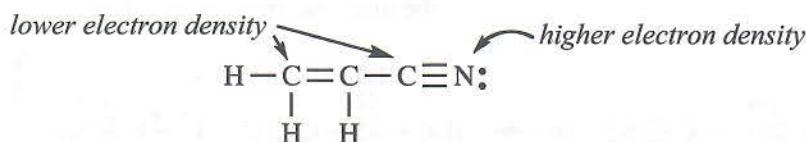
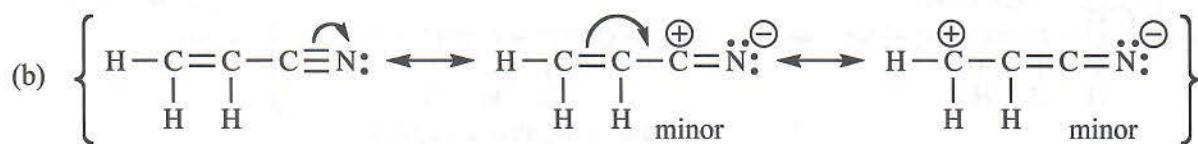
- (f) The lone pair of electrons on C cannot be delocalized to the C=C.



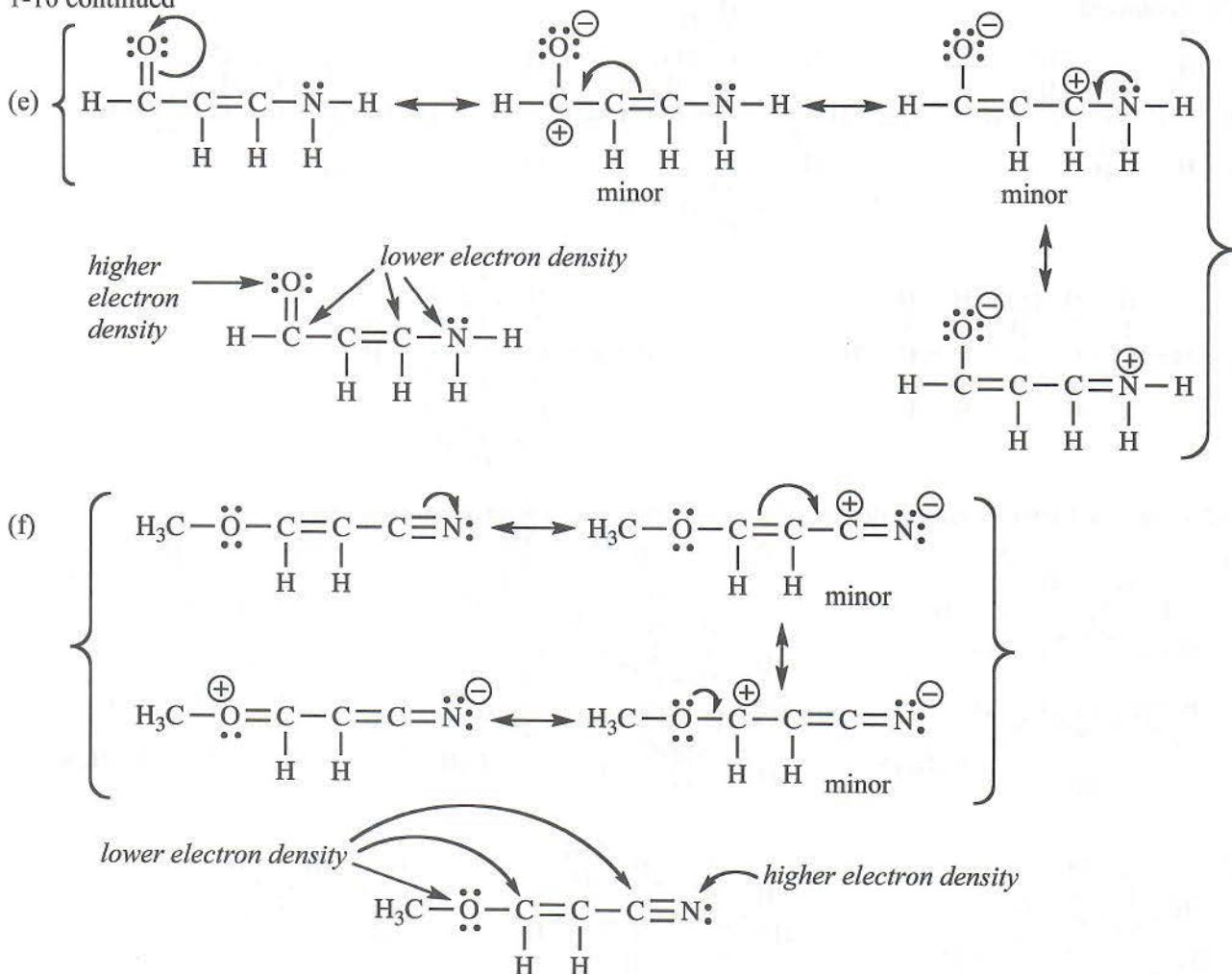
1-10 Resonance structures depict the distribution of electrons around the molecule. The significant resonance contributors suggest the areas of highest and lowest electron density.



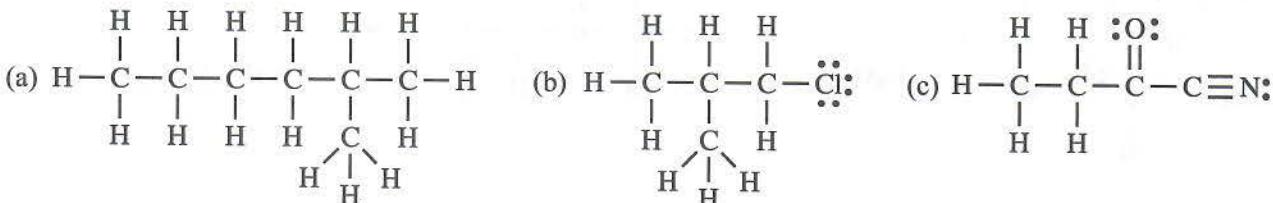
Although the N has a (+) charge in all resonance forms, it still has an octet and is not as electron-deficient as the CH<sub>2</sub> in the form where the CH<sub>2</sub> bears a (+) charge.



1-10 continued

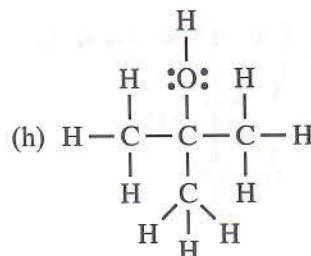
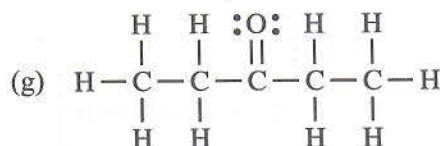
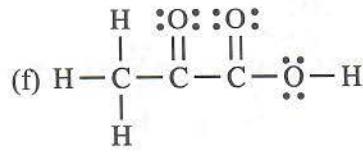
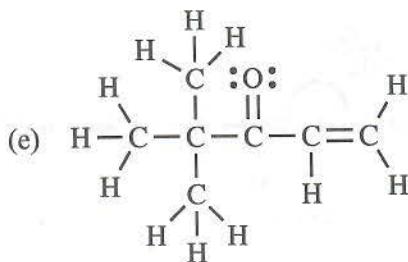
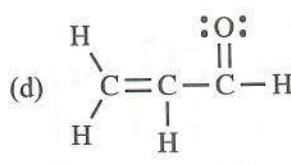


1-11 Your Lewis structures may *appear* different from how these are drawn. As long as the atoms are connected in the same order and by the same type of bond, they are equivalent structures. For now, the exact placement of the atoms on the page is not significant. A Lewis structure is "complete" with unshared electron pairs shown.

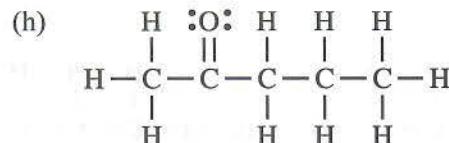
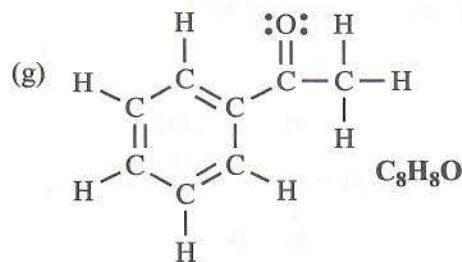
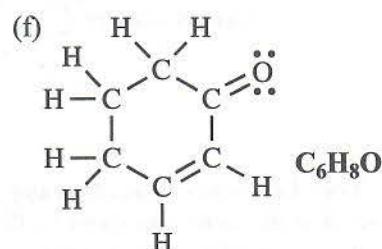
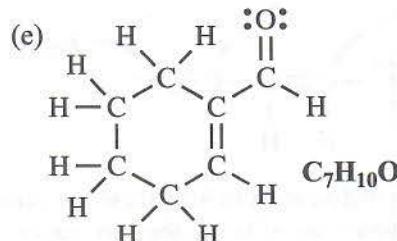
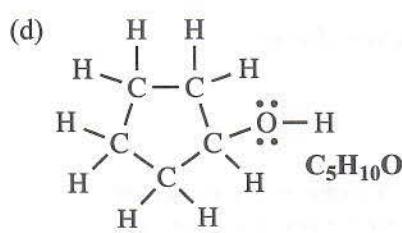
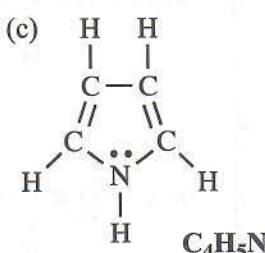
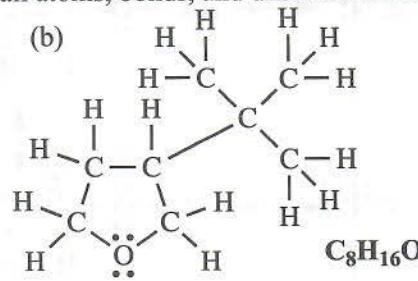
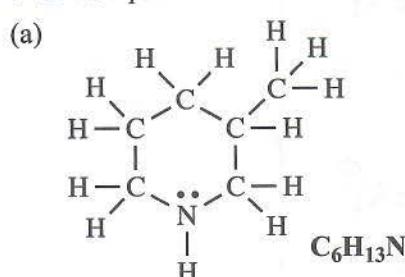


Always be alert for the implied double or triple bond. Remember that the normal valence of C is four bonds, nitrogen has three bonds, oxygen has two bonds, and hydrogen has one bond. The only exceptions to these valence rules are structures with formal charges. (We will see other unusual exceptions in later chapters.)

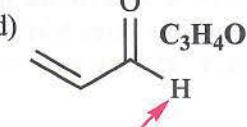
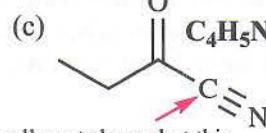
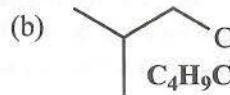
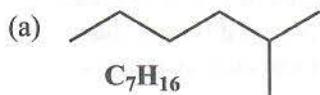
1-11 continued



1-12 Complete Lewis structures display all atoms, bonds, and unshared electron pairs.



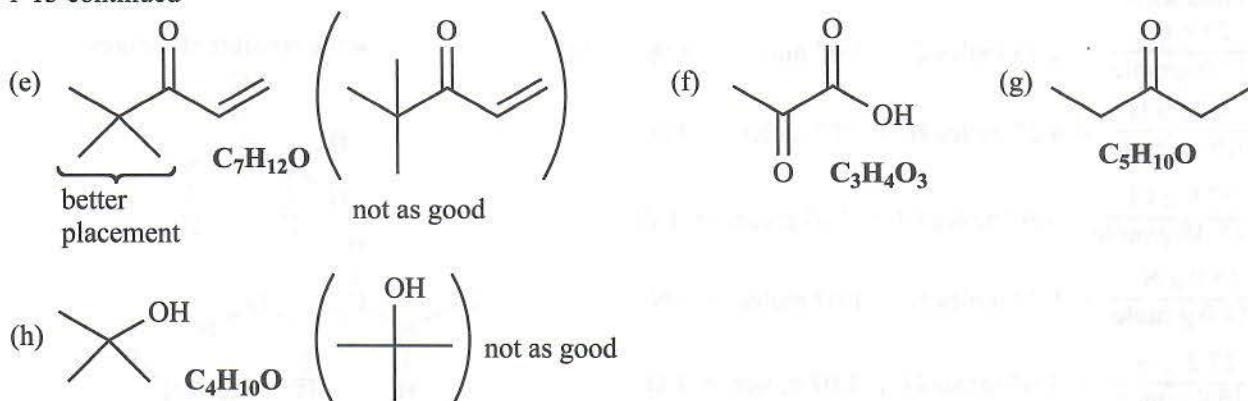
1-13 Line-angle structures, sometimes called "stick" figures, usually omit unshared electron pairs.



C is usually not shown but this clarifies what ends this triple bond.

H on C is usually not shown but this is an exception; it clarifies what ends this chain.

1-13 continued



1-14 If the percent values do not sum to 100%, the remainder must be oxygen. Assume 100 g of sample; percents then translate directly to grams of each element.

There are usually MANY possible structures for a molecular formula. Yours may be different from the examples shown here and they could still be correct.

(a)  $\frac{40.0 \text{ g C}}{12.0 \text{ g/mole}} = 3.33 \text{ moles C} \div 3.33 \text{ moles} = 1 \text{ C}$

$$\frac{6.67 \text{ g H}}{1.01 \text{ g/mole}} = 6.60 \text{ moles H} \div 3.33 \text{ moles} = 1.98 \approx 2 \text{ H}$$

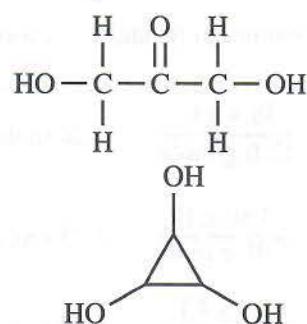
$$\frac{53.33 \text{ g O}}{16.0 \text{ g/mole}} = 3.33 \text{ moles O} \div 3.33 \text{ moles} = 1 \text{ O}$$

empirical formula =  $\boxed{CH_2O}$   $\Rightarrow$  empirical weight = 30.02

molecular weight = 90, three times the empirical weight  $\Rightarrow$

three times the empirical formula = molecular formula =  $\boxed{C_3H_6O_3}$

some possible structures:



Other structures  
are possible.

(b)  $\frac{32.0 \text{ g C}}{12.0 \text{ g/mole}} = 2.67 \text{ moles C} \div 1.34 \text{ moles} = 1.99 \approx 2 \text{ C}$

$$\frac{6.67 \text{ g H}}{1.01 \text{ g/mole}} = 6.60 \text{ moles H} \div 1.34 \text{ moles} = 4.93 \approx 5 \text{ H}$$

$$\frac{18.7 \text{ g N}}{14.0 \text{ g/mole}} = 1.34 \text{ moles N} \div 1.34 \text{ moles} = 1 \text{ N}$$

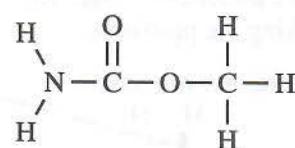
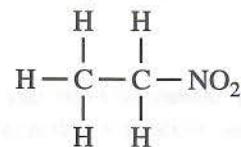
$$\frac{42.6 \text{ g O}}{16.0 \text{ g/mole}} = 2.66 \text{ moles O} \div 1.34 \text{ moles} = 1.99 \approx 2 \text{ O}$$

empirical formula =  $\boxed{C_2H_5NO_2}$   $\Rightarrow$  empirical weight = 75.05

molecular weight = 75, same as the empirical weight  $\Rightarrow$

empirical formula = molecular formula =  $\boxed{C_2H_5NO_2}$

some possible structures:



MANY other structures  
are possible.

1-14 continued

$$(c) \frac{25.6 \text{ g C}}{12.0 \text{ g/mole}} = 2.13 \text{ moles C} \div 1.07 \text{ moles} = 1.99 \approx 2 \text{ C}$$

$$\frac{4.32 \text{ g H}}{1.01 \text{ g/mole}} = 4.28 \text{ moles H} \div 1.07 \text{ moles} = 4 \text{ H}$$

$$\frac{37.9 \text{ g Cl}}{35.45 \text{ g/mole}} = 1.07 \text{ moles Cl} \div 1.07 \text{ moles} = 1 \text{ Cl}$$

$$\frac{15.0 \text{ g N}}{14.0 \text{ g/mole}} = 1.07 \text{ moles N} \div 1.07 \text{ moles} = 1 \text{ N}$$

$$\frac{17.2 \text{ g O}}{16.0 \text{ g/mole}} = 1.07 \text{ moles O} \div 1.07 \text{ moles} = 1 \text{ O}$$

empirical formula =  $\boxed{\text{C}_2\text{H}_4\text{ClNO}}$   $\Rightarrow$  empirical weight = 93.49

molecular weight = 93, same as the empirical weight  $\Rightarrow$

empirical formula = molecular formula =  $\boxed{\text{C}_2\text{H}_4\text{ClNO}}$

$$(d) \frac{38.4 \text{ g C}}{12.0 \text{ g/mole}} = 3.20 \text{ moles C} \div 1.60 \text{ moles} = 2 \text{ C}$$

$$\frac{4.80 \text{ g H}}{1.01 \text{ g/mole}} = 4.75 \text{ moles H} \div 1.60 \text{ moles} = 2.97 \approx 3 \text{ H}$$

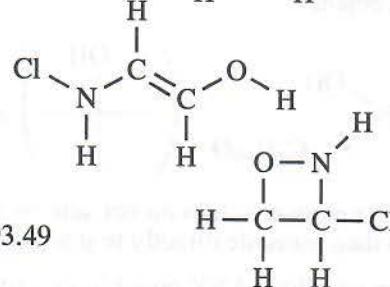
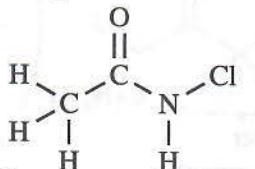
$$\frac{56.8 \text{ g Cl}}{35.45 \text{ g/mole}} = 1.60 \text{ moles Cl} \div 1.60 \text{ moles} = 1 \text{ Cl}$$

empirical formula =  $\boxed{\text{C}_2\text{H}_3\text{Cl}}$   $\Rightarrow$  empirical weight = 62.45

molecular weight = 125, twice the empirical weight  $\Rightarrow$

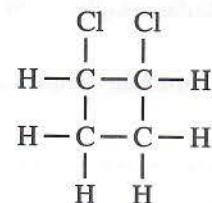
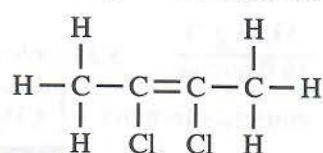
twice the empirical formula = molecular formula =  $\boxed{\text{C}_4\text{H}_6\text{Cl}_2}$

some possible structures:



MANY other structures  
are possible.

some possible structures:

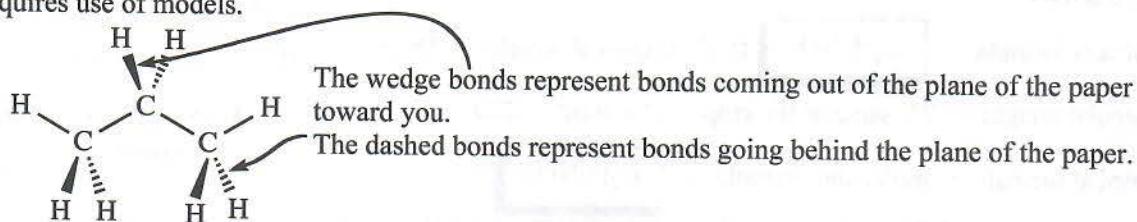


MANY other structures  
are possible.

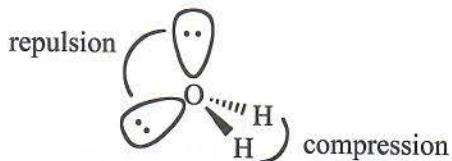
1-15 The fundamental principle of organic chemistry is that a molecule's chemical and physical properties depend on the molecule's structure: the structure-function or structure-reactivity correlation. It is essential that you understand the three-dimensional nature of organic molecules, and there is no better device to assist you than a molecular model set. You are strongly encouraged to use models regularly when reading the text and working the problems.

(a) Requires use of models.

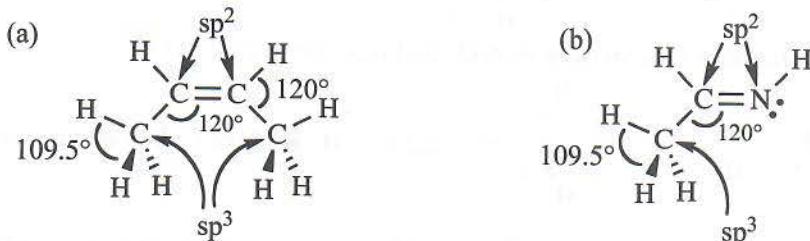
(b)



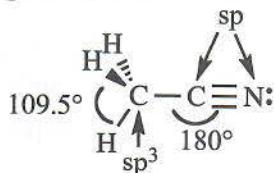
1-16 (a) The hybridization of oxygen is  $sp^3$  since it has two sigma bonds and two pairs of nonbonding electrons. The reason that the bond angle of  $104.5^\circ$  is less than the perfect tetrahedral angle of  $109.5^\circ$  is that the lone pairs in the two  $sp^3$  orbitals are repelling each other more strongly than the electron pairs in the sigma bonds, thereby compressing the bond angle.



1-17 Each double-bonded atom is  $sp^2$  hybridized with bond angles about  $120^\circ$ ; geometry around  $sp^2$  atoms is trigonal planar. In (a), all four carbons and the two hydrogens on the  $sp^2$  carbons are all in one plane. Each carbon on the end is  $sp^3$  hybridized with tetrahedral geometry and bond angles about  $109^\circ$ . In (b), the two carbons, the nitrogen, and the two hydrogens on the  $sp^2$  carbon and nitrogen are all in one plane. The  $CH_3$  carbon is  $sp^3$  hybridized with tetrahedral geometry and bond angles about  $109^\circ$ .

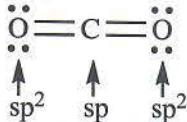


1-18 The hybridization of the nitrogen and the triple-bonded carbon are  $sp$ , giving linear geometry ( $C—C—N$  are linear) and a bond angle around the triple-bonded carbon of  $180^\circ$ . The  $CH_3$  carbon is  $sp^3$  hybridized, tetrahedral, with bond angles about  $109^\circ$ .

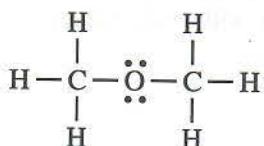


1-19

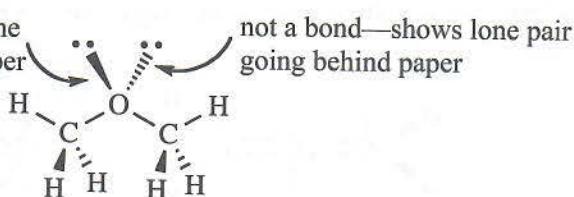
(a) linear, bond angle  $180^\circ$



(b) All atoms are  $sp^3$ ; tetrahedral geometry and bond angles of  $109^\circ$  around each atom.

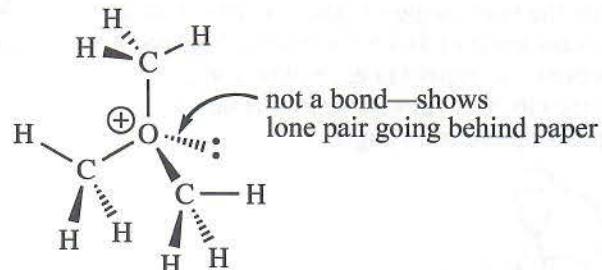
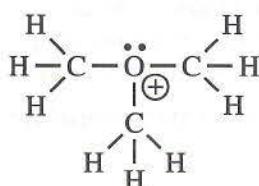


not a bond—shows lone pair coming out of paper

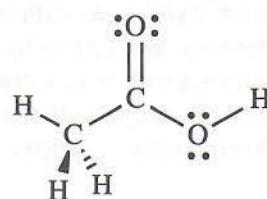
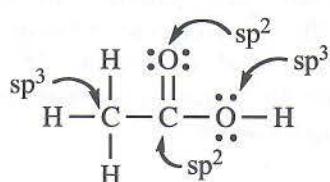


1-19 continued

(c) All atoms are  $sp^3$ ; tetrahedral geometry and bond angles of  $109^\circ$  around each atom.

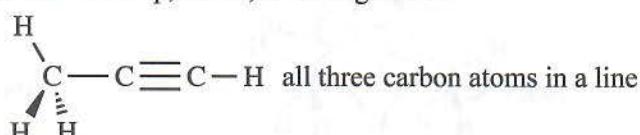
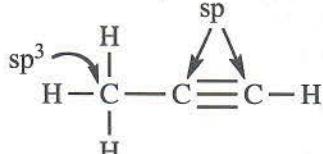


(d) trigonal planar around the carbonyl carbon ( $C=O$ ), bond angles  $120^\circ$ ; tetrahedral around the single-bonded oxygen and the  $CH_3$ , bond angles  $109^\circ$

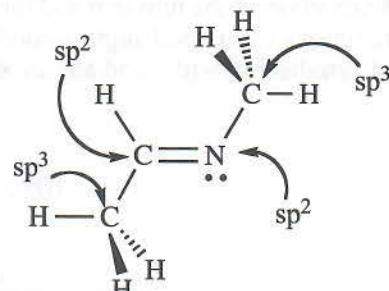
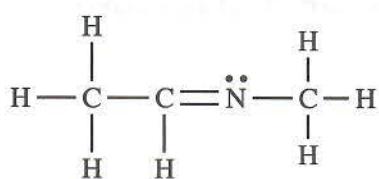


All atoms are in one plane except for the two H atoms on the  $sp^3$  C.

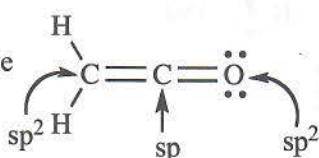
(e) tetrahedral around the  $sp^3$  carbon; the other two carbons both  $sp$ , linear, bond angle  $180^\circ$



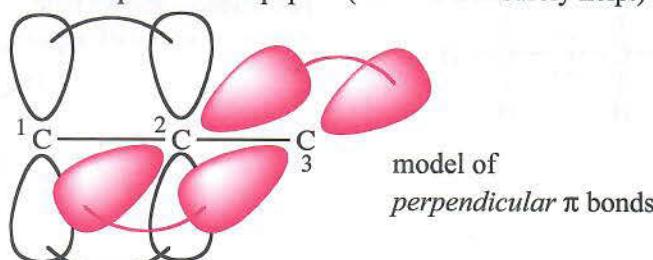
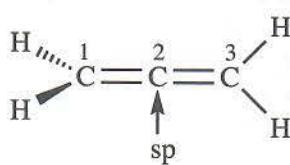
(f) trigonal planar around the  $sp^2$  carbon and nitrogen, bond angles  $120^\circ$ ; tetrahedral geometry and  $109^\circ$  bond angles around the  $sp^3$  carbons



(g) linear,  $180^\circ$  bond angle, around the central carbon; trigonal planar,  $120^\circ$  bond angles, around the  $sp^2$  carbon

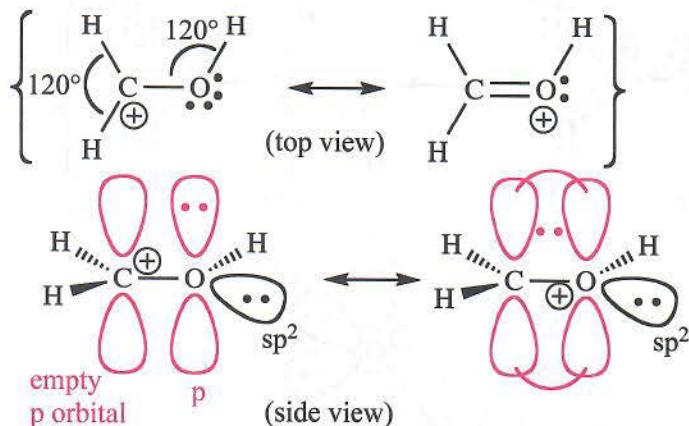


1-20 Carbon-2 is  $sp$  hybridized. If the p orbitals making the pi bond between C-1 and C-2 are in the plane of the paper (putting the hydrogens in front of and behind the paper), then the other p orbital on C-2 must be perpendicular to the plane of the paper, making the pi bond between C-2 and C-3 perpendicular to the paper. This necessarily places the hydrogens on C-3 in the plane of the paper. (Models will surely help.)



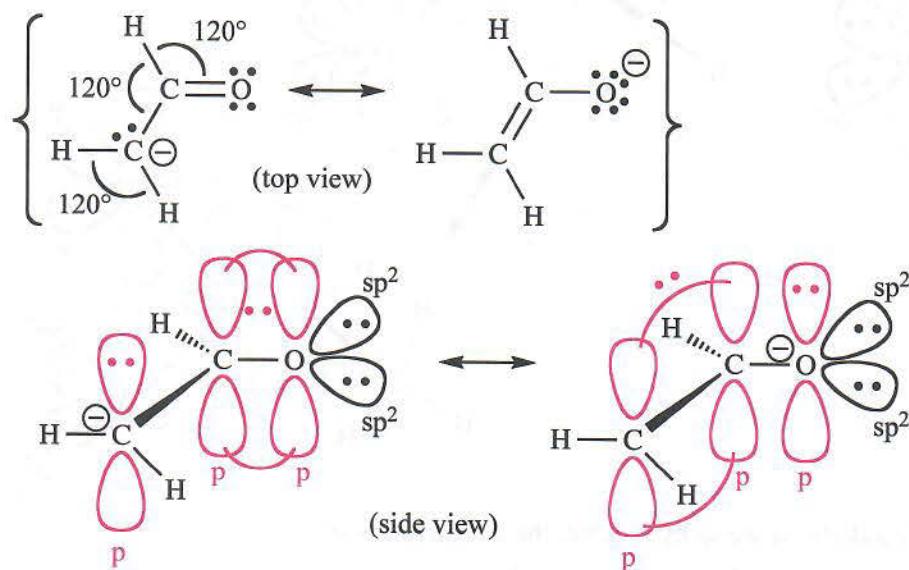
1-21 For clarity, electrons in sigma bonds are not shown. Part (a) has been solved in the text.

(b) Carbon and oxygen are both  $sp^2$  hybridized.



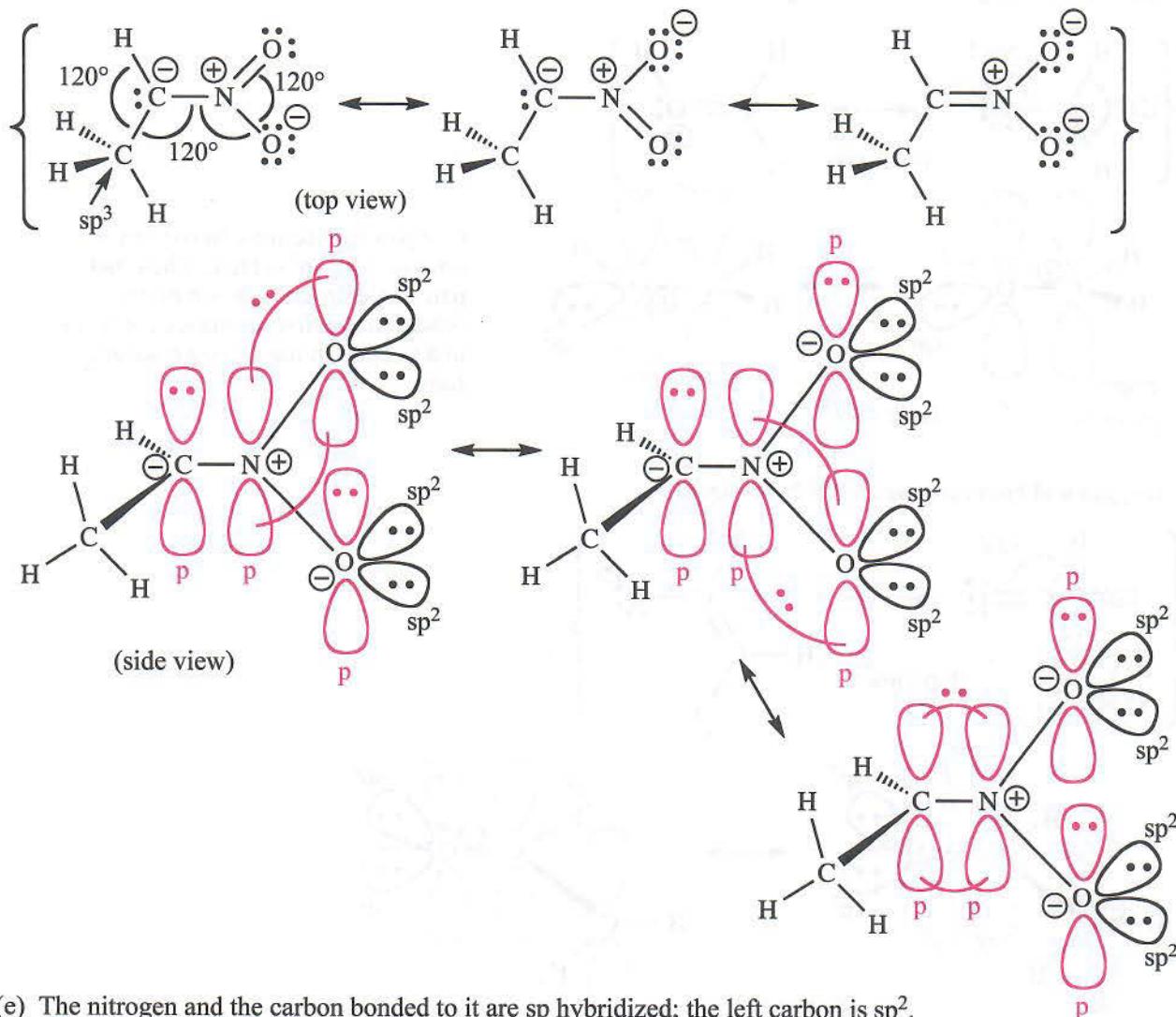
One pair of electrons on oxygen is always in an  $sp^2$  orbital. The other pair of electrons is shown in a p orbital in the first resonance form, and in a pi bond in the second resonance form.

(c) Oxygen and both carbons are  $sp^2$  hybridized.

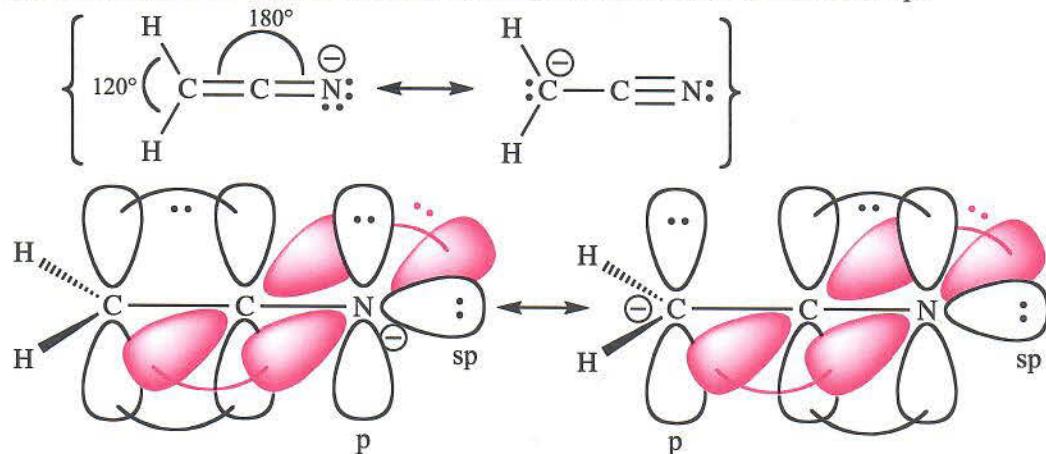


1-21 continued

(d) All atoms are  $sp^2$  hybridized except the C labeled as  $sp^3$  (and H which is NEVER hybridized); all bond angles around the  $sp^3$  carbon are  $109^\circ$ .

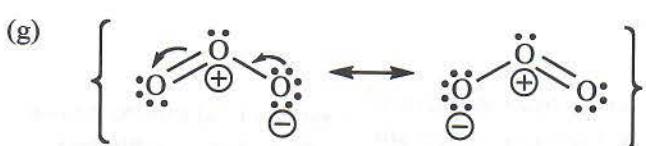
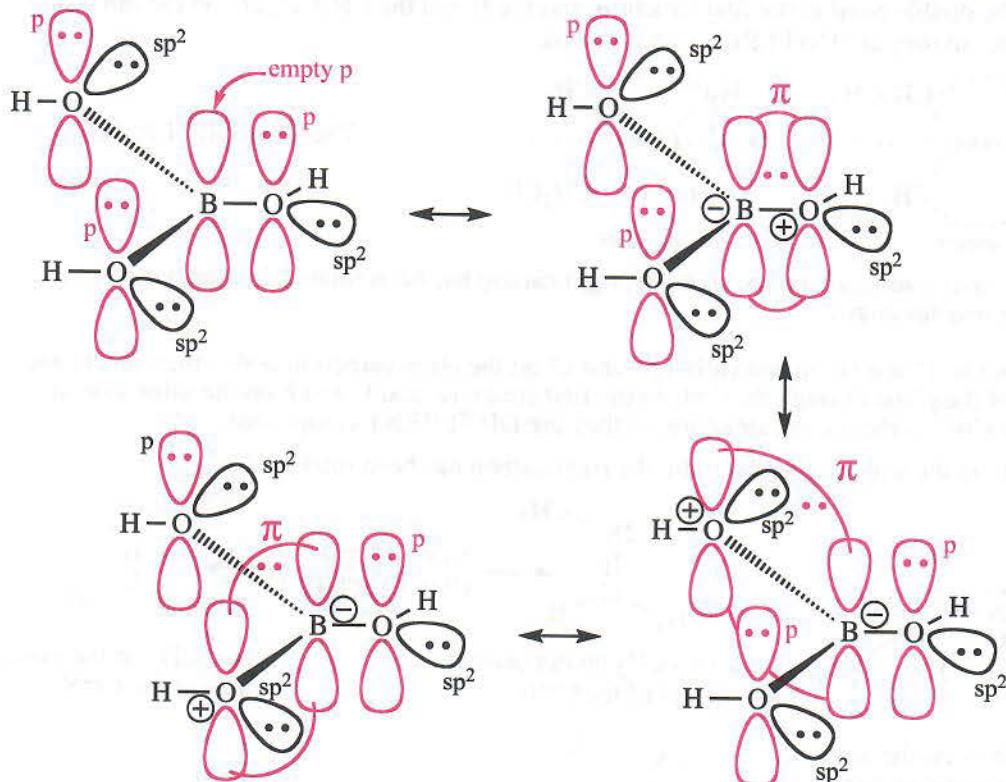
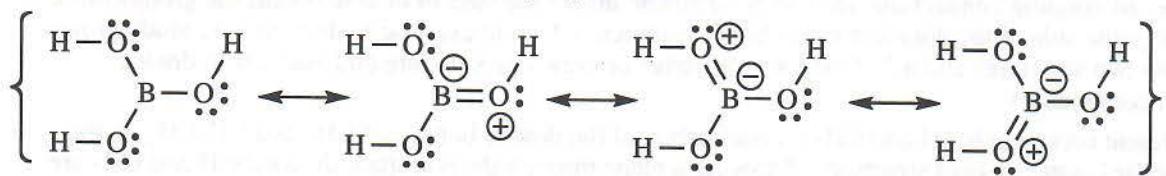


(e) The nitrogen and the carbon bonded to it are  $sp$  hybridized; the left carbon is  $sp^2$ .

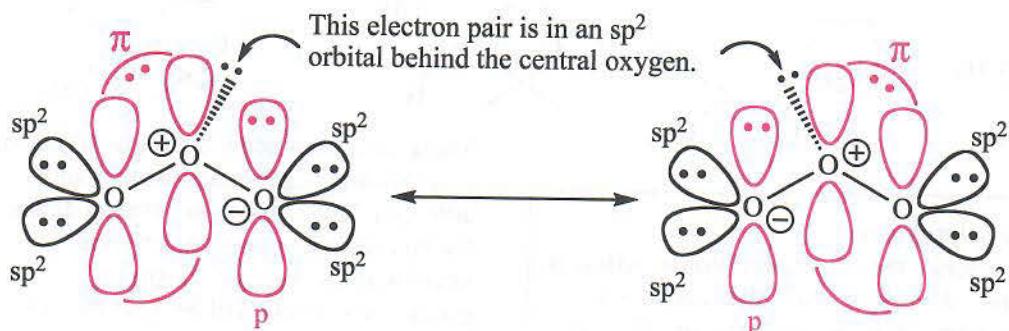


1-21 continued

(f) The boron and the oxygens bonded to it are  $sp^2$  hybridized.

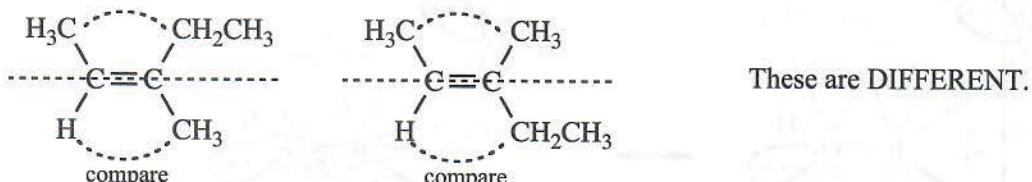


All oxygens are  $sp^2$  with bond angle  $120^\circ$ .



1-22 Very commonly in organic chemistry, we have to determine whether two structures are the same or different, and if they are different, what structural features are different. In order for two structures to be the same, all bonding connections have to be identical, and in the case of double bonds, the groups must be on the same side of the double bond in both structures. (A good exercise to do with your study group is to draw two structures and ask if they are the same; or draw one structure and ask how to draw a different compound.)

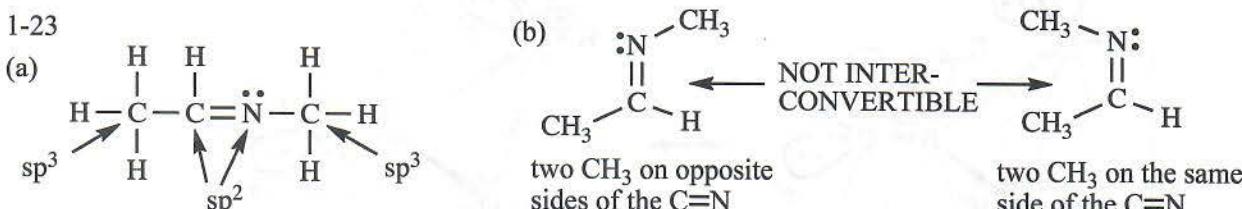
(a) Different compounds; H and CH<sub>3</sub> on one carbon of the double bond, and CH<sub>3</sub> and CH<sub>2</sub>CH<sub>3</sub> on the other carbon—same in both structures. Drawing a plane through the p orbitals shows the H and CH<sub>3</sub> are on the same side of the double bond in the first structure, and the H and the CH<sub>2</sub>CH<sub>3</sub> are on the same side in the second structure, so they are DIFFERENT compounds.



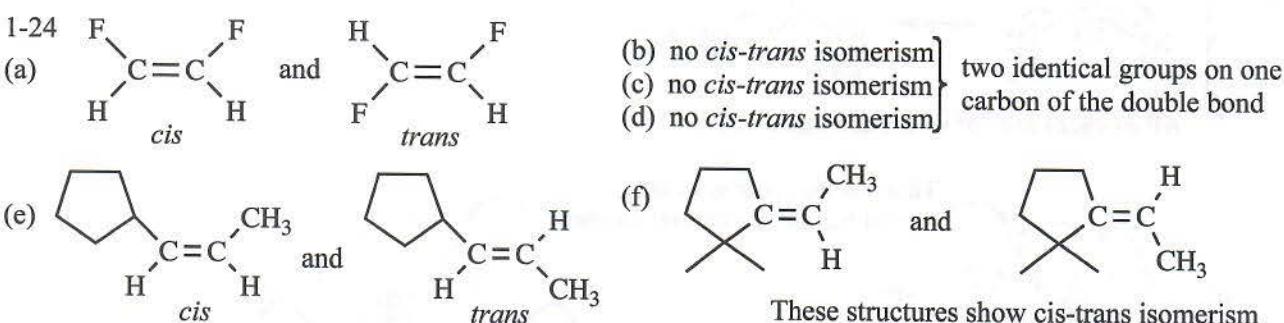
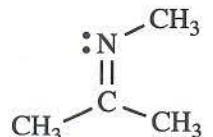
(b) Same compound; in the structure on the right, the right carbon has been rotated, but the bonding is identical between the two structures.

(c) Different compounds; H and Br on one carbon, F and Cl on the other carbon in both structures; H and Cl on the same side of the plane through the C=C in the first structure, and H and F on the same side of the plane through the C=C in the second structure, so they are DIFFERENT compounds.

(d) Same compound: in the structure on the right, the right carbon has been rotated 120°.



(c) The CH<sub>3</sub> on the N is on the same side as another CH<sub>3</sub> no matter how it is drawn—only one possible structure.



These structures show cis-trans isomerism (also known as geometric isomerism), although "cis" and "trans" are not defined for this particular case. A different, unambiguous system for naming geometric isomers will be described in Chapter 7.

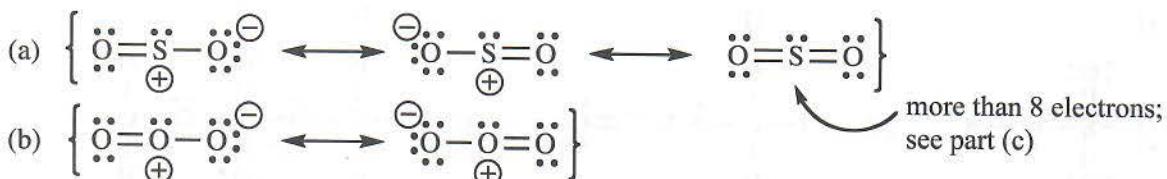
1-25 Models will be helpful here.

- (a) Constitutional isomers—the carbon skeleton is different.
- (b) Cis-trans isomers—the first is trans, the second is cis.
- (c) Constitutional isomers—the bromines are on different carbons in the first structure, on the same carbon in the second structure.

1-25 continued

- (d) same compound—just flipped over
- (e) same compound—just rotated
- (f) same compound—just rotated
- (g) not isomers—different molecular formulas
- (h) Constitutional isomers—the double bond has changed position.
- (i) same compound—just reversed
- (j) Constitutional isomers—the CH<sub>3</sub> groups are in different relative positions.
- (k) Constitutional isomers—the double bond is in a different position relative to the CH<sub>3</sub> and an H has moved.

1-26



(c) The last resonance form of SO<sub>2</sub> has no equivalent form in O<sub>3</sub>. Sulfur, a third-row element, can have more than eight electrons around it because of d orbitals, whereas oxygen, a second-row element, must adhere strictly to the octet rule.

1-27 (a) CARBON! (the best element)      (b) oxygen      (c) phosphorus      (d) chlorine

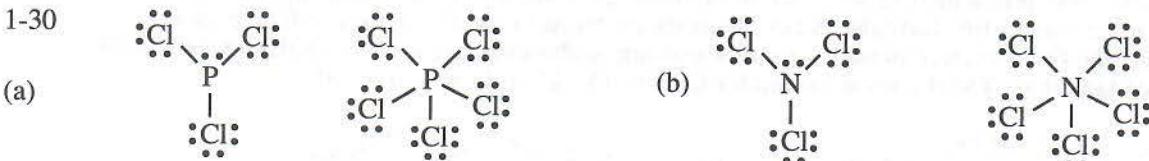
1-28

valence e <sup>-</sup> →	1	2	3	4	5	6	7	8
	H							He (2e <sup>-</sup> )
	Li	Be	B	C	N	O	F	Ne
				P	S	Cl		
						Br		
						I		

1-29

- (a) ionic only      (b) covalent (H—O<sup>-</sup>) and ionic (Na<sup>+</sup>—OH)
- (c) covalent (H—C and C—Li), but the C—Li bond is strongly polarized
- (d) covalent only      (e) covalent (H—C and C—O<sup>-</sup>) and ionic (Na<sup>+</sup>—OCH<sub>3</sub>)
- (f) covalent (H—C and C=O and C—O<sup>-</sup>) and ionic (HCO<sub>2</sub><sup>-</sup> Na<sup>+</sup>)      (g) covalent only

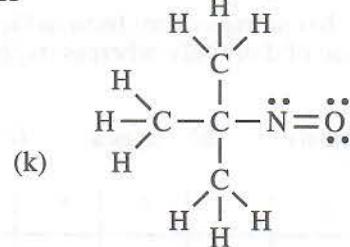
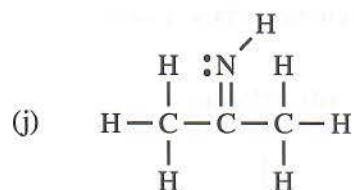
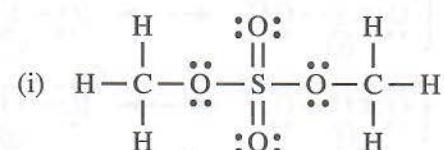
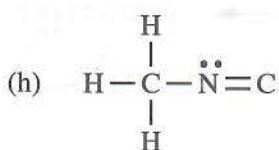
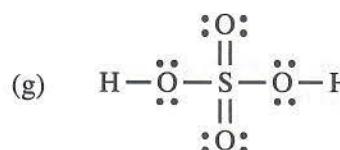
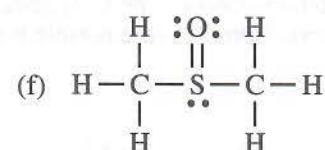
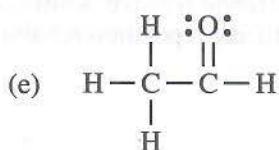
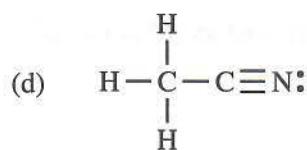
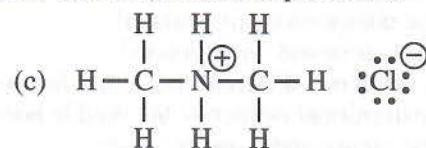
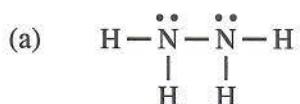
1-30



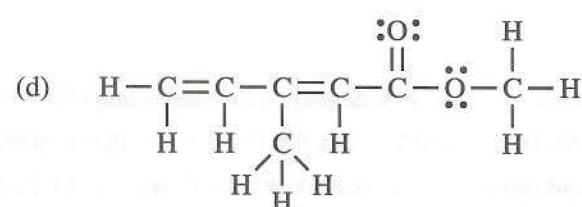
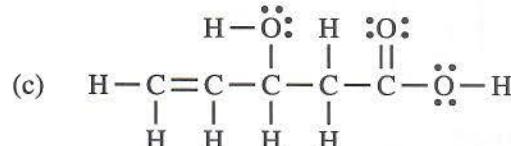
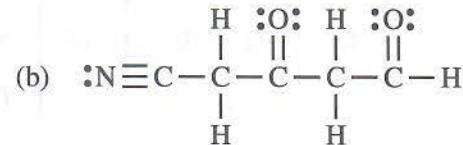
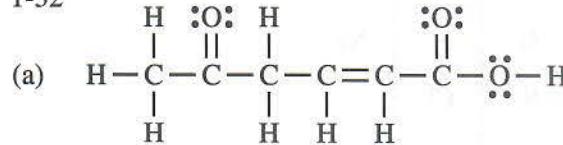
CANNOT EXIST

NCl<sub>5</sub> violates the octet rule; nitrogen can have no more than eight electrons (or four atoms) around it. Phosphorus, a third-row element, can have more than eight electrons because phosphorus can use d orbitals in bonding, so PCl<sub>5</sub> is a stable, isolable compound.

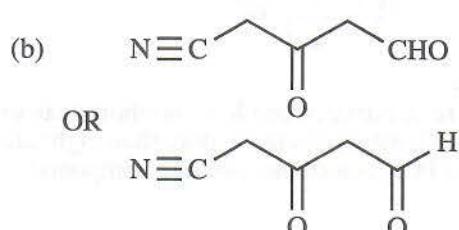
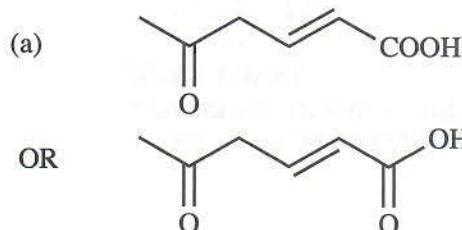
1-31 Your Lewis structures may look different from these. As long as the atoms are connected in the same order and by the same type of bond, they are equivalent structures. For now, the exact placement of the atoms on the page is not significant.



1-32



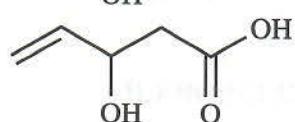
1-33 (Structures from problem 1-32 are redrawn in line-angle format.) In each set below, the second structure is a more correct line formula. Since chemists are human (surprise!), they will take shortcuts where possible; the first structure in each pair uses a common abbreviation, either COOH or CHO. Make sure you understand that COOH does not stand for C—O—O—H. Likewise for CHO.



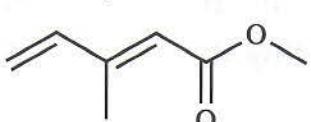
1-33 continued



OR

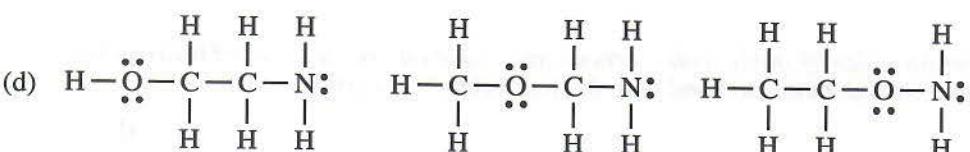
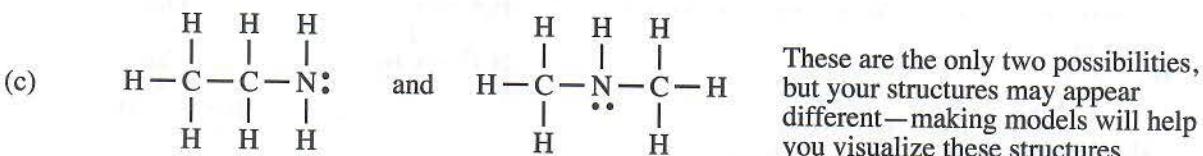
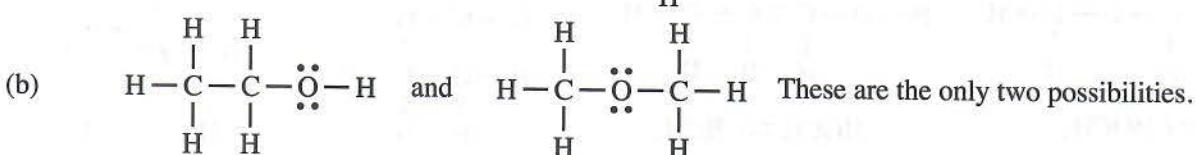
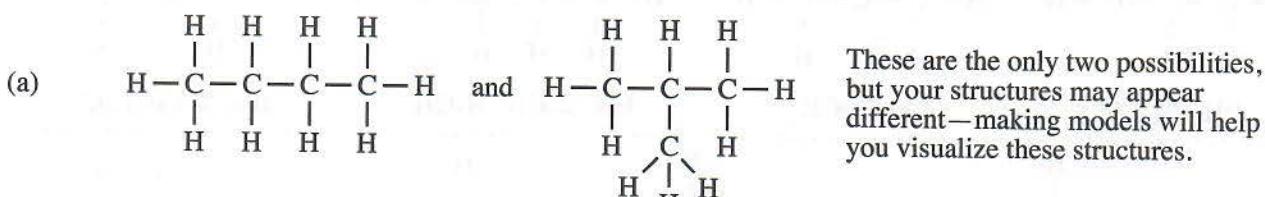


OR



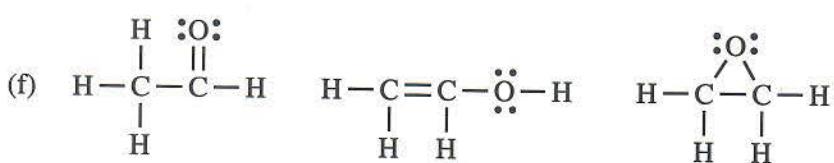
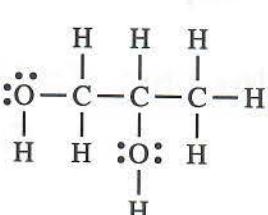
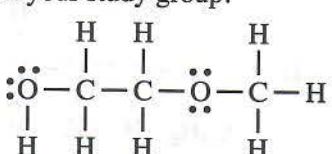
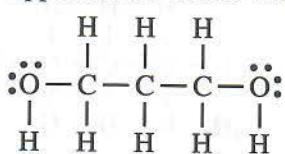
1-34

In some cases, you are asked for the maximum number of structures possible for a molecular formula containing a small number of atoms. In other cases, however, there may be many more structures possible, and your structures can be correct even if they are not the ones shown here.



Think of all the ways an oxygen could be added to the structures in (c). There are many more!

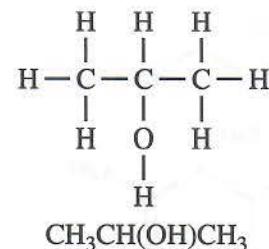
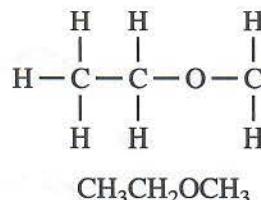
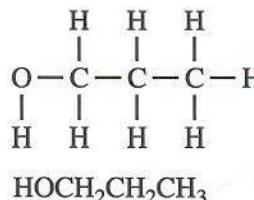
(e) There are several other possibilities as well. Your answer may be correct even if your structures do not appear here. Check with others in your study group.



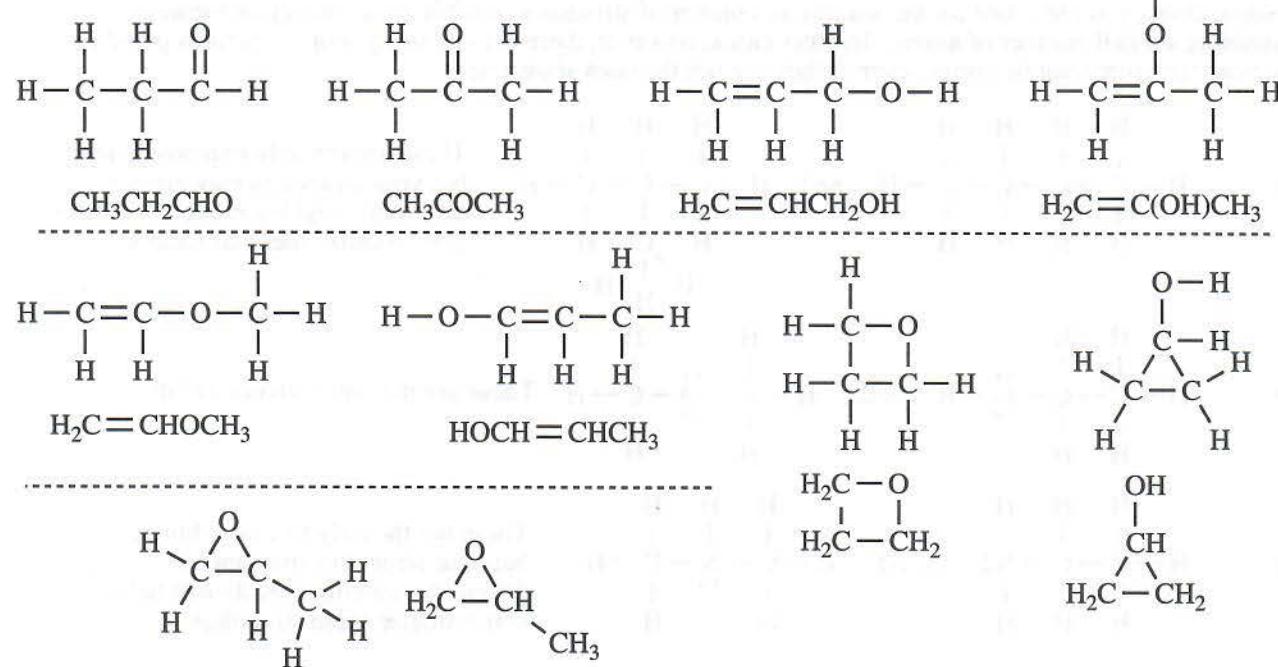
These are the only three structures with this molecular formula.

1-35

(a) only three possible structures

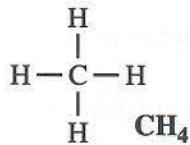


(b) This is most (maybe all) of the possible structures.

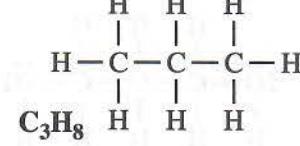
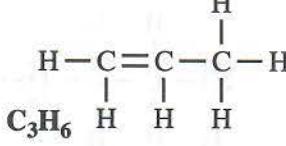
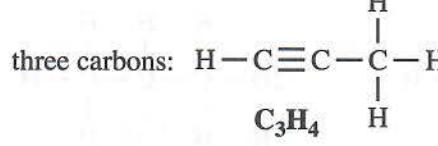
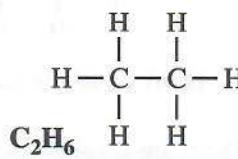


1-36 General rule: *molecular formulas of stable hydrocarbons must have an even number of hydrogens.*  
The formula  $\text{CH}_2$  does not have enough atoms to bond with the four orbitals of carbon.

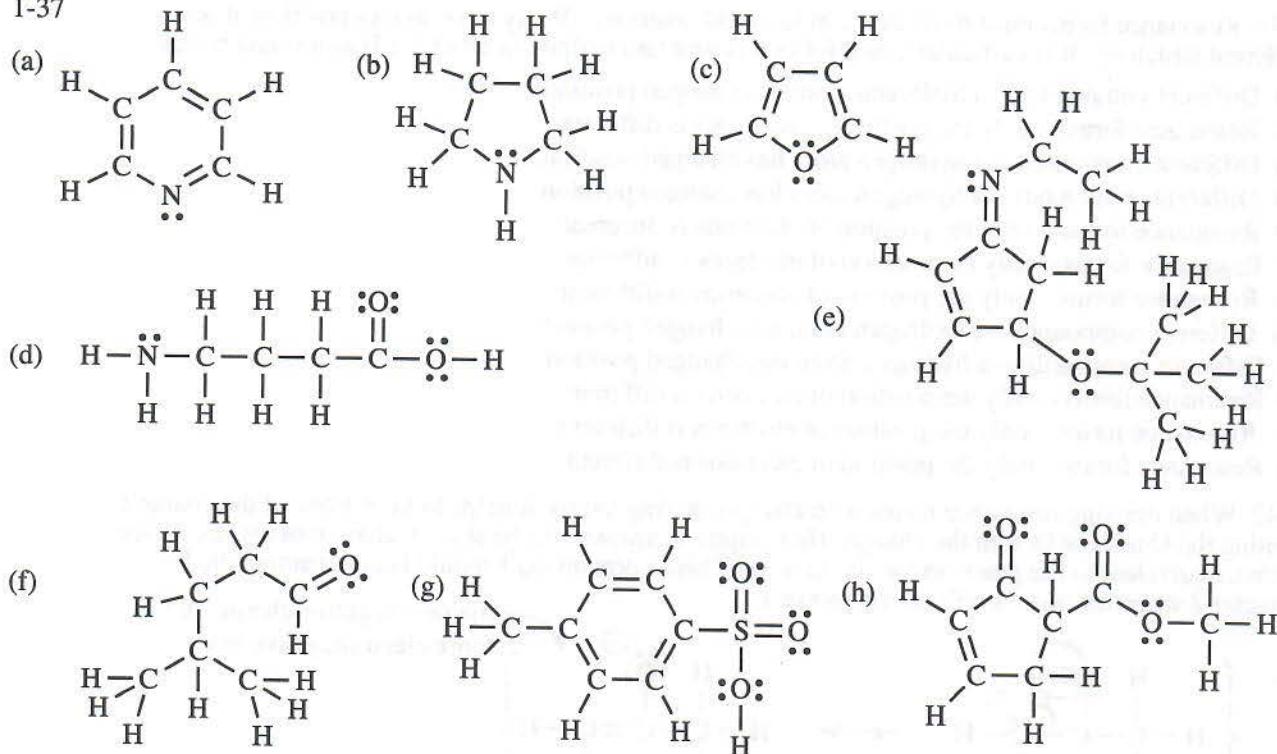
one carbon:



two carbons:



1-37



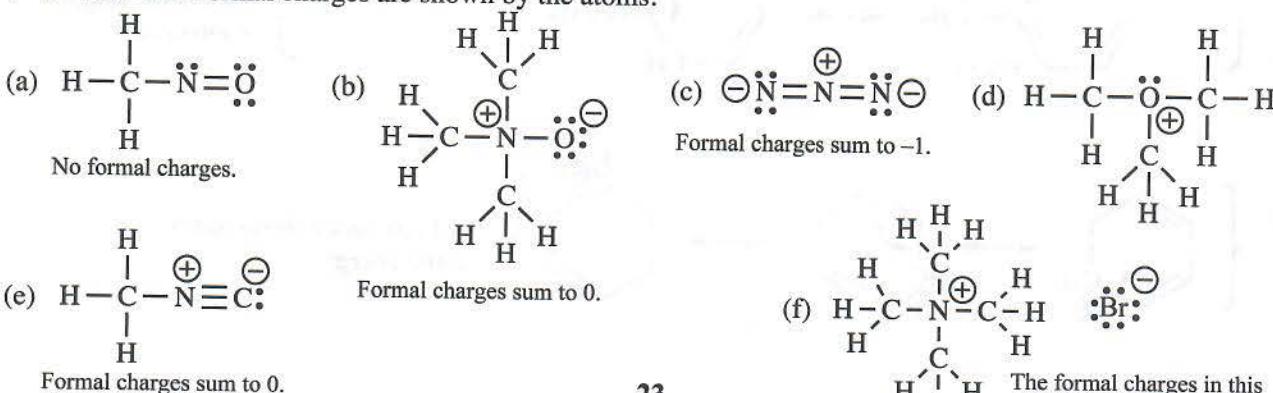
1-38 Molecular formulas of the structures in problem 1-37.

- (a) C<sub>5</sub>H<sub>5</sub>N      (b) C<sub>4</sub>H<sub>9</sub>N      (c) C<sub>4</sub>H<sub>4</sub>O      (d) C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub>      (e) C<sub>11</sub>H<sub>19</sub>NO  
 (f) C<sub>6</sub>H<sub>12</sub>O      (g) C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S      (h) C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>

1-39 The symbols "δ+" and "δ−" indicate bond polarity by showing partial charge. Electronegativity differences greater than or equal to 0.5 are considered large.

- |                            |                            |                            |                           |                            |
|----------------------------|----------------------------|----------------------------|---------------------------|----------------------------|
| (a) δ+ δ-<br>C—Cl<br>large | (b) δ- δ+<br>C—H<br>small  | (c) δ- δ+<br>C—Li<br>large | (d) δ+ δ-<br>C—N<br>small | (e) δ+ δ-<br>C—O<br>large  |
| (f) δ- δ+<br>C—B<br>large  | (g) δ- δ+<br>C—Mg<br>large | (h) δ- δ+<br>N—H<br>large  | (i) δ- δ+<br>O—H<br>large | (j) δ+ δ-<br>C—Br<br>small |

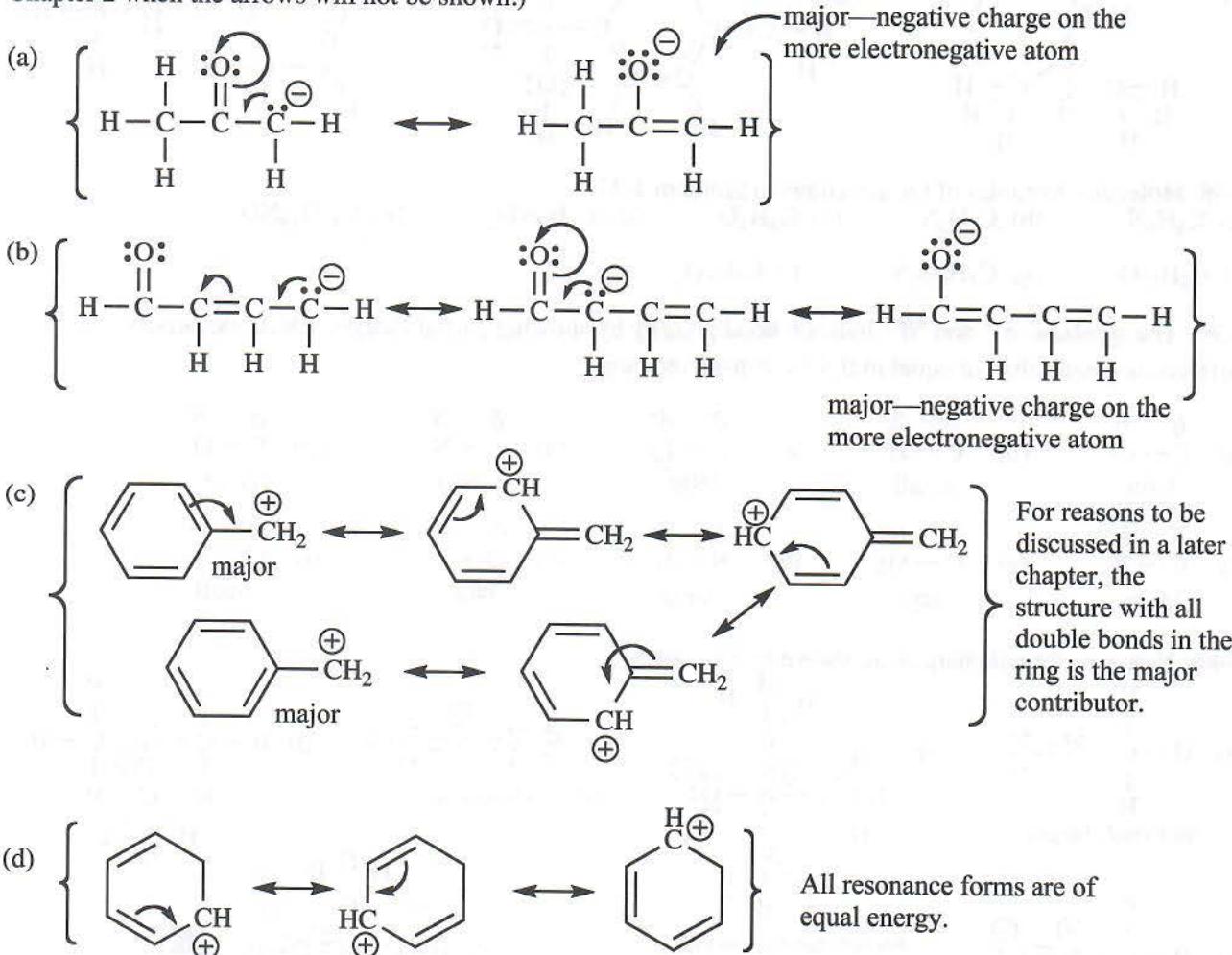
1-40 Non-zero formal charges are shown by the atoms.



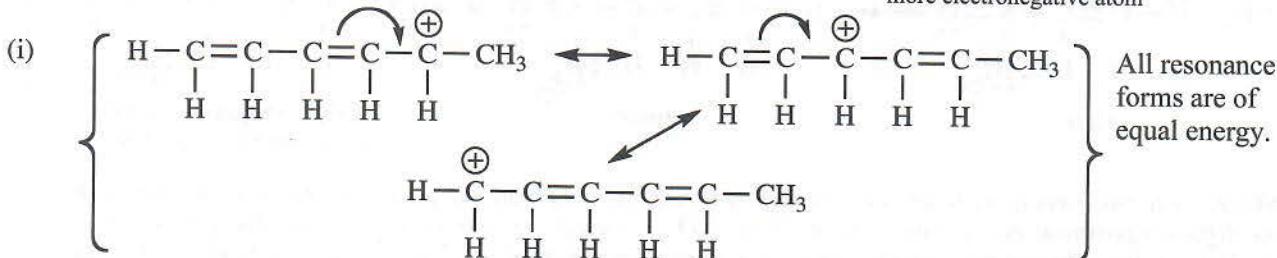
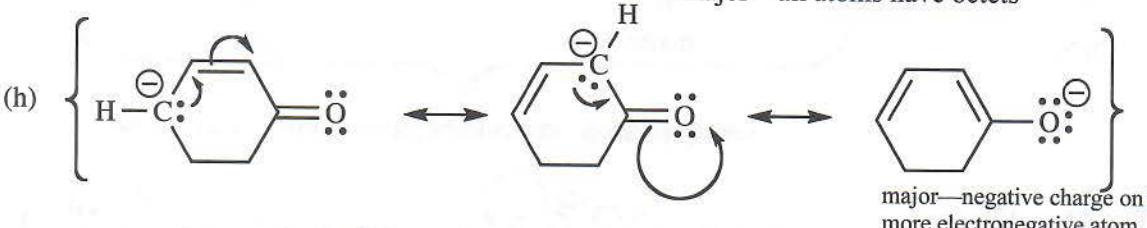
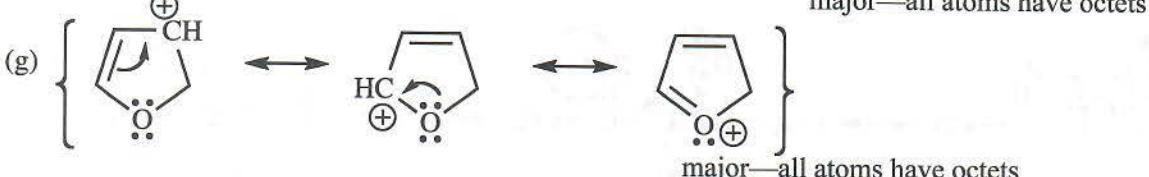
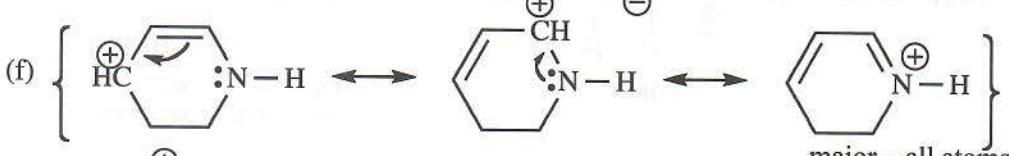
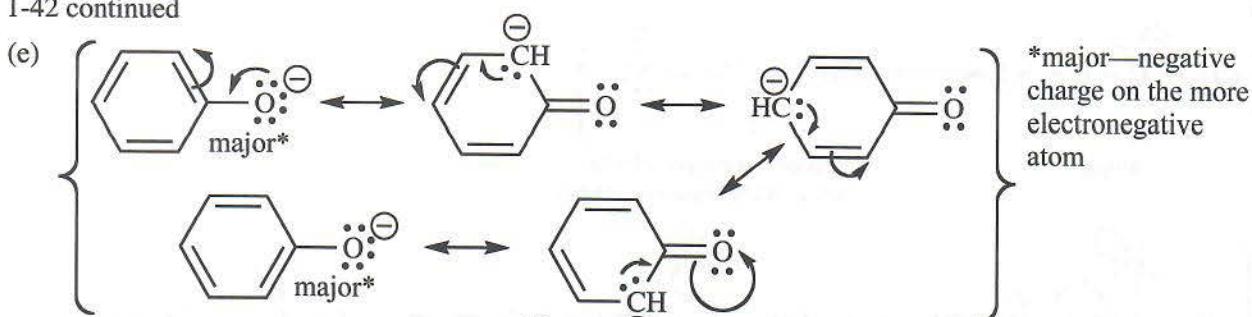
1-41 Resonance forms must have atoms in identical positions. If any atom moves position, it is a different structure. It is particularly helpful in this problem to draw in all of the H atoms and bonds.

- (a) Different compounds—a hydrogen atom has changed position.
- (b) Resonance forms—only the position of electrons is different.
- (c) Different compounds—a hydrogen atom has changed position.
- (d) Different compounds—a hydrogen atom has changed position.
- (e) Resonance forms—only the position of electrons is different.
- (f) Resonance forms—only the position of electrons is different.
- (g) Resonance forms—only the position of electrons is different.
- (h) Different compounds—a hydrogen atom has changed position.
- (i) Different compounds—a hydrogen atom has changed position.
- (j) Resonance forms—only the position of electrons is different.
- (k) Resonance forms—only the position of electrons is different.
- (l) Resonance forms—only the position of electrons is different.

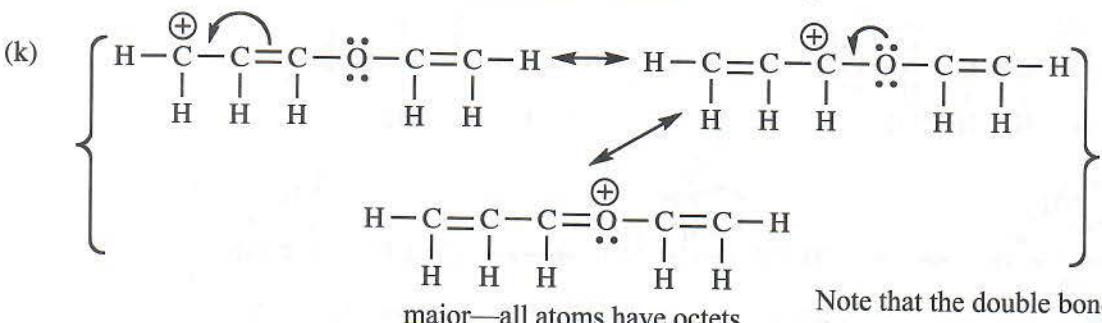
1-42 When drawing resonance forms with charges on ring atoms, it helps to keep track of the charge by writing the C or N or O with the charge. (In Chapter 1, arrows will be shown when drawing resonance forms, equivalent to the green arrows in the text. This important skill should become automatic by Chapter 2 when the arrows will not be shown.)



1-42 continued

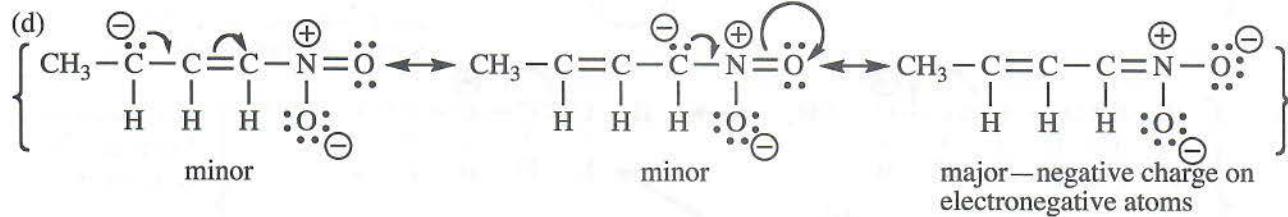
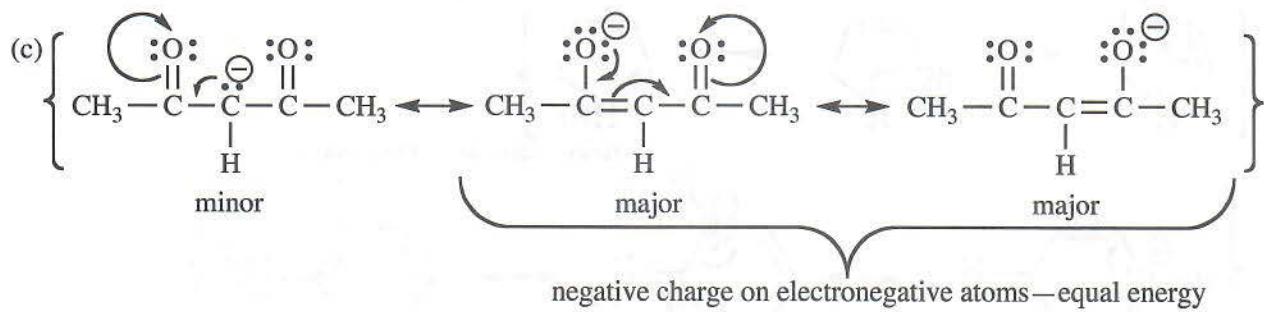
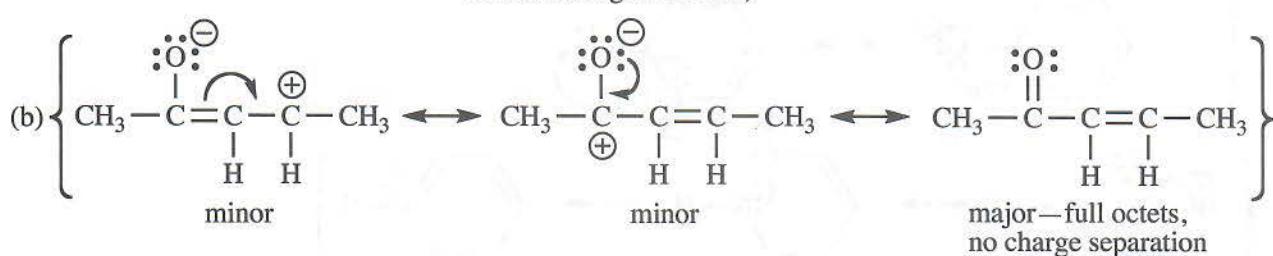
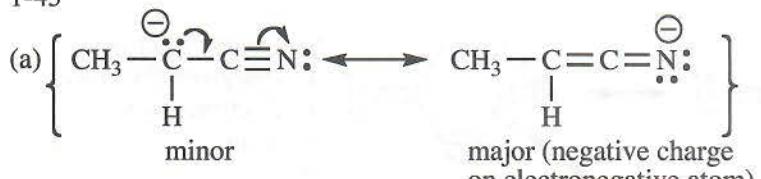


(j) No resonance forms—the charge must be on an atom next to a double or triple bond, or next to a non-bonded pair of electrons, in order for resonance to delocalize the charge.

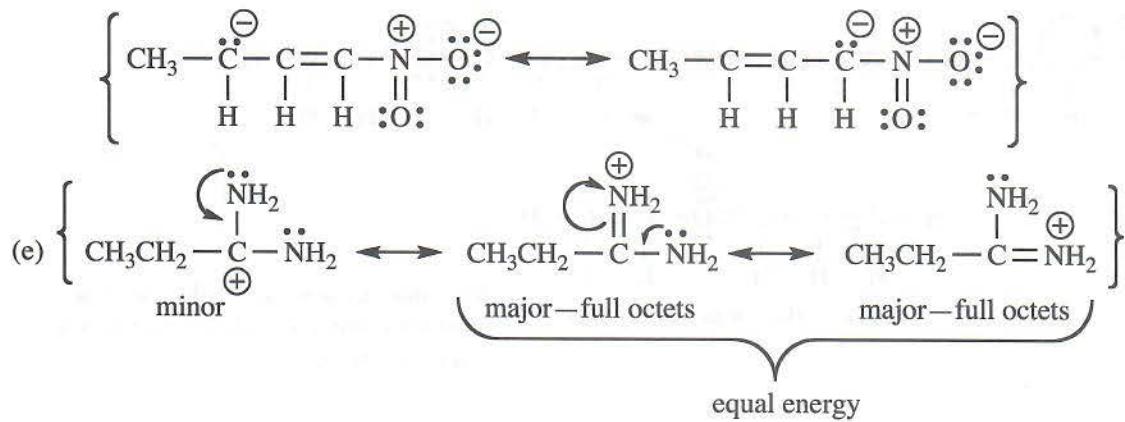


Note that the double bond on the right does not contribute its electrons to the resonance forms.

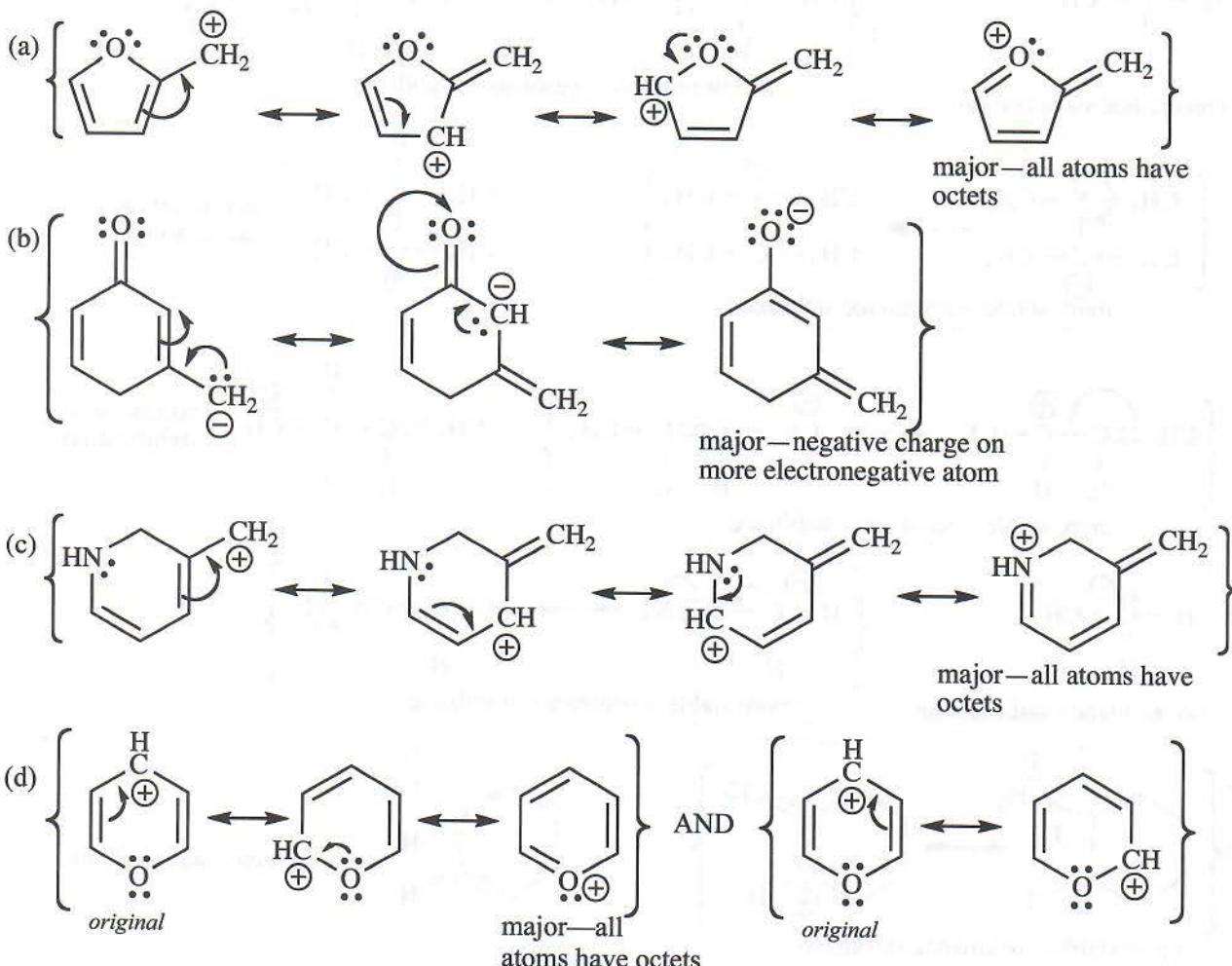
1-43



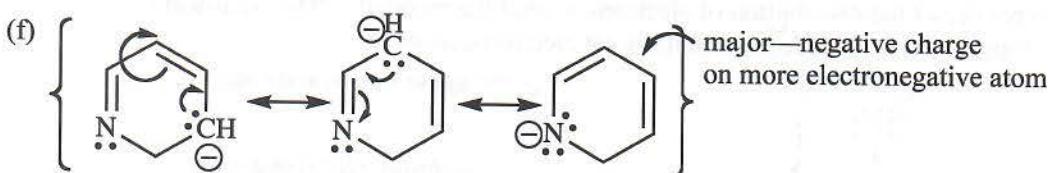
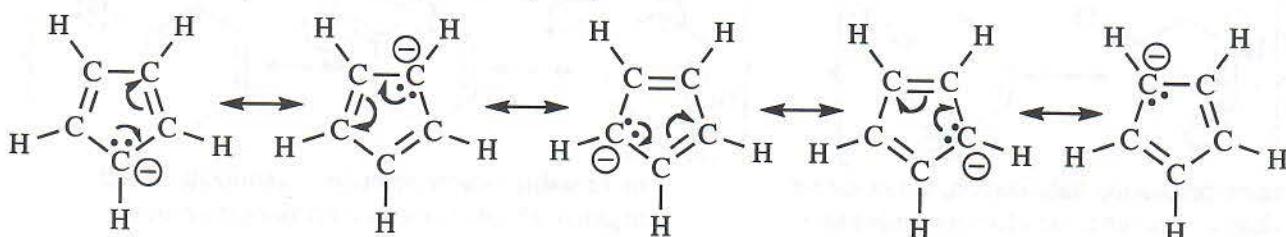
NOTE: The two structures below are resonance forms, varying from the first two structures in part (d) by the different positions of the double bonds in the  $\text{NO}_2$ . Usually, chemists omit drawing the second form of the  $\text{NO}_2$  group although we all understand that its presence is implied. It is a good idea to draw all of the resonance forms until they become second nature. The importance of understanding resonance forms cannot be overemphasized.



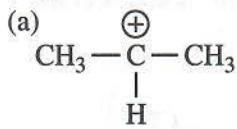
1-44 In Chapter 1, arrows will be shown when drawing resonance forms. This important skill should become automatic by Chapter 2 when the arrows will not be shown.



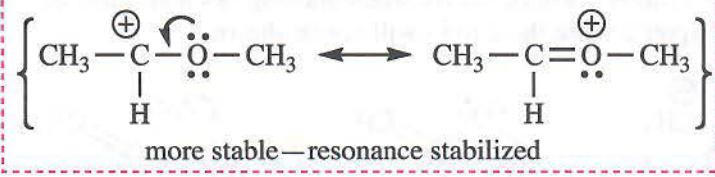
(e) This remarkable anion has five equivalent resonance forms, distributing the negative charge equally on all five carbons. (Braces omitted to save space.)



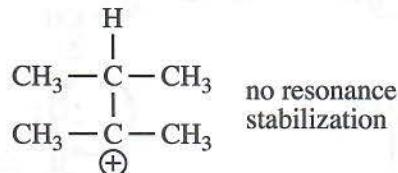
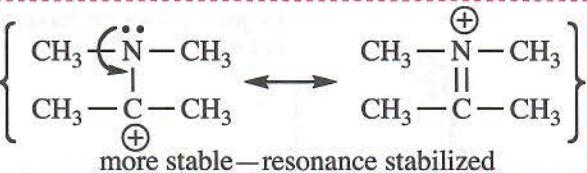
1-45



no resonance stabilization

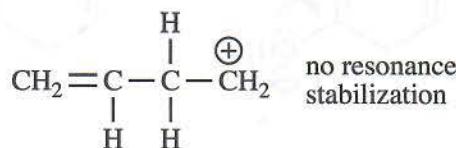
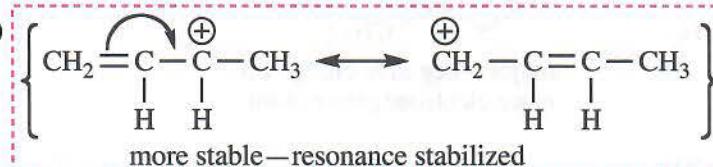


(b)



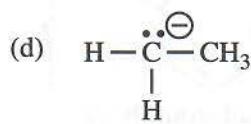
no resonance stabilization

(c)



no resonance stabilization

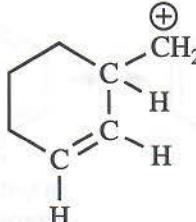
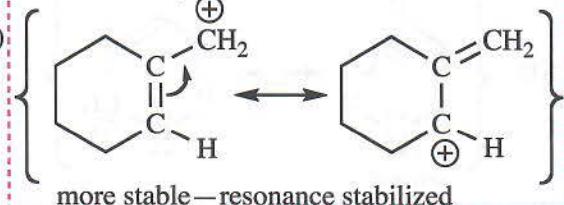
(d)



no resonance stabilization

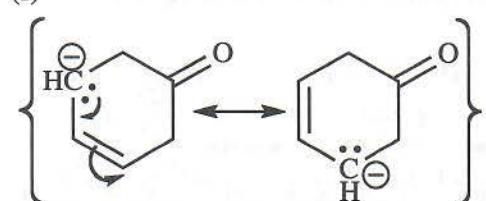


(e)

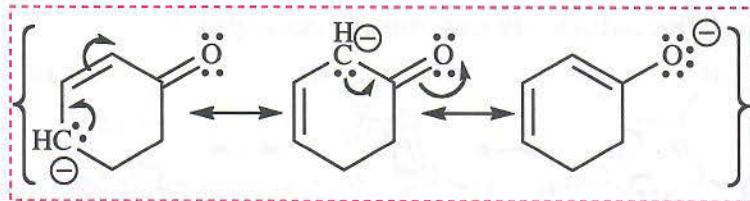


no resonance stabilization

(f)



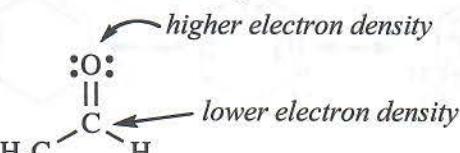
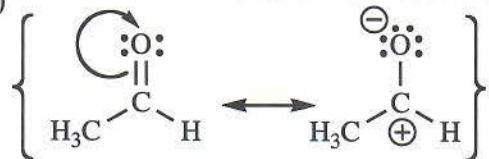
some resonance stabilization, but negative charge is never on an electronegative atom



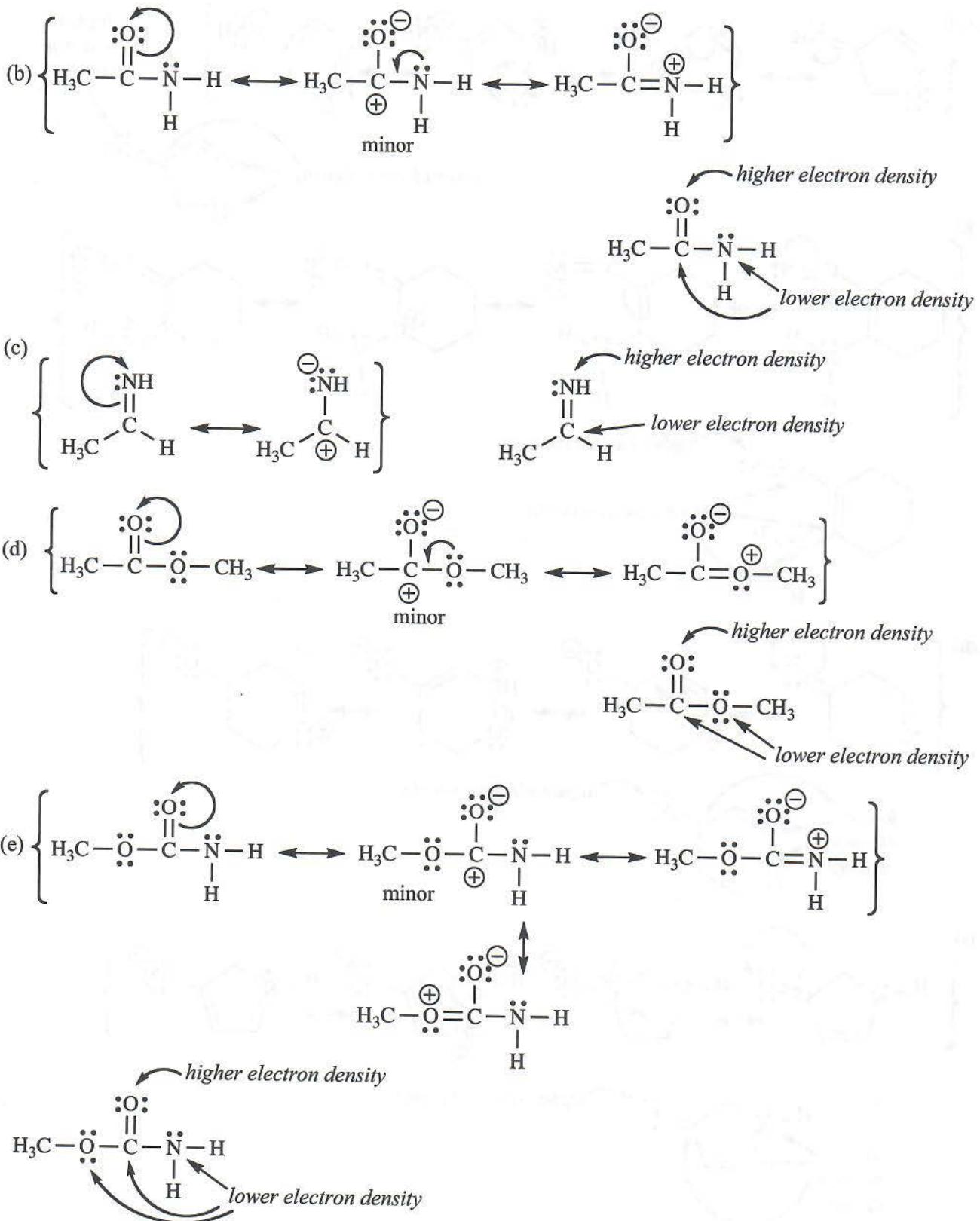
more stable—more resonance stabilization, and negative charge is on an electronegative atom

1-46 Resonance structures depict the distribution of electrons around the molecule. The significant resonance contributors suggest the areas of highest and lowest electron density.

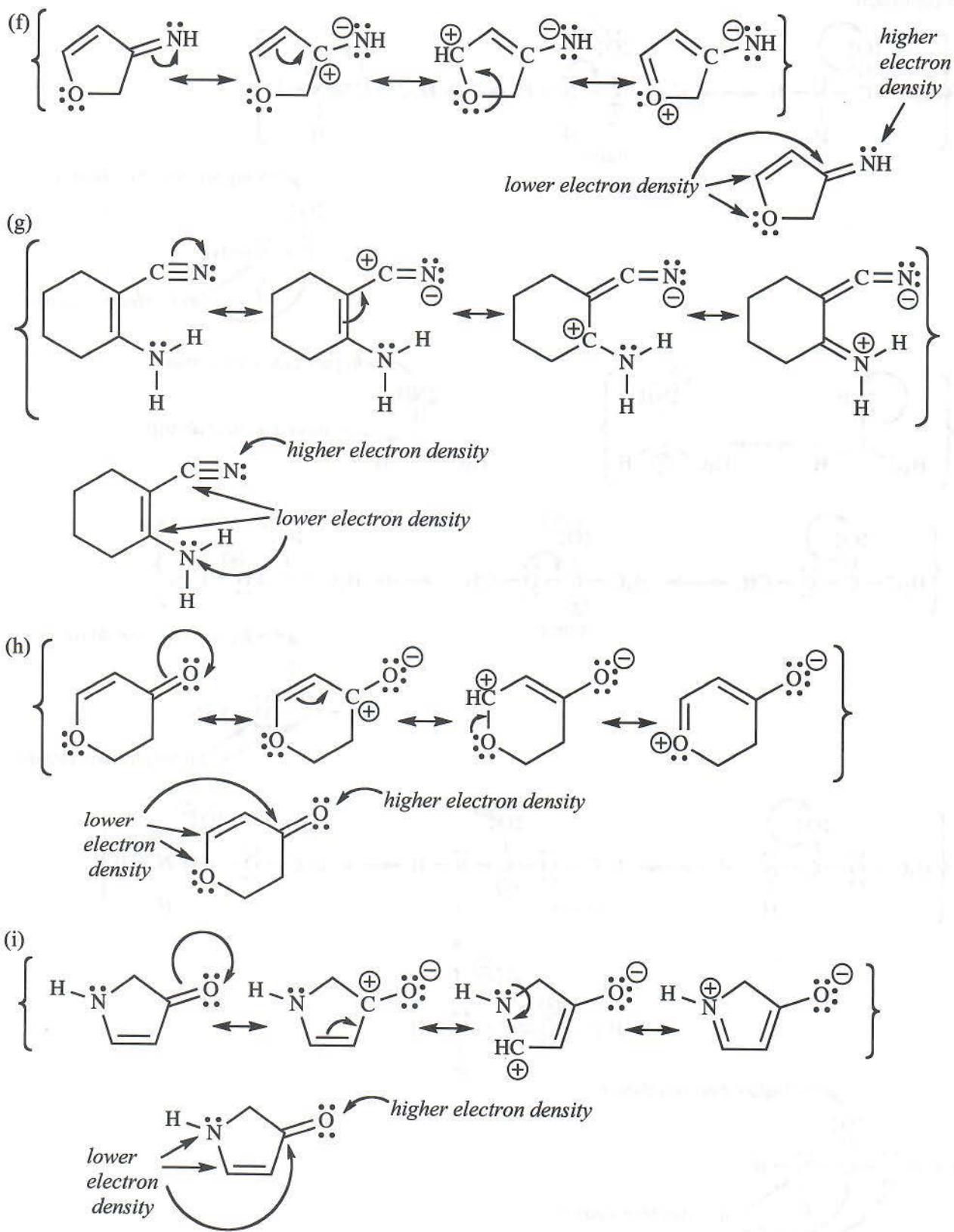
(a)



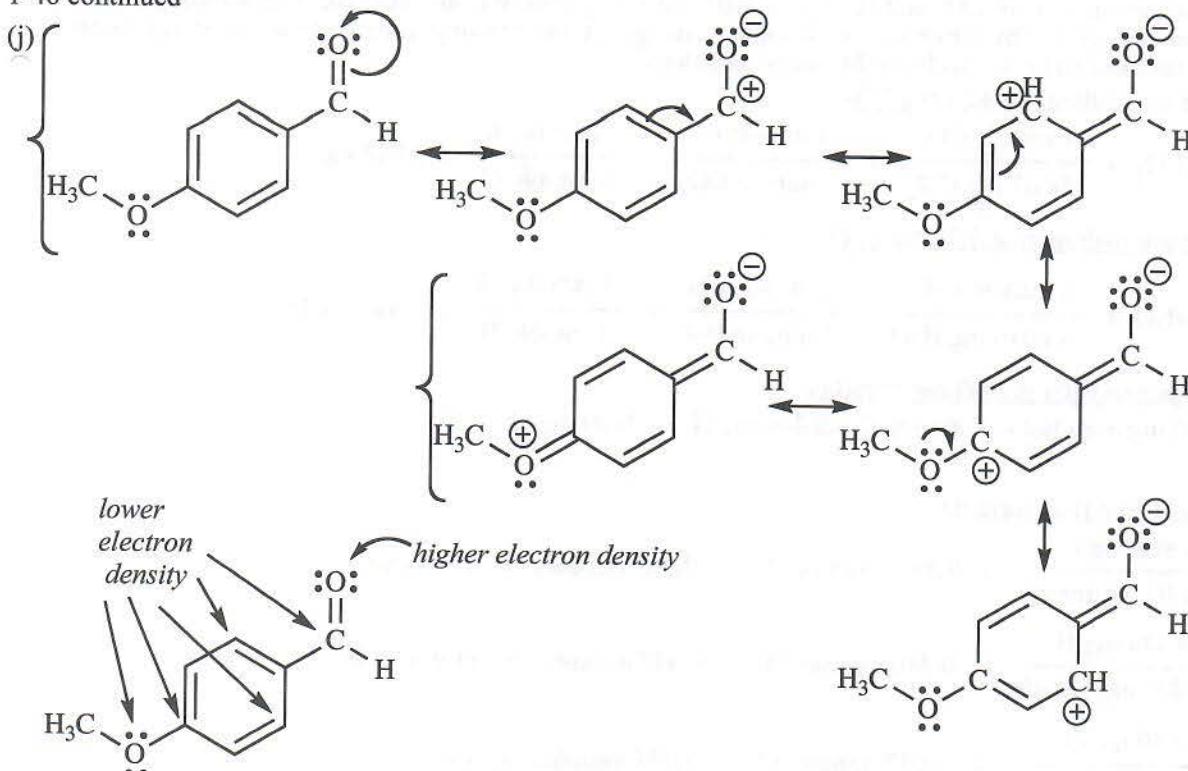
1-46 continued



1-46 continued



1-46 continued



1-47

(a) 100% - 62.0% C - 10.4% H = 27.6% oxygen

$$\frac{62.0 \text{ g C}}{12.0 \text{ g/mole}} = 5.17 \text{ moles C} \div 1.73 \text{ moles} = 2.99 \approx 3 \text{ C}$$

$$\frac{10.4 \text{ g H}}{1.01 \text{ g/mole}} = 10.3 \text{ moles H} \div 1.73 \text{ moles} = 5.95 \approx 6 \text{ H}$$

$$\frac{27.6 \text{ g O}}{16.0 \text{ g/mole}} = 1.73 \text{ moles O} \div 1.73 \text{ moles} = 1 \text{ O}$$

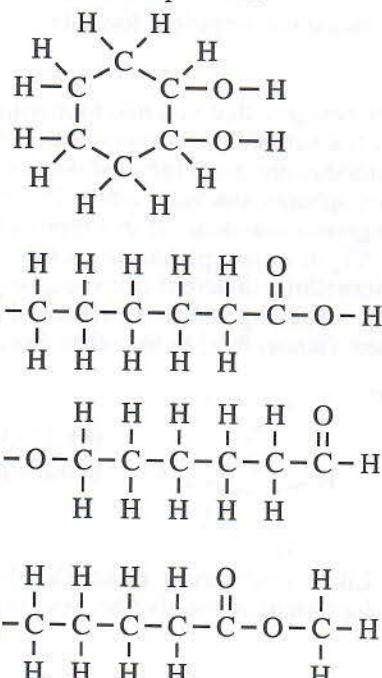
(b) empirical formula = C<sub>3</sub>H<sub>6</sub>O  $\Rightarrow$  empirical weight = 58

molecular weight = 117, about double the empirical weight

$\Rightarrow$  double the empirical formula = molecular formula =

C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>

(c) some possible structures—MANY other structures are possible:



1-48 From the amounts of CO<sub>2</sub> and H<sub>2</sub>O generated, the milligrams of C and H in the original sample can be determined, thus giving by difference the amount of oxygen in the 5.00-mg sample. From these values, the empirical formula and empirical weight can be calculated.

(a) how much carbon in 14.54 mg CO<sub>2</sub>

$$14.54 \text{ mg CO}_2 \times \frac{1 \text{ mmole CO}_2}{44.01 \text{ mg CO}_2} \times \frac{1 \text{ mmole C}}{1 \text{ mmole CO}_2} \times \frac{12.01 \text{ mg C}}{1 \text{ mmole C}} = 3.968 \text{ mg C}$$

how much hydrogen in 3.97 mg H<sub>2</sub>O

$$3.97 \text{ mg H}_2\text{O} \times \frac{1 \text{ mmole H}_2\text{O}}{18.016 \text{ mg H}_2\text{O}} \times \frac{2 \text{ mmoles H}}{1 \text{ mmole H}_2\text{O}} \times \frac{1.008 \text{ mg H}}{1 \text{ mmole H}} = 0.444 \text{ mg H}$$

how much oxygen in 5.00 mg estradiol

$$5.00 \text{ mg estradiol} - 3.968 \text{ mg C} - 0.444 \text{ mg H} = 0.59 \text{ mg O}$$

calculate empirical formula

$$\frac{3.968 \text{ mg C}}{12.01 \text{ mg/mmole}} = 0.3304 \text{ mmoles C} \div 0.037 \text{ mmoles} = 8.93 \approx 9 \text{ C}$$

$$\frac{0.444 \text{ mg H}}{1.008 \text{ mg/mmole}} = 0.440 \text{ mmoles H} \div 0.037 \text{ mmoles} = 11.9 \approx 12 \text{ H}$$

$$\frac{0.59 \text{ mg O}}{16.00 \text{ mg/mmole}} = 0.037 \text{ mmoles O} \div 0.037 \text{ mmoles} = 1 \text{ O}$$

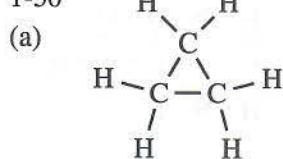
empirical formula = C<sub>9</sub>H<sub>12</sub>O       $\Rightarrow$       empirical weight = 136

(b) molecular weight = 272, exactly twice the empirical weight

twice the empirical formula = molecular formula = C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>

1-49 Imagine that you had four tennis balls, two yellow and two green. If you are asked to arrange them on a flat surface, how many different ways could you do it? There are two possible "square" arrangements (diamonds are the same, just oriented differently): one has the two yellow spheres touching and the two green spheres touching, while the other arrangement has the two yellow diagonal to each other, and the two greens diagonal. If this represented CH<sub>2</sub>Cl<sub>2</sub>, with carbon at the center, there should be two isomers of CH<sub>2</sub>Cl<sub>2</sub> in square planar geometry—and yet only one CH<sub>2</sub>Cl<sub>2</sub> has ever been isolated. The geometry must be something different from square planar, and the only other way of arranging the five atoms in CH<sub>2</sub>Cl<sub>2</sub>, while satisfying carbon's valence of 4, is tetrahedral. In tetrahedral geometry, the relationship of each sphere (tennis ball) to the other three is equivalent, no matter how the spheres are arranged.

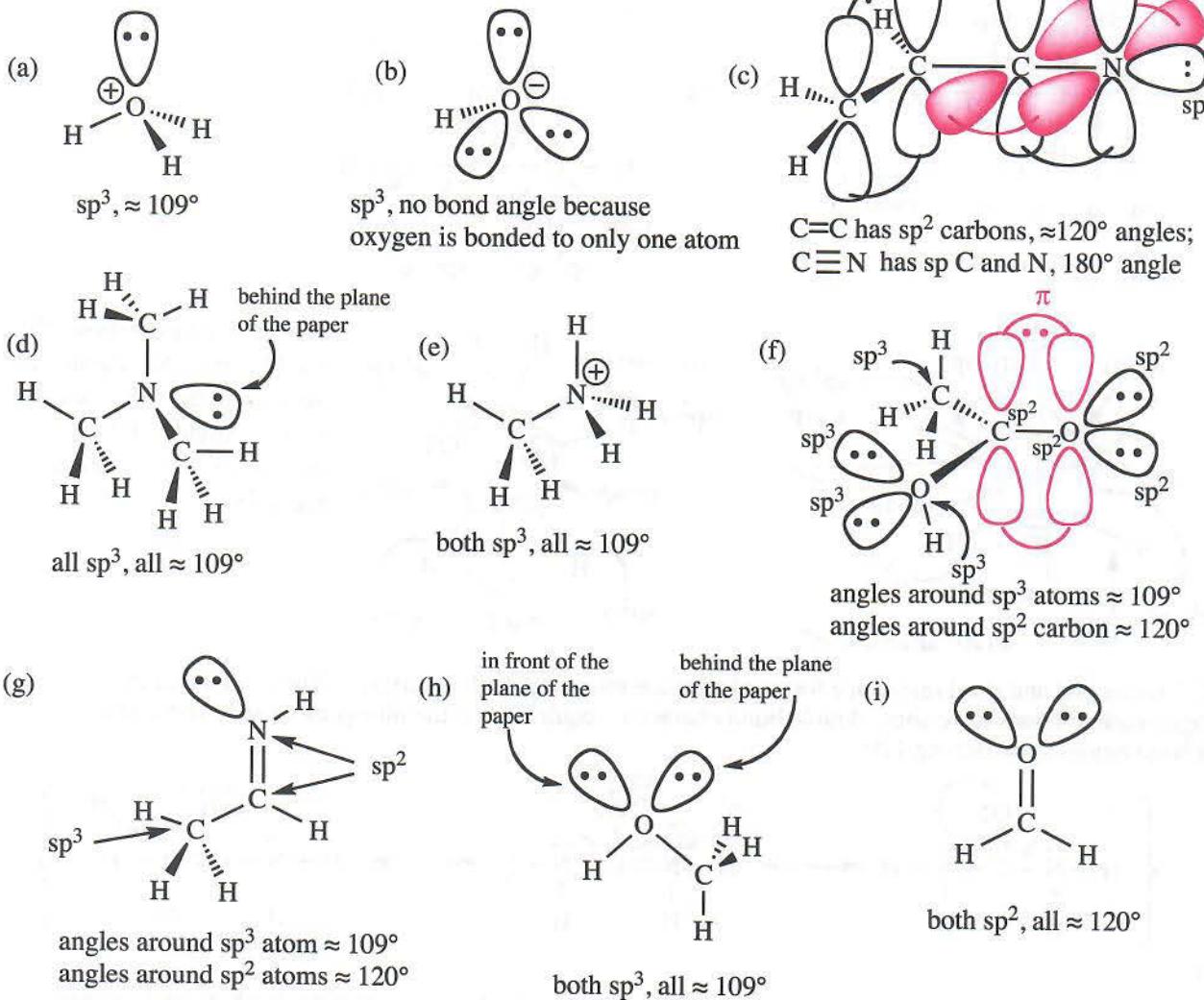
1-50



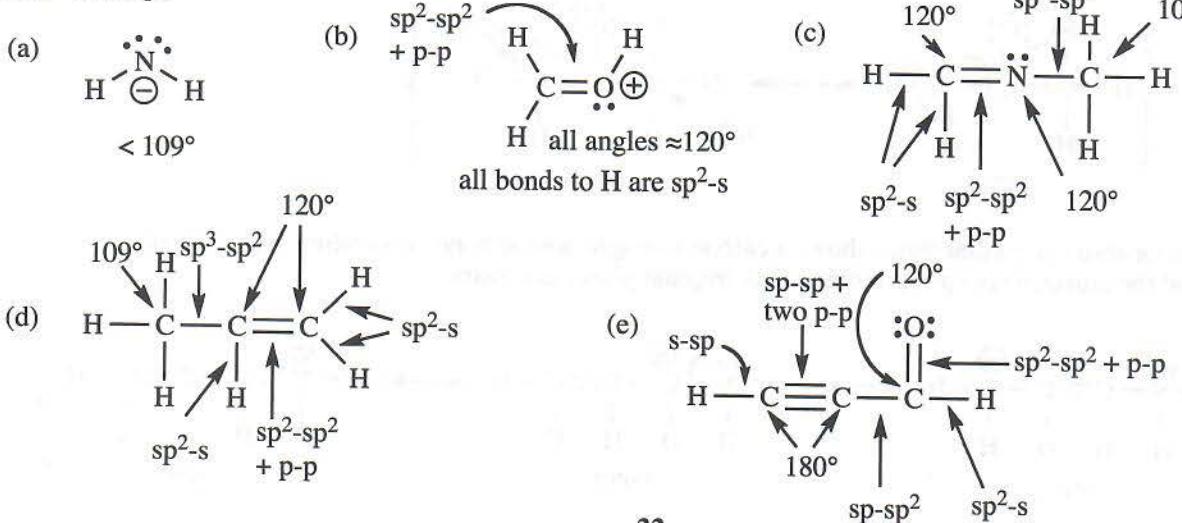
(b) Cyclopropane must have 60° bond angles compared with the usual sp<sup>3</sup> bond angle of 109.5° in an acyclic molecule.

(c) Like a bent spring, bonds that deviate from their normal angles or positions are highly strained. Cyclopropane is reactive because breaking the ring relieves the strain.

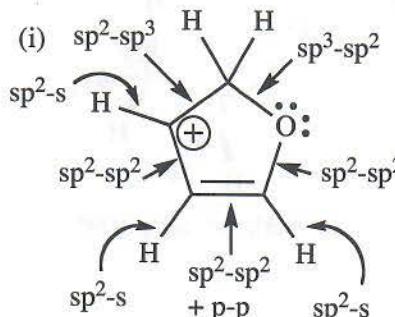
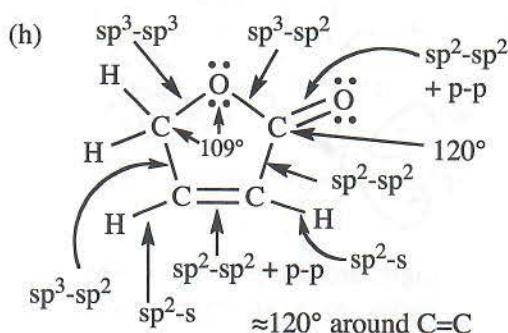
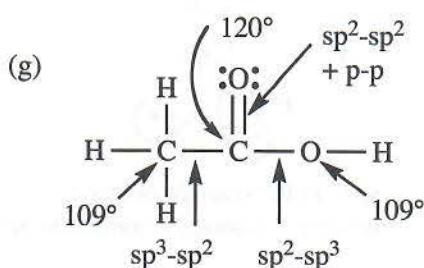
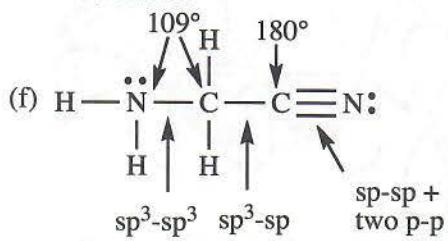
1-51



1-52 For clarity in these pictures, bonds between hydrogen and an sp<sup>3</sup> atom are not labeled; these bonds are s-sp<sup>3</sup> overlap.

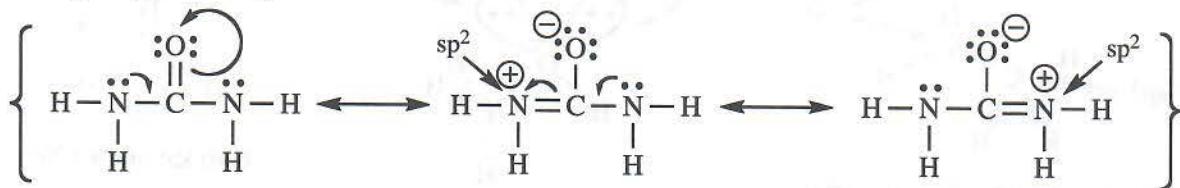


1-52 continued



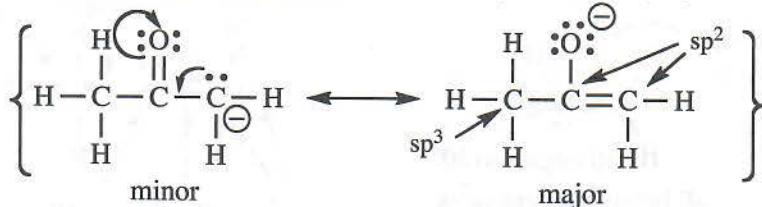
Resonance forms show that the O is  $sp^2$ . All atoms are  $sp^2$  except the top C which is  $sp^3$ . Angles  $\approx 120^\circ$  around  $sp^2$ ,  $\approx 109^\circ$  around the  $sp^3$  C.

1-53 The second and third resonance forms of urea are minor but still significant. They show that the nitrogen-carbon bonds have some double bond character, requiring that the nitrogens be  $sp^2$  hybridized with bond angles approaching  $120^\circ$ .

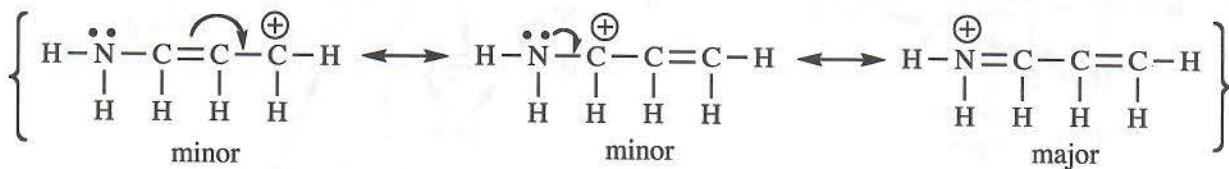


1-54

(a) The major resonance contributor shows a carbon-carbon double bond, suggesting that both carbons are  $sp^2$  hybridized with trigonal planar geometry. The  $CH_3$  carbon is  $sp^3$  hybridized with tetrahedral geometry.

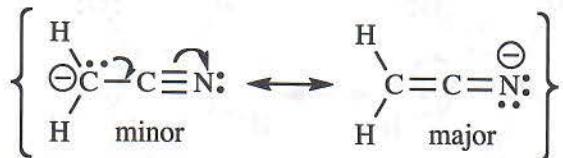


(b) The major resonance contributor shows a carbon-nitrogen double bond, suggesting that all three carbons and the nitrogen are  $sp^2$  hybridized with trigonal planar geometry.

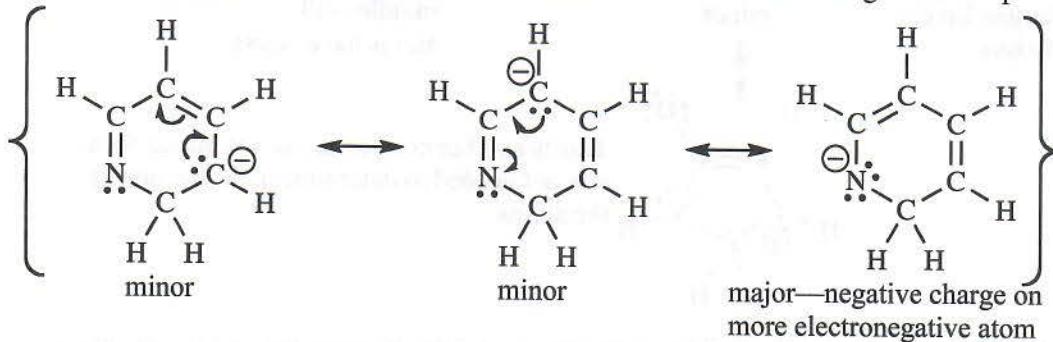


1-54 continued

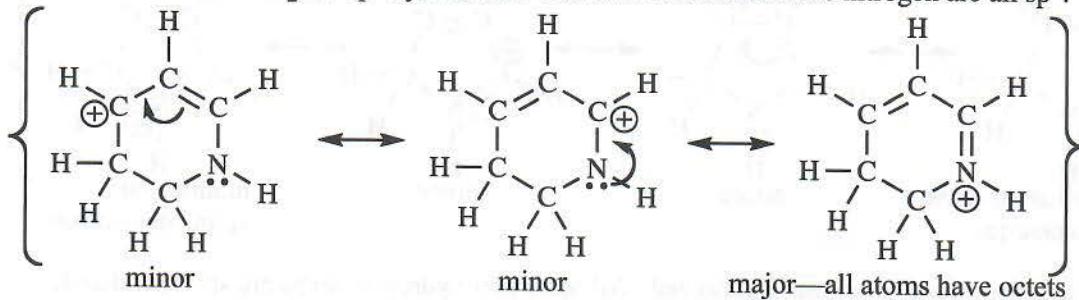
- (c) The nitrogen and the carbon bonded to it are  $sp$  hybridized; the other carbon is  $sp^2$ . This ion has linear geometry. See the solution to 1-21(e) in this manual for an orbital picture.



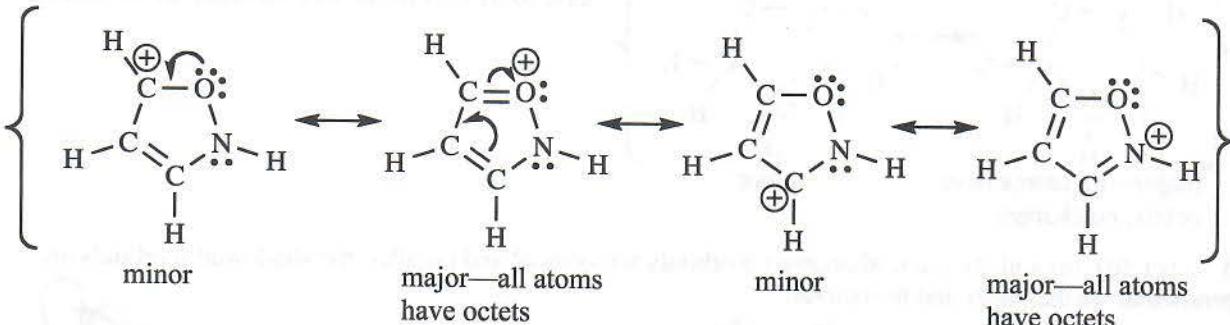
- (d) The carbon of the  $\text{CH}_2$  is  $sp^3$  hybridized. The other carbons and the nitrogen are all  $sp^2$ .



- (e) The two carbons of  $\text{CH}_2$  are  $sp^3$  hybridized. The other carbons and the nitrogen are all  $sp^2$ .

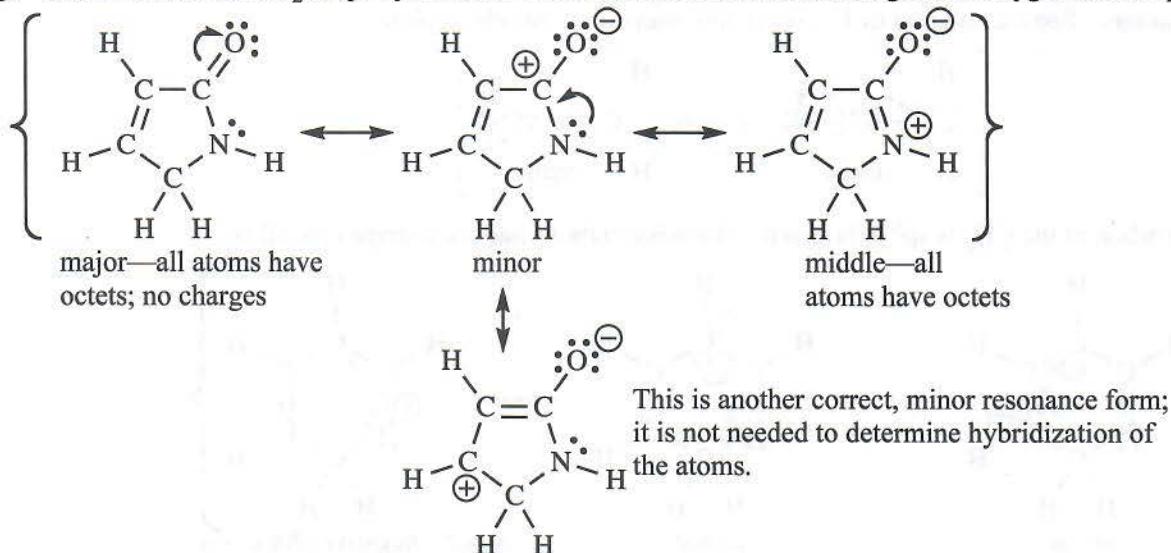


- (f) All of the non-hydrogen atoms in this molecule are  $sp^2$  hybridized.

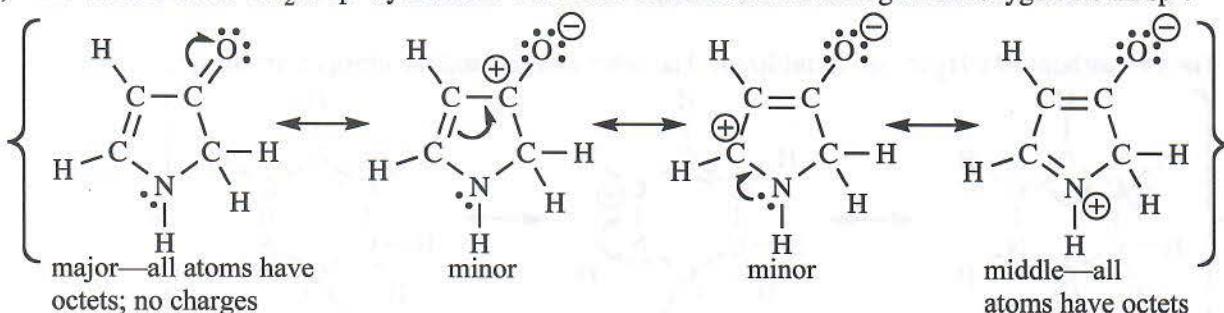


1-54 continued

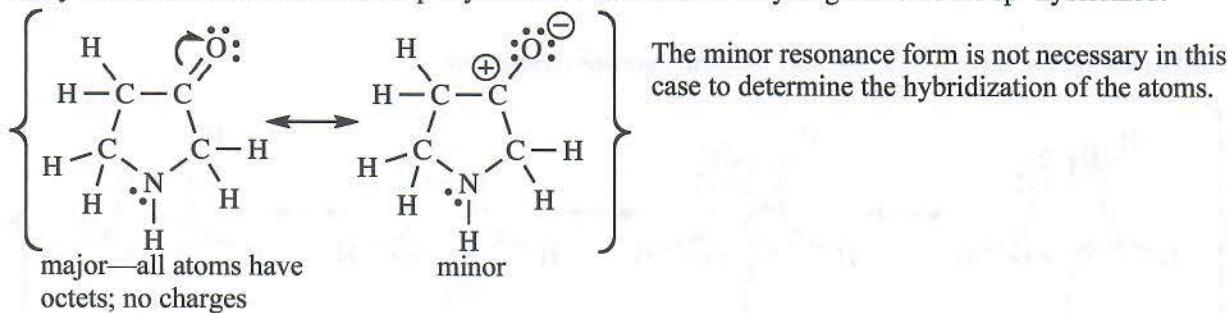
- (g) The carbon of the  $\text{CH}_2$  is  $\text{sp}^3$  hybridized. The other carbons and the nitrogen and oxygen are all  $\text{sp}^2$ .



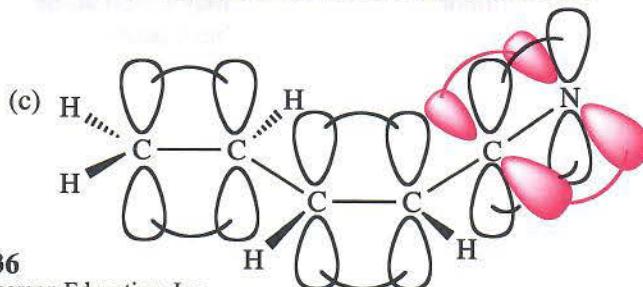
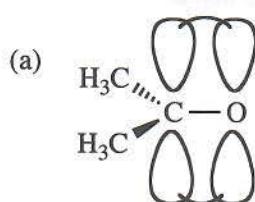
- (h) The carbon of the  $\text{CH}_2$  is  $\text{sp}^3$  hybridized. The other carbons and the nitrogen and oxygen are all  $\text{sp}^2$ .



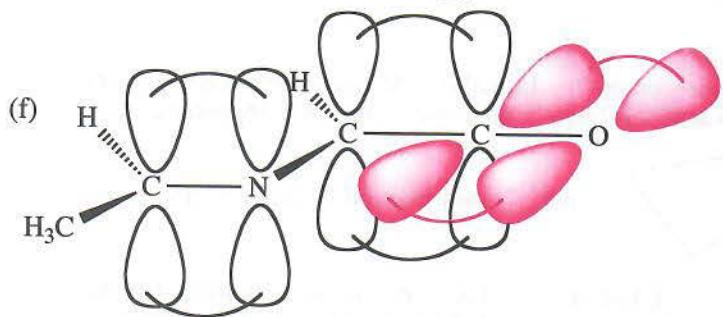
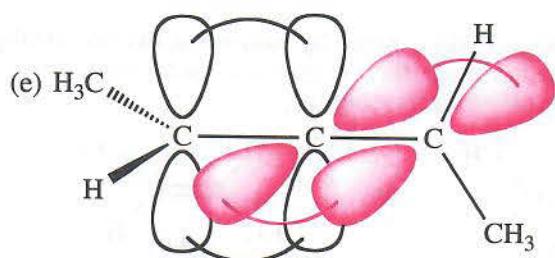
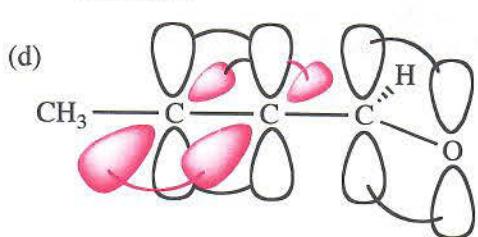
- (i) Only the C and O of the  $\text{C=O}$  are  $\text{sp}^2$  hybridized. All other non-hydrogen atoms are  $\text{sp}^3$  hybridized.



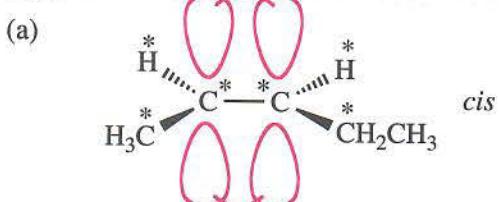
1-55 In (c), (d), (e) and (f), the unshadowed p orbitals are vertical and parallel; the shadowed p orbitals are perpendicular to the paper and horizontal.



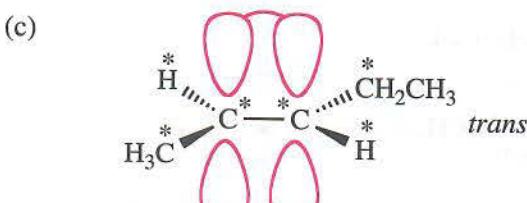
1-55 continued



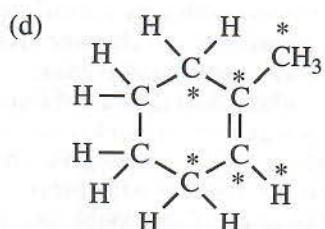
1-56



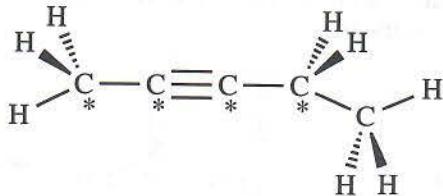
(b) The coplanar atoms in the structures to the left and below are marked with asterisks.



There are still six coplanar atoms.

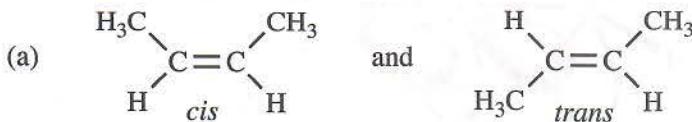


1-57 Collinear atoms are marked with asterisks.

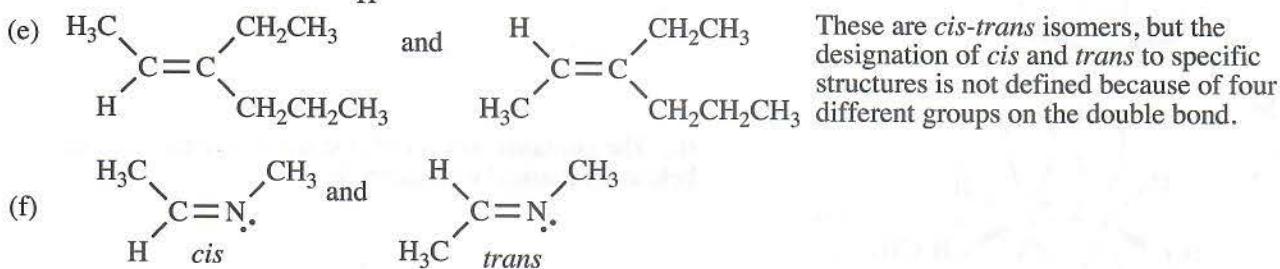
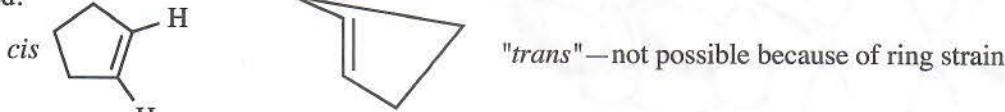


1-58

Cis and trans isomers are determined by comparing two identical groups on the two carbons of the double bond, and determining their relative position: same side of the double bond = *cis*; opposite side = *trans*. Drawing in H atoms is a big help!



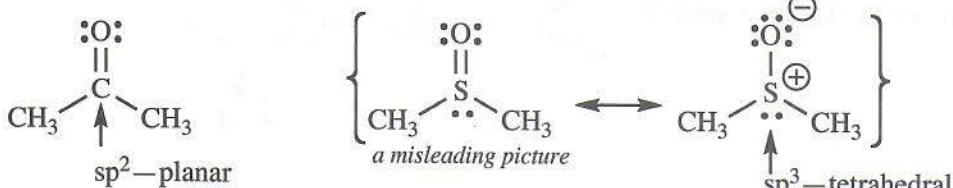
- (b) no *cis-trans* isomerism around a triple bond
- (c) no *cis-trans* isomerism; two groups on each carbon are the same
- (d) Theoretically, cyclopentene could show *cis-trans* isomerism. In reality, the *trans* form is too unstable to exist because of the necessity of stretched bonds and deformed bond angles. *trans*-Cyclopentene has never been detected.



1-59

- (a) constitutional isomers—The carbon skeletons are different.
- (b) constitutional isomers—The position of the chlorine atom has changed.
- (c) *cis-trans* isomers—The first is *cis*, the second is *trans*.
- (d) constitutional isomers—The carbon skeletons are different.
- (e) *cis-trans* isomers—The first is *trans*, the second is *cis*. (The  $-\text{CH}_2\text{CH}_3$  groups decide.)
- (f) same compound—Rotation of the first structure gives the second.
- (g) *cis-trans* isomers—The first is *cis*, the second is *trans*.
- (h) constitutional isomers—The position of the double bond relative to the ketone has changed (while it is true that the first double bond is *cis* and the second is *trans*, in order to have *cis-trans* isomers, the rest of the structure must be identical).

1-60



The key to this problem is understanding that sulfur has a *lone pair of electrons*. The second resonance form shows four pairs of electrons around the sulfur atom, an electronic configuration requiring  $\text{sp}^3$  hybridization. Sulfur in DMSO cannot be  $\text{sp}^2$  like carbon in acetone, so we would expect sulfur's geometry to be pyramidal (the four electron pairs around sulfur require tetrahedral geometry, but the three atoms around sulfur define its shape as pyramidal). The first resonance form is a misleading picture because it suggests a p-p pi bond in DMSO that does not exist. Sulfur might use a d orbital for some pi bonding but it is definitely not a p-p pi bond.