

## CFQ & PP: Fundamentals of Organic Structure and Reactivity

### Reading

- Brown and Foote: Chapter 1
- Oxtoby, Gillis and Nachtrieb: Sections 3.3 - 3.8
- Weeks: Chapters 1 and 2

### Lecture Supplement

Some Important Functional Groups (page 5 this Thinkbook)

### Optional Web Site Reading

More on Lewis Structures ([www.towson.edu/~ladon/lewis.html](http://www.towson.edu/~ladon/lewis.html))

### Suggested Text Exercises

- Brown and Foote Chapter 1: 3 – 18, 23 - 70
- Oxtoby, Gillis and Nachtrieb Chapter 3 (ignore questions about bond lengths): 11, 27 - 45 (odd), 53 - 63 (odd)

### Related Tutorials ([web.chem.ucla.edu/~harding/tutorials/tutorials.html](http://web.chem.ucla.edu/~harding/tutorials/tutorials.html))

- Drawing Lewis Dot Structures
- Formal Charge
- Curved Arrows
- Resonance: Vocabulary  
Drawing Resonance Structures  
Most Important Resonance Structure

### Optional Interactive Organic Chemistry CD and Workbook

Supporting Concepts: Formal Charge (p. 67)  
Resonance (p. 68)

### Common Questions About Organic Chemistry Problems

*I don't have time to do all these problems!* As you look through this Thinkbook, you will find many problems: the Concept Focus Questions (CFQ), the Practice Problems (PP), as well as suggested problems from the text and other sources. Working all these problems can be time-consuming, but this task is essential to your understanding of the course material. Rarely do students who skimp on problem solving get good grades. Most students who study a topic for the first time really do need to work all the problems. Problem solving is an excellent way to reinforce the concepts in your mind. If you can honestly say to yourself that you have a firm grasp on the concept, then feel free to skip the problem. On the other hand if you are not 100% sure, then work the problem. Even students who have a firm conceptual grasp should work a few "obvious" problems every now and then to stay sharp.

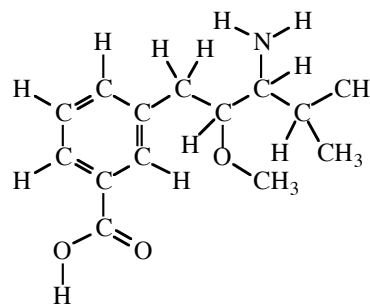
*Which problems are most important?* Here is a suggested order of priority:

1. The CFQ: Always read these *before* lecture, and then again when you study the chapter. They outline the fundamental concepts presented in lecture, and are the most important problems in this course.
2. The PP: Written by the same person who writes the exam.
3. All other problems, including the optional ones. Different students get the most out of different problem sources, although most students seem to get more out of the textbook problems than from the other sources. Pushing Electrons and the Hardinger tutorials focus on specific topics, and should be examined if you are having trouble with these specific topics.

### Concept Focus Questions

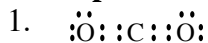
1. Draw the Lewis dot structure for CO<sub>2</sub>.
2. How are the electrons distributed in the bonds of CO<sub>2</sub>? What consequences does this have for the ways in which this molecule might react with other electron-rich or electron-poor molecules?
3. Define "resonance," and give an example.

4. Draw a stick (bond-line) structure for the molecule shown. Include all lone pairs.



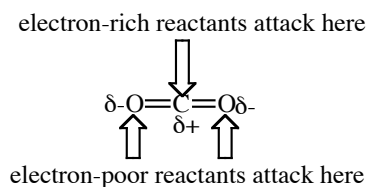
5. Define "functional group." Why are functional groups important to a systematic study of organic chemistry? (Be prepared to name or draw functional groups, but please do not memorize specific examples.)
6. What is the single most important factor that controls the geometry of any molecule?
7. Describe the bond lengths, bond angles, and overall geometry of methane.
8. Why does the carbon of methane use hybrid orbitals and not atomic orbitals to bond with hydrogen?
9. Draw the orbitals that overlap to form the bonds in ethylene.

## Concept Focus Questions Solutions



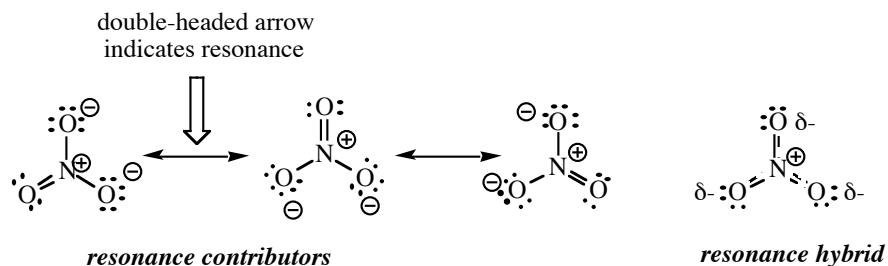
Use of the abbreviated procedure for drawing Lewis dot structures that naturally leads to multiple bonds. (Tutorial: <http://web.chem.ucla.edu/~harding/tutorials/tutorials.html>)

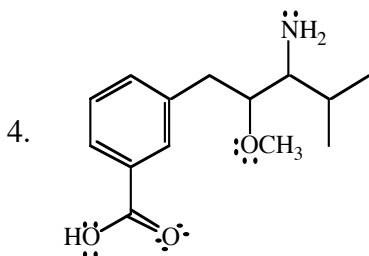
2. The distribution of bonding electron density is influenced by the electronegativity of the atoms that comprise the bond. A more electronegative atom attracts more electron density toward itself. Thus, end of the bond with the more electronegative atom will have a small negative charge ( $\delta^-$ ). The less electronegative atom loses electron density, as so has a small positive charge ( $\delta^+$ ). Carbon is less electronegative than oxygen, so the carbon has a  $\delta^+$  charge and each oxygen atom has a  $\delta^-$  charge. To predict reactivity, recall from basic physics that opposite charges attract and like charges repel. Atoms with a  $\delta^-$  charge will be attracted to electron-poor reactants and repel electron-rich reactants. Atoms with a  $\delta^+$  charge will attract electron-rich reactants and repel electron-poor reactants. Thus, the electron-rich reactants will attack the carbon, whereas electron-poor reactants will attack the oxygen. The oxygen lone pairs are also available to react, and also serve to attract electron-poor reactants to the oxygen.



3. **Resonance:** When a molecule can be represented by the weighted hybrid of two or more hypothetical but reasonable Lewis structures that differ only in the distribution of bonding and nonbonding electrons, and in which the positions of the nuclei are constant.

**Example:** Nitrate ion ( $\text{NO}_3^-$ ) has three important resonance contributors. None of these is a good representation of reality. The resonance hybrid is a weighted average of all resonance contributors, and is the structure closest to actual structure of this ion.

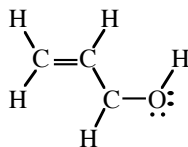




- A functional group is a set of atoms, bonded together, that gives a molecule particular chemical and physical properties. Because chemical reactions involve changes in electron distribution and bonds, functional groups with similar electronic structures will react in similar ways. This is just one reason why the study of functional groups is so critical to a systematic study of organic chemistry.
- The single most important factor that controls the geometry of any molecule or ion is electron repulsion. (VSEPR is not a reason, but rather a theory that describes how and why electron repulsion controls geometry.)
- All the C-H bonds in methane are equivalent, so all the C-H bond lengths and H-C-H bond angles are equal. The C-H bonds are 1.091 Å, a fairly typical  $\sigma$  bond length. The H-C-H bond angles are all 109.47°. The hydrogen atoms point toward the corners of a tetrahedron.
- Methane prefers to adopt a geometry that places the hydrogen atoms as far away from each other as possible yet still maintains the C-H bonds. The best way to achieve this is through tetrahedral geometry, with H-C-H bond angles of 109.47°. The atomic orbitals that carbon has available for bonding are the  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  orbitals. The carbon  $2s$  orbital cannot overlap with a hydrogen  $1s$  orbital, because this hydrogen orbital already has one electron. (We cannot place three electrons in the new bond.) The set of carbon  $p$  orbitals are mutually perpendicular (orthogonal). Overlap of the hydrogen  $1s$  orbitals with the carbon  $2p$  orbitals would result in H-C-H bonds of 90°. The  $sp^3$  hybrid orbitals have the desired angles and electron occupancy to allow C-H bonding to occur with the desired bond angles.
- Your orbital drawing should look like Figure 1.18 of the Brown and Foote text.

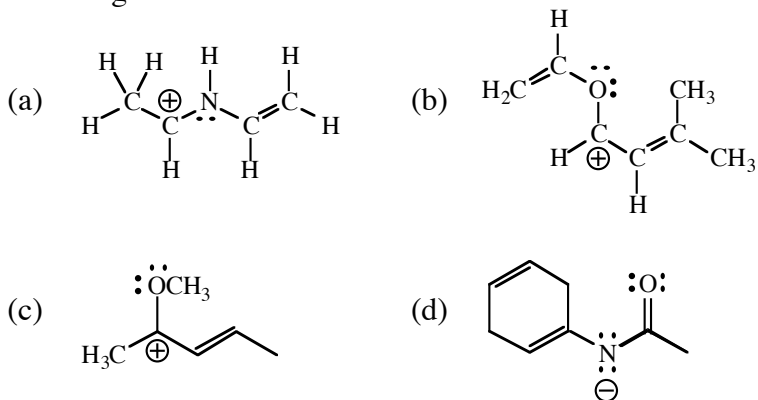
### Practice Problems

Questions 1- 4 concern this structure:

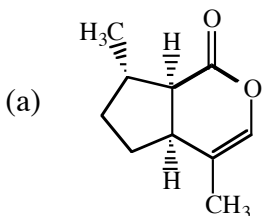


- Label each carbon and oxygen with its formal charge.
- Draw all the important resonance contributors for this structure.
- Draw the resonance hybrid for this structure.

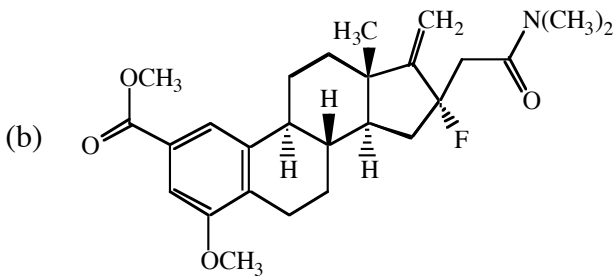
4. Select the one structure that you have drawn which is the best representation of reality.
5. Draw all the significant resonance contributors as well as the resonance hybrid for the following molecules or ions.



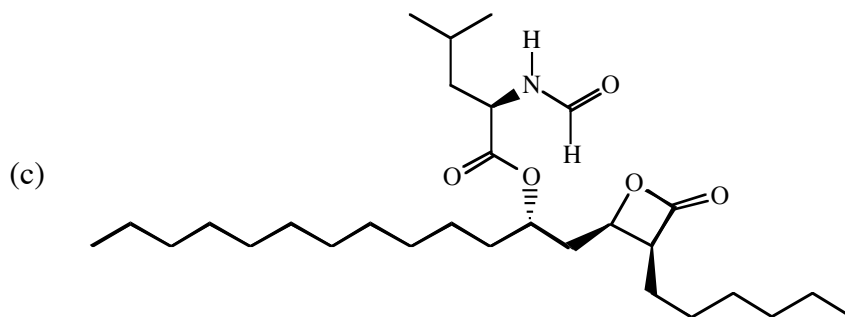
6. Very briefly explain why the study of functional groups is critical to an understanding of organic chemistry.
7. Circle and label all functional groups of the following molecules.



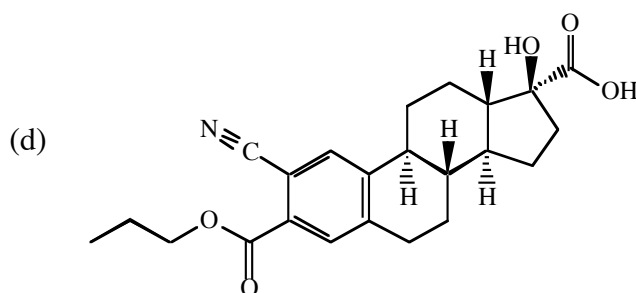
Nepetalactone, the active component of catnip.



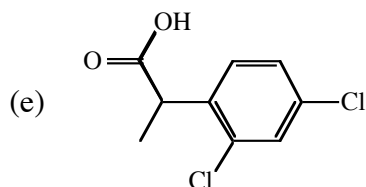
Methyl stressonate, isolated from the sweat of Bruins taking organic finals.



Xenical (orlistat), a weight loss drug that work by irreversibly blocking stomach and intestinal enzymes involved in fat metabolism.



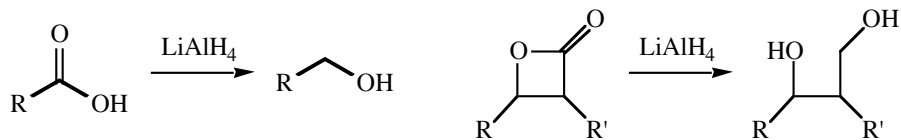
Pepperonione, a molecule found in pizza that helps the Bruin brain recognize patterns and therefore makes organic chemistry much easier to learn.



2,4-DP, a herbicide (a chemical used to kill plants).

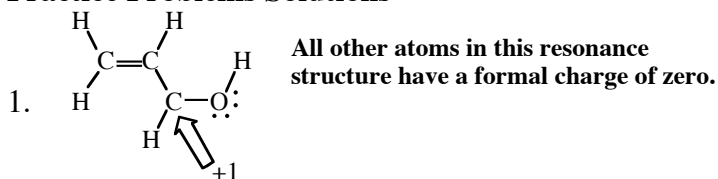
8. Draw a single molecule that contains the listed functional groups. Do not use any abbreviations such as R or X.
  - (a) Ester, amide, primary alcohol.
  - (b) Carboxylic acid, alkene, benzene ring, ether.
  - (c) Alkyl chloride, nitrile, ketone, aldehyde.
  
9. Based on their Lewis structures, what can we conclude about the chemical reactions of the ester and amide functional groups?
  
10. Why are the reactions of aldehydes and imines very similar? Be very specific.
  
11. A carboxylic acid reacts with  $\text{LiAlH}_4$  to form a primary alcohol. We can therefore conclude that the four-membered ring of Xenical (question 7), which contains a

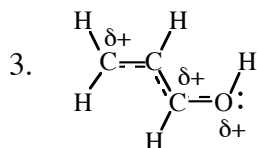
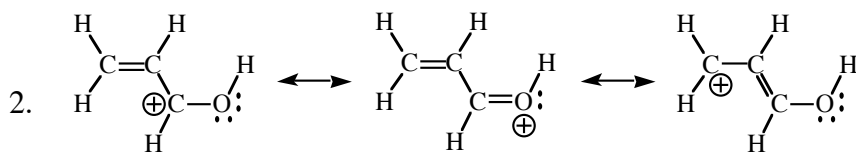
functional group called a lactone, reacts in a similar manner. Briefly explain why we can make this conclusion.



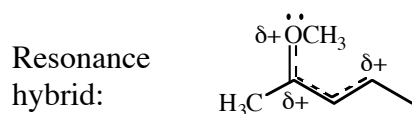
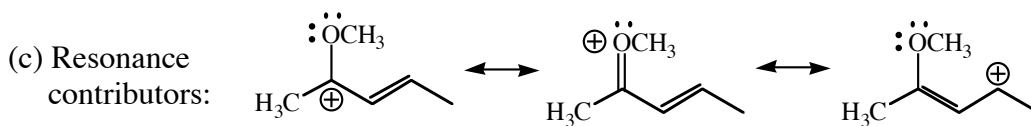
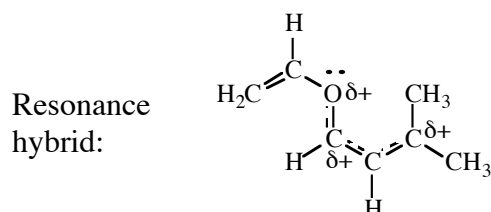
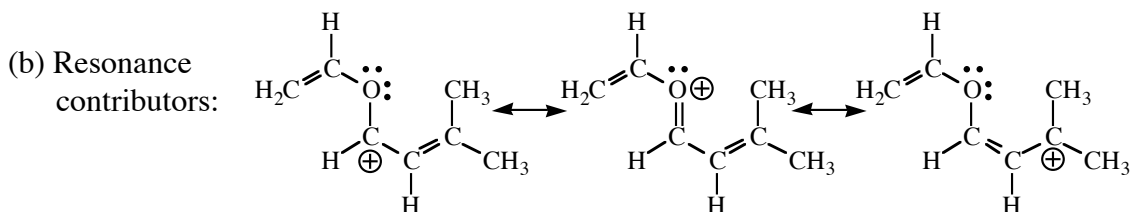
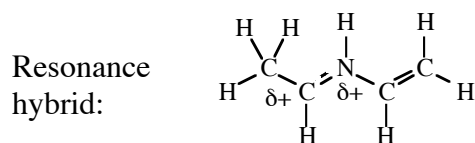
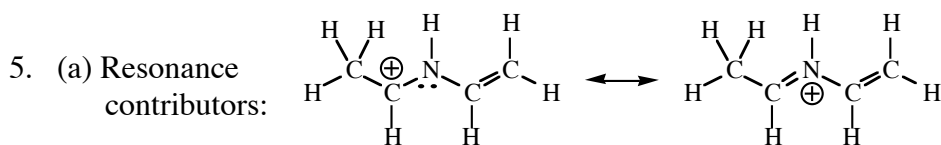
- If the ester of methyl stressonate (question 7b) reacts with  $\text{LiAlH}_4$  to form a primary alcohol, what other functional group in methyl stressonate is expected to undergo a similar reaction?
- Which two of the following three functional groups has the most similar chemistry: ester, amide, and alcohol? Briefly explain.
- Very briefly explain why we would expect many similarities in reactions of alcohols and water.
- Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a common reactant in organic chemical reactions. Draw a Lewis structure for sulfuric acid. Briefly describe how the polarity of a chemical bond is estimated by using only the Lewis structure of a molecule. Illustrate your answer with the S-O bond in sulfuric acid.
- Consider the structure of allyl alcohol ( $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$ ). Estimate the O-C-C and H-O-C bond angles. Briefly explain your reasoning for the H-O-C bond angle.
- Consider the structure of ethyl methyl ether ( $\text{CH}_3\text{OCH}_2\text{CH}_3$ ). What is the hybridization of the oxygen atom, and the approximate C-O-C bond angle?
- Briefly discuss the molecular geometry of methane and the methyl carbanion ( $:\text{CH}_3$ ).
- Draw the structure of  $\text{SF}_6$ , clearly showing the molecular geometry. Very briefly explain why  $\text{SF}_6$  adopts this molecular geometry.
- Draw a picture that clearly shows how atomic or hybrid orbitals overlap to form a carbonyl group. Include all lone pairs. Specify the geometry and hybridization of each atom.
- What is the most polar bond in 2,4-DP (structure in question 7)?

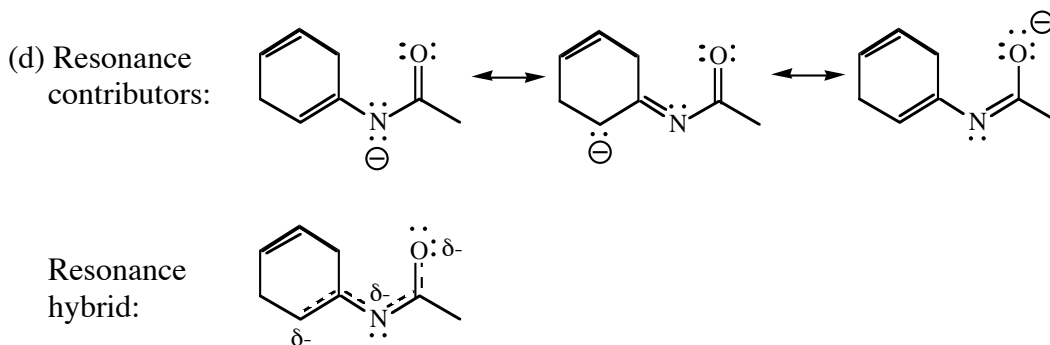
### Practice Problems Solutions



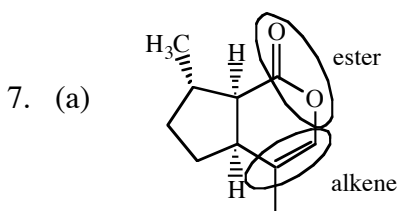


4. The resonance hybrid is the best representation of the actual structure of this ion.

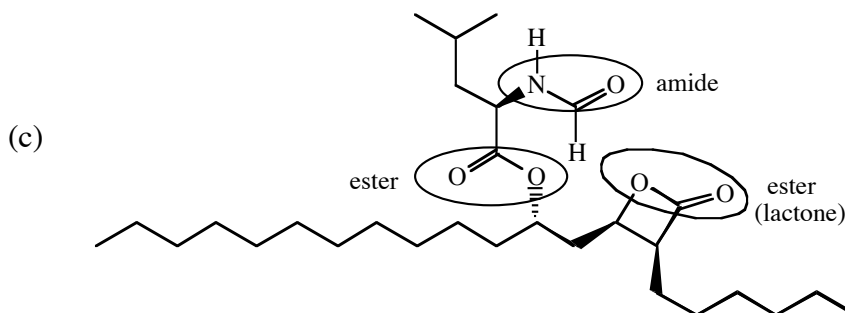
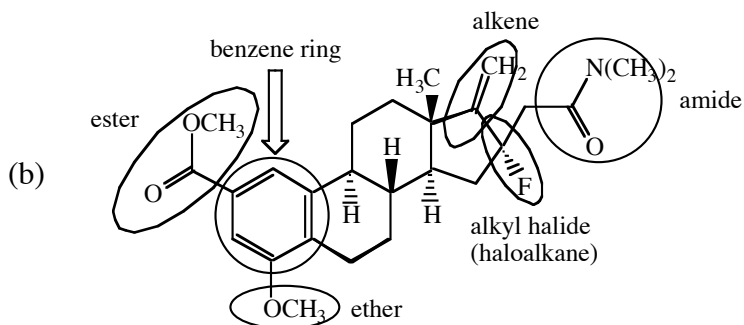


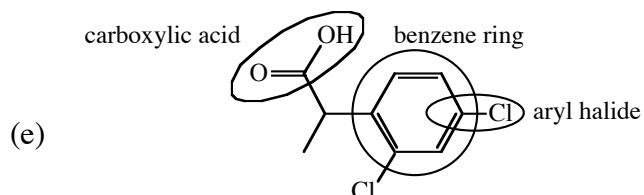
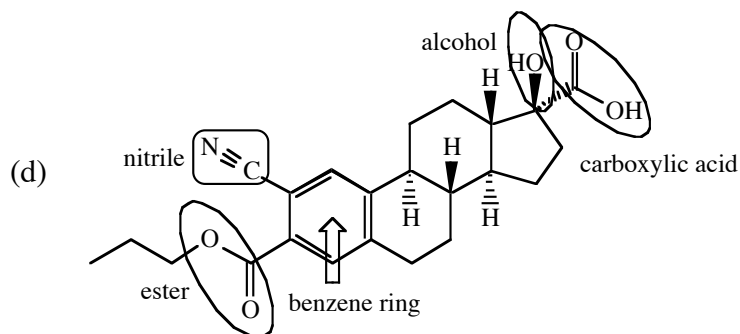


6. A functional group is defined as a group of atoms that are common between compounds and give rise to the characteristic physical and chemical properties of a compound. Chemical reactivity and physical properties are both strongly influenced by electron molecular structure. Therefore compounds with similar functional groups will have similar physical and chemical properties. By considering the functional groups in a compound, we can make many predictions about a compound that we have never before encountered, and perhaps never even been synthesized.



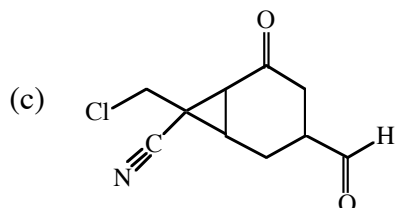
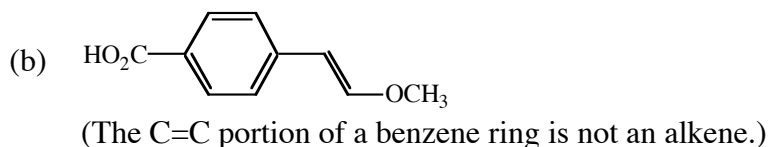
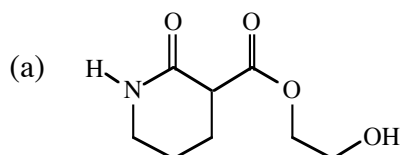
(A cyclic ester is also called a lactone.)





(An aryl halide is a halogen atom attached to a benzene ring, similar to an alkyl halide.)

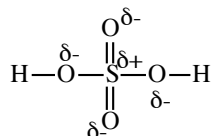
8. Functional groups may share atoms, but one functional group may not be wholly contained within another. (For instance, a carboxylic acid ( $\text{RCO}_2\text{H}$ ) contains the  $\text{OH}$  group, but it is not an alcohol. However, we still expect some similarities on the chemistry of carboxylic acids and alcohols because they both contain an  $-\text{OH}$  group.) One example for each set of functional groups is given, but any molecule that contains all of required functional groups is acceptable.



9. These functional groups have similar structures. As can be seen from their Lewis structures in the previous question, both have a carbonyl group ( $\text{C}=\text{O}$ ), and both have a heteroatom (an atom other than carbon or hydrogen; nitrogen or oxygen in this case) attached to the carbonyl group. Both heteroatoms have a lone pair of electrons.

Because these functional groups have similar structures, we can predict their chemical reactions will also be somewhat similar.

10. Aldehydes and imines are expected to have similar chemistry because the functional groups are similar. Both consist of a double bond between a carbon and a heteroatom with at least one lone pair of electrons. In both cases this carbon bears a  $\delta+$  charge due to the effect of a neighboring atom that is more electronegative.
11. The carboxylic acid and lactone functional groups both have a carbonyl group attached to an oxygen atom, so they are similar (but not identical) functional groups. Because bonding arrangements in functional groups control chemical reactions, similar functional groups react in similar ways. Thus, because the carboxylic acid and lactone functional groups are similar in structure we expect them to undergo similar reactions.
12. Chemical reactions, such as reduction by  $\text{LiAlH}_4$ , are controlled by the electronic and atomic structure of the functional groups. Therefore functional groups with similar electronic and atomic structure are expected to react in a similar fashion. The functional group that is most similar to an ester in this case is the amide.
13. Chemical reactions can be described in terms of electron and bonding changes. Thus one expects the greatest similarities in reactivity for functional groups that have the greatest similarity in electronic and bonding structure. The ester and amide functional groups are the closest pair of the three. They each contain a carbonyl group attached to a heteroatom with at least one lone pair. The alcohol does not contain a carbonyl or the extra heteroatom.
14. These compounds both have very similar functional groups: C-O-H in alcohols, and H-O-H in water. Because these functional groups have very similar electronic and atomic arrangements, we expect them to have somewhat similar chemical and physical properties.
15. Any legitimate Lewis structure for sulfuric acid is acceptable in this case. Formal charges are considered a part of any Lewis structure, and must be included as well. Bond polarity is a result of uneven distribution of the electron density within a covalent bond. This is analyzed by considering the electronegativities of the bonded atoms. Oxygen (EN = 3.5) is more electronegative than sulfur (EN = 2.5), so the bonding electron density is greater toward the oxygen. The slight negative charge that results on oxygen is designated with a  $\delta-$ . This leaves a deficiency of bonding electron density on the sulfur. The slight positive charge on sulfur is indicated by  $\delta+$ .



16. The O-C-C bond angle is slightly more than the normal tetrahedral angle of  $109.47^\circ$ , while the H-O-C bond angle is slightly less than the normal tetrahedral angle of  $109.47^\circ$ . The oxygen atom at the vertex of this bond angle has four things attached to it: H atom, C atom, and two lone pairs. Because electrons repel, the most stable molecular geometry will be that which places these four things as far away from each other as possible, yet still maintains the bonds. This is best achieved by pointing the four bonds at the corners of a tetrahedron, providing bond angles of  $109.47^\circ$ . However, a lone pair occupies more space than a bonding pair, and thus repels more strongly than a bonding pair. This results in a compression of the H-O-C bond angle to a value that is a few degrees less than the normal tetrahedral angle of  $109.47^\circ$ .
17. The hybridization of the oxygen atom is  $sp^3$ . Because the methyl ( $\text{CH}_3$ ) and ethyl ( $\text{CH}_3\text{CH}_2$ ) groups are larger than the oxygen lone pairs, the C-O-C bond angle is predicted to be greater than  $109.47^\circ$ .
18. Methane ( $\text{CH}_4$ ): The carbon atom is attached to four hydrogen atoms and is therefore  $sp^3$  hybridized. Because all attachments to the carbon atom are identical, they all repel each other equally, and the bond angles are all equal at  $109.47^\circ$ . All C-H bond lengths are equal.

Methyl carbanion ( $:\text{CH}_3$ ): The carbon atom has four attachments (three hydrogen atoms and one lone pair) and is therefore  $sp^3$  hybridized. However the attachments are not all identical so the bond angles cannot all be identical either. A lone pair occupies more space than a bonding electron pair, so the lone pair repels the hydrogen atoms more strongly than the hydrogen atoms repel each other. This means the H-C-H bond angle is a bit smaller than a perfect tetrahedron (less than  $109.47^\circ$ ).

19. In simple terms, the structure of any molecule is such that placing the various atoms as far apart as possible yet still maintaining the bonds minimizes electron repulsion. For a central atom surrounded by six atoms, the best way to achieve this maximum spread is by use of octahedral geometry.



20. Your drawing should look something like Figure 1.19c, page 38, of the Brown and Foote text. Because both atoms have three attachments, both atoms are trigonal planar and  $sp^2$  hybridized. (There is some experimental evidence that suggests the lone pairs of a carbonyl oxygen atom are different, and lie in atomic instead of hybrid orbitals. Using VSEPR only, this is an unexpected result. In actuality, hybridization costs energy that is recovered to some extent by bonding. If the energy recovery is greater than the hybridization cost, then the atom uses hybrid orbitals. If the energy recovery is not enough, then the atom uses atomic orbitals.)

21. Bond polarity is a function of the difference in electronegativity of the atoms that make up a bond. The greatest difference in electronegativity between two attached atoms in 2,4-DP is in an O-H bond.