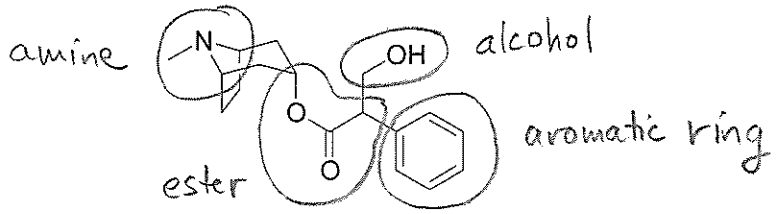
Summer 2008
Exam #1

Key

1. Write the letter that corresponds to the best answer for each question in the space provided (32 pts total).

A 1a. Atropine is an example of an organic compound called an *alkaloid*. It is produced by the "deadly nightshade" plant and causes dilated pupils, impaired vision and other unpleasant physiological effects. Which functional groups are present in atropine? (4 pts)



atropine

a) alcohol, amine, aromatic ring, ester
b) alcohol, amine, aromatic ring, ether
c) amide, ether, ketone, phenol
d) amide, aromatic ring, carboxylic acid, phenol

C 1b. What is the hybridization of the nitrogen atom in atropine? (All atoms have zero formal charge, and lone pairs are *not* shown in the drawing.) (4 pts)

a) sp
b) sp^2
(c) sp^3
d) The nitrogen atom is not hybridized

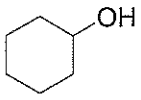
B 1c. What is the hybridization of the carbonyl oxygen in atropine? (4 pts)

a) sp
(b) sp^2
c) sp^3
d) The carbonyl oxygen atom is not hybridized

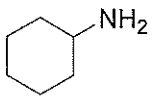
D 1d. According to valence bond theory, the bond between the oxygen atom and the hydrogen atom in atropine (note that there is only one O-H bond) is formed by the overlap of (4 pts):

a) a "p" orbital on oxygen and an "s" orbital on hydrogen
b) an "sp" orbital on oxygen and an "sp" orbital on hydrogen
c) an "sp^2" orbital on oxygen and an "s" orbital on hydrogen
(d) an "sp^3" orbital on oxygen and an "s" orbital on hydrogen

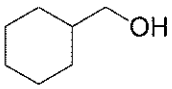
1e. Label each of the alcohols and amines shown below as primary (1°), secondary (2°), or tertiary (3°). (4 pts)



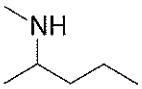
2°



1°

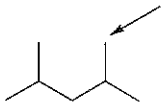


1°



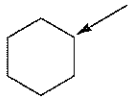
2°

1f. For each structure, label the indicated carbon atom (the one shown by the arrow) as primary (1°), secondary (2°), or tertiary (3°). (4 pts)

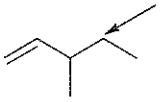


1°

3°

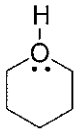


2°

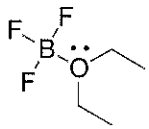


2°

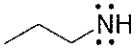
1g. Calculate the formal charge on the indicated atom in each molecule. All lone pairs are shown. (8 pts)



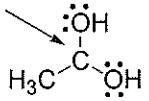
Oxygen: +1



Boron: −1

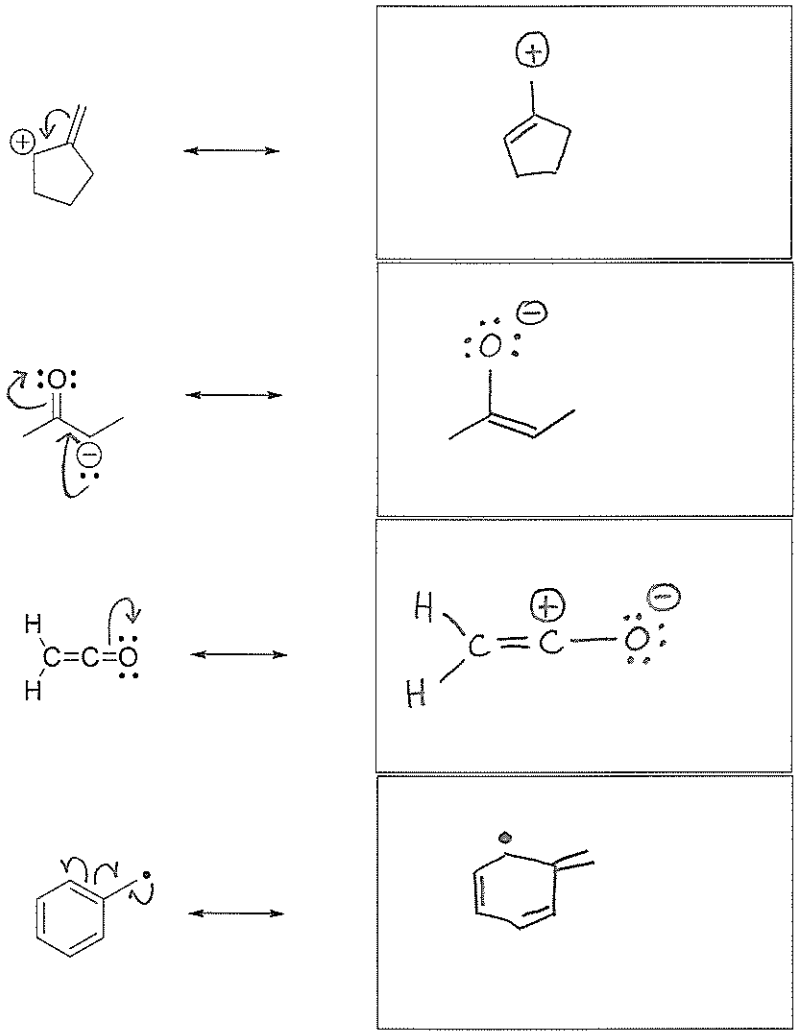


Nitrogen: −1



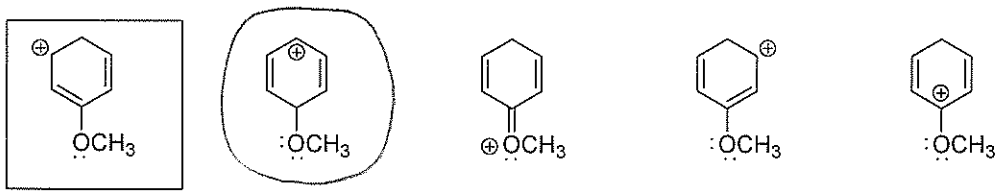
Carbon: +1
(All hydrogens are explicitly shown; show formal charge for the indicated C.)

2a. Draw **one** other acceptable resonance contributor for each of the chemical species shown. Show the conversion of the original structure to your new structure using the appropriate curved arrow(s). Include all lone pairs and formal charges to receive full credit (16 pts).

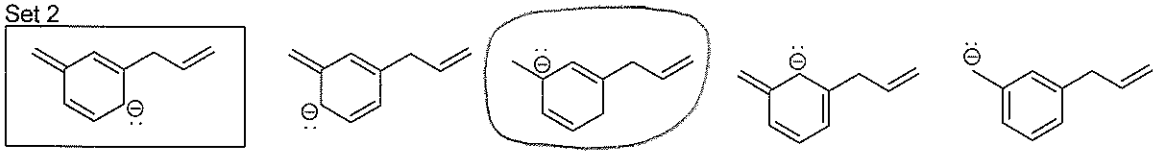


2b) Each of the following sets of resonance structures has a structure that is *not* related to the structure in the box. Circle the structure in each set that is not a valid resonance structure of the boxed structure. All lone pairs are shown. Space is left below each set for you to use, but only your circled answer will be graded (10 pts).

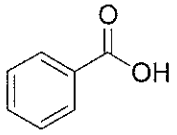
Set 1



Set 2



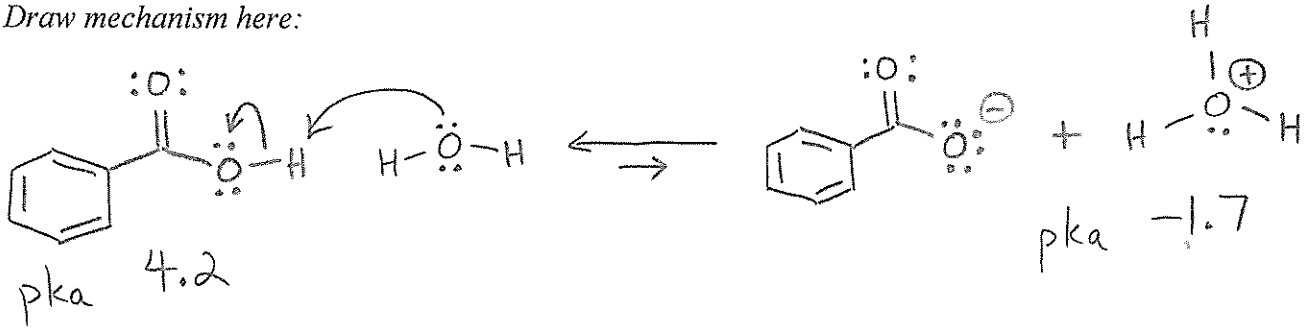
3. Draw an arrow-pushing mechanism for the reaction of benzoic acid and water. Show all lone pairs, curved arrows and formal charges for full credit. Show the products of the reaction. Use the pK_a of water and the other values given to determine which side of the reaction is favored at equilibrium. (15 pts)



benzoic acid

Potentially useful pK_a values:	
Benzoic acid	4.2
Hydronium ion	-1.7

Draw mechanism here:



Which side of the reaction is favored at equilibrium (circle it)? **Reactants** **Products**

4) Circle the correct answer to each question (18 pts).

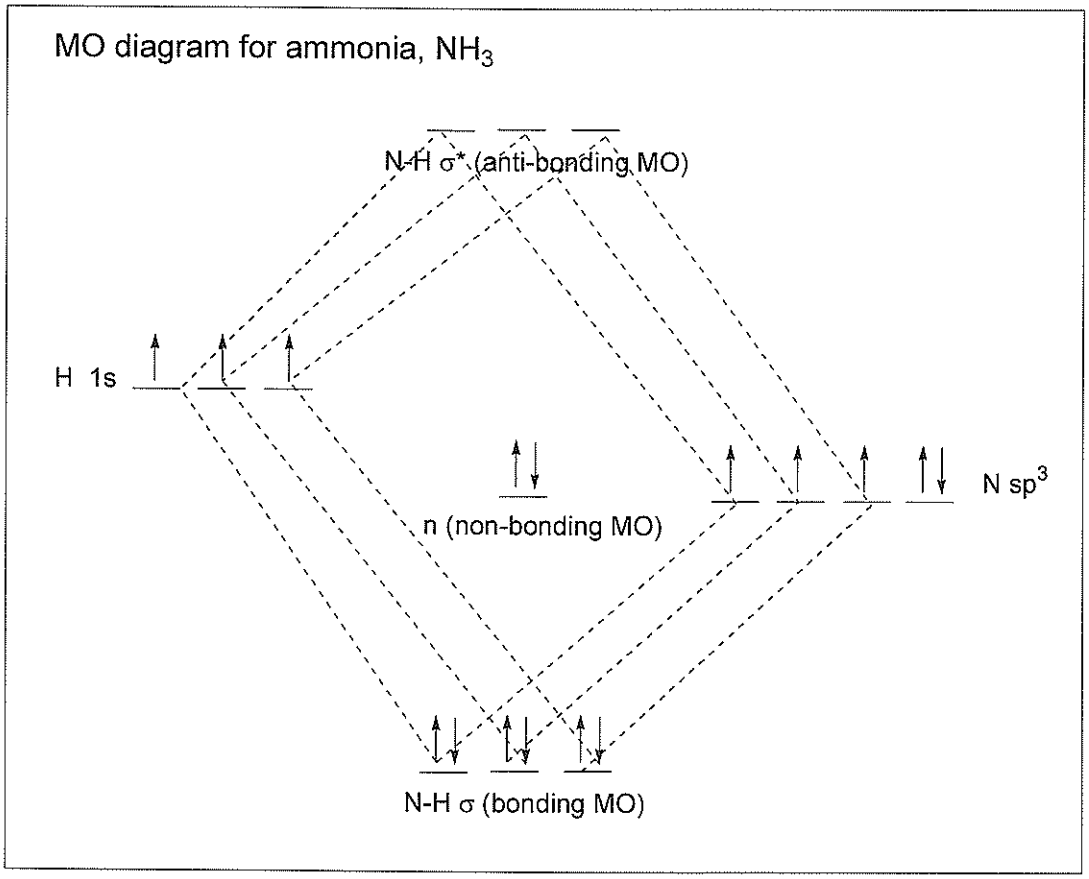
4a) How many nodes are there in the H_2 σ* MO? **Zero** **One** **Two**

4b) How many nodes are there in a C=C π MO? **Zero** **One** **Two**

4c) Which is higher in energy, a 1s orbital on H or an H_2 σ MO? **1s** **H_2 σ** **Neither**

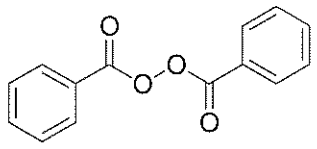
4d) A certain MO diagram has four bonding orbitals and four anti-bonding orbitals. How many atomic orbitals were mixed to produce this diagram?
Four **Eight** **Millions**

The molecular orbital diagram for ammonia, NH_3, is shown here. Although it is more complicated than the examples shown in class, the diagram is constructed in the same way, and the same concepts apply.



4e) What is the HOMO in this diagram?
H 1s **N sp^3** **N-H σ** **Non-bonding** **N-H σ***

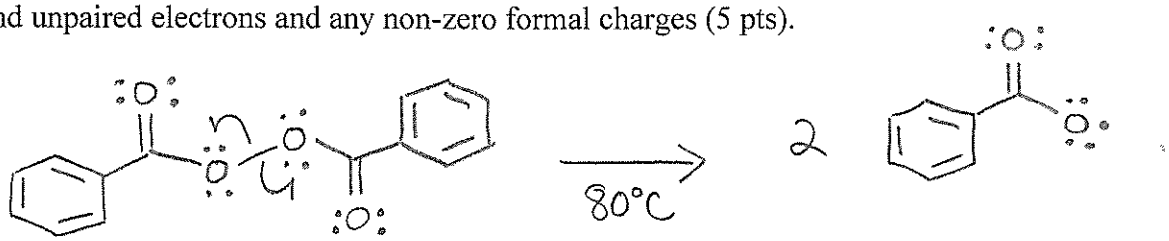
4f) What is the LUMO in this diagram?
H 1s **N sp^3** **N-H σ** **Non-bonding** **N-H σ***



benzoyl peroxide
(lone pairs not shown)

5) Benzoyl peroxide is a commonly used "free-radical initiator", a chemical used to initiate a particular series of radical reactions. When heated to about 80 °C, the relatively weak O-O bond breaks homolytically and two identical radicals are produced.

5a) Draw a mechanism showing the process described above (the conversion of benzoyl peroxide to the two radicals). For full credit, show all curved arrows, lone pairs and unpaired electrons and any non-zero formal charges (5 pts).



5b) Redraw one of the radicals produced in the reaction and draw an equivalent resonance contributor for it. For full credit, show all lone pairs, unpaired electrons and any non-zero formal charges. Show the appropriate curved arrows to convert your original structure to the new resonance structure. Include the resonance arrow that shows the relationship of your two structures as resonance structures (4 pts)