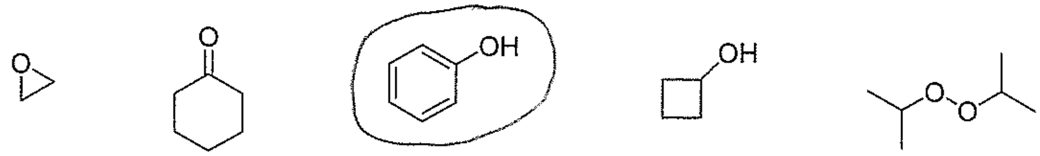
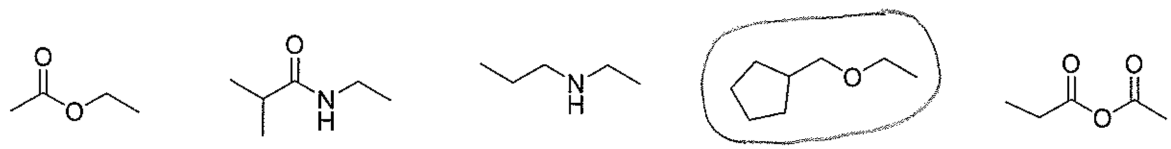
Key - Exam #1 - Summer '09

1) Circle the best answer to each of the following questions. (3 pts each)

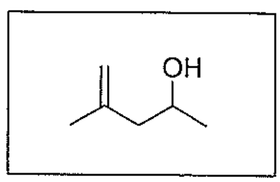
1a) Which of the following structures is a phenol?



1b) Which of the following structures is an ether?

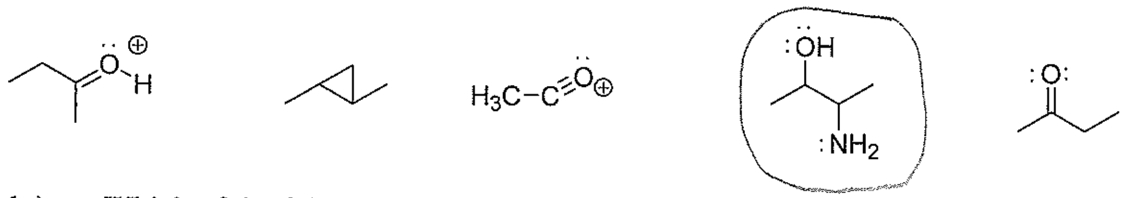


1c) How many electrons are there in the C-O σ bonding molecular orbital in the molecule shown here?

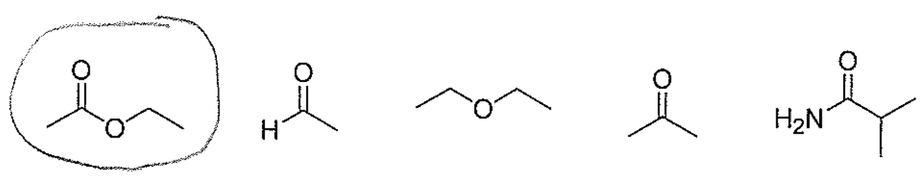


Zero One Two Four

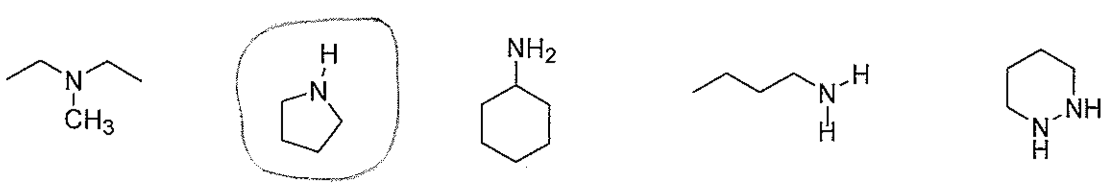
1d) Which of the following structures contains an oxygen atom with sp^3 hybridization?



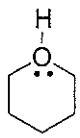
1e) Which of the following is an ester?



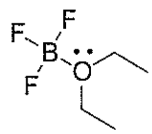
1f) Which of the following is a *secondary amine*?



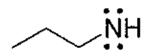
2a) Calculate the formal charge on the indicated atoms in each structure below. All lone pairs you need for the calculation are shown. (8 pts)



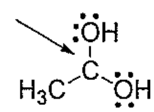
Oxygen: 1+



Boron: 1−

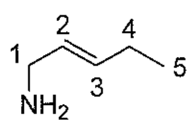


Nitrogen: 1−



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

2b) Indicate the two orbitals that overlap to form each of the indicated bonds in the structure shown here. All atoms are neutral, but lone pairs are not shown. The carbons atoms are numbered for reference. (10 pts)



C-N σ sp^3 on C and sp^3 on N

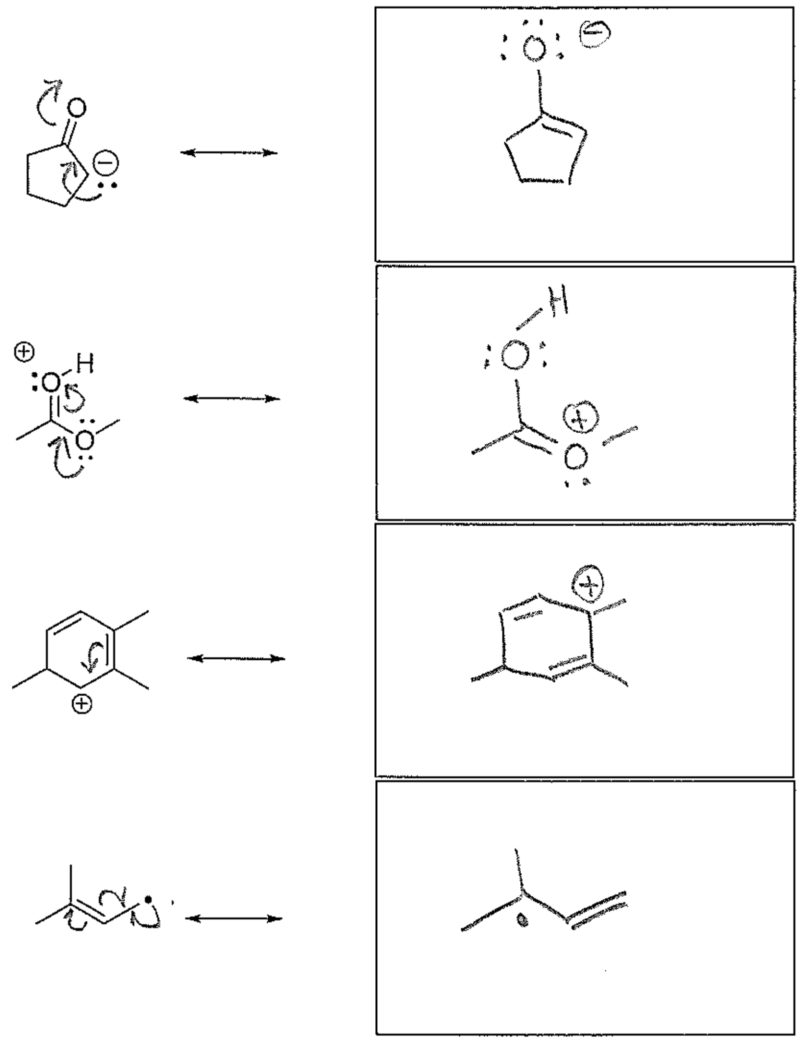
N and H sp^3 on N and s on H

C1 and C2 σ sp^3 on C1 and sp^2 on C2

C2 and C3 π p on C2 and p on C3

C4 and C5 σ sp^3 on C4 and sp^3 on C5

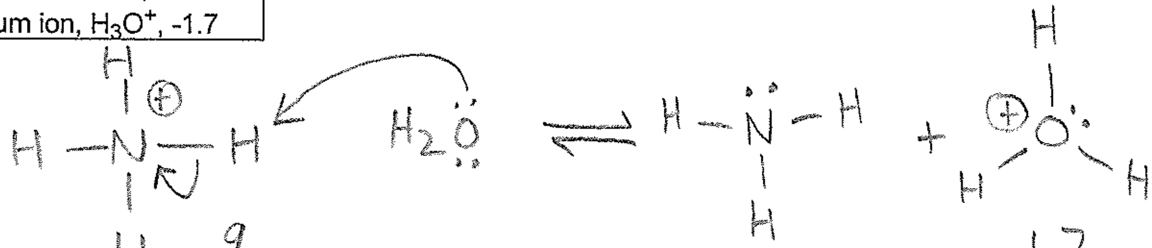
3) Draw **one** other acceptable resonance contributor for each of the chemical species shown. Show the conversion of the original structure to your new structure using the appropriate curved arrow(s). Include all lone pairs and formal charges to receive full credit (16 pts).



(Other structures may also be acceptable.)

4) Draw an arrow-pushing mechanism for the Bronsted-Lowry acid-base mechanism that occurs between ammonium ion (NH_4^+) and water. For full credit, include all curved arrows, lone pairs of electrons, and non-zero formal charges. Show the products of the reaction and indicate which side of the equation is favored at equilibrium. A table of pK_a values is provided (10 pts).

Potentially useful pK_a values:
Ammonia, 36
Ammonium ion, NH_4^+ 9
Hydronium ion, H_3O^+, -1.7



Reactants favored

4b) Identify the HOMO and the LUMO in the reaction above. Specify both the orbital and the molecule that contains it. (6 pts)

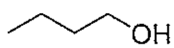
HOMO: non bonding MO in H_2O (sp^3 on O in H_2O)

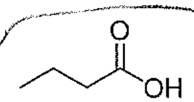
LUMO: N-H σ^* in NH_4^{+}

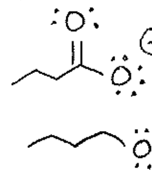
5a) For each of the following pairs, circle the more acidic molecule. The acidic hydrogen is explicitly shown in cases where it may not be obvious. (10 pts)

$HS^{\ominus}$ vs $:\ddot{O}H^{\ominus}$: S more polarizable than O; charge is dispersed/delocalized over larger area

H_2S H_2O



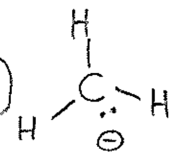




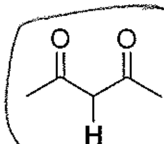
⊖ stabilized by resonance while

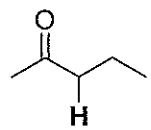
⊖ not

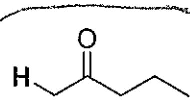
CH_4 H_2O

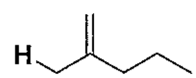


vs $^{\ominus}:\ddot{O}H$ O more electronegative than C; holds e⁻ more closely to nucleus, which is more stable



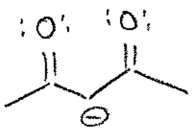




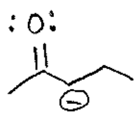


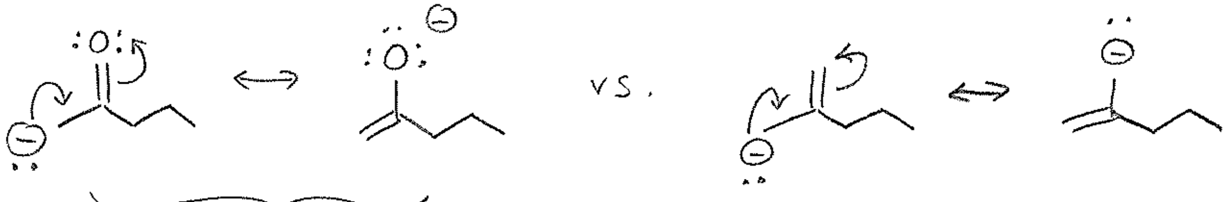
5b) Select any **one** of the pairs listed above and explain your answer by comparing the stabilities of the conjugate bases of the acids shown. You must include appropriate structures of the bases in your explanation for full credit. (6 pts)

(Answers vary ... see above also)



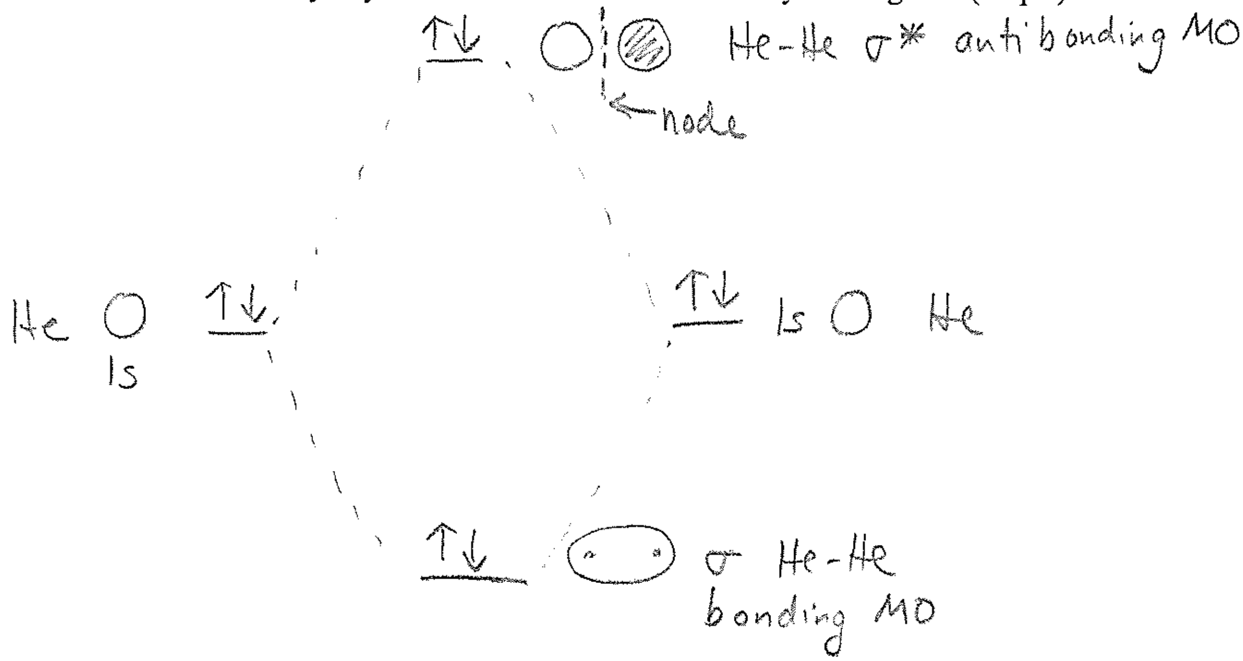
has more acceptable resonance contributors than





more stable – the ⊖ is delocalized to a more electronegative element (O vs. C)

6a) Draw a molecular orbital diagram for He_2. Include all atomic and molecular orbitals at the proper relative energy levels, clearly labeled and identified. Draw a picture of each orbital and identify any nodes. Include all electrons in your diagram. (10 pts)



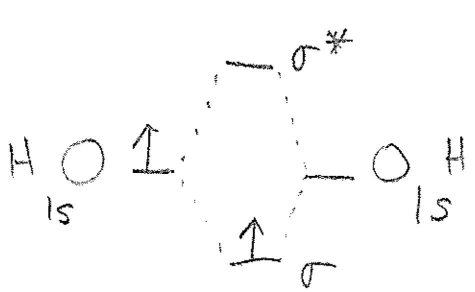
6b) Based on the information contained in your diagram, explain whether you expect He_2 can exist. Recall that

$$\text{bond order} = \frac{(\text{electrons in bonding orbitals} - \text{electrons in anti-bonding orbitals})}{2}$$

(3 pts) For He_2: $\frac{2-2}{2} = 0$

Bond order is 0; He-He bond cannot exist. The two e⁻ in the anti-bonding orbital destabilize the system, offsetting the stabilization conferred by the two e⁻ in the bonding orbital

6c) Do you expect that the molecule H_2^+ could exist? Why or why not? (3 pts)



Yes, though the bond would be weak (bond order of $\frac{1}{2}$). Lowering the 1s electron to a σ MO would be stabilizing.