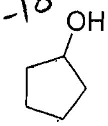
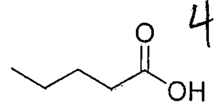
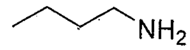
Key Exam 2 Summer 2018

1a) Arrange the three acids in order of **decreasing** pK_a. (Highest to lowest) (5 pts)

15-18  4-5  36 

W X Y

C

a. W > X > Y
b. Y > X > W
c. Y > W > X
d. W > Y > X
e. X > Y > W

1b) Using a conjugate base stability argument, which of these factors is the <u>best</u> explanation for the difference in acidity between structures **W and X** in question 1a? (5 pts)

A

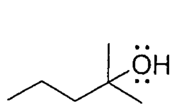
a. Resonance
b. Electronegativity
c. Charge
d. Size/Polarizability

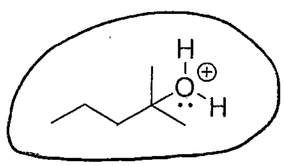
1c) Using a conjugate base stability argument, which of these factors is the <u>best</u> explanation for the difference in acidity between structures **W and Y** in question 1a? (5 pts)

B

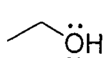
a. Resonance
b. Electronegativity
c. Inductive effect
d. Size/Polarizability

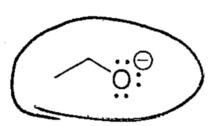
1d) Circle the stronger acid (5 pts):





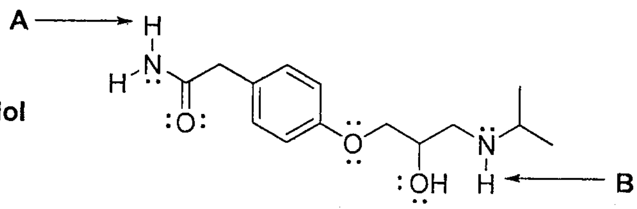
1e) Circle the stronger base (5 pts):





2) Atenolol is a beta blocker used to treat high blood pressure. Which proton is more acidic, A or B? Explain your reasoning, using a conjugate base stability argument. To receive credit, you must explain WHY one conjugate base is more stable than the other. (10 pts)

Atenolol

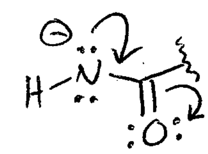


The more acidic proton is (circle one):

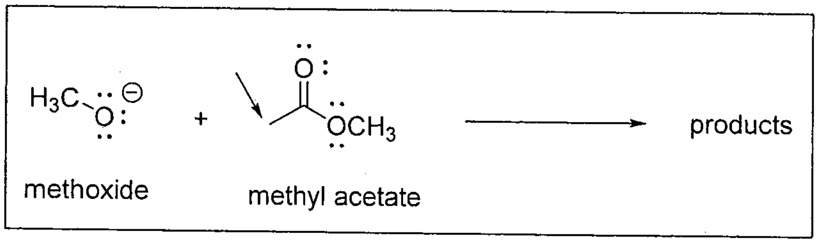
A B

Reason (one or two sentences):

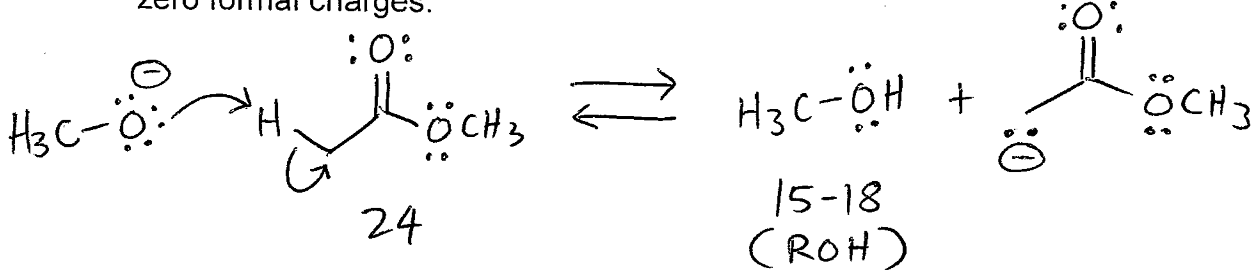
Conjugate base of A is stabilized by resonance; conjugate base of B is not



3) When methoxide ion, a Bronsted base, is combined with methyl acetate, a Bronsted acid (pK_a = 24), as shown in this partial equation, a proton transfer occurs. The most acidic protons in methyl acetate are attached to the carbon designated with the arrow. You will need to draw one of these hydrogens explicitly in your mechanism.



3a) (10 pts) Using curved arrows, draw a mechanism for this proton transfer reaction. (Redraw the structures below. Do not draw your mechanism on the structures shown above.) Draw the products of this reaction. Show all lone pairs and non-zero formal charges.

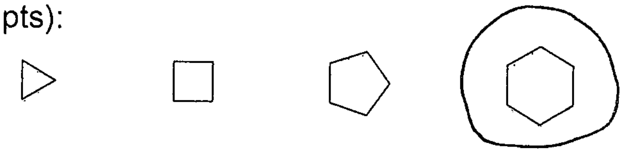


3b) (3 pts) Estimate the equilibrium constant for the reaction: K = $10^6 - 10^9$

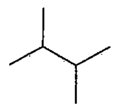
3c) (2 pts) State which side of ~~the reaction is~~ favored at equilibrium by circling the correct response: **Reactants (left)** **Products (right)**

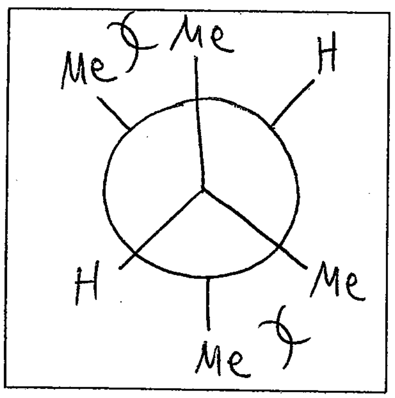
4a) Circle the ring with the MOST strain (4 pts):

4b) Circle the ring with the LEAST strain (4 pts):

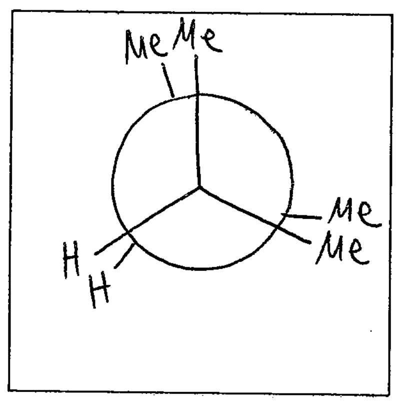


4c) Draw the requested Newman projections of 2,3-dimethylbutane looking down the C2-C3 bond. Then identify the type(s) of strain present in each conformation by circling the correct response. *Hint:* Be sure you are drawing the correct molecule, or you will not get full credit. (10 pts)





Most stable



Least stable

4d) (7 pts) Identify all type(s) of strain present in the MOST stable conformation you just drew. Possibilities include torsional, angle, steric, and "none".

Steric

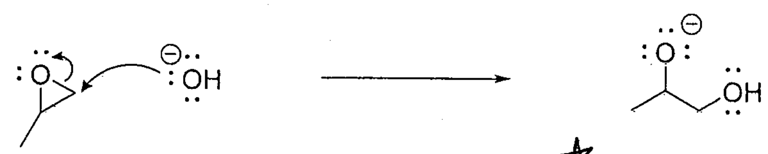
Identify all type(s) of strain present in the LEAST stable conformation you just drew. Possibilities include torsional, angle, steric, and "none".

Steric, torsional

How many gauche butane interactions are there in the MOST stable conformation? Write the number here: 2

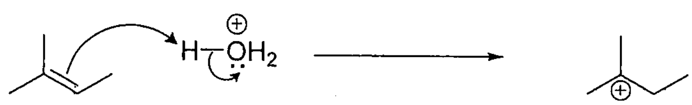
How many gauche butane interactions are there in the LEAST stable conformation? Write the number here: 0

5a) Identify the requested orbital for each of the following mechanisms (e.g. what kind of orbital is the HOMO or LUMO in each case) (16 pts).

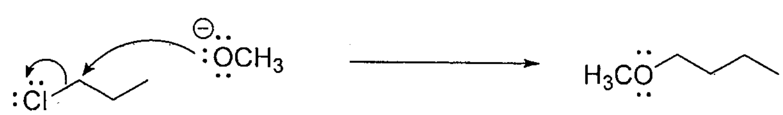


Identify the LUMO: $C-O\ \sigma^*$

Identify the LUMO: p



Identify the HOMO: $C-C\ \pi$



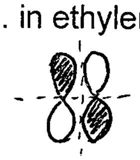
Identify the HOMO: sp^3 or n MO

5b) True or False? Write the correct response on the line before each statement (9 pts)

F A bonding molecular orbital is the result of an out-of-phase combination of atomic orbitals. Bonding = in phase combination

F The bond order of H_2 is 2. It's 1

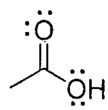
F A C-C π* orbital (e.g. in ethylene) has one nodal plane (one node).



It has 2

6) Extra credit. (10 pts)

In the presence of a strong acid like HCl, a carboxylic acid will be protonated. Which of the two oxygen atoms is most likely to get protonated (i.e., which oxygen atom is more basic), and why? Support your answer using appropriate chemical structures that include all lone pairs and nonzero formal charges.

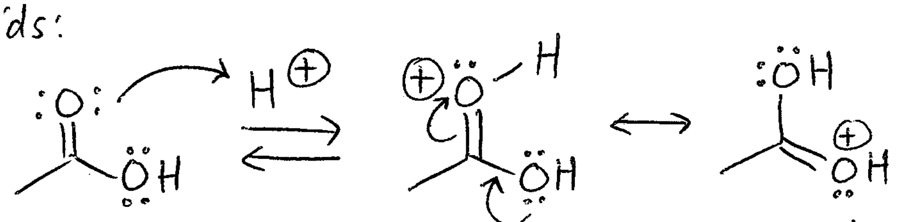


The more basic oxygen atom is (circle one):

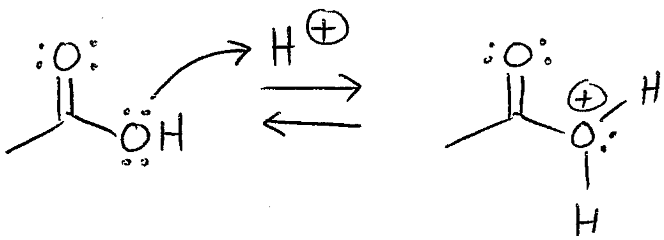
The carbonyl oxygen **The OH group oxygen**

Now show why using structures and explanations:

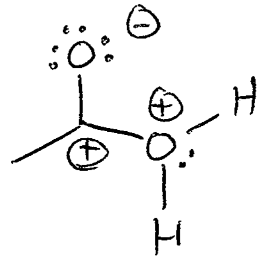
Protonate each O separately and analyze the conjugate acids:



Conjugate acid is stabilized by resonance



The only other resonance structure you can draw would be:



Two ⊕ charges adjacent → unstable

Protonating the carbonyl O leads to a more stable conjugate acid = weaker conjugate acid; thus carbonyl O is more basic