Organic Chemistry 2
Third Examination
May 2, 2008
Prof. Malachowski

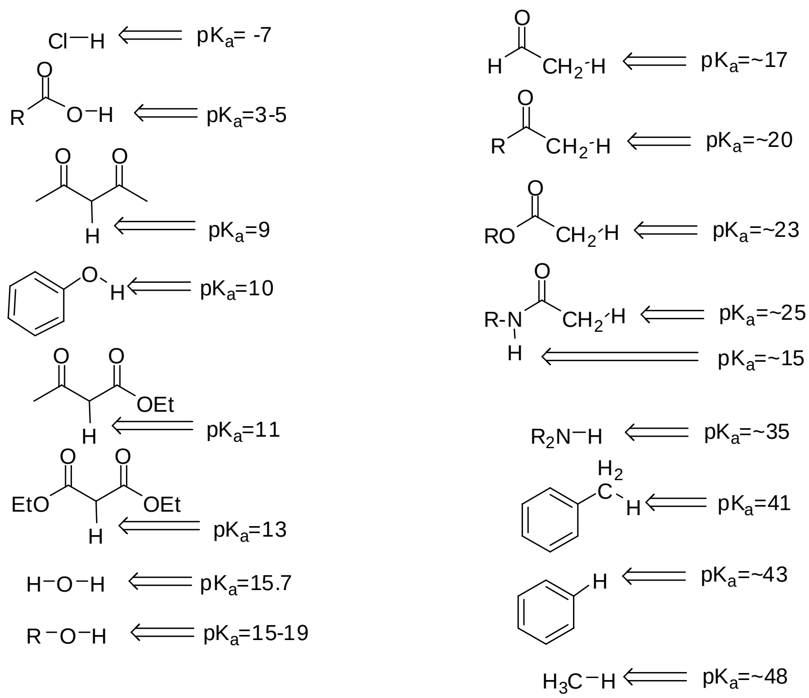
Name:_______________________________

The examination has six questions on four pages. The point values for each question are found with the question. Partial credit where appropriate will be given.

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex , then you may need to rethink the question. Keep in mind the intended examination topics.

In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include lone pairs of electrons and formal charges when appropriate.

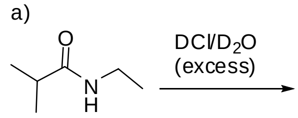
pK_a information:



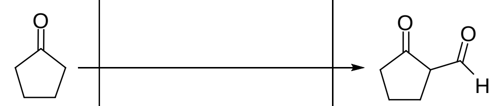
Note: R=alkyl

1. Complete the following reactions by providing the necessary information: reagent or major product. (3 pts. each)

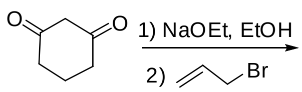
a)



b)

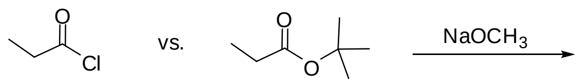


c)

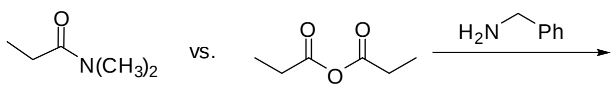


2. Circle the starting material that is more reactive with the reagents shown (2 pts. each) and provide the product of this reaction in the box to the right. (3 pts. each)

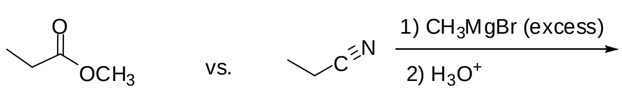
a)



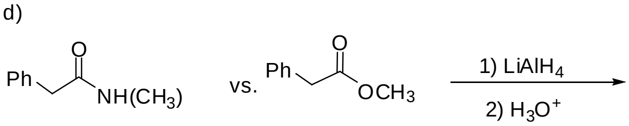
b)



c)

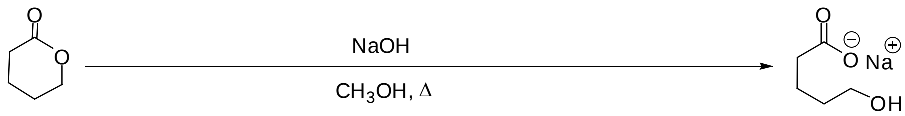


d)



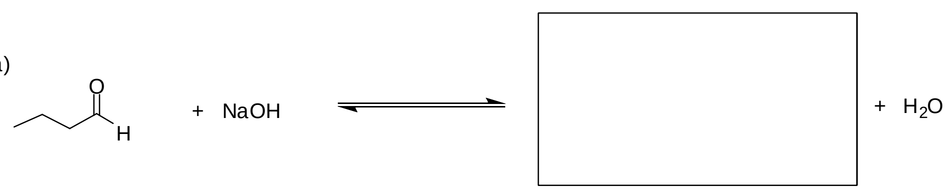
29 total pts.

3. Draw the curved arrow electron flow mechanism for the following reaction. In addition, (a) label the tetrahedral intermediate by writing "tet. int." under the structure. (b) Identify the acid-base equilibrium step by circling the acidic proton and writing "pK_a=X"(fill in the X with the proper value) next to the acid on each side of the equilibrium. (15 pts.)

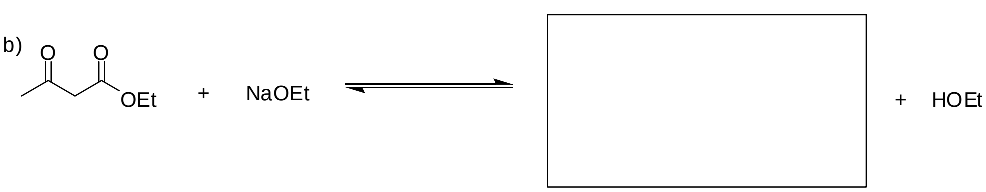


4. a) Draw the structure of the most stable resonance form of the conjugate base in the box on the right. (3 pts. each)
b) Circle the products or starting materials to indicate which side of the acid-base equilibium will be favored. (2 pts. each)

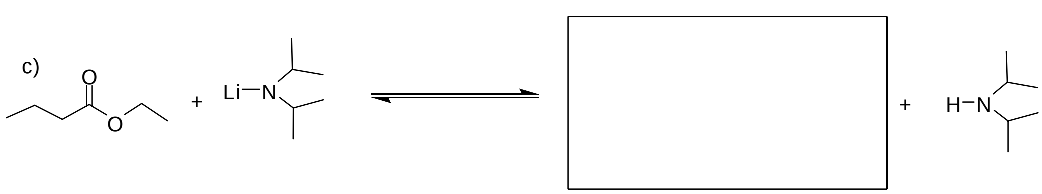
a)



b)



c)

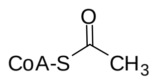


30 total pts.

5. As I've mentioned on several occassions, reactions in nature often occur by fundamentally the same mechanism and provide the same outcome as reactions that happen in the chemistry laboratory. One such example can be found in the citric acid cycle, a key oxidative metabolic cycle in eukaryotes and prokaryotes alike. The first step in the cycle is an enzyme catalyzed crossed aldol addition. Answer the following questions based on our discussions of aldol reactions in class.

a) Draw the enol form of acetyl coenzyme A (acetyl-CoA) in the box below. (3 pts.)

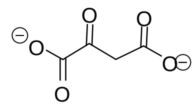
b) Circle the most electrophilic carbon in oxaloacetate. (3 pts.)



acetyl-CoA

enol form of acetyl-CoA

+



oxaloacetate

c) The enol in part a engages in an aldol addition with the most electrophilic carbon in part b. Draw the curved electron flow arrows that show the aldol on the structures above. (3 pts.)

d) Draw the product of this aldol reaction in the box to the right. (3 pts.)

e) A hydrolysis reaction occurs in the second part of the citrate synthase catalyzed reaction. Show the product of the hydrolysis of the thiol (sulfur) ester in the box below. (3 pts.)

d) aldol product from enol + oxaloacetate

H_2O

e) hydrolysis product

f) After the aldol addition and the hydrolysis reaction, the hydrolysis product (box e) undergoes a dehydration or elimination reaction as in the second part of aldol condensation reactions. Draw this product in the box below. (3 pts.)

f) dehydration (or aldol condensation) product

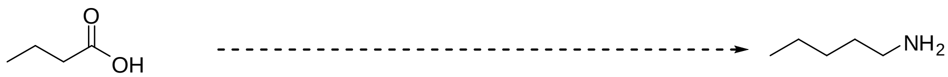
g) The product formed in box f is a thermodynamically favorable outcome. Why? (Circle one, 3 pts.)

(1) The product has a symmetrical structure that makes it stable.
(2) Carboxylic acids always cause elimination to occur due to their many resonance forms which have a stabilizing effect.
(3) The product has an alkene in conjugation with a carbonyl system which is a thermodynamically stable arrangement.
(4) Dehydration products are always stable because they afford highly substituted alkenes which are more thermodynamically stable than less substituted alkenes.
(5) Molecules like to exercise and "dehydrate" because then they get to rehydrate with funky-colored mini-sports drinks that have awesome names like "Claisen-sation".

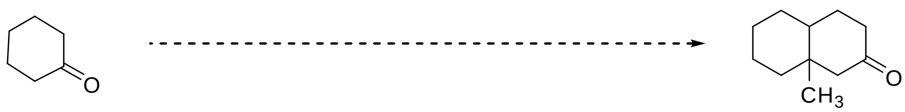
_______ 21 total pts.

6. Synthesize the molecule on the right from the starting material on the left. You may use any inorganic or organic materials. (10 pts. each)

a)



b)



___ 20 total pts.