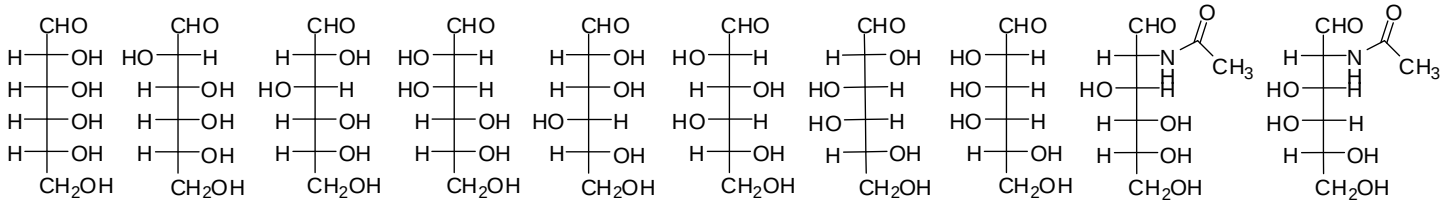
Organic Chemistry 2 Name:_____
Final Examination
May 6, 2010
Prof. Malachowski

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

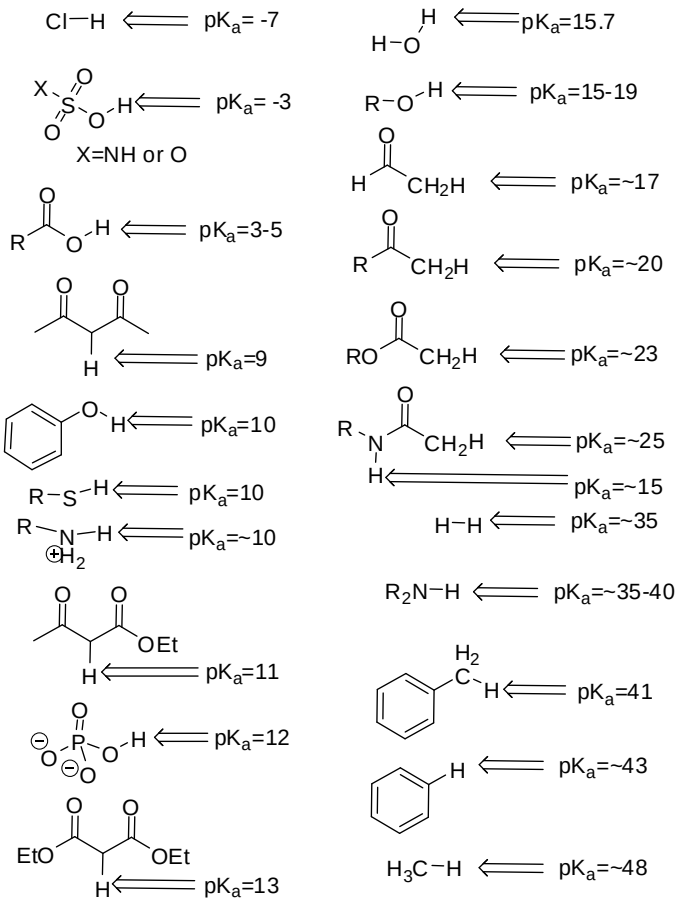
Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex , then you may need to rethink the question. Keep in mind the intended examination topics.

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.

Carbohydrate structures:



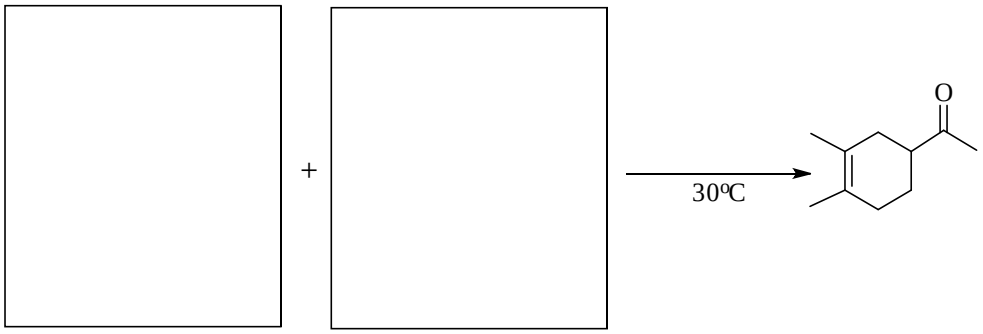
pK_a information



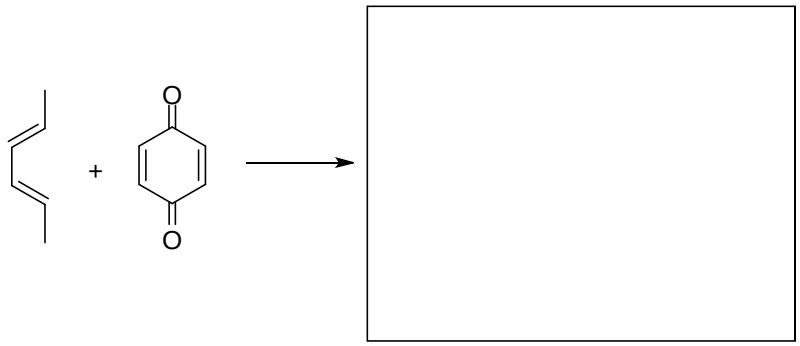
Note: R=alkyl

1. Provide the necessary information, product, reagents, or starting materials, to complete the following reactions. (4 pts. per question)

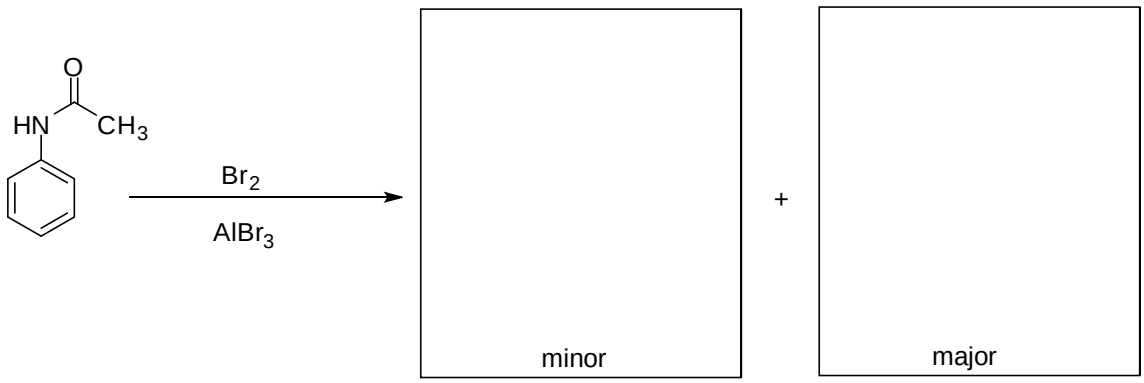
a)



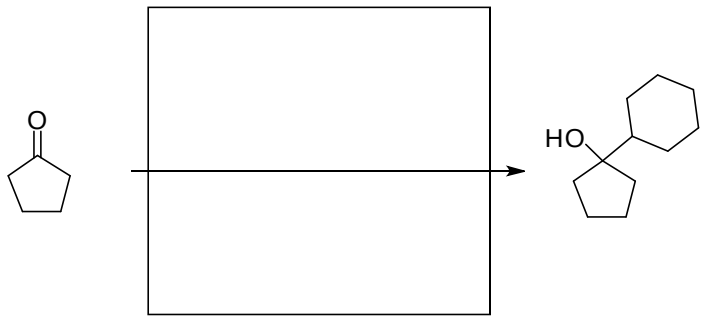
b)



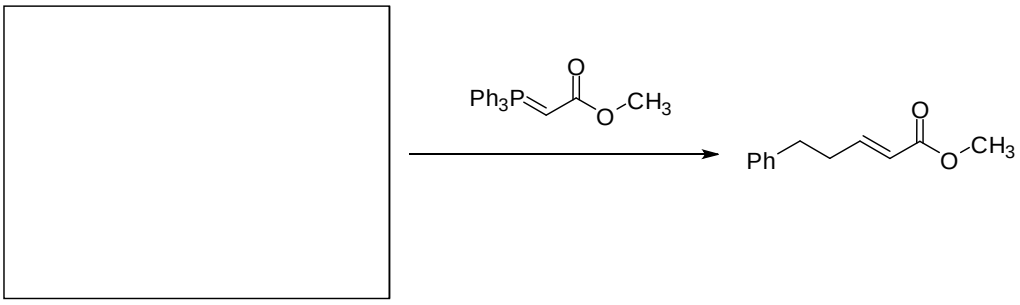
c)



d)

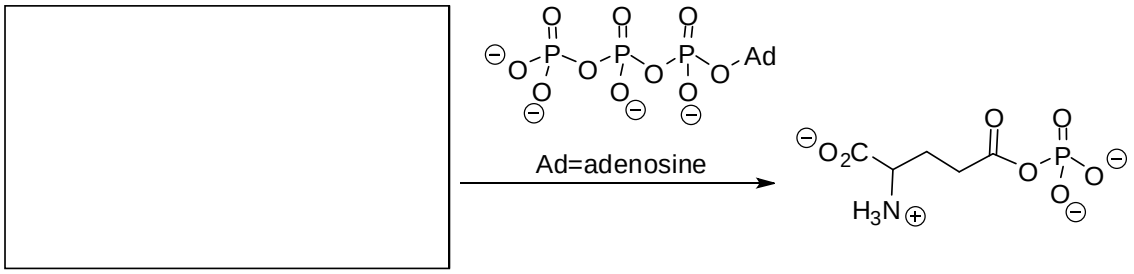


e)

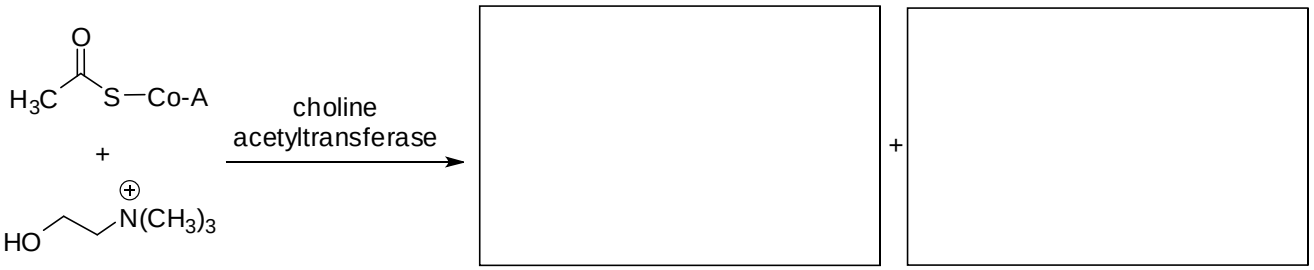


/20 pts.

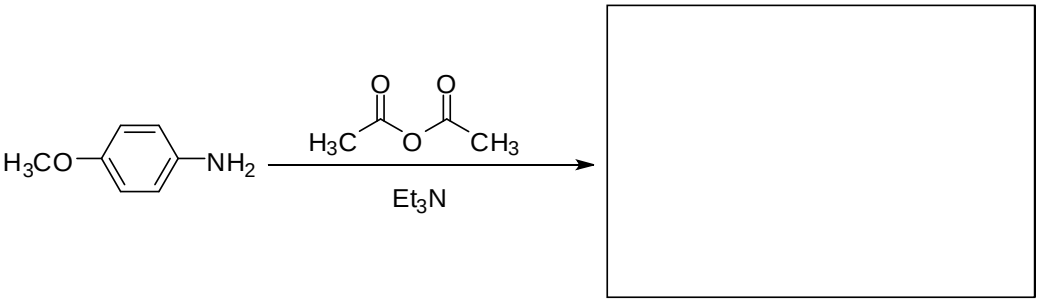
f)



g)

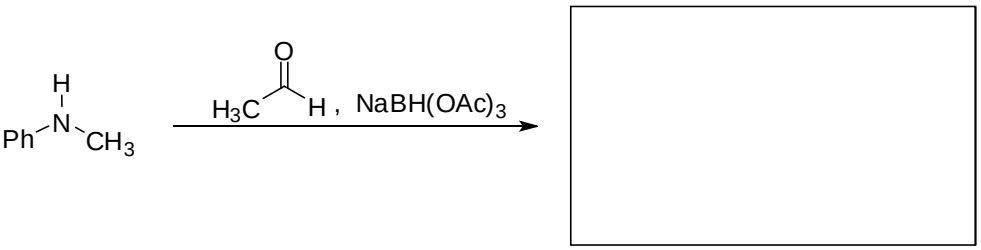


h)



i)

j)

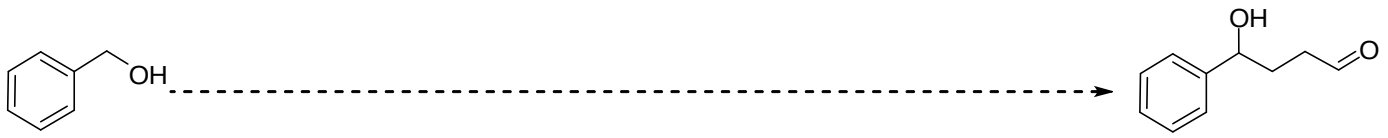


2. Suggest a synthesis to take the starting material on the left to the product on the right. This will require more than one step, but can be accomplished in three steps or less. You may use any inorganic or organic reagent. (7 pts. each)

a)

/27 pts.

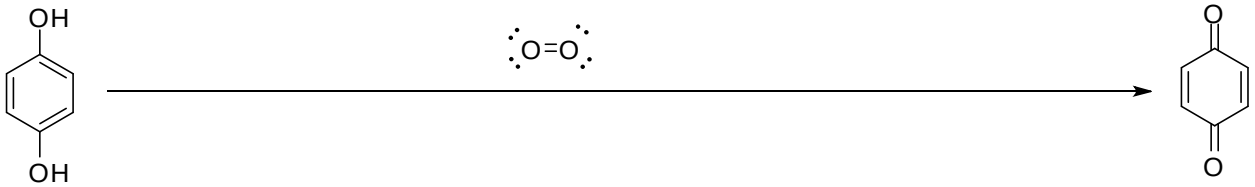
b)



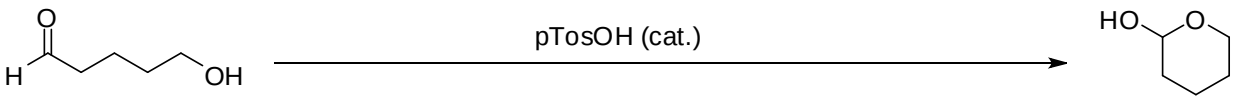
c)

3. Draw the mechanisms for the reactions shown below. Your mechanism should include formal charges, counter ions and curved electron flow arrows. You do NOT need to draw important resonance structures. (10 pts. each)

a)

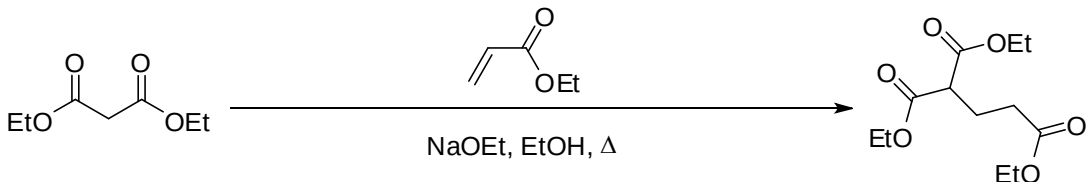


b)

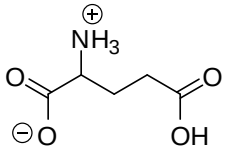


/34 pts.

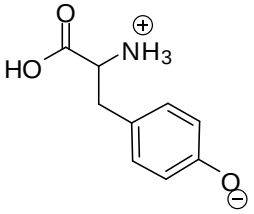
c)



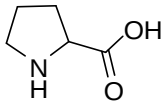
4. Three natural alpha-amino acids are drawn below in various forms of ionization and without any stereochemistry. Add the correct stereochemistry and the correct state of ionization of all functional groups in a physiological solution of pH~7 in the box below each. (9 pts.)



glutamic acid



tyrosine



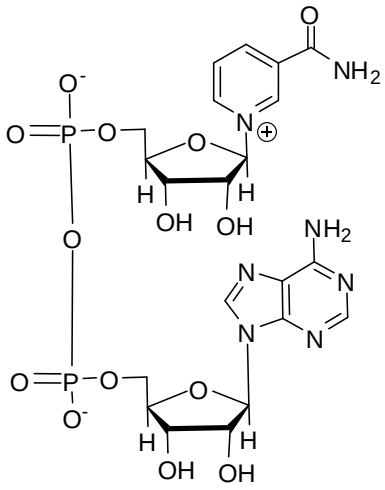
proline

5. The structure of nicotinamide adenine dinucleotide, NAD^+, is shown below. Answer the following questions about NAD^+'s structure based on course discussions. (7 pts.)

a) Circle all the aromatic parts of NAD^+ and place an Ar next to them.

b) Place a box around the carbohydrate portions of NAD^+ and write 'carb' next to them.

c) Of the NAD^+/NADH pair, NAD^+ is the oxidized / reduced (circle one) form.



NAD^+=nicotinamide adenine dinucleotide

/26 pts.

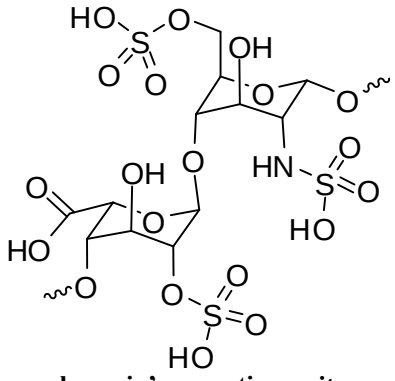
6. Heparin is an important anti-coagulant polysaccharide used in medicine. The Wikipedia site for heparin shows the following structure for one unit of heparin. Answer the questions below about the structure of heparin based on your understanding of carbohydrate structures and related biochemical topics. (24 pts.)

Circle the correct answer to complete the phrases below.

a) Heparin's core repeating unit is a…
(1) monosaccharide
(2) disaccharide
(3) trisaccharide
(4) tetrasaccharide
(5) pentasaccharide

b) The carbohydrate farthest to the right in the heparin repeating unit is a derivative of…
(1) D-idose
(2) D-galactose or D-galactosamine
(3) D-glucose or D-glucosamine
(4) D-mannose
(5) D-pantyhose

c) The glycosidic linkage shown in the repeating unit is a(n)…
(1) α-1,2 (2) β-1,2 (3) α-1,3 (4) β-1,3 (5) α-1,4



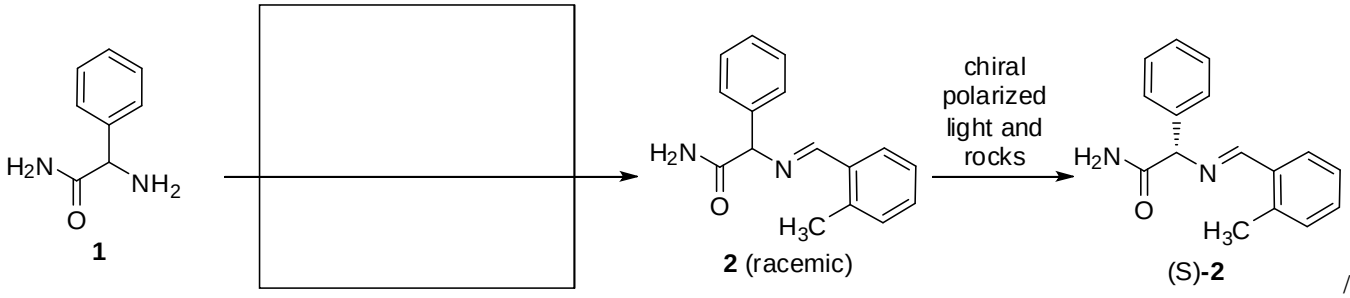
heparin's repeating unit

d) At physiological pH (~7), heparin is considered to have the highest negative charge density of any biological macromolecule. What is the total negative charge on heparin's repeating unit?
(1) -2 (2) -3 (3) -4 (4) -5 (5) -6

e) The carbohydrate farthest to the left in the heparin structure is a(n)…
(1) aldopentose (2) aldohexose (3) ketopentose (4) ketohexose (5) aldoheptose

f) The Wikipedia structure is really not the most thermodynamically stable form based on our discussions of carbohydrate conformations. Draw a more stable conformation for heparin's repeating unit. You may abbreviate side groups as necessary to make the structure clearer.

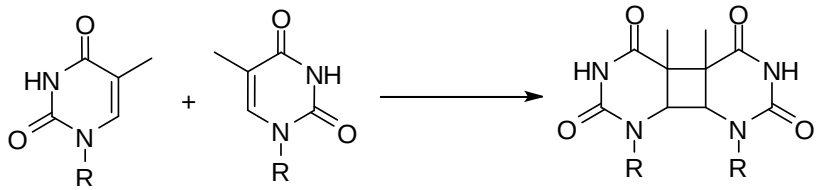
7. Dutch researchers recently reported a study of how chirality may have arisen during the earliest days on earth. In particular, they studied the transformation of racemic **2** to only one enantiomer of **2**.
a) The researchers synthesized their starting material **2** from **1**. In the box below, provide the reagent that allowed for the synthesis of racemic **2**. (3 pts.)



/27 pts.

b) As with all good experimentalists, the researchers made a very conscious choice in selecting compound **2** to study the evolution of chirality. This was not a random choice, rather it gave them an easy case to study the evolution of chirality. Why is the chiral center in **2** particularly good for a study of this process? What type of intermediates might form that would facilitate the transformation of (R/S)-**2** to predominantly (S)-**2**? (4 pts.)

8. Skin cancer is frequently the result of UV damage to the DNA in skin cells. One important reaction that occurs to initiate carcinogenesis is the photochemical dimerization of two thymine molecules.



thymine thymine dimer

Answer the following questions based on our discussions this semester. (3 pts. each)

a) Select the answer that best explains why the thymine alkene is good at absorbing UV radiation.
(1) The alkene is part of the aromtic thymine system, therefore it will have especially stable highest occupied molecular orbitals (HOMO's).
(2) There is excellent orbital overlap between the two nitrogen atoms in the thymine rings.
(3) Thymine has two carbonyls that can both absorb UV radiation through their low lying LUMO orbitals.
(4) Thymine has a conjugated pi system, therefore it will have a smaller HOMO-LUMO gap leading to easier, lower energy absorptions.
(5) Six member rings are lower in energy and therefore have good UV radiation absorption properties.

b) Assuming a *syn addition* like in the Diels-Alder reaction, molecular orbital analysis of the cycloaddition reaction between the two alkenes in thymine in their ground state suggests the reaction will not work. Draw the alkene (and just the alkene!) molecular orbital diagram and explain why the reaction between the two alkenes is symmetry forbidden or not likely to work.

/10 pts.

c) Show the molecular orbital diagram of the alkene (and just the alkene!) if UV absorption leads to electron excitation and the promotion of one electron in the alkene molecular orbitals. Label the HOMO of the resulting molecular orbital diagram.

d) This photochemical excitation from UV absorption allows the dimerization reaction to occur, i.e. the reaction is now symmetry allowed. Briefly explain.

/6 pts.