

Organic Chemistry 2
Final Examination
May 8, 2006
Prof. Malachowski

Name: _____

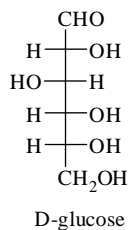
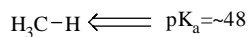
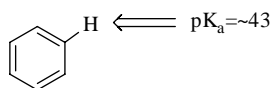
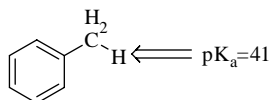
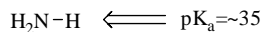
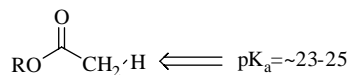
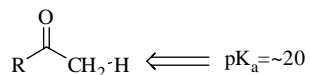
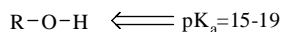
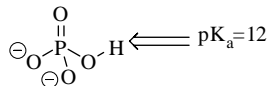
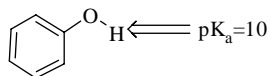
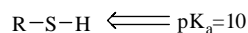
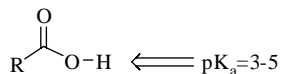
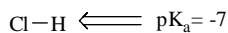
The examination has nine questions on six pages. The point values for each question are found with the question. Partial credit where appropriate will be given.

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.

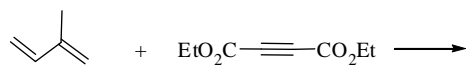
There is a periodic table on the back of this cover sheet for your reference.

pK_a information:

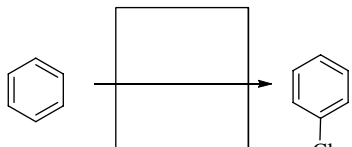


1. Complete the following reactions by providing the necessary information: starting material, reagent or major product, unless otherwise instructed. (3 pts. each box)

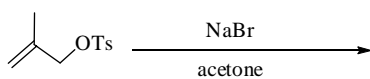
a)



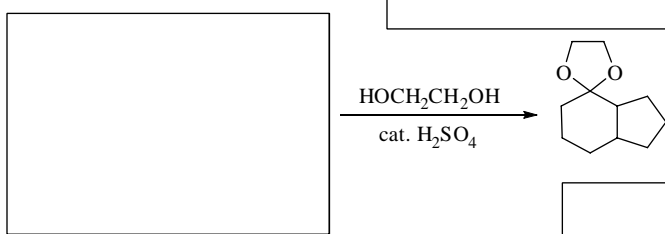
b)



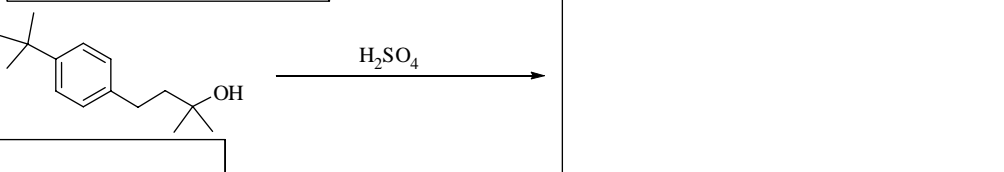
c)



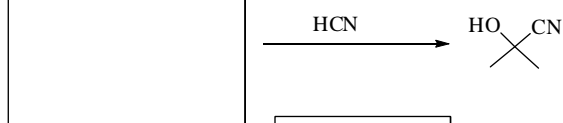
d)



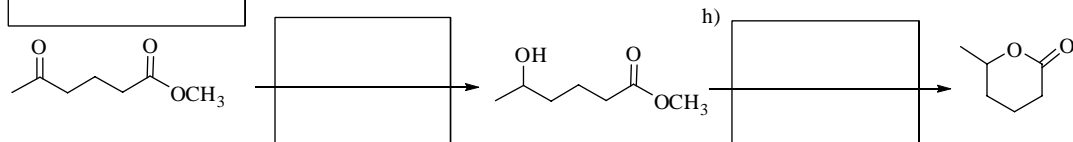
e)



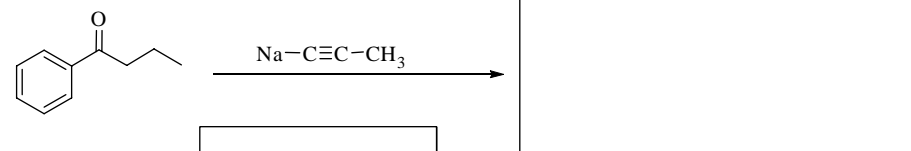
f)



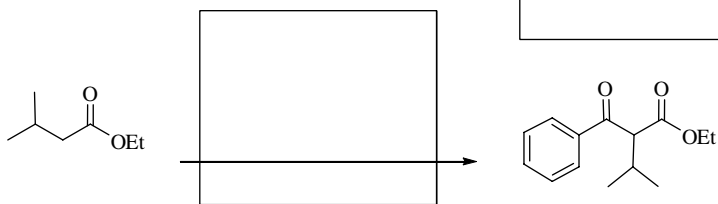
g)

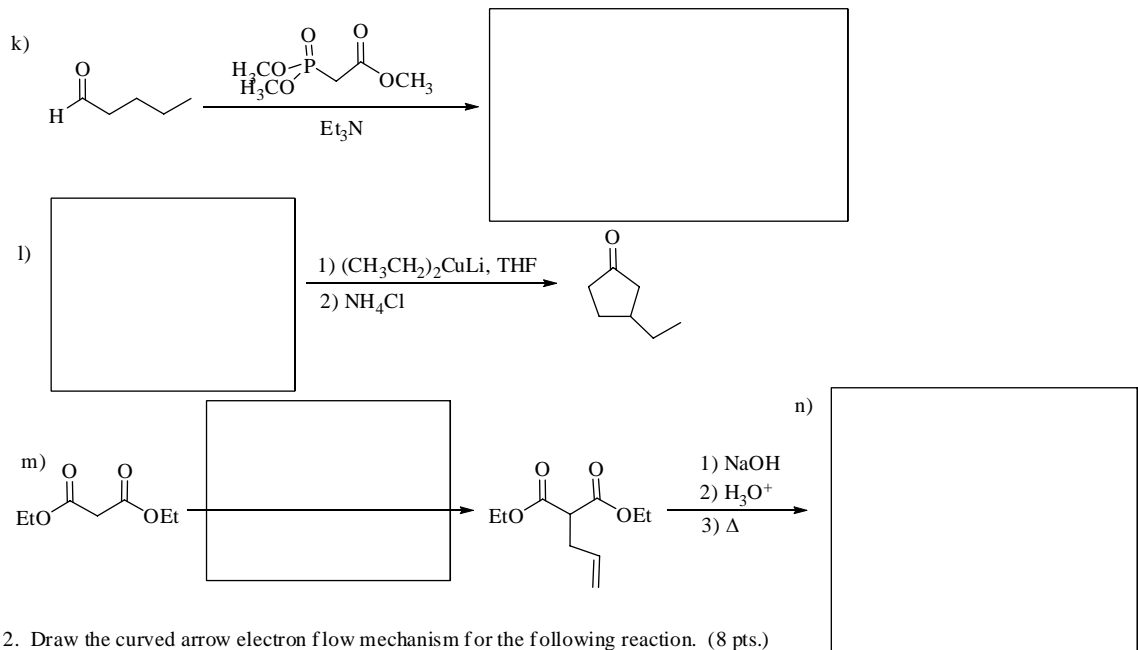


i)

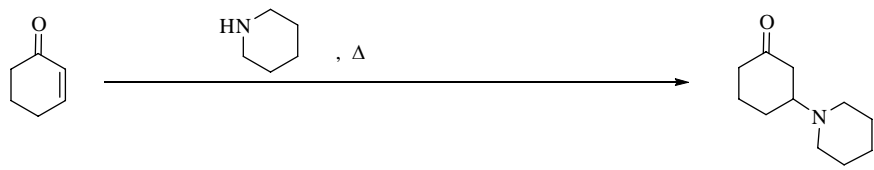


j)





2. Draw the curved arrow electron flow mechanism for the following reaction. (8 pts.)



3. Draw the HOMO of 1,3,5-hexatriene using conventional depictions of the molecular orbitals. (6 pts.)

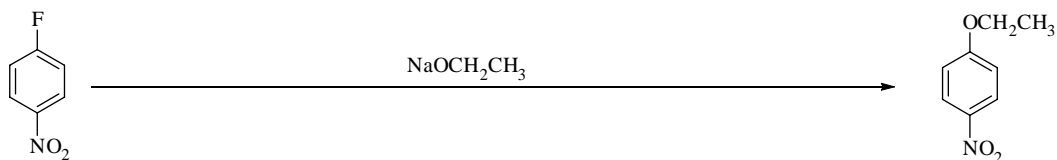
4. a) Suggest two reasons why the equilibrium in the base-catalyzed aldol addition between ketones does not favor the products, but the equilibrium in the base-catalyzed aldol addition between two aldehydes does favor the product. (8 pts.)

b) Briefly describe how chemists achieve a product from the base-catalyzed reaction of a ketone with itself (under thermodynamic conditions) and what makes this process successful. (6 pts.)

5. Crossed aldol reactions represent a useful way to make new C-C bonds, however without a careful selection of reaction conditions they afford a complex mixture of products. Show one reaction example of a crossed aldol reaction which is selective for one product and briefly explain why the reaction is selective. (8 pts.)

6. Glucosamine is a commonly found structure in nature. It is D-glucose with an amine group replacing the hydroxyl group in the C-2 position. Draw the most stable pyranose chair form of α -D-glucosamine. (4 pts.)

7. a) Draw the curved arrow electron flow mechanism for the following reaction. You do NOT need to include resonance forms of intermediates in this part of the question. (6 pts.)



b) Draw four important resonance contributors of the intermediate shown in the mechanism of part a. Be sure to include the curved electron flow arrows to indicate how one resonance form is transformed into another. (6 pts.)

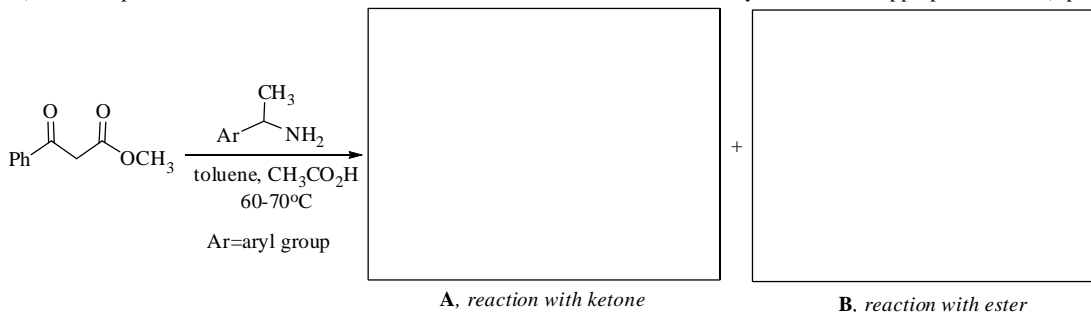
c) Circle the resonance form that best illustrates the involvement of the nitro group in the reaction mechanism. (2 pts.)

d) What general type of reaction mechanism is this reaction? (1 pts.) _____

This space intentionally left blank so that you can sketch some relaxing images or favorite chemical structures that may have been omitted from the exam.

8. The following reaction was recently reported in a chemistry journal. There are two possible products from this reaction; in particular, the amine can react with either one of the carbonyl groups shown. Answer the following questions about this process.

a) Draw the products of the reaction with the ketone and the reaction with the carboxylic ester in the appropriate boxes. (6 pts.)



b) These two reactions occur by two different general mechanisms. Identify the mechanisms by name. (2 pts.)

reaction mechanism to form **A**: _____

reaction mechanism to form **B**: _____

c) What is the name of the functional group formed in the reaction with the ketone? (1 pt.) _____

What is the name of the functional group formed in the reaction with the ester? (1 pt.) _____

d) Both the reaction to form **A** and the reaction to form **B** are equilibria, and the researchers encountered difficulties in trying to form one product in preference to the other. The researchers controlled the reaction outcome for the formation of **A** by specifically removing a byproduct of this equilibrium reaction. What was this byproduct? (2 pts.)

e) If the researchers wanted to form product **B** chemoselectively, what could they remove to shift the equilibrium towards **B**? (2 pts.)

f) Controlling equilibria as described in part d and e is an example of the application of what concept? (3 pts.)

g) The researchers found greater formation of **B** at higher temperatures (~110°C) and needed to run the reaction at lower temperatures to form predominantly **A**. Based on this fact, what type of product is **B**? (3 pts.)

h) Normally the reaction between a ketone and an amine is rapid, however in this case it was a little slower due to the presence of the phenyl group. Why did the phenyl group make the ketone less reactive? (3 pts.)

9. Devise a synthesis for the product on the right from the starting material on the left. You may use any inorganic or organic reagents. (10 pts. each)

