

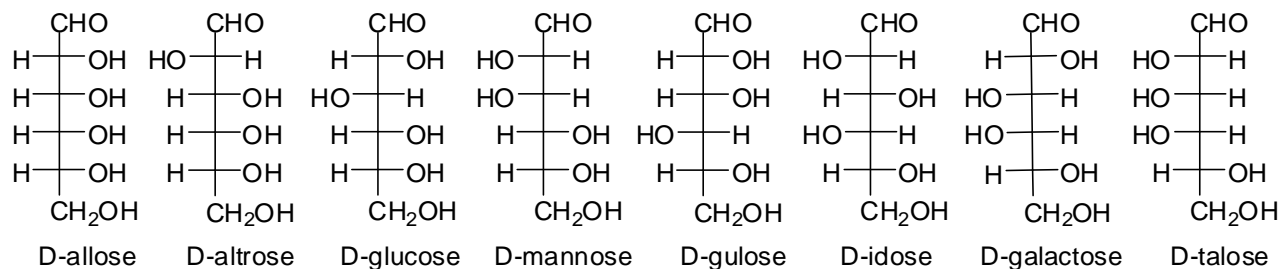
Organic Chemistry 2
Second Examination
March 27, 2009
Prof. Malachowski

Name: AIG executive #10

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

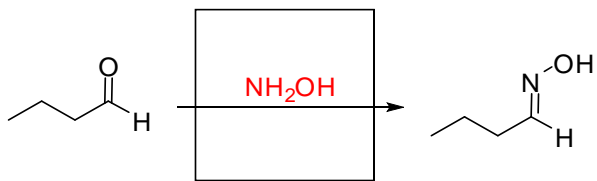
Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics.

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.

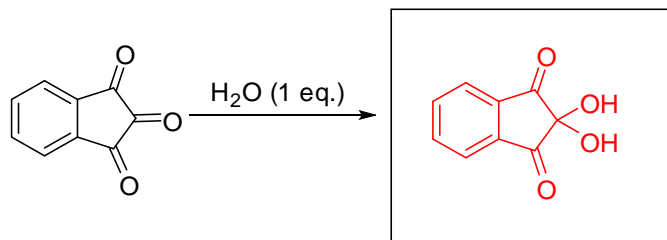


1. Provide the necessary information, product(s), reagents or starting materials, to complete the following reactions. (3 pts. per question)

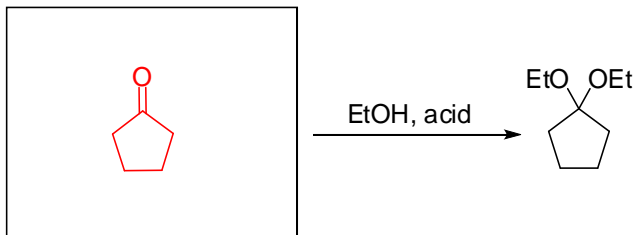
a)



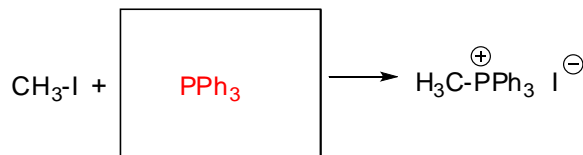
b)



c)

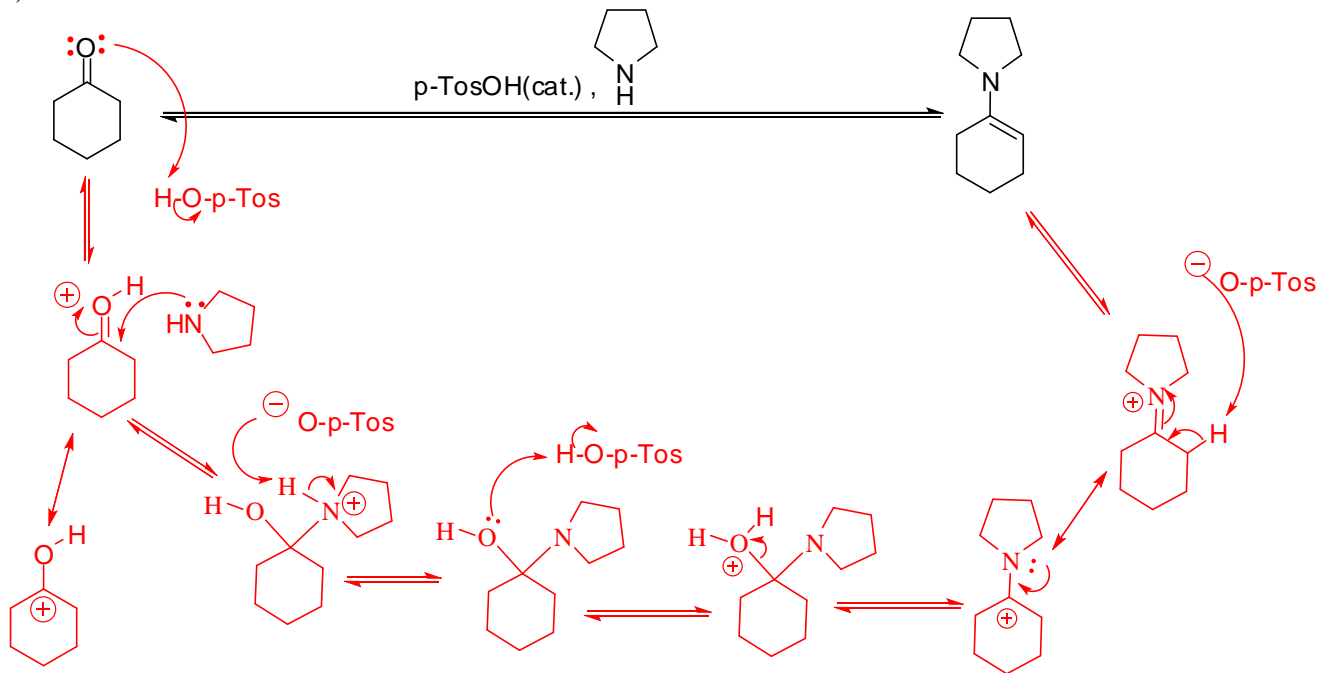


d)

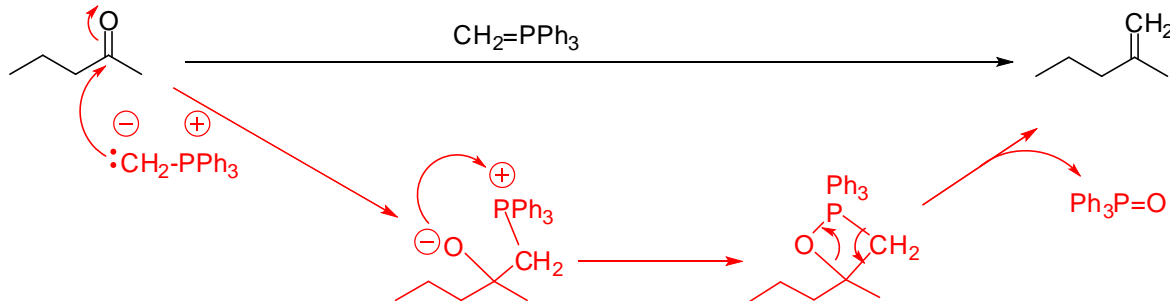


2. Draw the mechanisms for the reactions shown below. Your mechanism should include important resonance structures, formal charges and curved electron flow arrows. (10 pts. each)

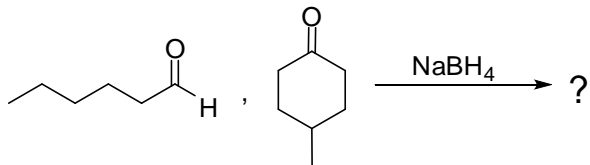
a)



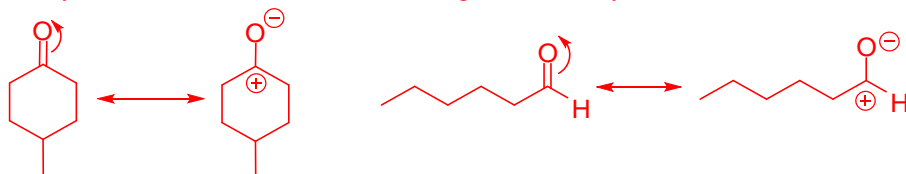
b)



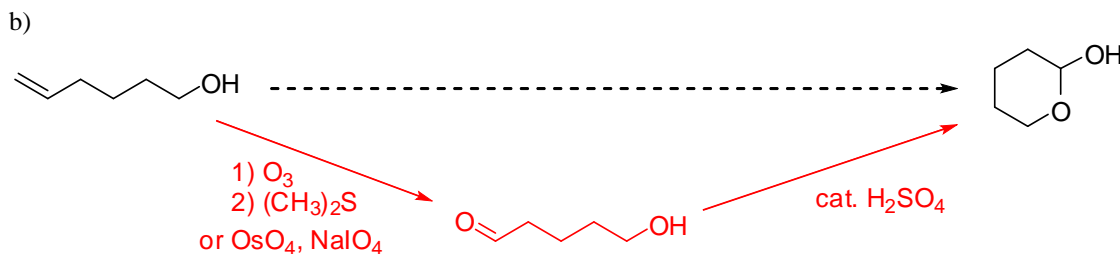
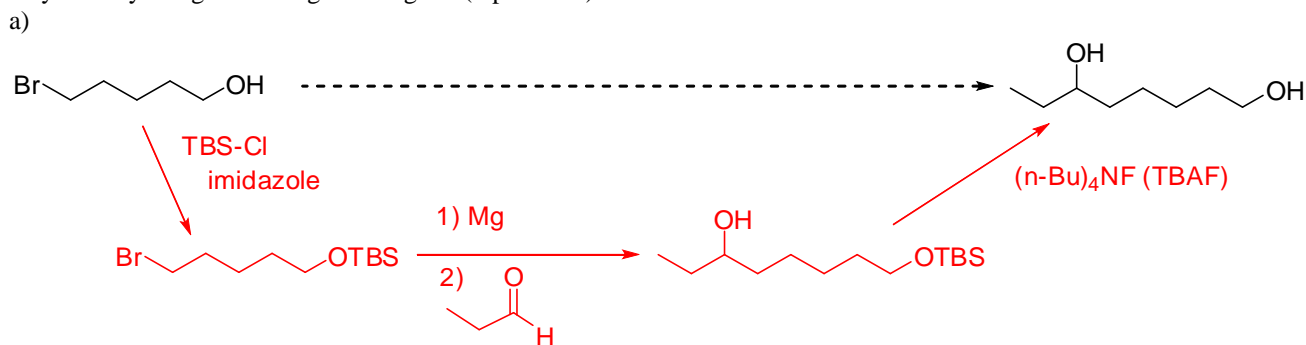
3. The following reaction was reported in the chemical literature and lead to almost exclusive reduction of the aldehyde over the ketone. Briefly explain why the aldehyde reacts more readily than the ketone. (8 pts.)

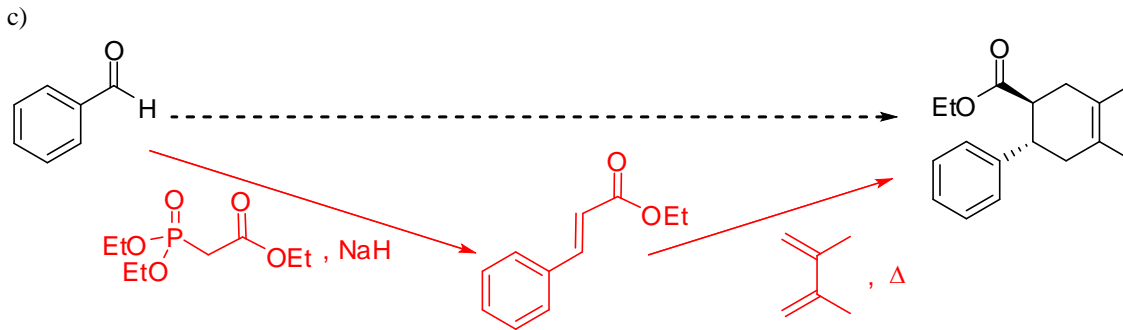


The aldehyde is more electrophilic than the ketone for both steric and electronic reasons. A nucleophile is less likely to add to the carbon of the ketone C=O for steric reasons, i.e. due to the presence of two bulky alkyl groups around the C=O. The carbon of the aldehyde carbonyl is more electrophilic because the hydrogen donates much less electron density to the aldehyde carbonyl carbon, whereas the ketone carbonyl carbon has two alkyl groups stabilizing the carbon with electron density. The resonance forms of both the aldehyde and ketone (below) illustrate the greater stability of the ketone carbocation resonance form due to the two alkyl groups.

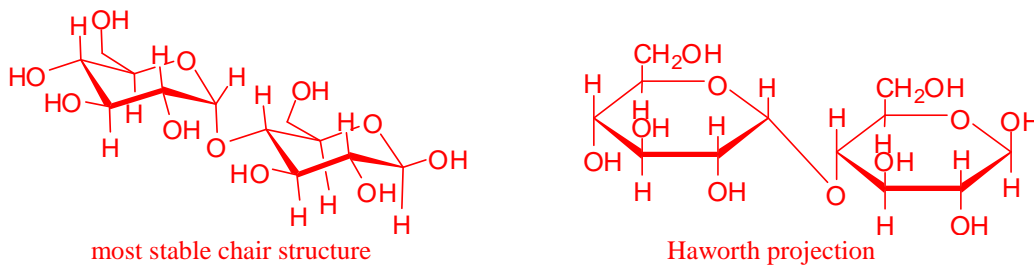


4. Suggest a synthesis to take the starting material on the left to the product on the right. This will require more than one step. You may use any inorganic or organic reagent. (8 pts. each)

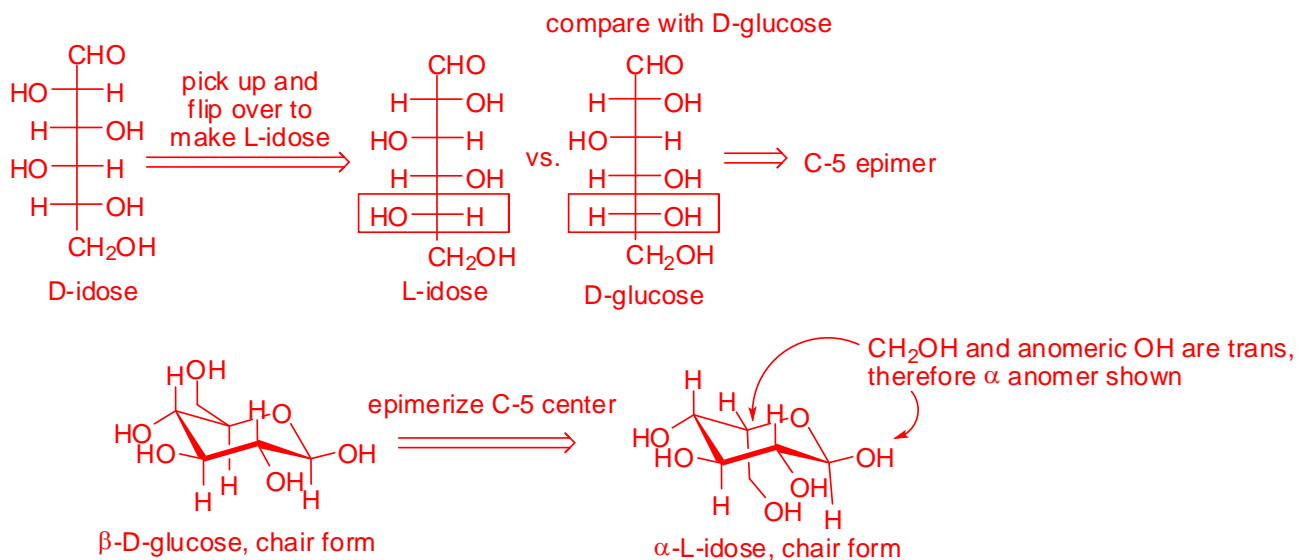




5. Maltose, or mal-toes, was discovered and named by my great grandfather, Stanislaw Malachowski, based on his important studies of the sweet component in toe jam. It is a disaccharide consisting of two glucose molecules with an α -1,4 linkage, official name: 4-O-(α -D-glucopyranosyl)-D-glucopyranose. Draw the most stable chair structure and the Haworth projection of this disaccharide. (8 pts.)



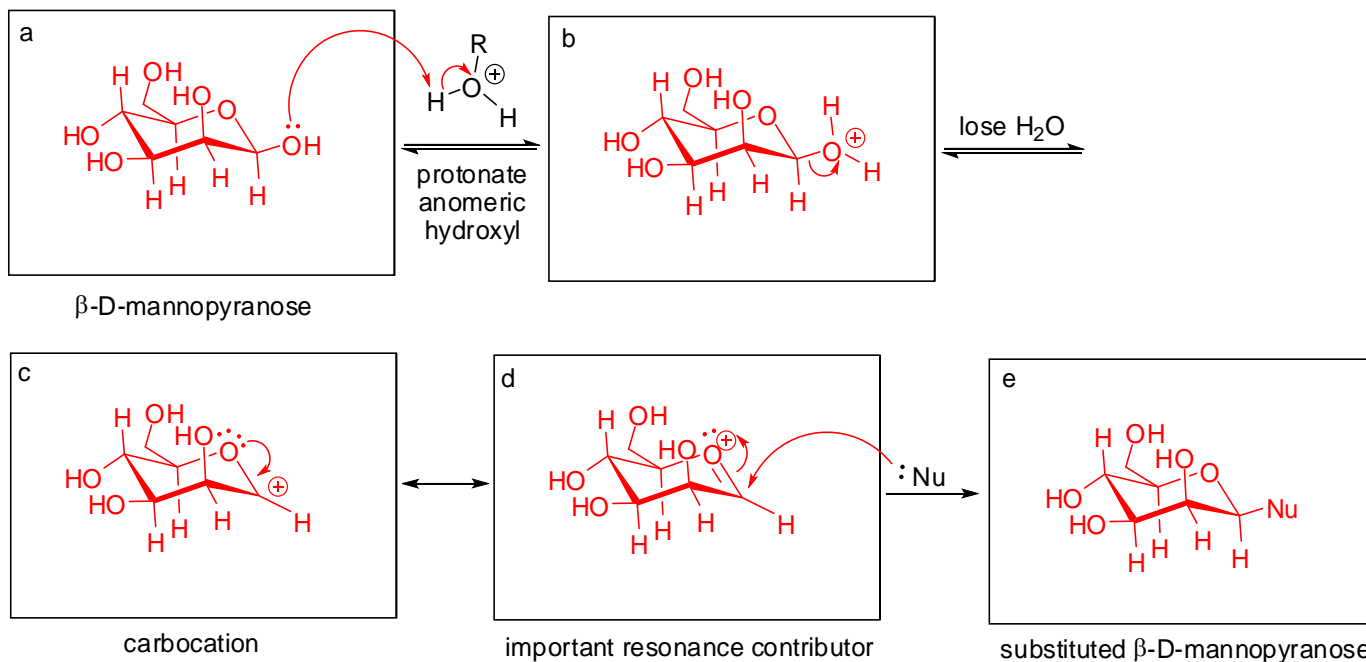
6. Although most sugars are found predominantly as the D stereochemical form, some are commonly found as the L form. One example is L-idose, a derivative of which is an important component of heparin, a widely used anti-coagulant polysaccharide. Draw the most stable chair configuration of α -L-idopyranose. (7 pts.)



/23 pts.

7. In nature and in the lab, all aldopyranoses readily undergo substitution by nucleophiles at the anomeric carbon through a process identical to the hemiacetal to acetal conversion or mechanism discussed in class. Fill in the boxes below to show how this process occurs. Draw ALL necessary electron flow arrows and formal charges.

- In box a, draw the most stable chair structure of β -D-mannopyranose. (3 pts.)
- In box b, draw the result of protonation of the alcohol at the anomeric carbon. (3 pts.)
- Show the carbocation that forms with the departure of water in box c. (3 pts.)
- Draw an important resonance contributor of the carbocation in box d. (3 pts.)
- Show electron flow arrows for the addition of a nucleophile and draw the product structure in box e. (3 pts.)



8. Describe the relationship between the following structures. (2 pts. each)

