

Organic Chemistry c3444y

4th Hour Exam

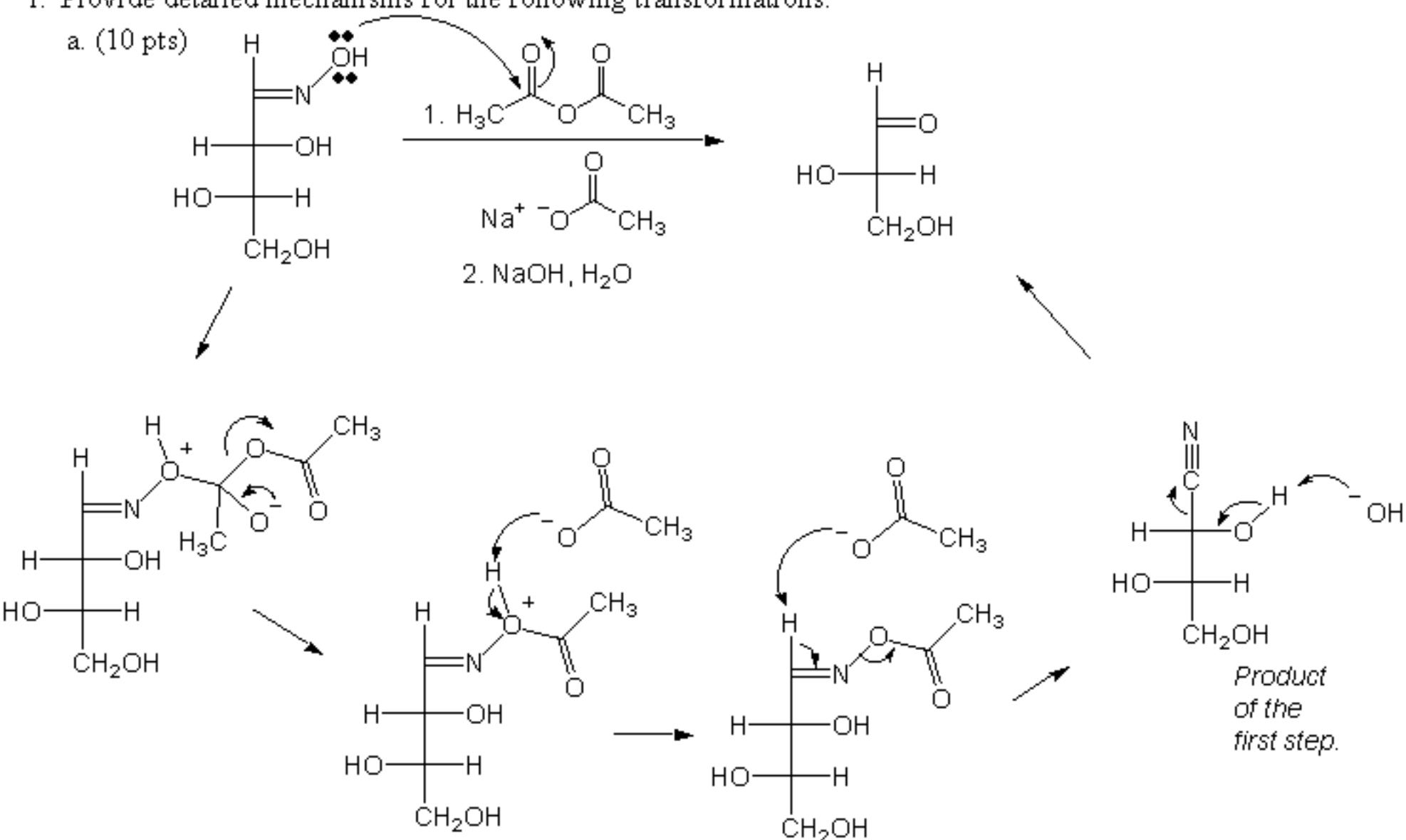
Wednesday, April 18, 2001

Prof. Leighton

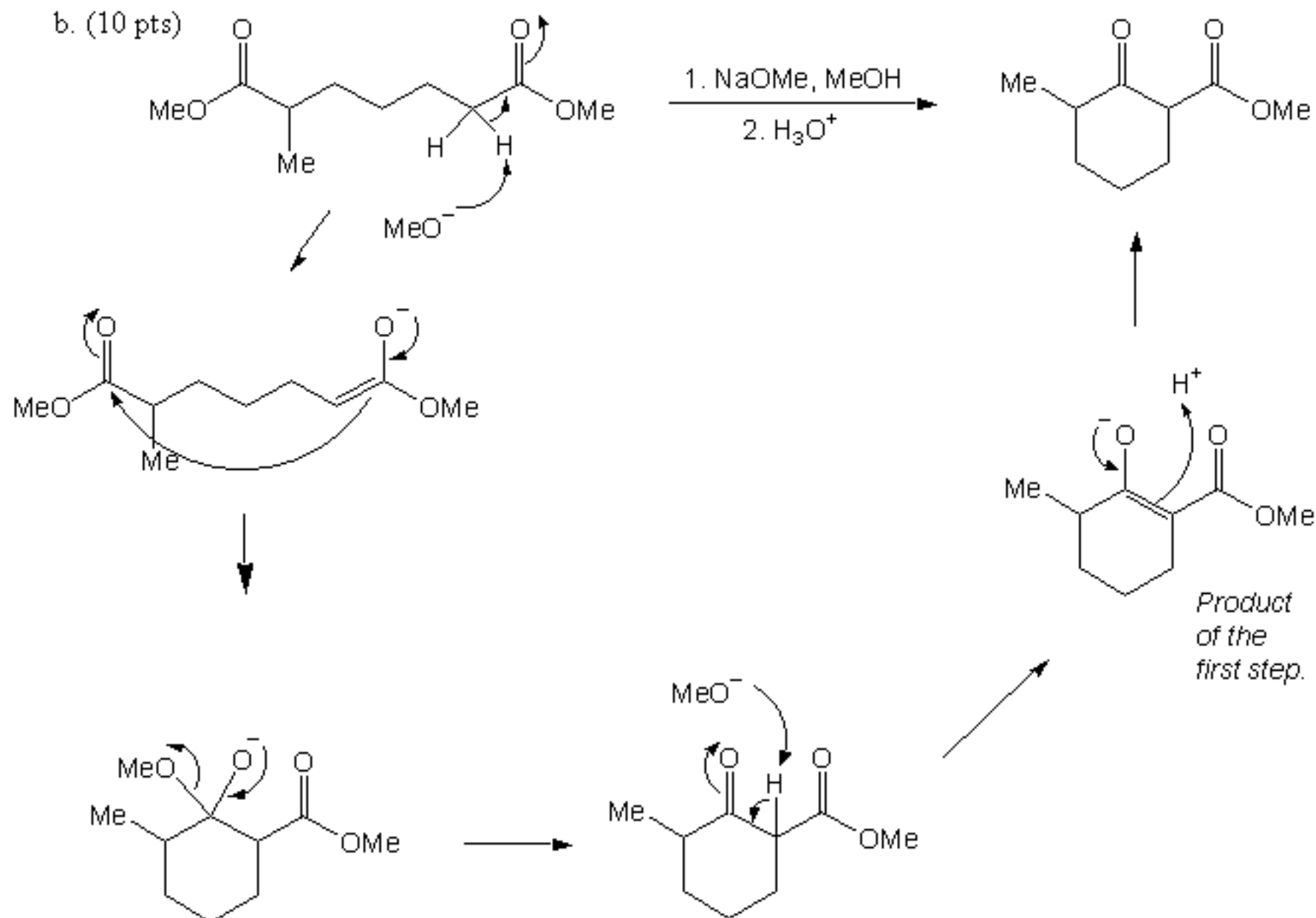
Answer Key

1. Provide detailed mechanisms for the following transformations:

a. (10 pts)

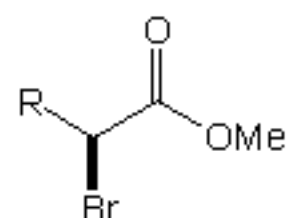
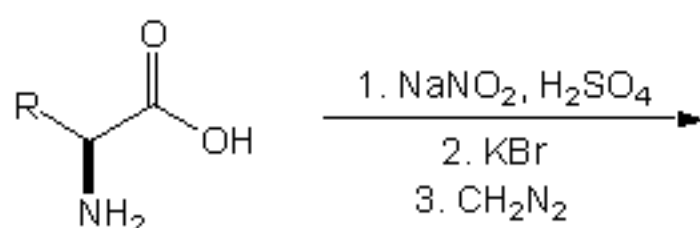


b. (10 pts)

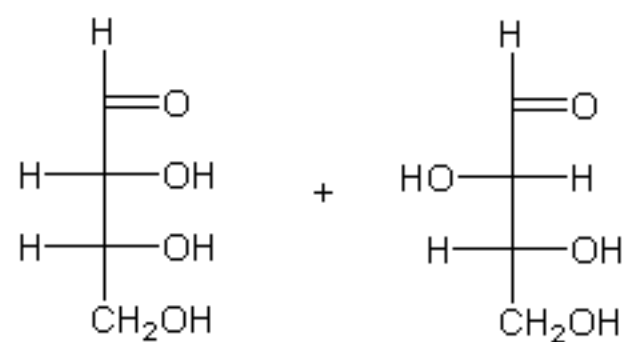
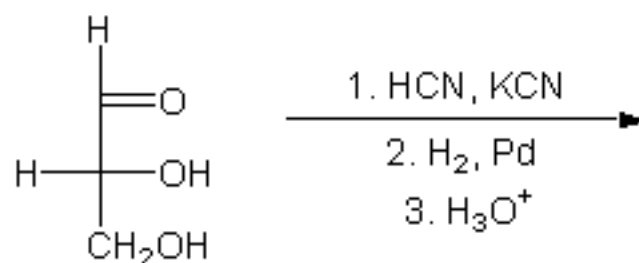


2. Predict the major product(s) of the following reactions:

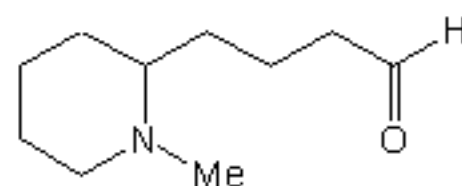
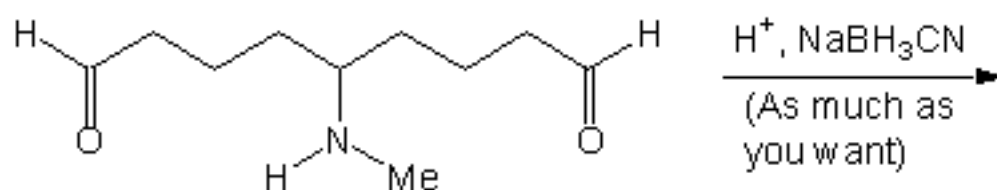
a. (8 pts)



b. (8 pts)



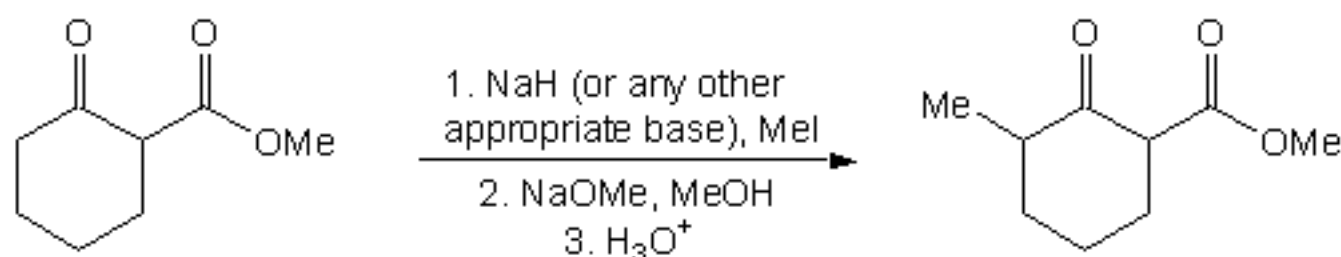
c. (8 pts)



3. Provide the reagents necessary to accomplish the following transformations:

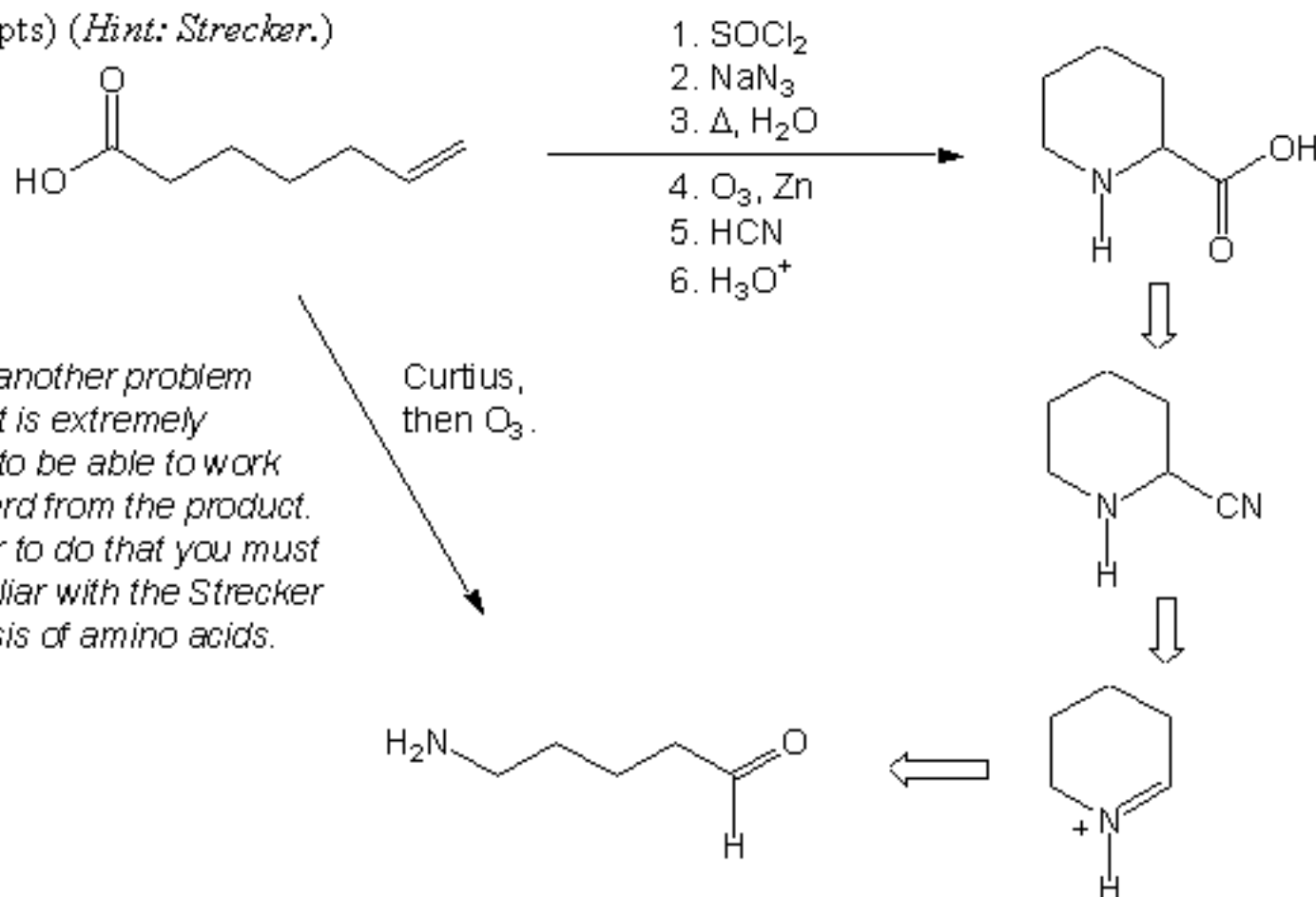
(*More than one step will be required.*)

a. (7 pts)

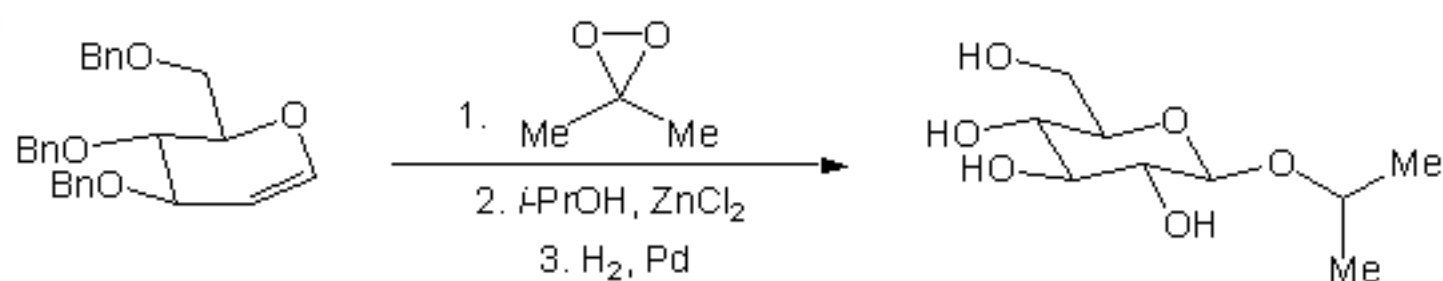


Direct alkylation will not work here because the desired enolate will not form. But the reversibility of the Dieckmann condensation gives us a way out. First alkylate between the carbonyls and then do a retro-Dieckmann-Dieckmann sequence.

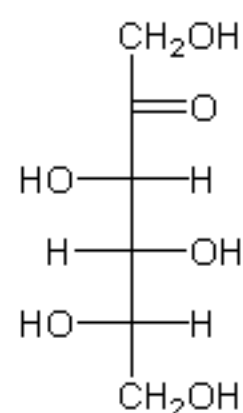
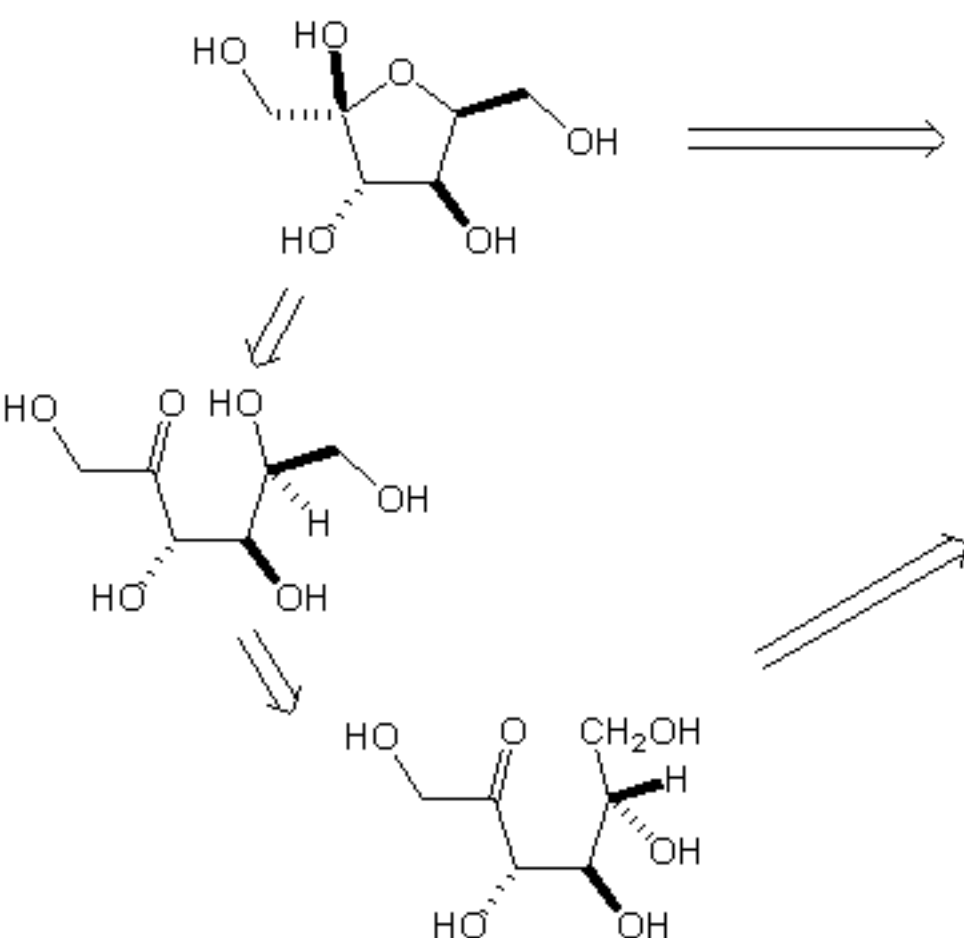
b. (7 pts) (*Hint: Strecker.*)



c. (7 pts)



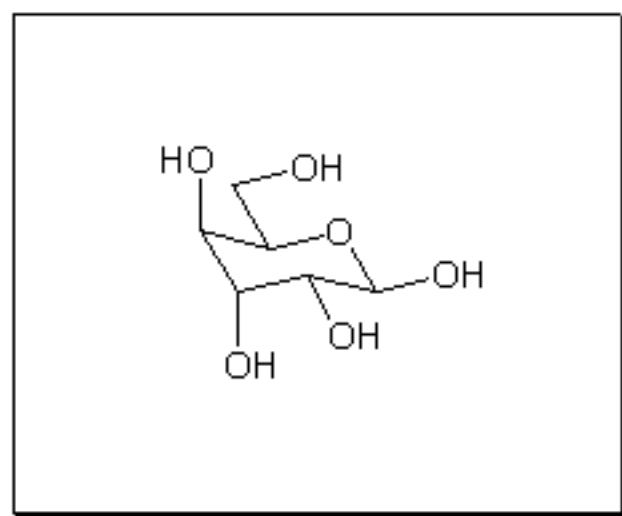
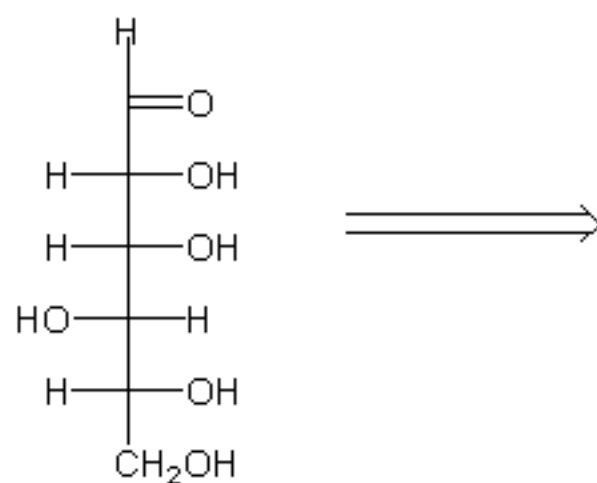
4. a. (10 pts) Provide a Fischer projection and a classification (*e.g.* D-aldotetrose) for the following carbohydrate:



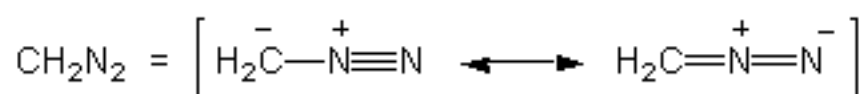
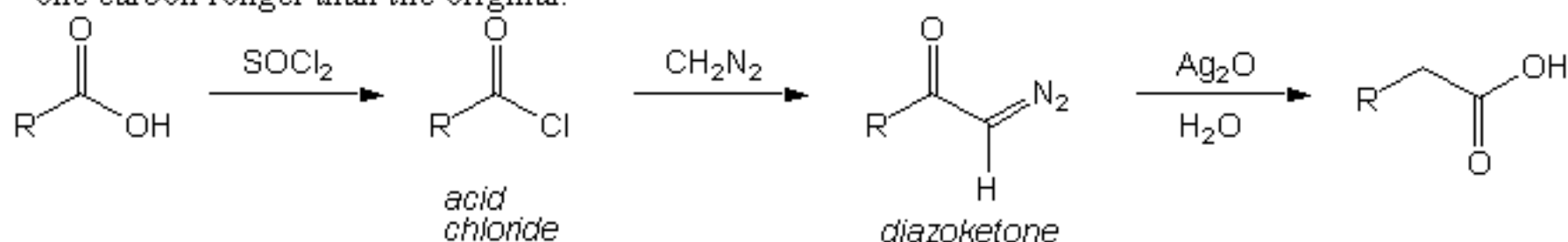
Fischer Projection

L-ketohexose
Classification

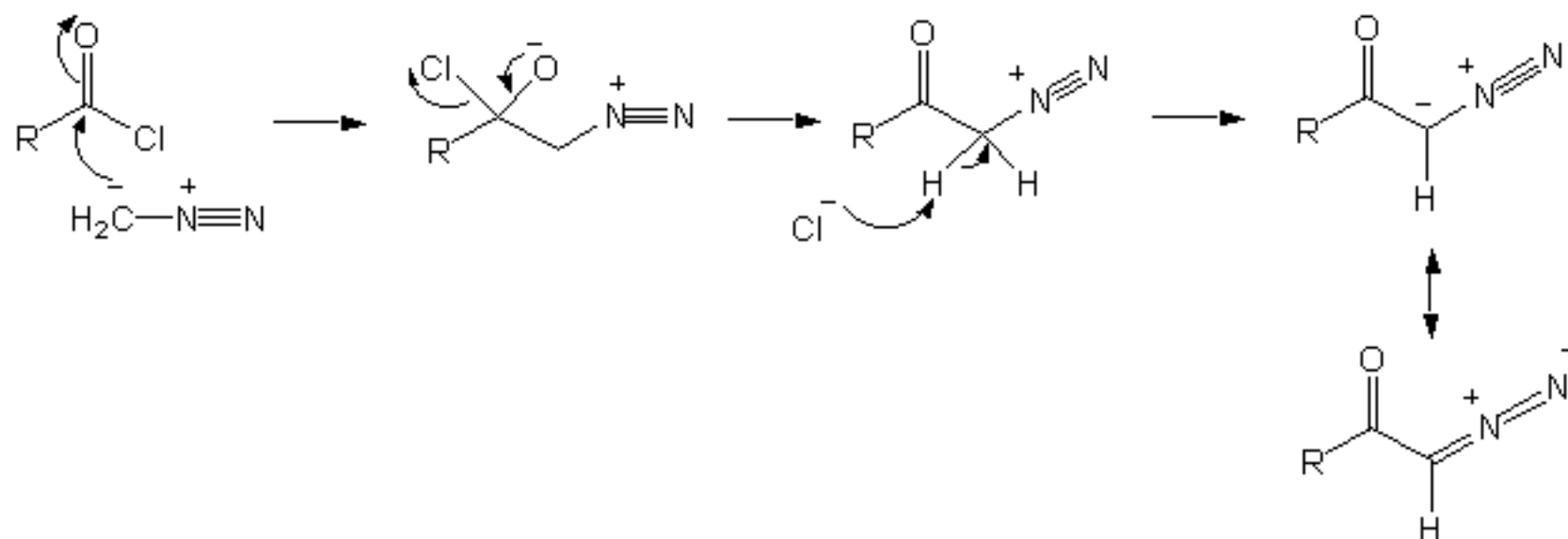
- b. (10 pts) Provide a clear drawing of the most stable **β -PYRANOSE** form of the following ketohexose.



5. Consider the following reaction sequence (known as the Arndt-Eistert Homologation). In the first part, a carboxylic acid is transformed into an acid chloride, and the acid chloride is then treated with diazomethane to give a diazo ketone. In the second part (known as the Wolff Rearrangement), the diazo ketone is treated with a silver salt in the presence of water to give a new carboxylic acid that is one carbon longer than the original.



- a. (5 pts) Provide a mechanism for the conversion of the acid chloride to the diazoketone.



- b. (10 pts) Given what you know about the **Curtius Rearrangement**, propose a reasonable mechanism to account for the conversion of the diazoketone to the product carboxylic acid. You may ignore the silver oxide, but you will need the water at some point in the mechanism.

