

Organic Chemistry c3444y

3rd Hour Exam

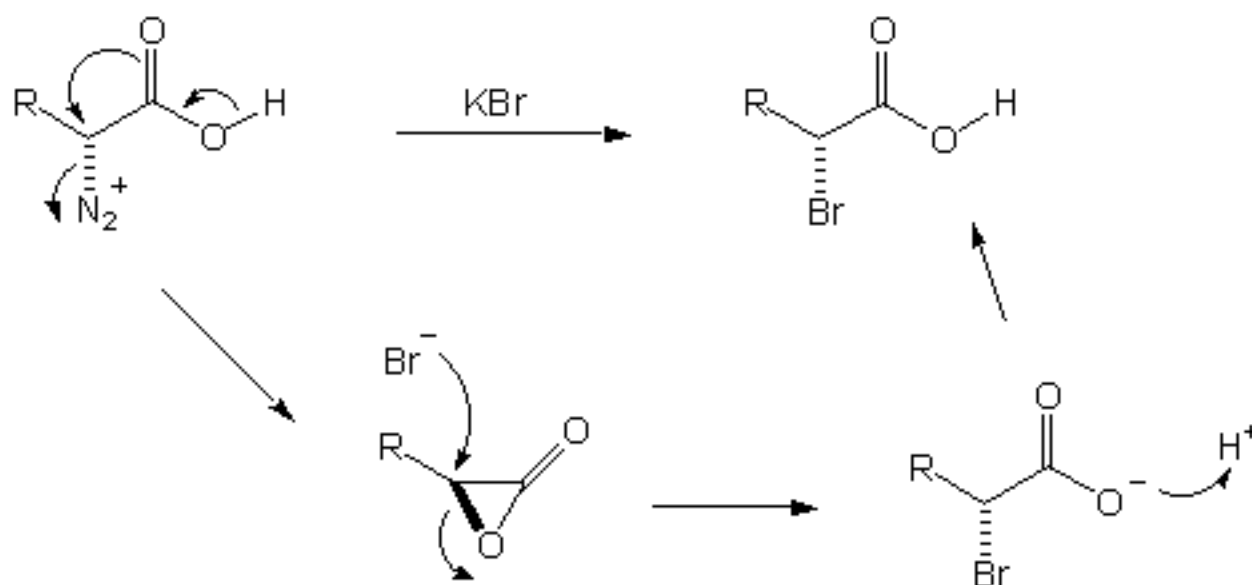
Monday, Apr. 26, 1999

Prof. Leighton

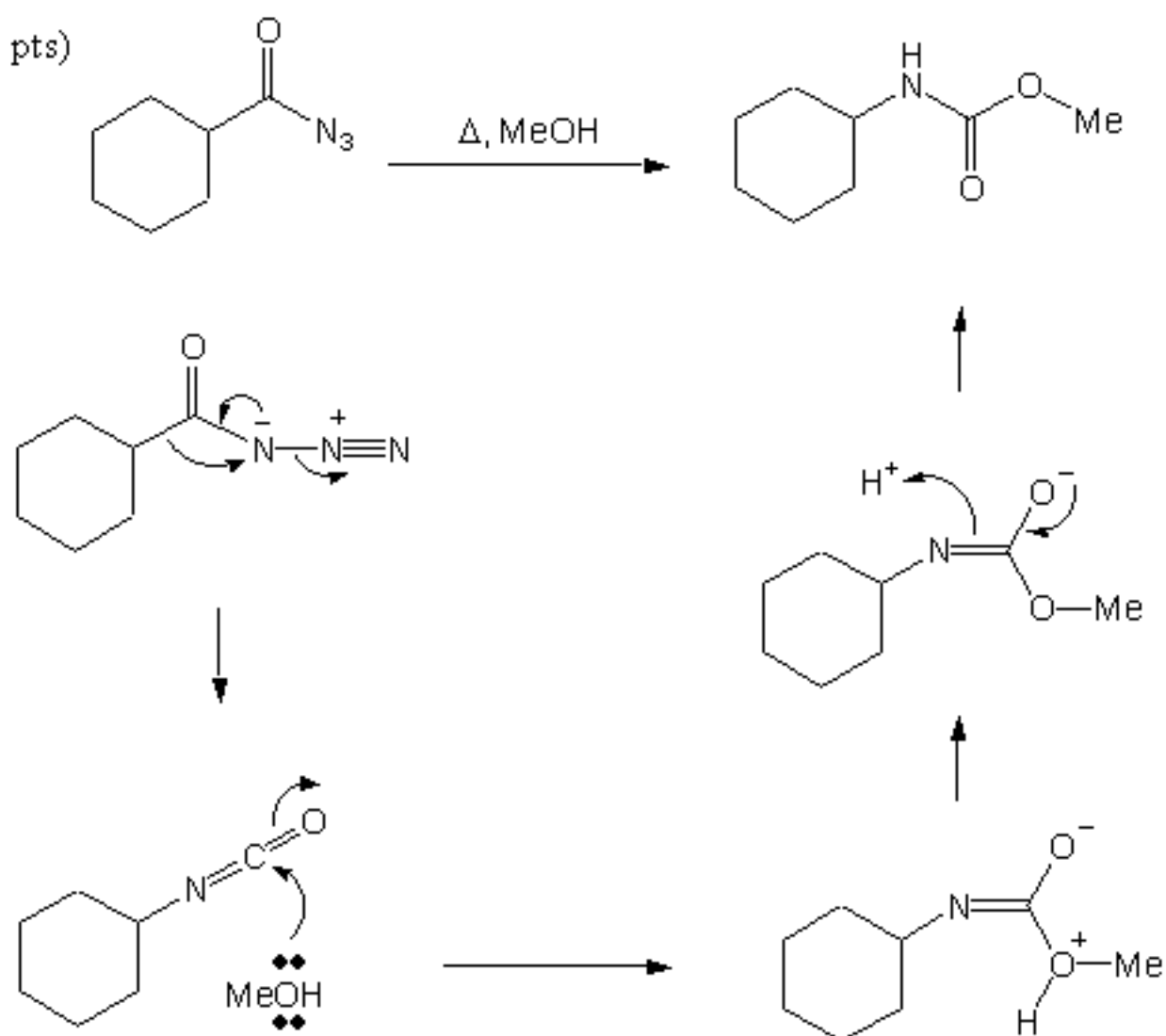
Answer Key

1. Provide detailed mechanisms for the following transformations:

a. (10 pts)

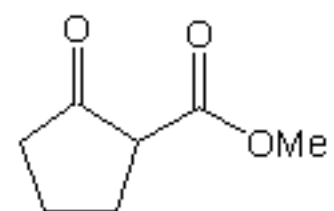
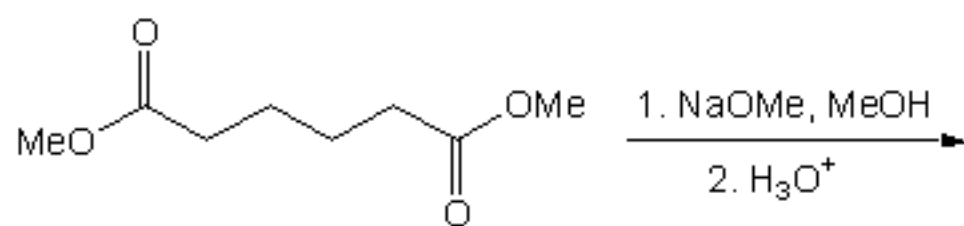


b. (10 pts)

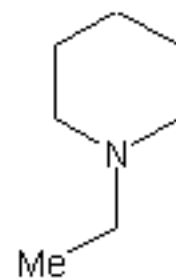
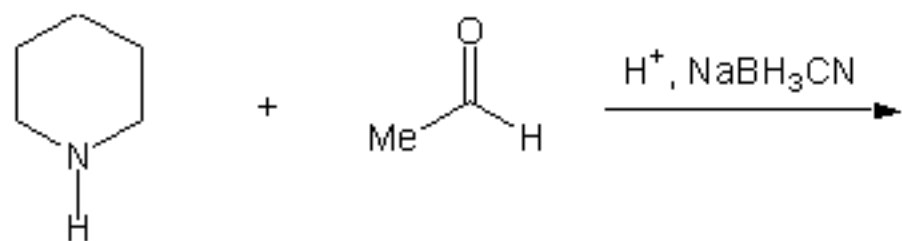


2. Predict the major product of the following reactions:

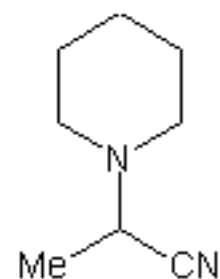
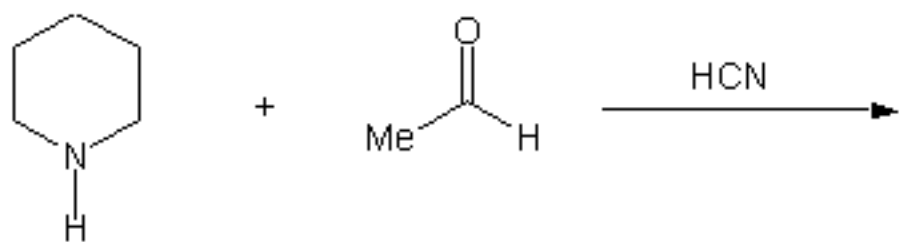
a. (10 pts)



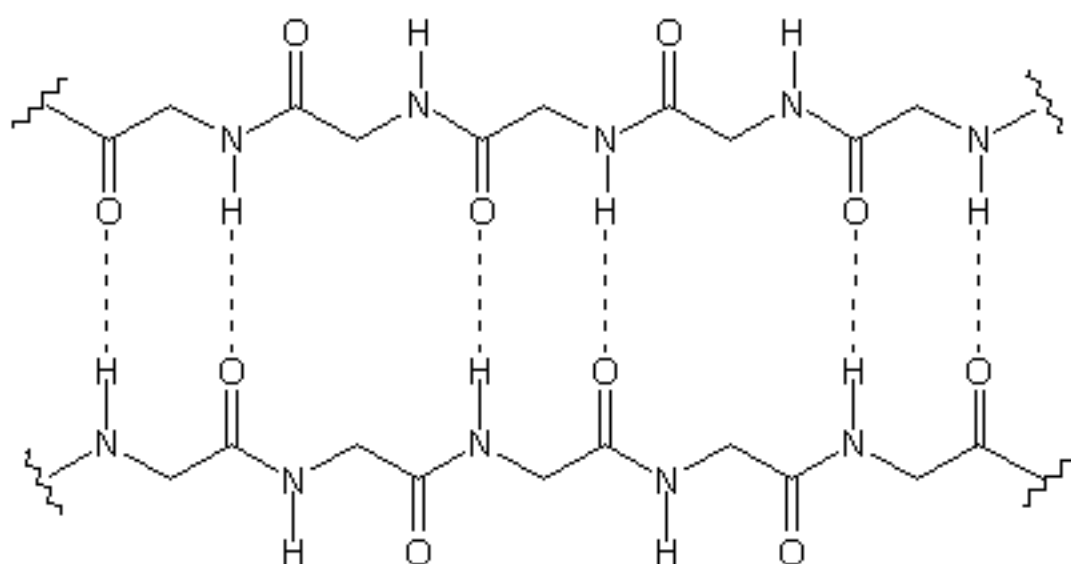
b. (5 pts)



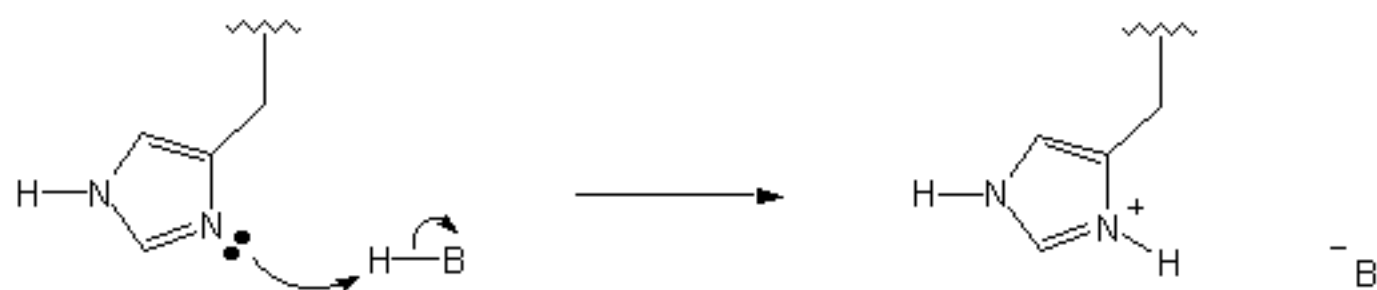
c. (5 pts)



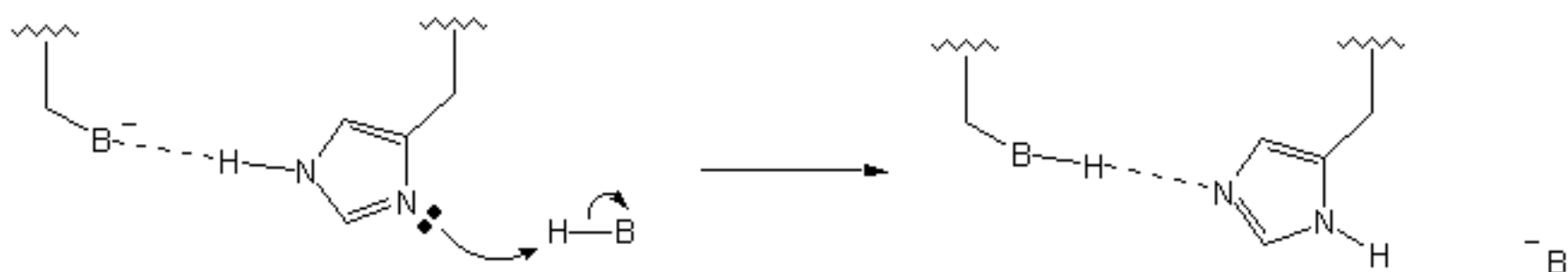
3. a. (10 pts) Shown below is a section of a peptide chain. Draw a second peptide chain underneath it such that you form an antiparallel β -sheet. Be sure to indicate the hydrogen bonds.



- b. (10 pts) The imidazole of histidine is often used by proteins as a base at the active site.

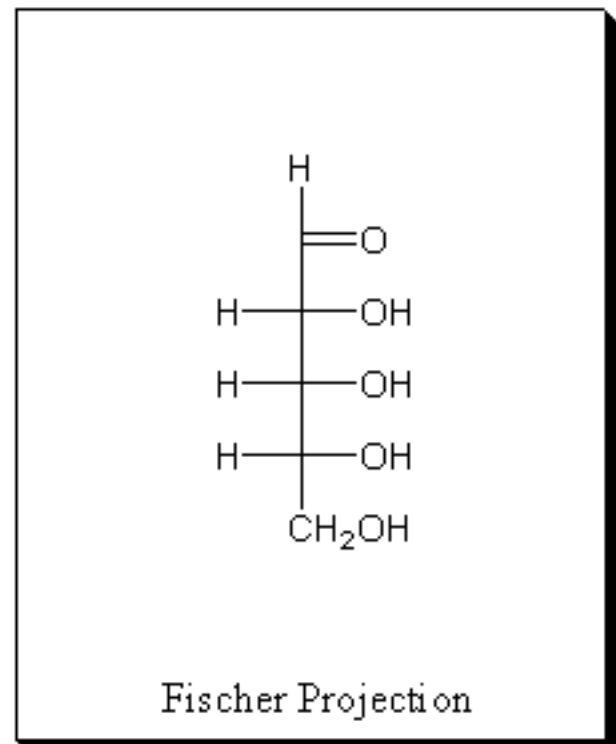
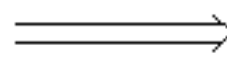
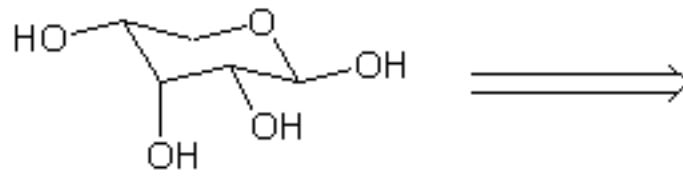


Although imidazole is a reasonably competent base (pK_a of protonated imidazole = 7), proteins often use a "trick" to increase its basicity. Show with structures how the basicity of imidazole may be increased. You may use any other reasonable chemical entity likely to be found in a protein that you desire.



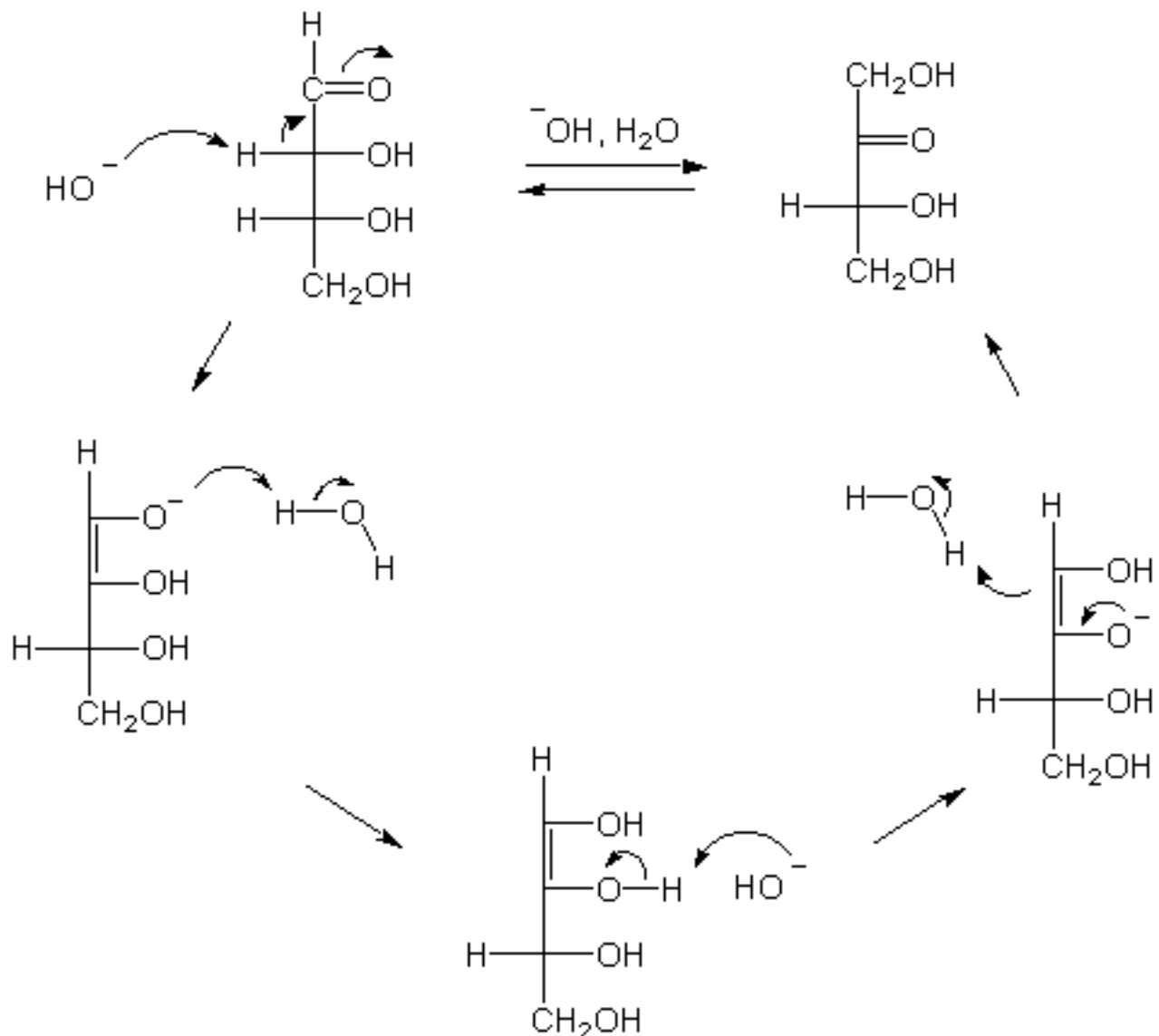
The protein can employ a base to deprotonate the imidazole during the reaction. In this way, the electron density of the imidazole is increased and it is thus a stronger base. Another way to look at this is that in the first reaction above we have created a positive charge on the imidazole. By using the other base, we avoid the creation of this charge.

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

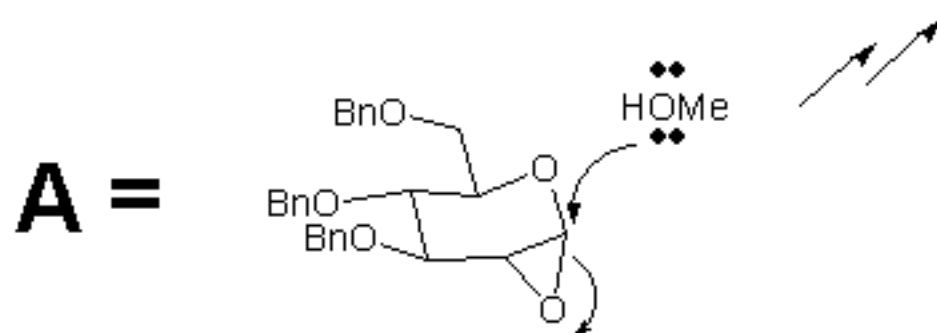
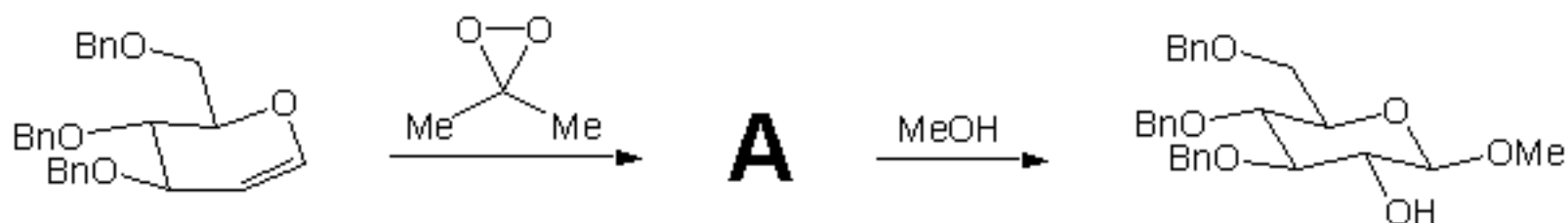


D-Aldopentose
Classification

b. (10 pts) Provide a mechanism for the following transformation:

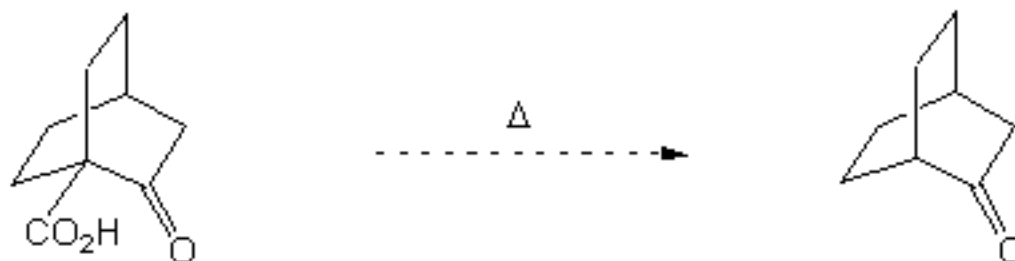


5. a. (10 pts) Provide the structure of intermediate **A**, and provide a *brief, concise* explanation for why this two step process leads to the indicated stereochemistry in the product.



The epoxide forms on the bottom face of the alkene because the nearest BnO group is blocking the top face. A direct S_N2 -like displacement then gives inversion leading to the observed stereochemical result.

- b. (10 pts) Because most β -ketoacids readily decarboxylate, your lab partner is planning to attempt the following decarboxylation:



Even though your lab partner routinely steals your food, you decide to explain why you believe this reaction might not work based on a careful mechanistic analysis:

