Chem. 310N, Spring 2008

Professor Krische

Midterm Exam II

Average = 50

Grading Scale

90-100 = A+

80-89 = A

70-79 = A-

65-69 = B+

60-64 = B

55-59 = B-

50-54 = C+

45-49 = C

40-44 = C-

37-39 = D+

33-36 = D

30-32 = D-

0-29 = F

Name:_____

Problem

1. (16 points)_____

2. (24 points)_____

3. (12 points)_____

4. (18 points)_____

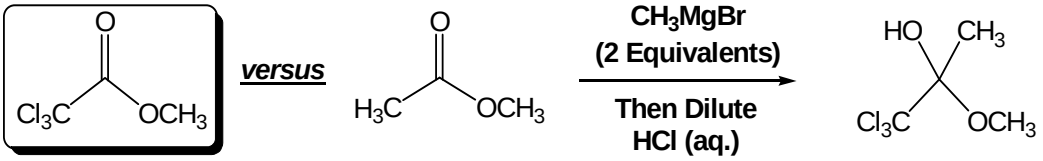
5. (20 points)_____

6. (10 points)_____

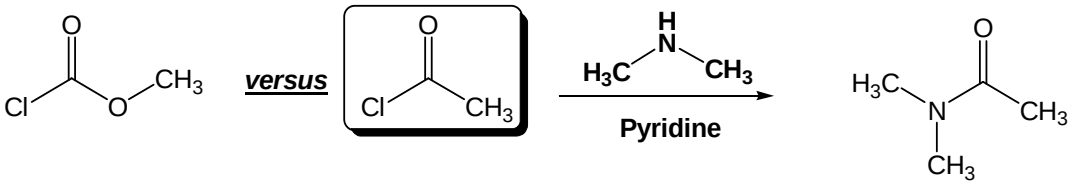
Total Points: _____ /100

1. (16 points) For the following pairs of compounds, circle the compound that reacts faster with the indicated nucleophile. For the faster reacting compound only, draw the product of its reaction with the indicated nucleophile.

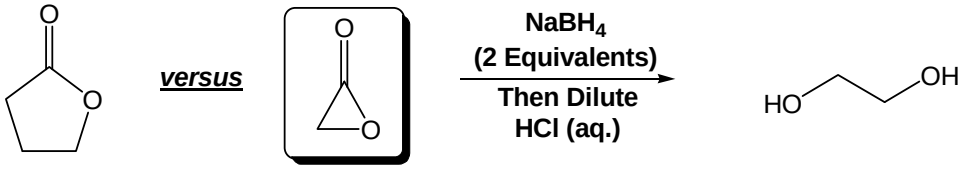
A.



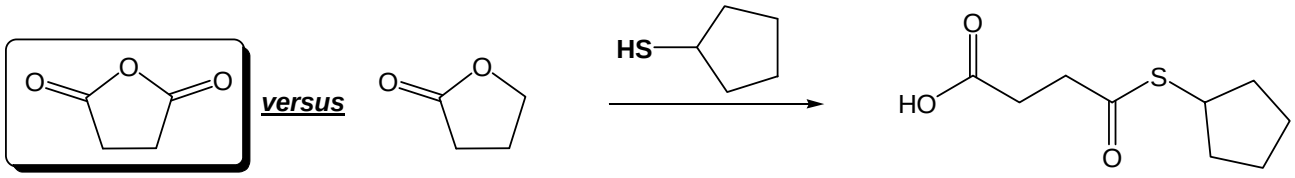
B.



C.

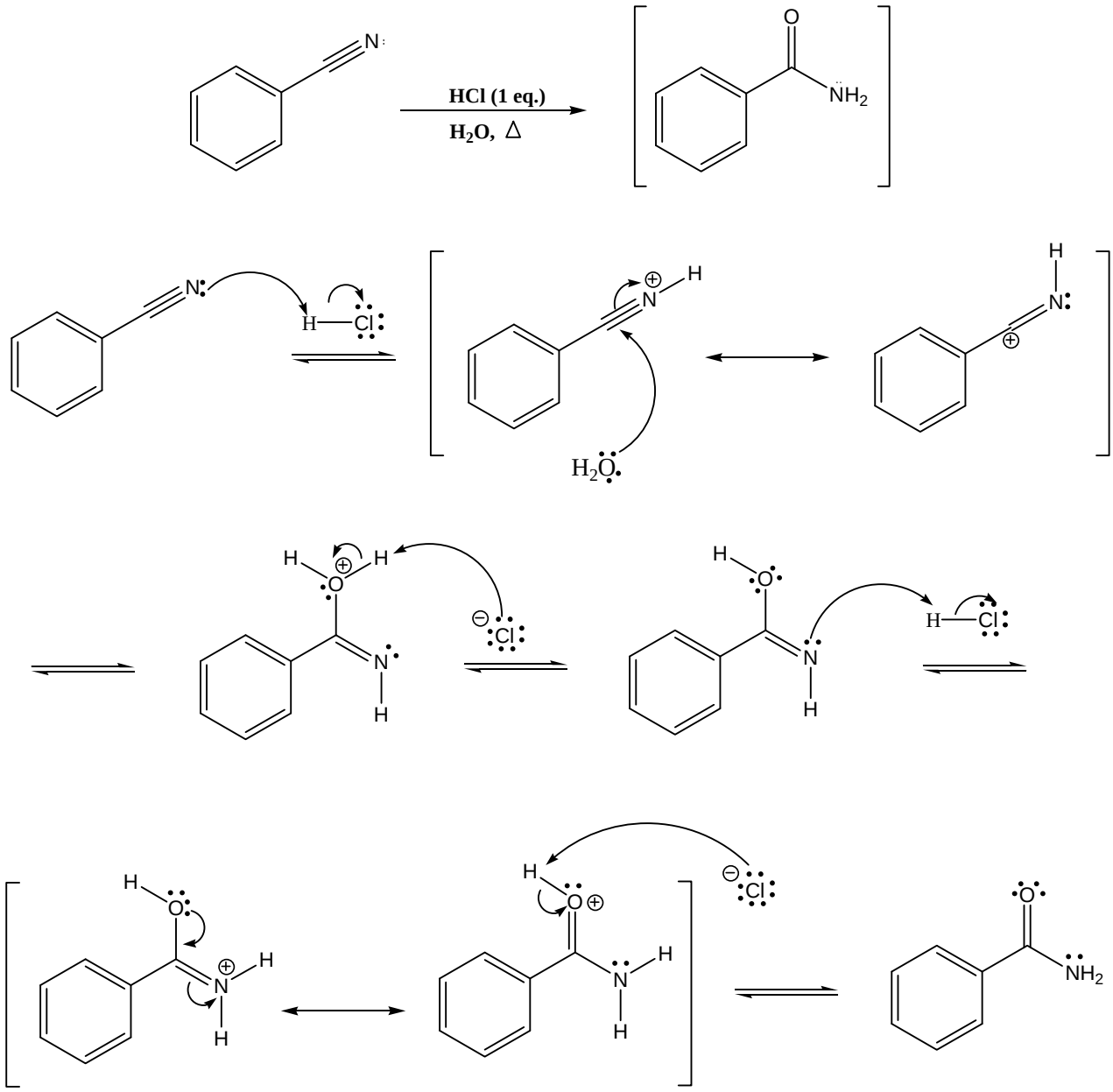


D.



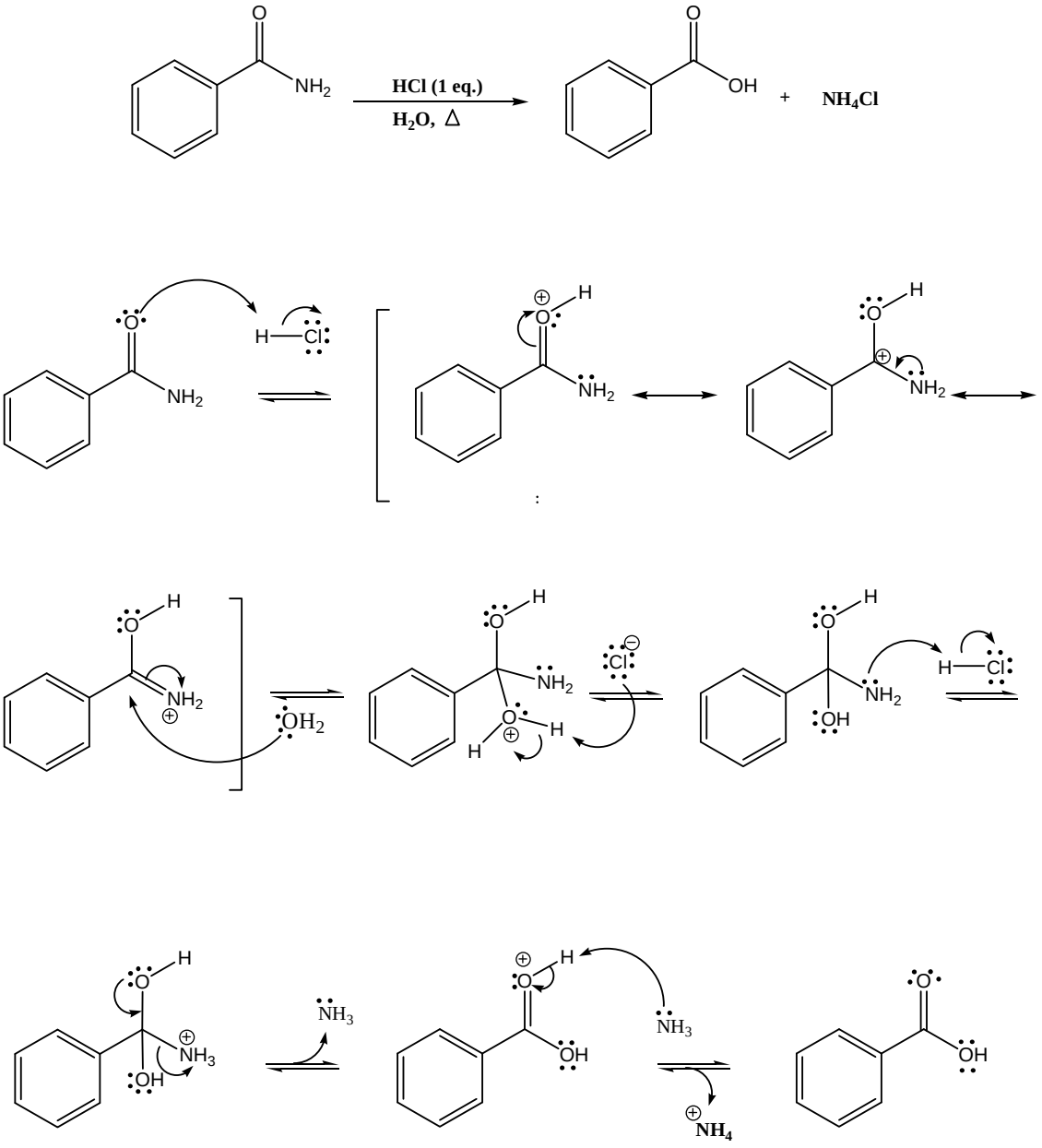
2. (24 points) Hydrolysis of benzonitrile produces benzoic acid. The hydrolysis occurs in two stages. The <u>first</u> stage involves hydrolysis of the nitrile to furnish an amide. The <u>second</u> stage involves hydrolysis of the amide to furnish an acid. Propose a mechanism to account for the benzonitrile hydrolysis. For each intermediate, draw all lone pair electrons, any formal charges, and all important resonance structures. Use the arrow pushing formalism to interconvert intermediates.

A. <u>First Stage</u>: Hydrolysis of the nitrile to furnish an amide.

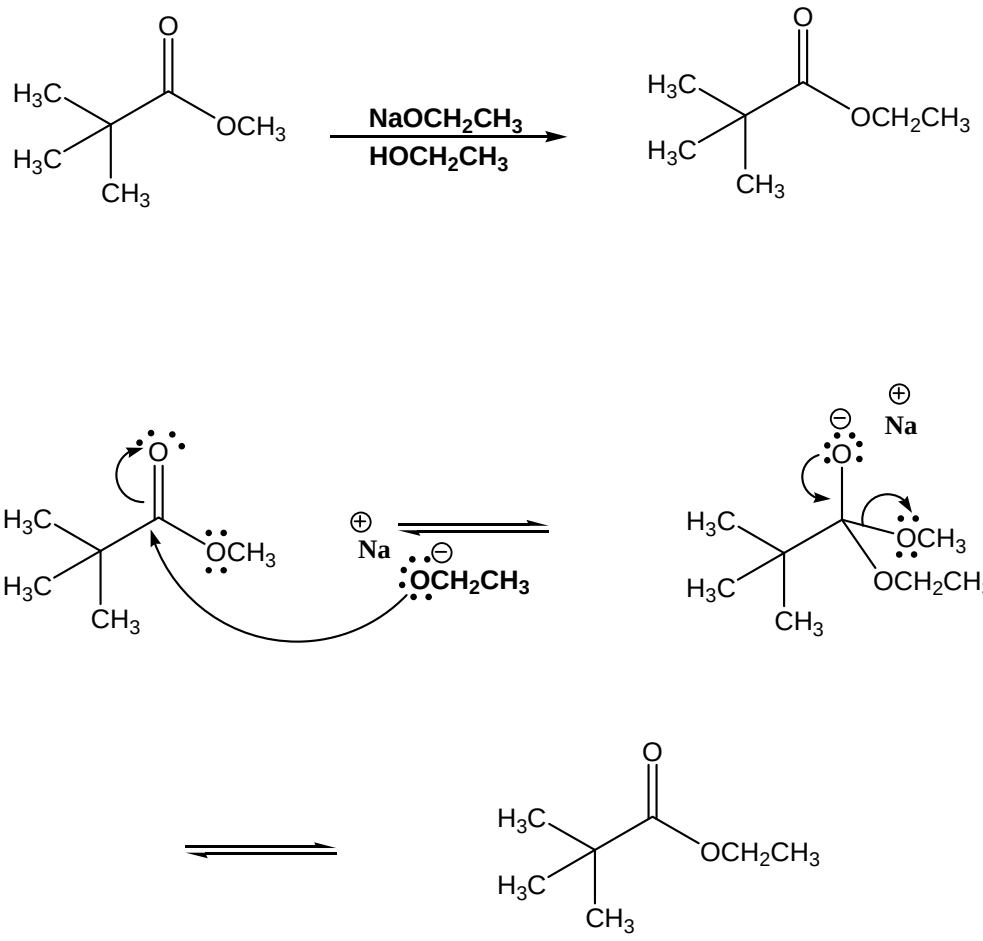


2 (continued)

B. <u>Second Stage</u>: Hydrolysis of the amide to furnish an acid.

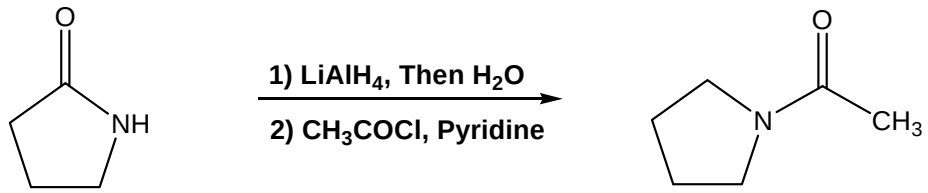


3. (12 points) Propose mechanisms to account for the following transformations. For each intermediate, draw all lone pair electrons, any formal charges, and all important resonance structures. Use the arrow pushing formalism to interconvert intermediates.

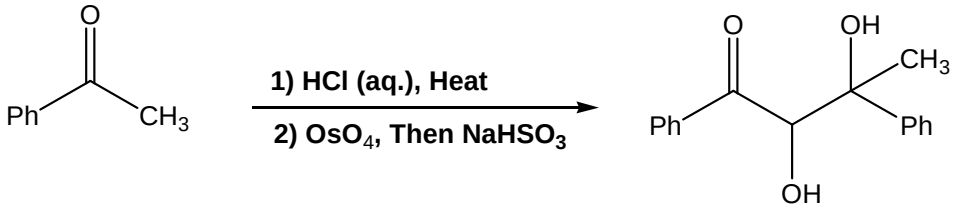


4. (18 points) Draw the major product expected when the indicated starting materials are subjected to the following multi-step transformations.

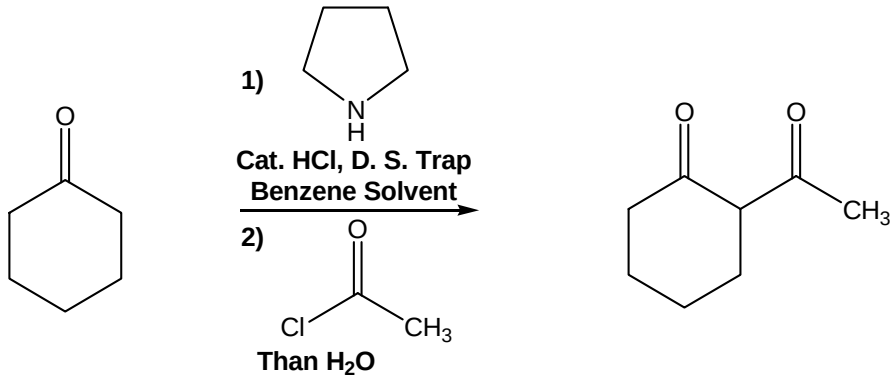
A.



B.

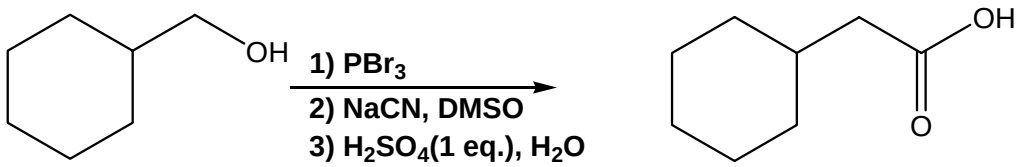


C.

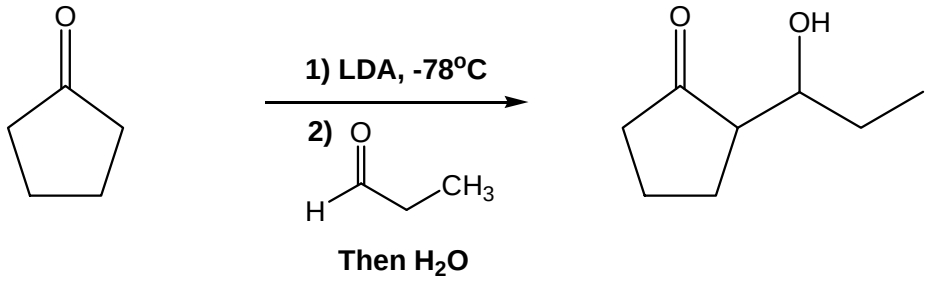


4. (Continued)

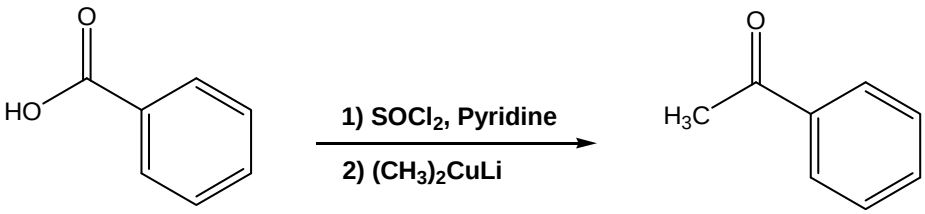
D.



E.

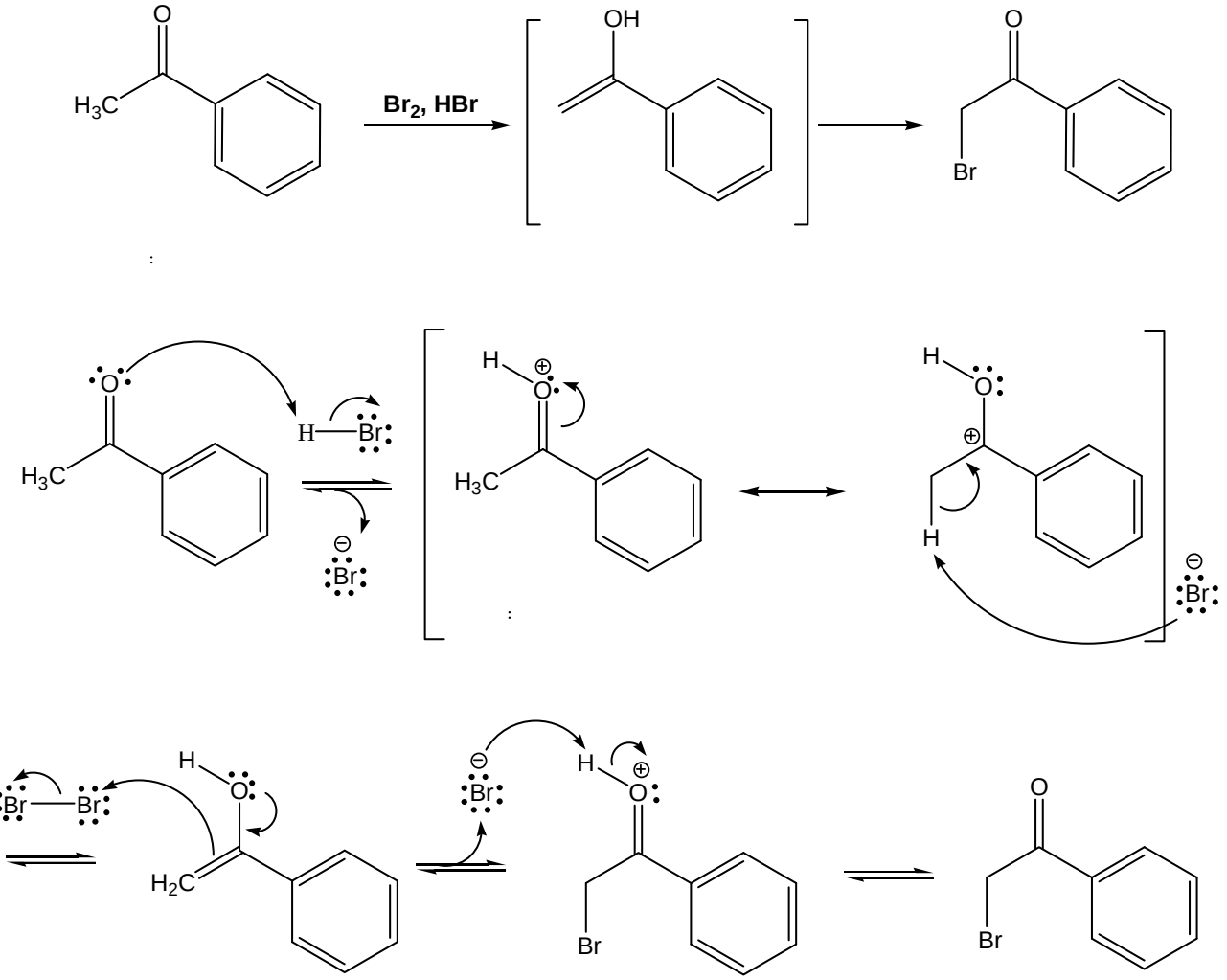


F.



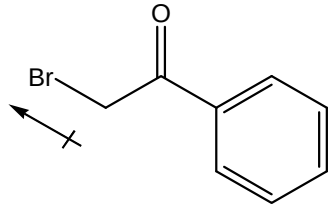
5. (20 points) The bromination of "acetophenone" under acidic conditions occurs by way of an enol intermediate.

A. (15points) Propose a mechanism for this transformation. For each intermediate, draw all lone pair electrons, any formal charges, and all important resonance structures. Use the arrow pushing formalism to interconvert intermediates.



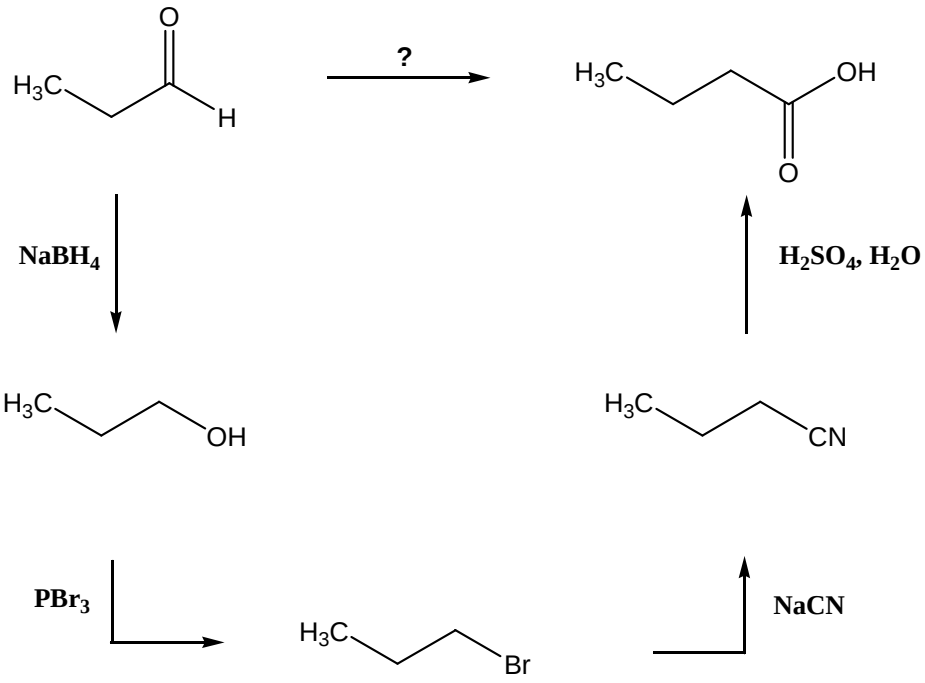
B. (05 points) Based on the mechanism you have proposed, clearly explain why products of "over-bromination" are not observed in this transformation. Draw structures that illustrate key points.

The first bromine atom removes electron density from the adjacent carbonyl through inductive effects causing the lone pairs on the carbonyl to be less basic. This hinders the reaction from proceeding because protonation of the carbonyl, which leads to enol formation, is significantly retarded.

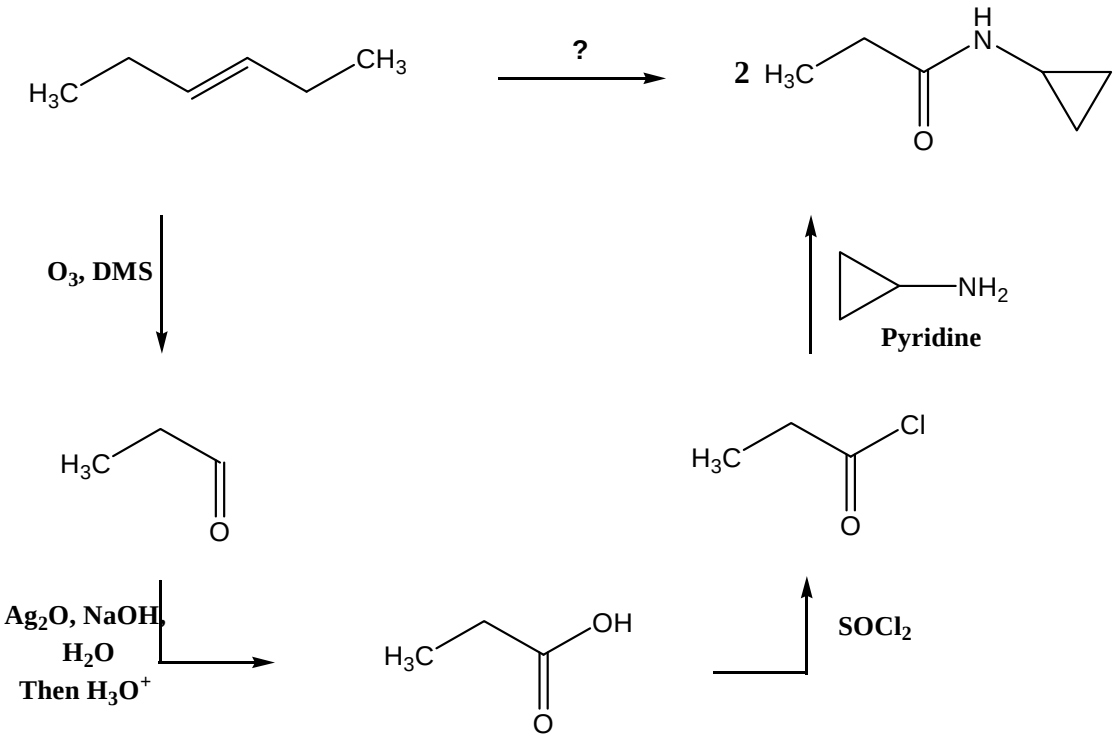


6. (10 points) Devise a synthetic route to accomplish the following transformations. Clearly number each step of your proposed sequence. (Hint: Try to work backwards)

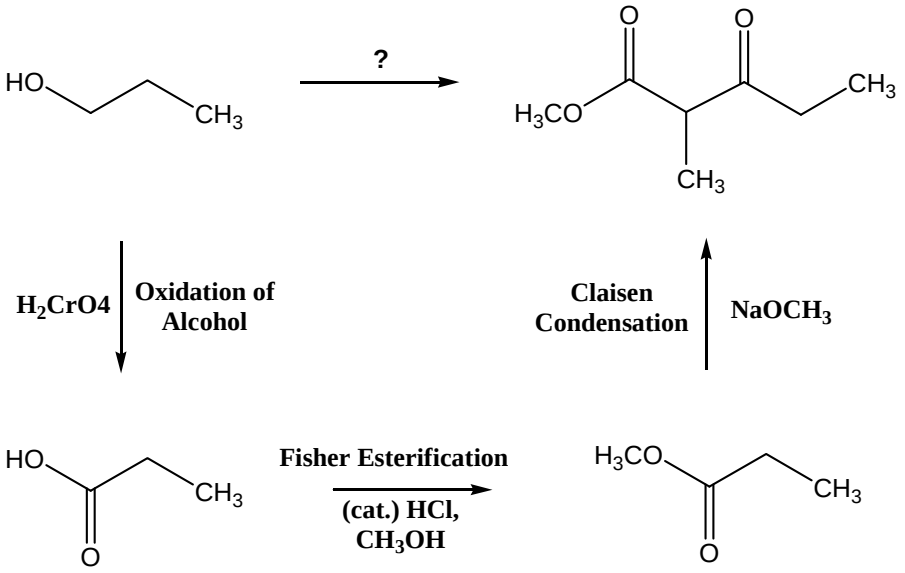
A. (Hint: Notice a 1-carbon homologation has occurred)



B. (Hint: Start with an ozonolysis reaction)



C. (Hint: Think Claisen condensation)



D. (Hint: Employ acetoacetic ester synthesis)