Name_____

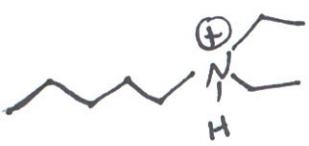
Exam 3
Chemistry 52
August 10, 2012
4-6 pm

Do not open or begin this exam until instructed. This exam consists of 7 pages plus the cover page, 2 scrap pages, and a periodic table. Before starting the exam, check to make sure that you have all of the pages. The exam has a total of 150 points and includes 15 questions. Only legible answers written on the exam will be considered for grading. All pertinent information needed for the exam is given. Notes, textbooks, and electronic communication devices are not permitted. This exam is administered under the Dartmouth College Honor Principle.

Use your time wisely.

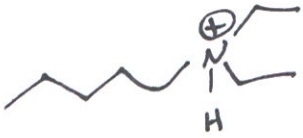
Page Number	Value	Points Awarded
1	30	
2	23	
3	36	
4	23	
5	8	
6	20	
7	10	
Total	150	

1. (6 points) What is the predominate form of N,N-diethylpentanamine at pH 3? pH 7? pH 12?



pH 3

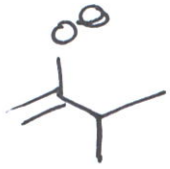
pka ~10 so mostly protonated pH < 10.



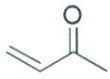
pH 7

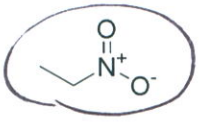
pH 12

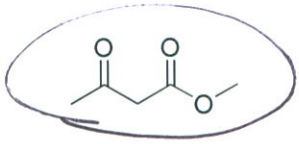
2. (4 points) Provide the structure of the kinetic enolate of 3-methyl-2-butanone.



3. (4 points, 1 each) Circle any of the following compounds that could be easily converted to a Michael donor.







4. (4 points, 1 each) Circle any compounds that are more acidic than methanol.

3-oxobutanal diethyl ether pyrrolidine 2,2,2-trifluoroethanol

5. (4 points, 1 each) Circle any compounds that are more basic than triethylamine.

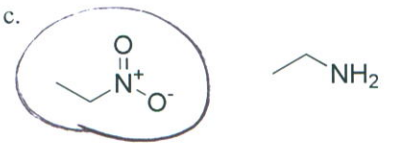
phenol sodium ethoxide sodium butanoate lithium diisopropylamide

6. (8 points, 2 each) For each set, circle the more acidic compound.

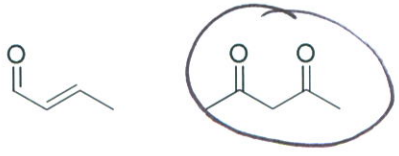
a.

b.

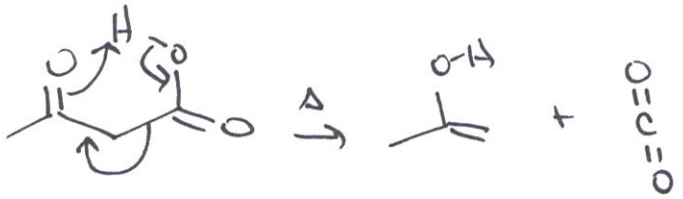
c.



d.



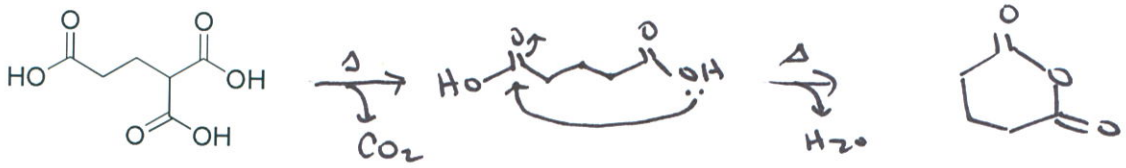
7. (4 points) Draw a β-ketoacid and show with mechanistic arrows how it loses carbon dioxide upon heating.



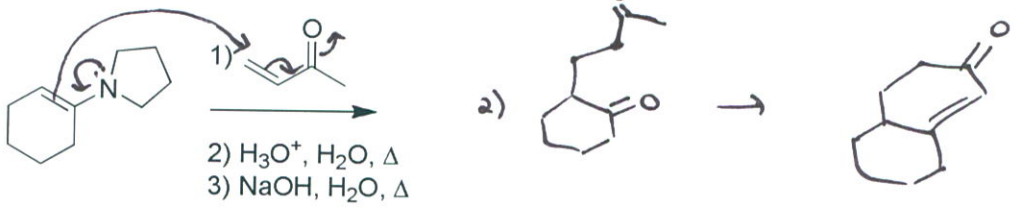
8. (3 points) In the space provided, briefly explain why a chemist might elect a 3-step reaction sequence converting a ketone to an enamine, alkylating the enamine, and then hydrolyzing the enamine back to the ketone over a 1-step direct alkylation of the ketone.

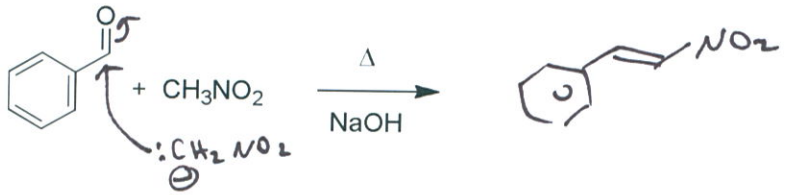
Method avoids over-alkylation.

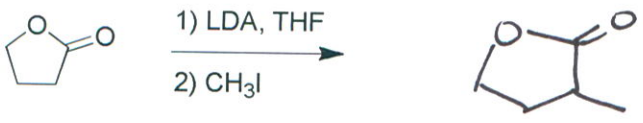
9. (4 points) When the following compound is heated to 230 °C, carbon dioxide and water are evolved. What compound results?

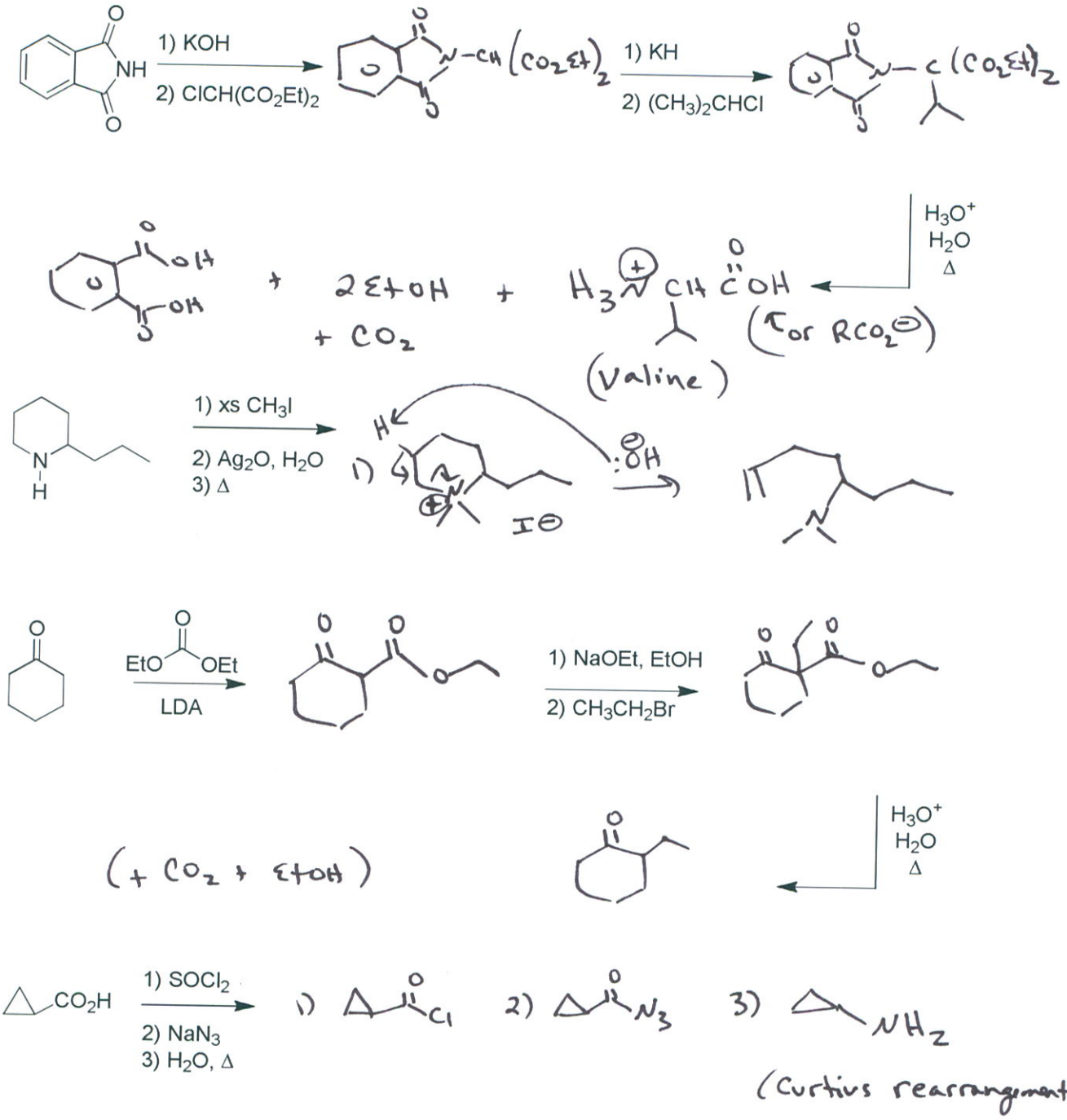


10. (44 points, 4 each) Provide the major organic products of the following reactions

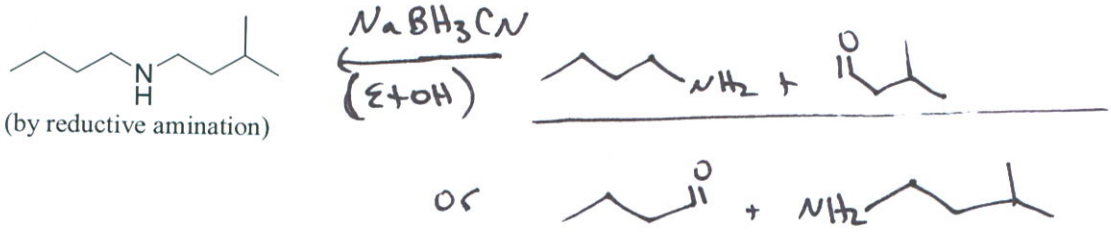


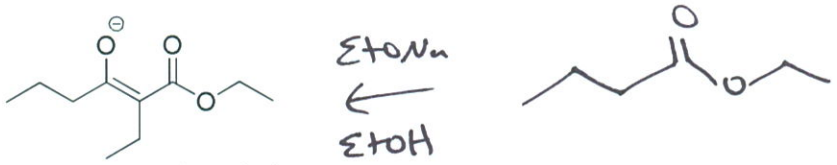




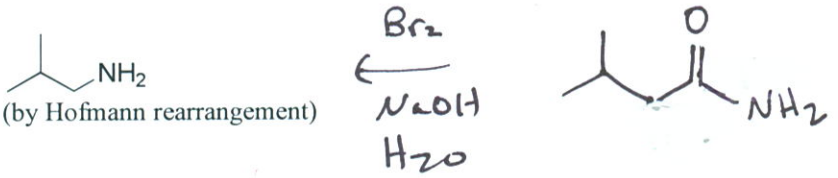


11. (12 points, 4 each) Show the starting materials required to prepare the given compounds by the methods indicated. Only one step is required for each synthesis.



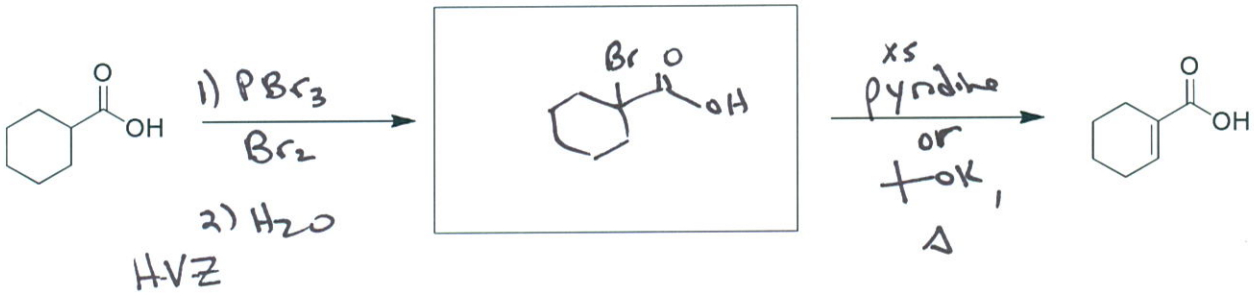


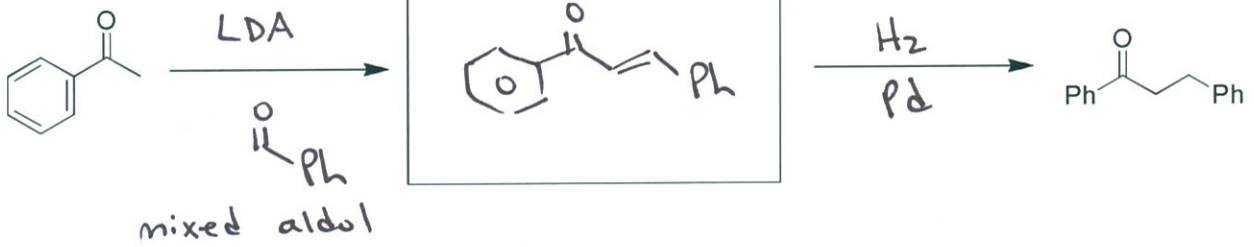
(by Claisen condensation)

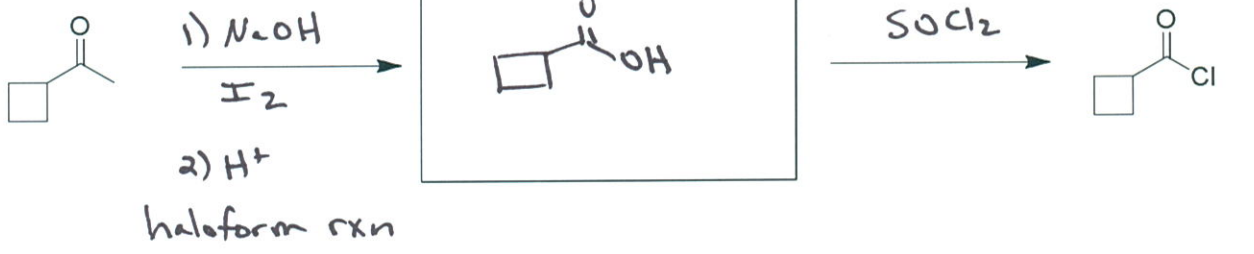


(by Hofmann rearrangement)

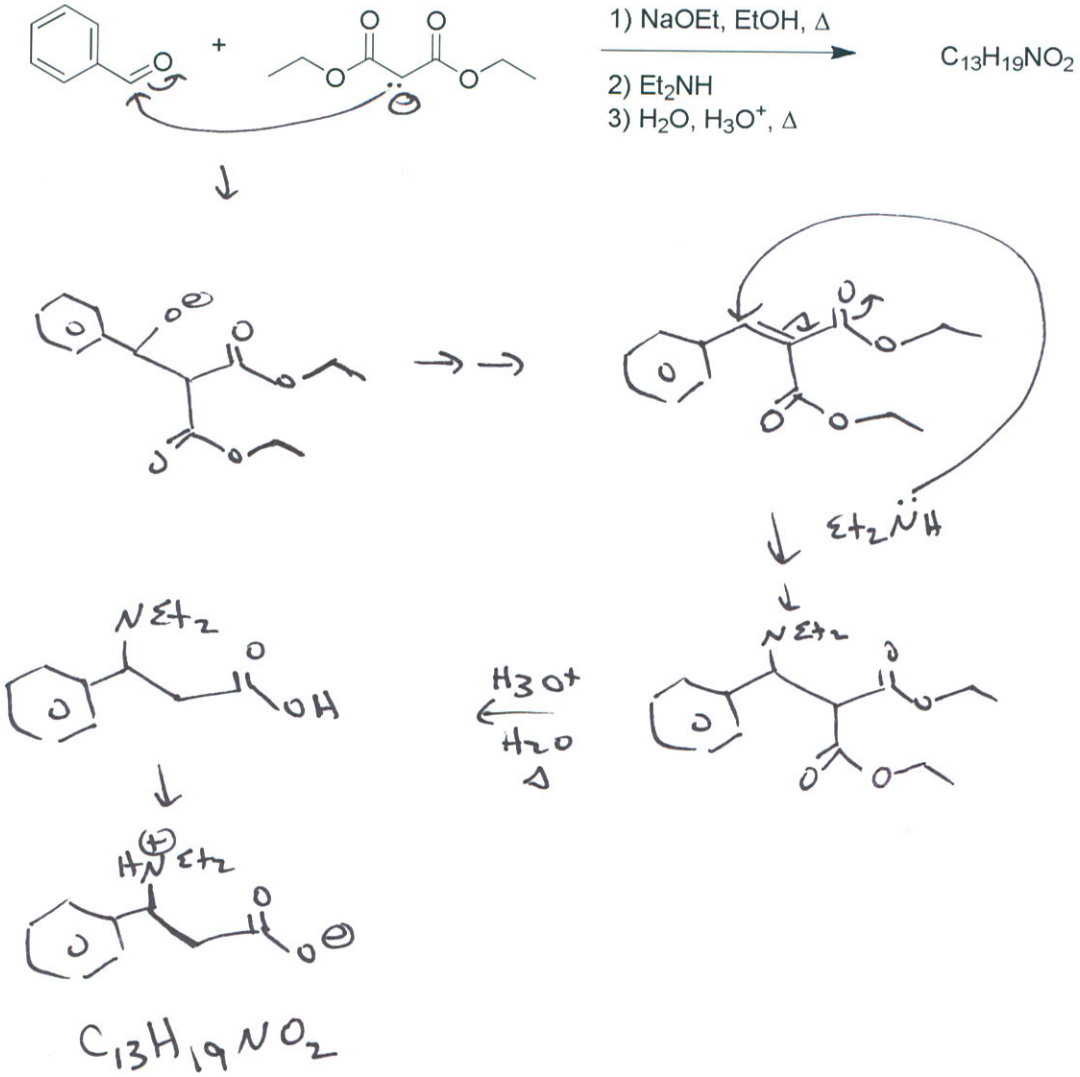
12. (15 points, 5 each) Complete the following short syntheses by providing reagents over arrows and intermediate compounds in the boxes. All can be completed in two or three steps.

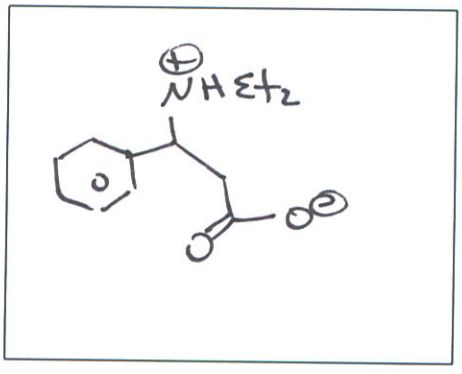




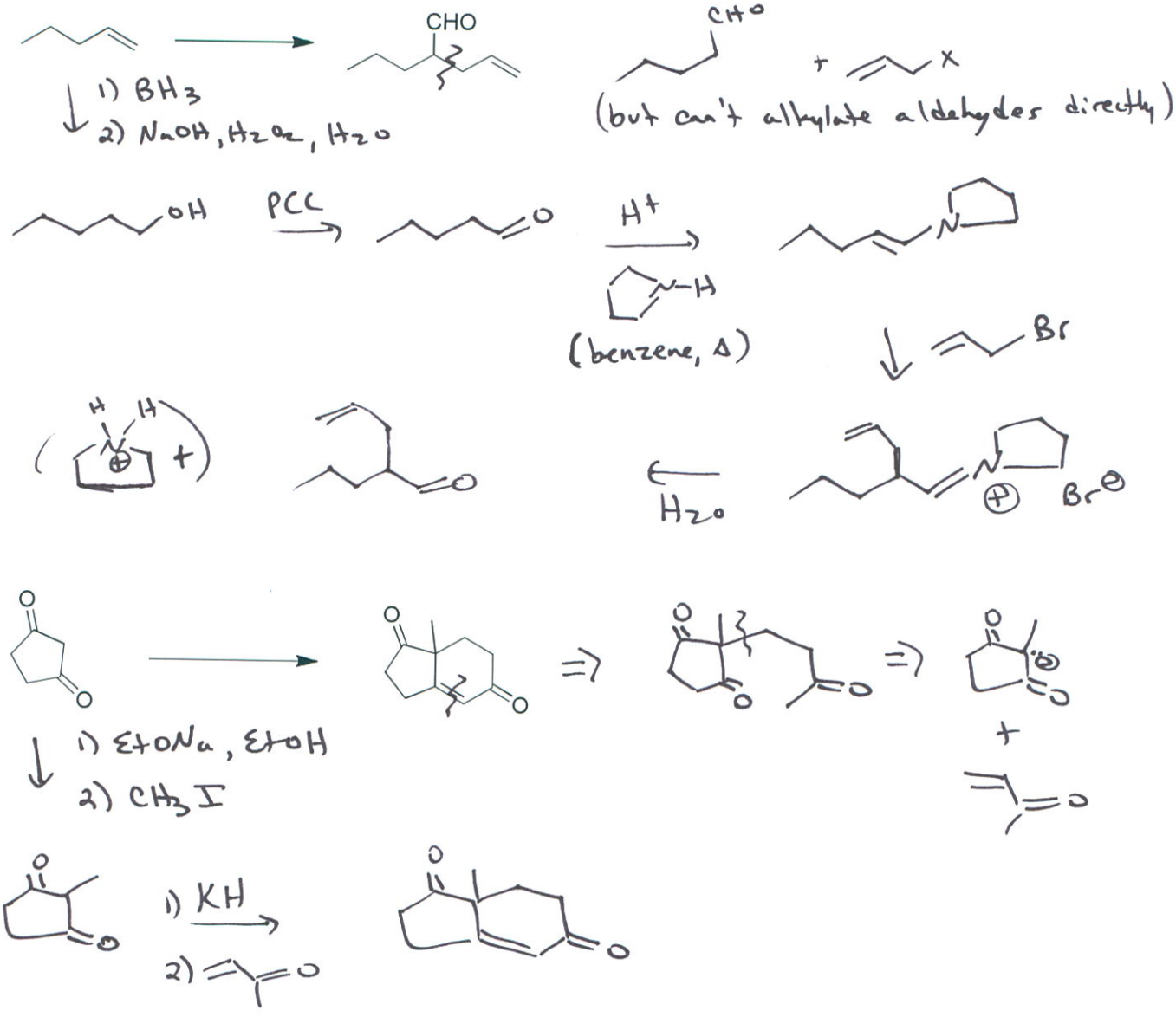


13. (8 points) Provide the structure of the product of the following reaction sequence. For partial credit, it is advisable to show intermediates as they are formed or an outline of the mechanism. Electron-pushing arrows are not required. Place your final answer in the box.





14. (20 points, 10 each) Provide the necessary reagents for the following conversions. Clearly separate the steps. In addition to the given starting material, you may use any reagents you need. You must make any organometallic reagents and ylides if you plan to use them. You are strongly encouraged to show the product of each step so that partial credit can be awarded when appropriate.



15. (10 points) Provide a complete electron-pushing mechanism for the following reaction. Clearly indicate each step of the reaction, including any proton transfers.