

CH 254, Spring 2008

Name

KEY

Exam #4, 9 May 2008

(PRINT CLEARLY PLEASE!)

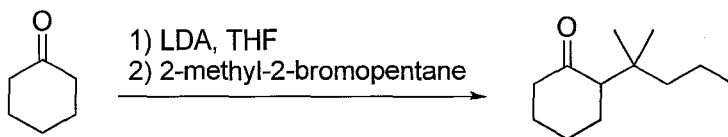
Question #	Points Possible	Points Received
1	20	
2	15	
3	15	
4	16	
5	8	
6	8	
7	18	
Subtotal	100	
Extra Credit	9	
Total	109	

1. (20 points) Multiple Choice. For each question, circle ONE answer.

A. Which is the only one of these compounds which cannot self-condense in the presence of dilute aqueous NaOH?

- a. phenylethanal
- b. propanal
- c. 2-methylpropanal
- d. 3-methylpentanal
- ☒ e. 2,2-dimethylpropanal

B. A student proposed the following synthesis. Why did it fail?



- a. The use of LDA results in the thermodynamic product instead of the desired kinetic product.
- b. LDA is insoluble in the THF solvent so the reaction is too slow to occur at a useful rate.
- c. LDA acts as a nucleophile instead of a base in its reaction with cyclohexanone.
- ☒ d. The tertiary bromide is too sterically hindered to be attacked by the enolate.
- e. Instead of 2-methyl-2-bromopentane, 2-bromo-3-methylpentane should have been used to anticipate a cationic rearrangement that would occur.

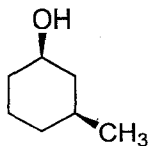
C. In the Michael reaction, addition to the  $\alpha,\beta$ -unsaturated carbonyl occurs in a:

- a. 1,2-fashion
- b. 1,3-fashion
- ☒ c. 1,4-fashion
- d. 1,5-fashion
- e. Diels-Alder reaction

D. In the chromic acid oxidation of alcohols, the chromium is:

- ☒ a. reduced from  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$
- b. oxidized from  $\text{Cr}^{+6}$  to  $\text{Cr}^{+3}$
- c. reduced from  $\text{Cr}^{+3}$  to  $\text{Cr}^{+6}$
- d. oxidized from  $\text{Cr}^{+3}$  to  $\text{Cr}^{+6}$
- e. none of the above

E. When the optically active alcohol shown here is oxidized by  $\text{H}_2\text{CrO}_4$ , the product is:

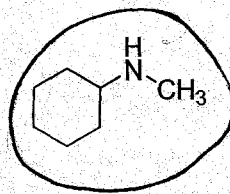
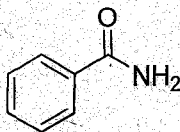
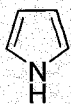
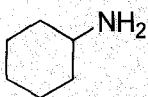


- a. a ketone which is meso and optically active
- ☒ b. an optically active ketone
- c. a racemic mixture of ketones which is optically inactive
- d. an aldehyde which is meso and optically active
- e. an acyclic carboxylic acid

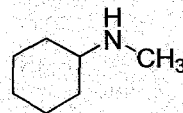
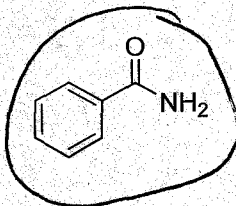
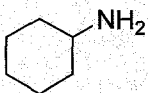
F. Which of the following reagents is not an oxidizing agent?

- a.  $\text{KMnO}_4$
- b.  $\text{CrO}_3$
- ☒ c.  $\text{NADH}$
- d. PCC
- e.  $\text{HIO}_4$

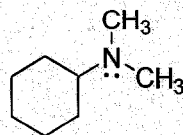
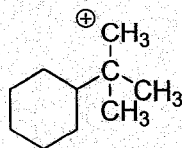
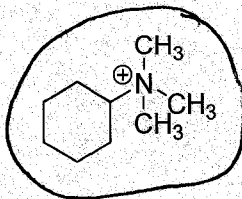
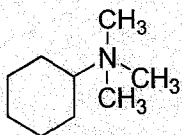
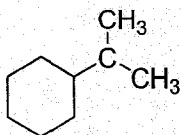
G. Which of the following is the most basic?



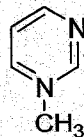
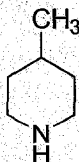
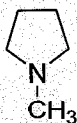
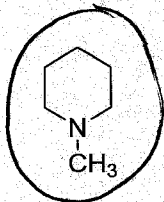
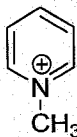
H. Which of the following is the least basic?



I. Which of the following is a quaternary ammonium ion?



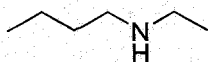
J. Which of the following is the correct structure of N-methylpiperidine?



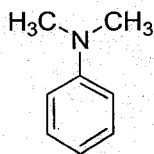
2. (15 points) Nomenclature. Name each of the following compounds using acceptable IUPAC nomenclature. Don't forget to indicate stereochemistry where appropriate.



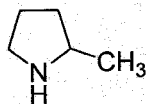
ammonia



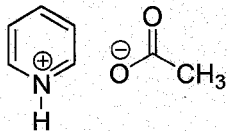
N-ethyl-1-butanamine



N,N-dimethylaniline

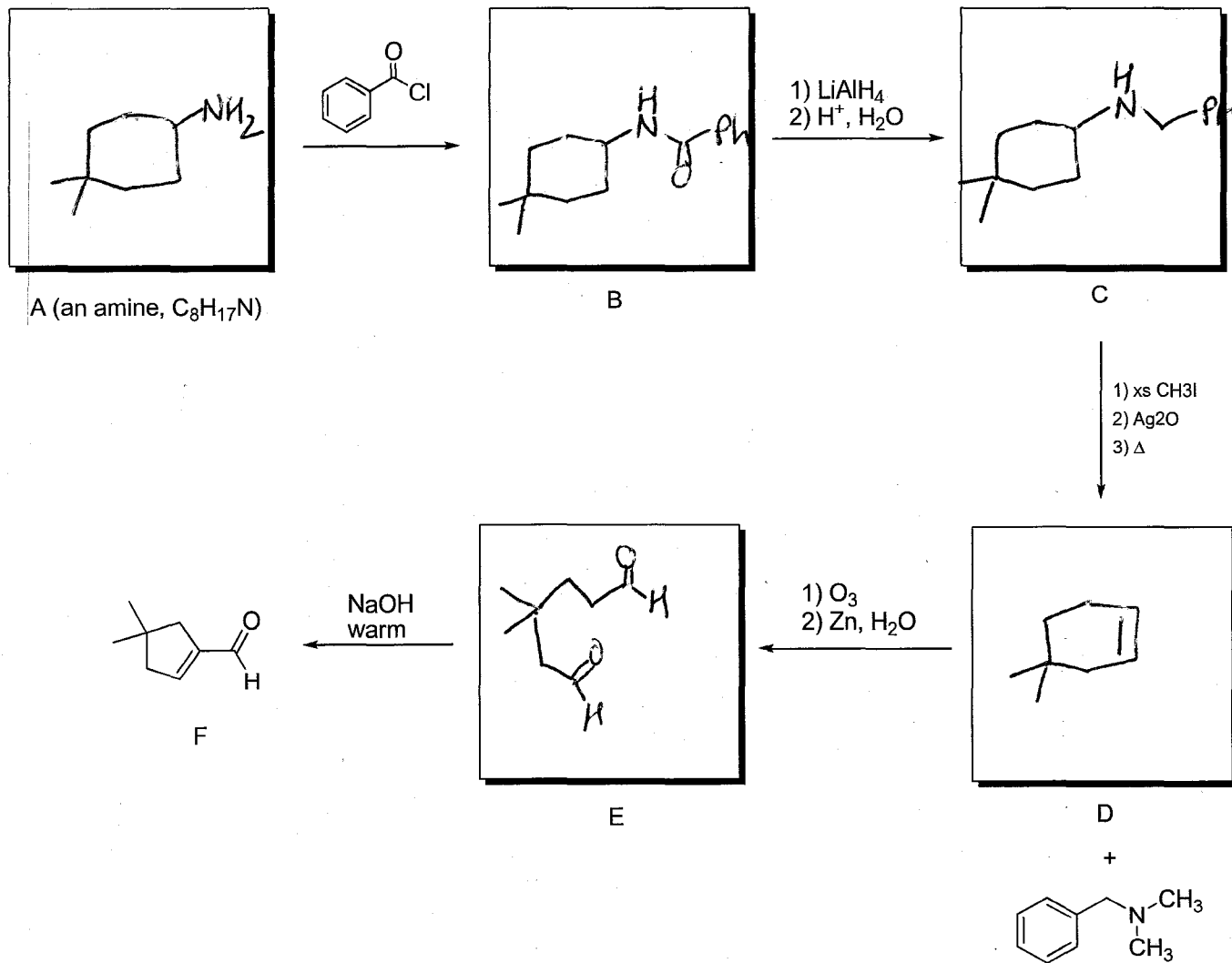


2-methylpyrrolidine



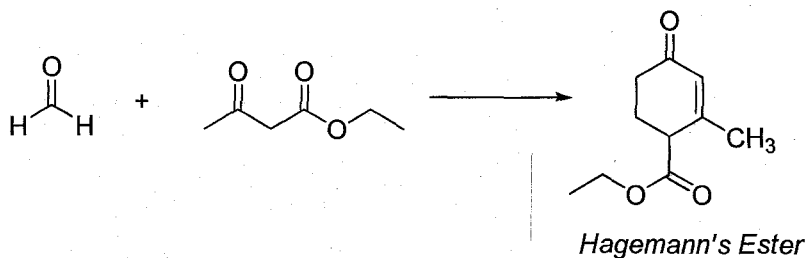
pyridinium acetate

3. (15 points) Box problem! Fill in the missing compounds so as to complete the scheme shown below.

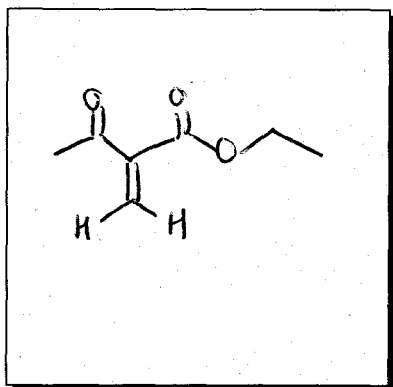


3 pts each

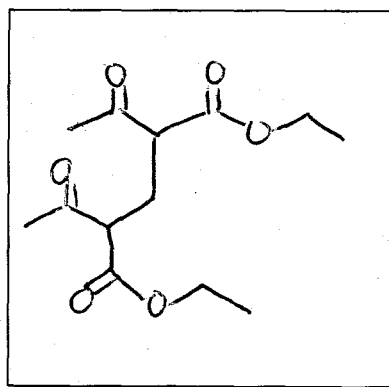
4. (16 points) A compound known as *Hagemann's Ester* can be prepared by treating a mixture of formaldehyde and ethyl acetoacetate first with base and then with acid and heat. Write the structure for the product of each step.



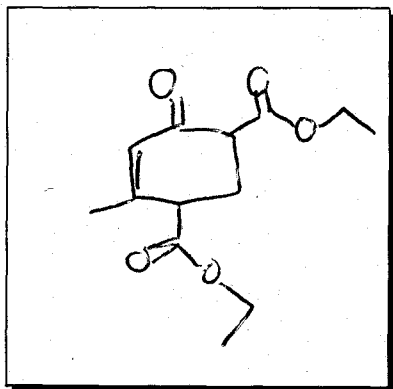
- The first step is an aldol-like condensation.
- The second step is a Michael addition.
- The third step is an intramolecular aldol condensation.
- The fourth step is a hydrolysis followed by a decarboxylation.



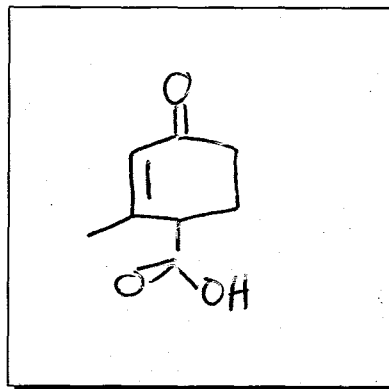
product of step (a)



product of step (b)

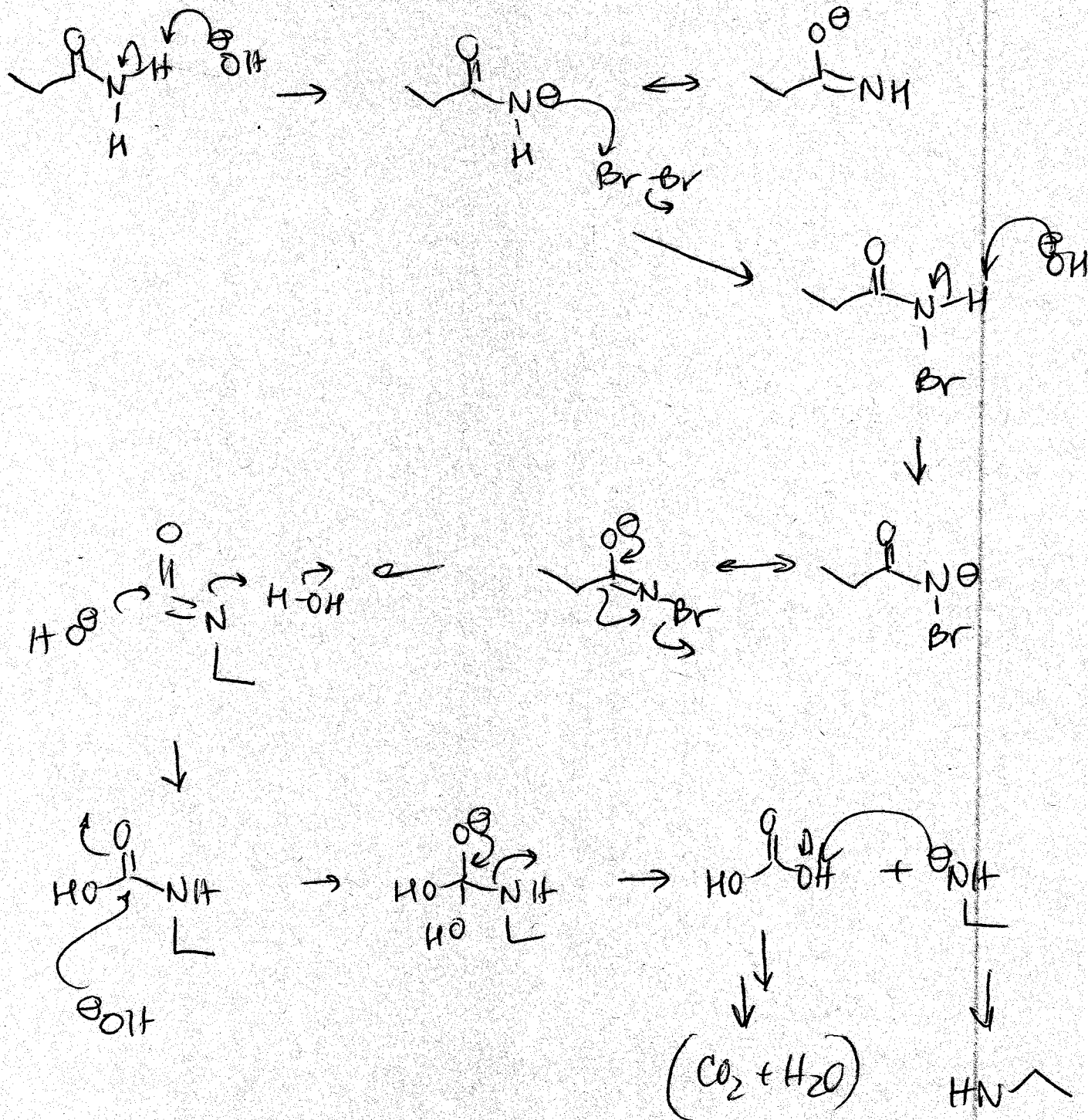
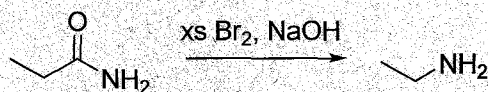


product of step (c)



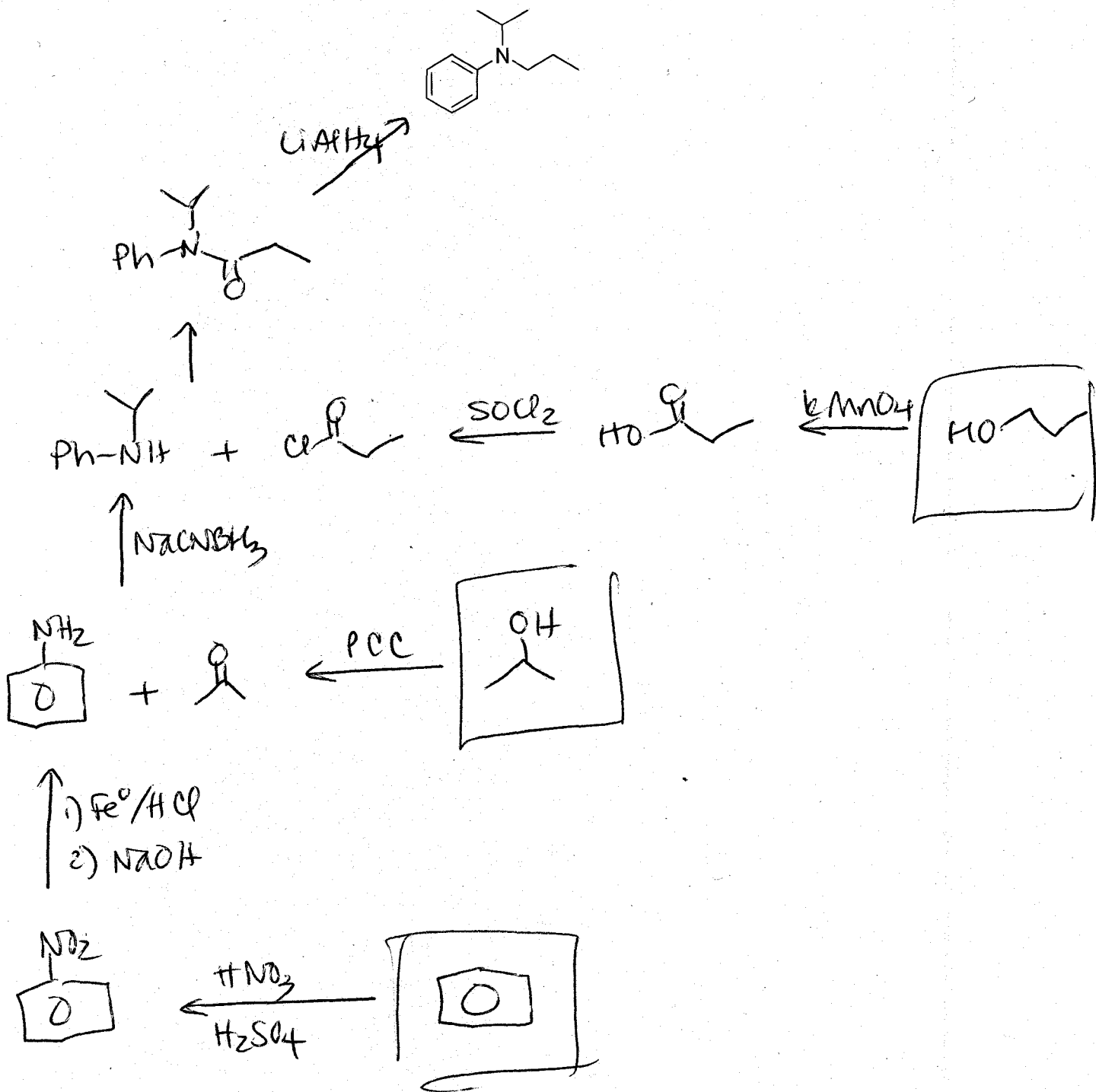
product of step (d)

5. (8 points) Provide a mechanism for the following transformation, using proper electron-pushing formalisms.

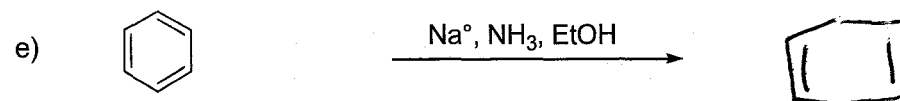
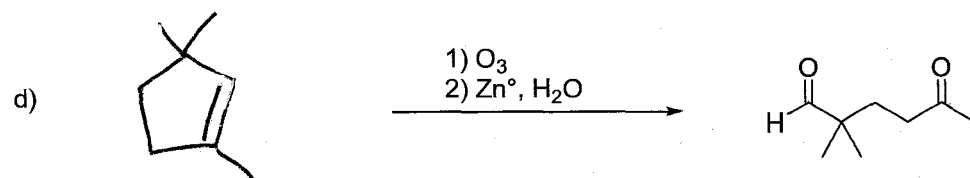
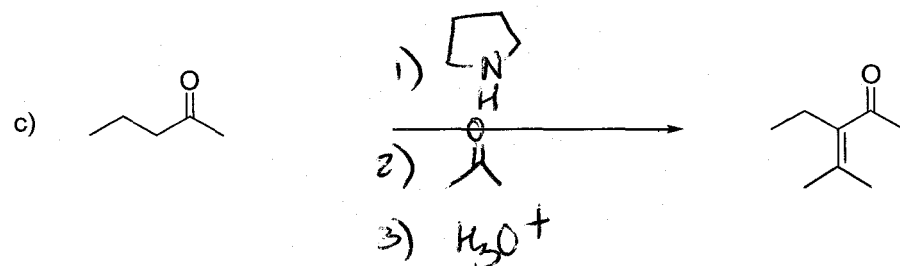
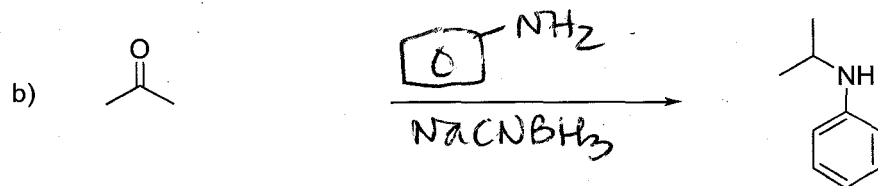
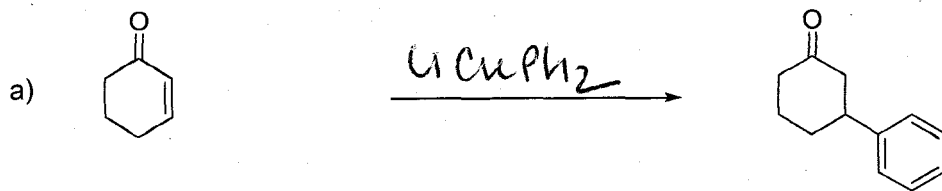




6. (8 points) Provide a synthesis of the following compound. Allowable starting materials include any three-carbon or less alcohol or alkyl halide, benzene, and any necessary inorganic reagents. Show all isolable intermediates. No mechanisms, please!

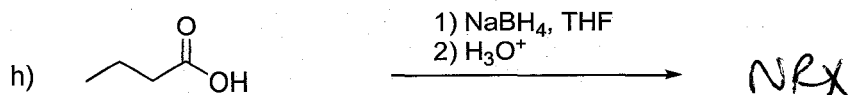
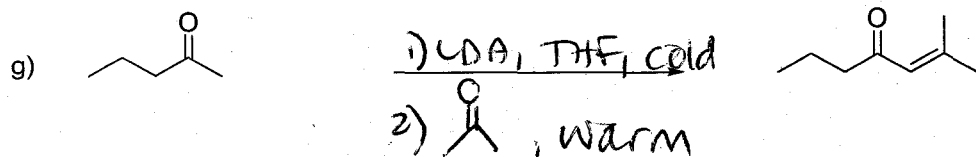
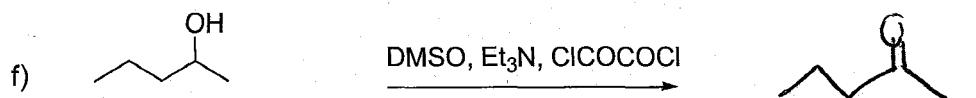


7. (18 points) Fill in the missing information so as to successfully complete each indicated reaction. (Keep in mind that "NRX" is always a viable product.) Your best five of the seven shown will be graded.



(continued on next page)

(from previous page)



**Extra Credit:**

1. Name the following reactions:

- a. C  $\rightarrow$  D in Problem #3    Hofmann elimination
- b. E  $\rightarrow$  F in Problem #3    aldol
- c. #5    Hofmann rearrangement
- d. #7c    Stork
- e. #7e    Birch reduction
- f. #7f    Swern oxidation
- g. #7g    aldol

2. The only member of this Texas trio who doesn't have a beard is named Beard. What's the name of the band?

ZZ Top