Massachusetts Institute of Technology

5.13: Organic Chemistry II *Dr. Sarah A. Tabacco*

Hour Exam #3
November 12, 2003

Printed Name Key **Signature**_____

MIT ID #_____ **Recitation TA**_____

General Instructions:

- **This is a closed book exam.** No books, notes, or calculators allowed. You are allowed to use molecular models.
- Make sure that your exam has **11 pages** (including cover, a blank page for extra work, and a periodic table).
- Write your name on each page.
- Write answers in the spaces provided. If you run out of room, use the blank page and **indicate this for your grader.**
- Show all of your work if you wish to receive partial credit.
- Read the instructions **carefully**, and budget your time.

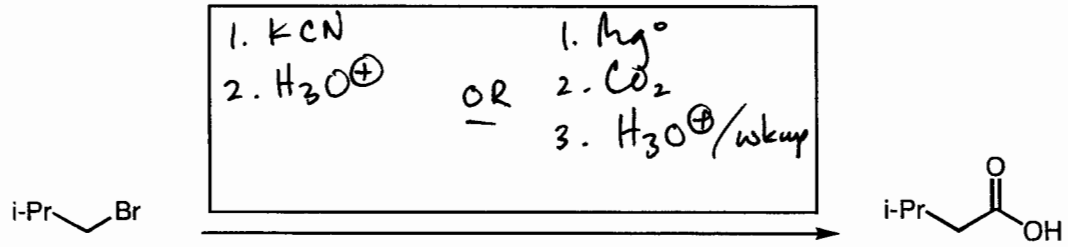
- **GOOD LUCK!!**

1	/8	
2	/8	
3	/16	
4	/12	
5	/12	
6	/11	
7	/22	
8	/11	

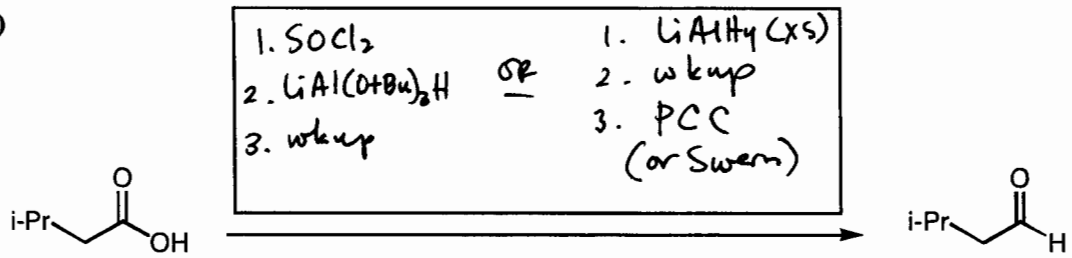
Total_____
(out of 100 points)

1. (4 points each, 8 points total) In the boxes, please provide the reagents for the illustrated transformations. More than one step may be required.

a)

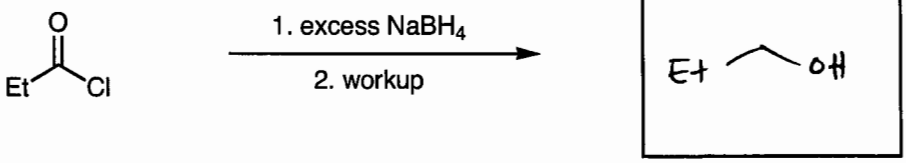


b)



2. (2 points each, 8 points total) Please provide the products of the following reactions. If no reaction is expected, write "NR".

a)



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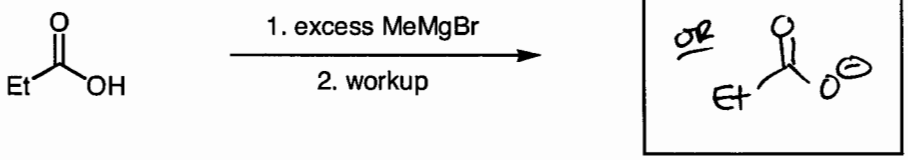
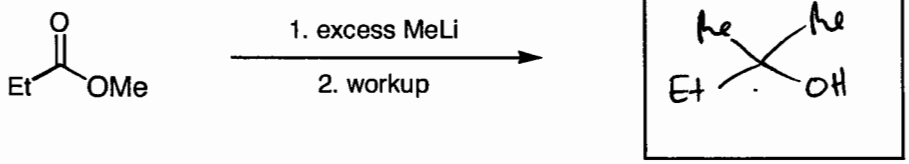
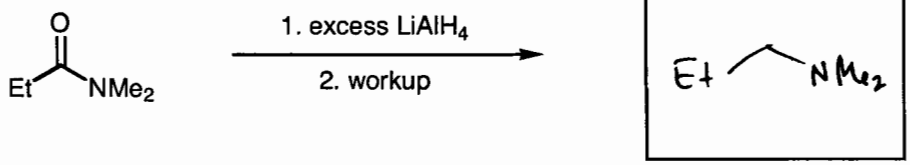


c)



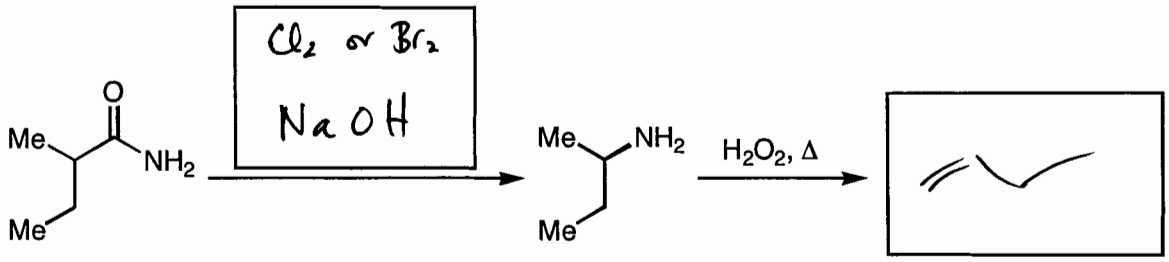
d)



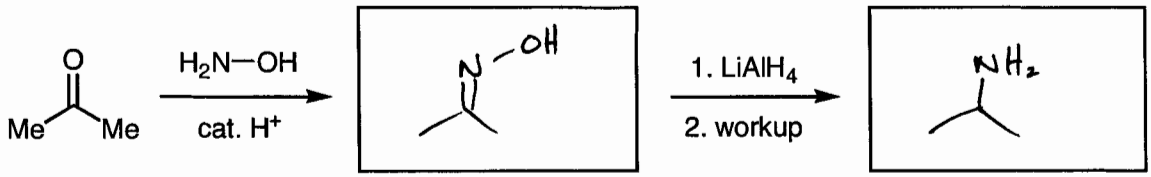
Name Key

3. (2 points each, 16 points total) Please provide the requested products or reagents. If no reaction is expected, write "NR".

a)



b)



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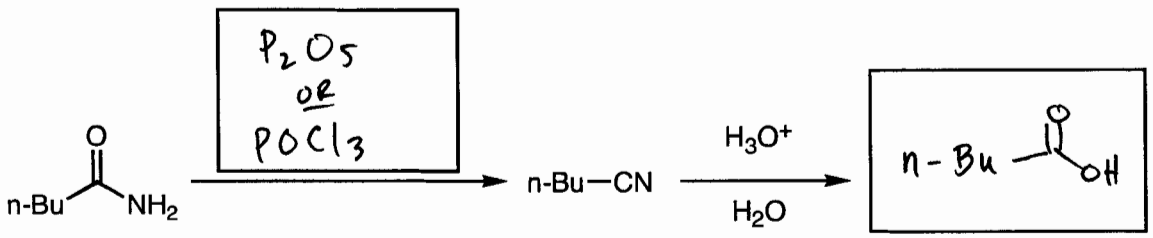
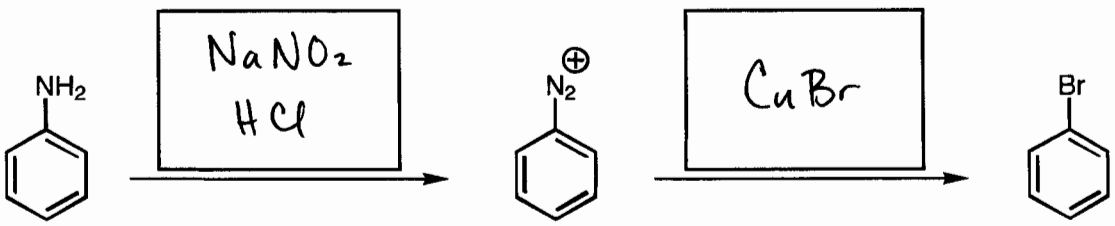


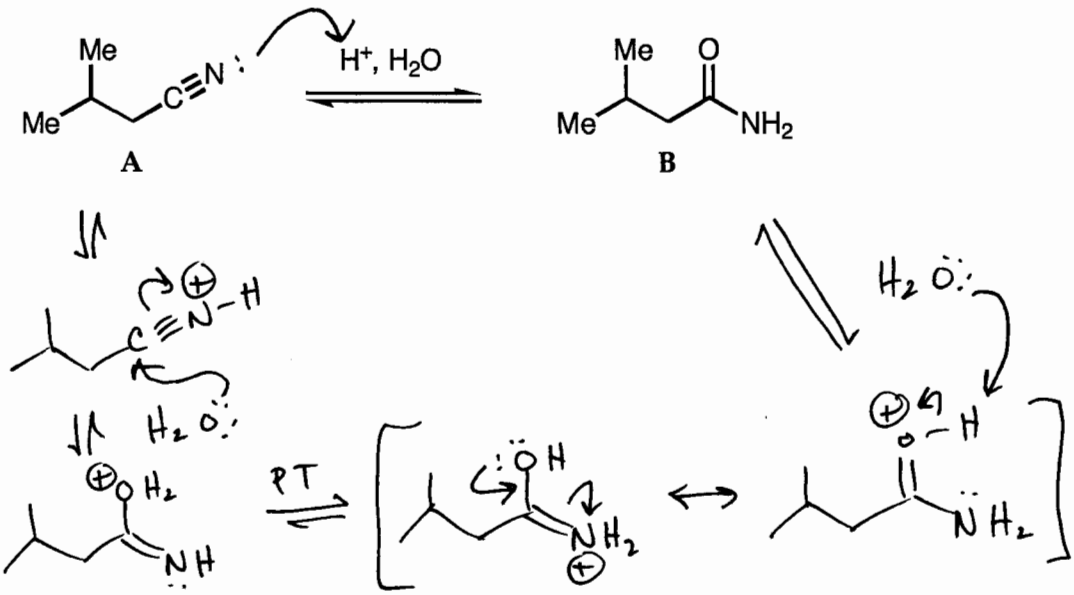
d)



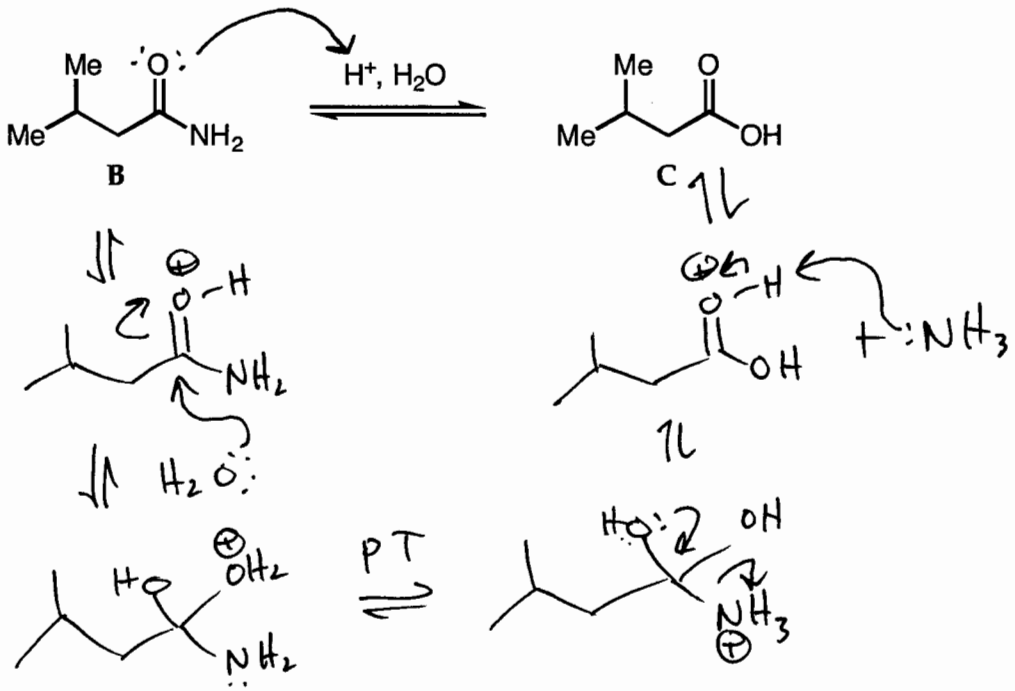
Name Key

4. (12 points) The hydrolysis of a nitrile (**A**) to a carboxylic acid (**C**) involves initial formation of a primary amide (**B**). Provide a detailed mechanism for each the following transformations.

a)

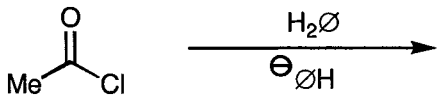


b)



Name Key

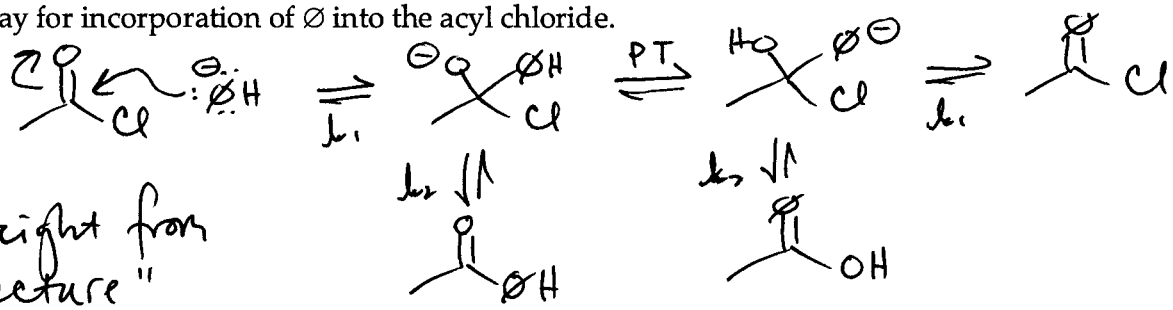
5. (12 points) Consider the labeling experiment outlined below:



stop the reaction at 50% conversion and examine the recovered acyl chloride for incorporation of Ø

Ø = isotopically labeled oxygen (^{18}O)

a) Please provide the mechanism for the hydrolysis reaction shown above, including the pathway for incorporation of Ø into the acyl chloride.



"straight from lecture"

(do not need to label k_1/k_{-1})

b) What level of Ø incorporation ("high" or "low") you would expect to observe in the recovered acyl chloride? Explain briefly.

Incorporation of the label into the acyl chloride would be very low. $Cl^\ominus$ is a much better LG than $^\ominus OH$, so hydrolysis is much faster than label incorporation.

($k_2 \gg k_1$)

c) Based on your answer to part **b**, do you think the results of this labeling study definitively prove the mechanism of this reaction? Explain briefly.

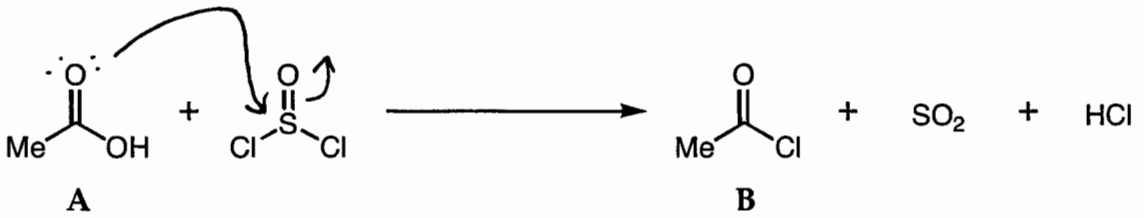
No. Explanation #1: It is impossible to definitively prove a mechanism!

Explanation #2: No incorporation of label is consistent w/ S_N2! add'n/elim.

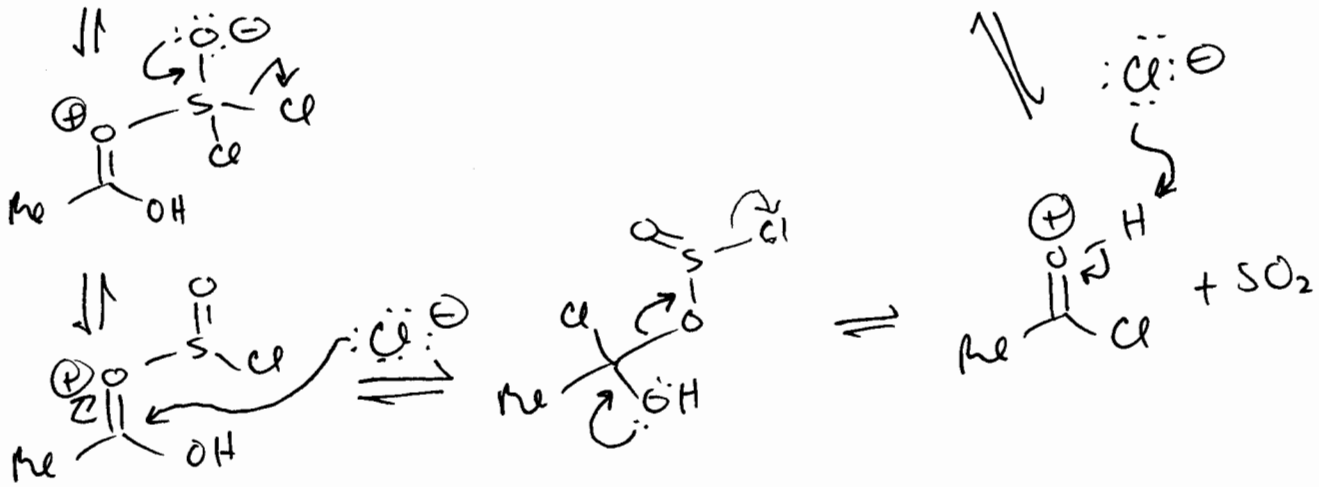
Name Key

6. (11 points) Provide a detailed mechanism for the illustrated conversion of acetic acid (**A**) to acetyl chloride (**B**).

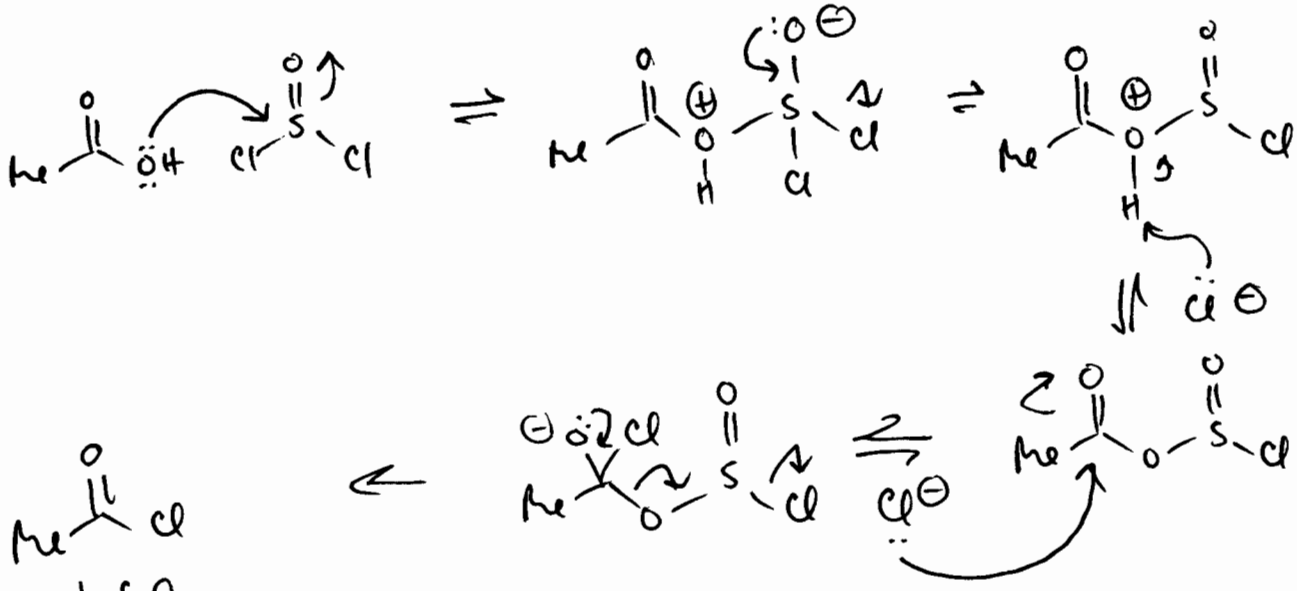
From lecture:



A **B**



From Wade:

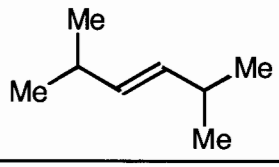


The mechanism given in lecture is more compelling for several reasons, but either one was accepted for full credit.

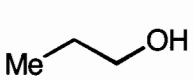
Name Key

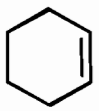
7. (11 points each, 22 points total) Please provide syntheses for **only two of the three** indicated compounds. All of the carbon atoms should be derived from the allowed starting materials. You may use any common reagents.

Allowed Starting Materials:



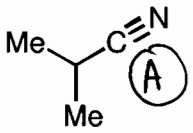
CO_2

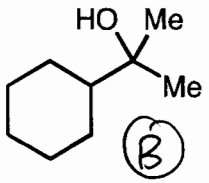




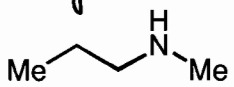
Me–OH

Pick Two:



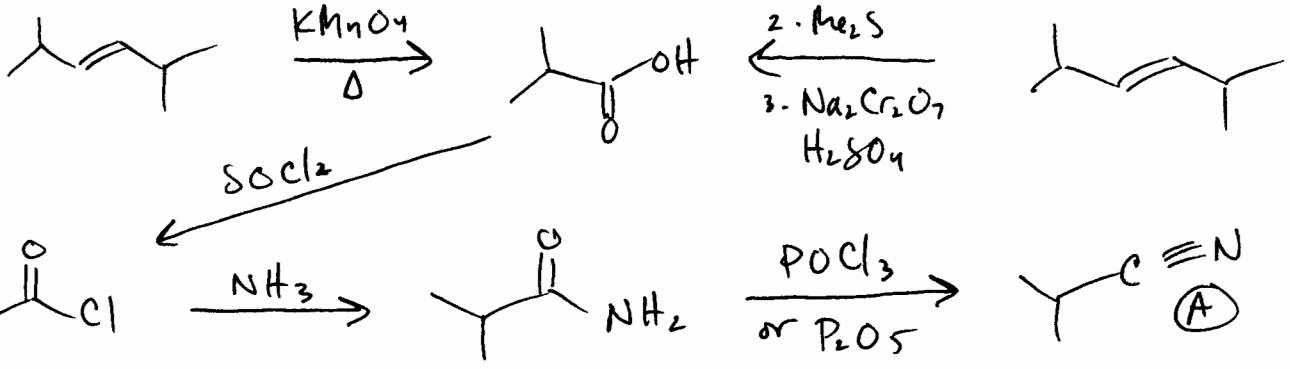


There are other acceptable ways to make all of these molecules.

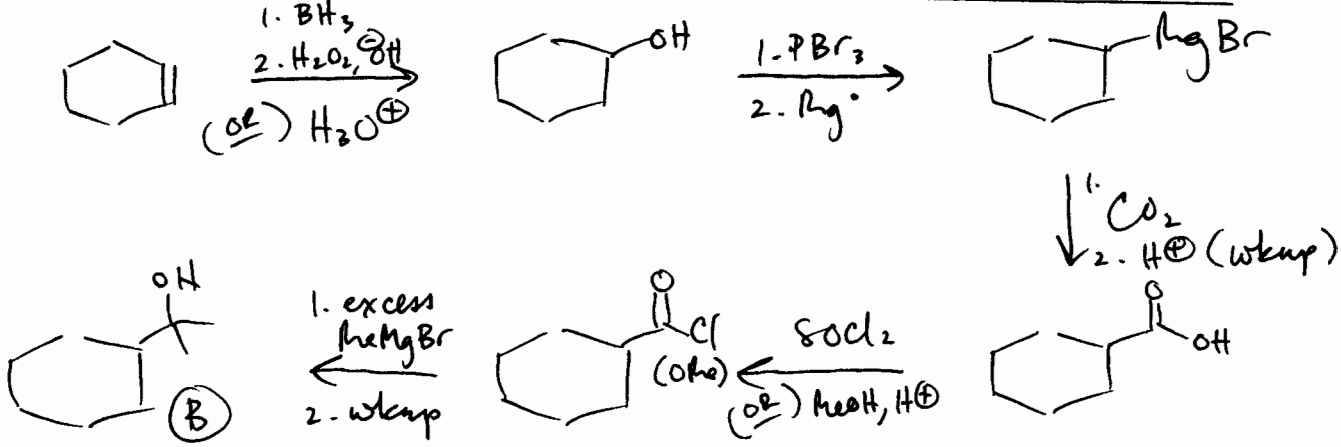


Synthesis #1:

(A)



(B)

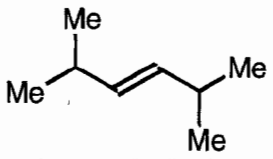


(MeOH $\xrightarrow[2.\ Mg^{\circ}]{1.\ PBr_3}$ MeMgBr)

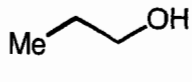
Name Key

7. (continued)

Allowed Starting Materials:

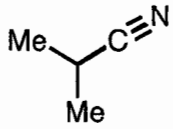


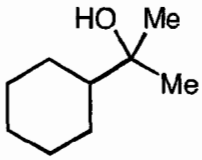
CO_2

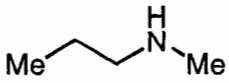


Me–OH

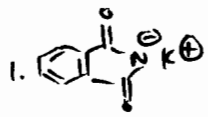
Pick Two:





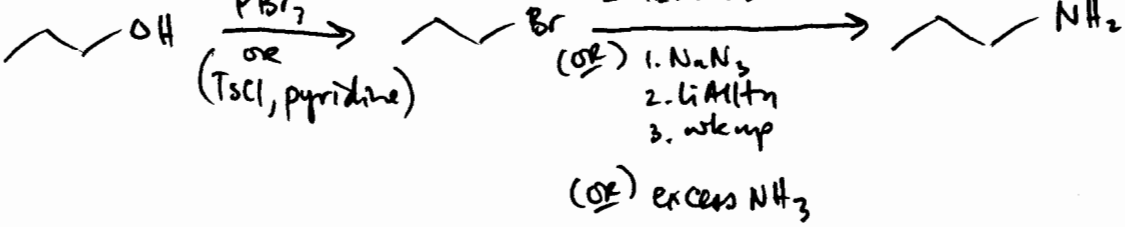


Synthesis #2:



2. H_2NNH_2

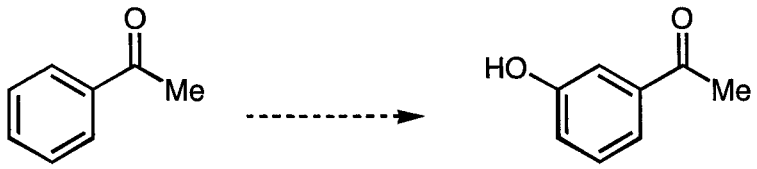
(c)



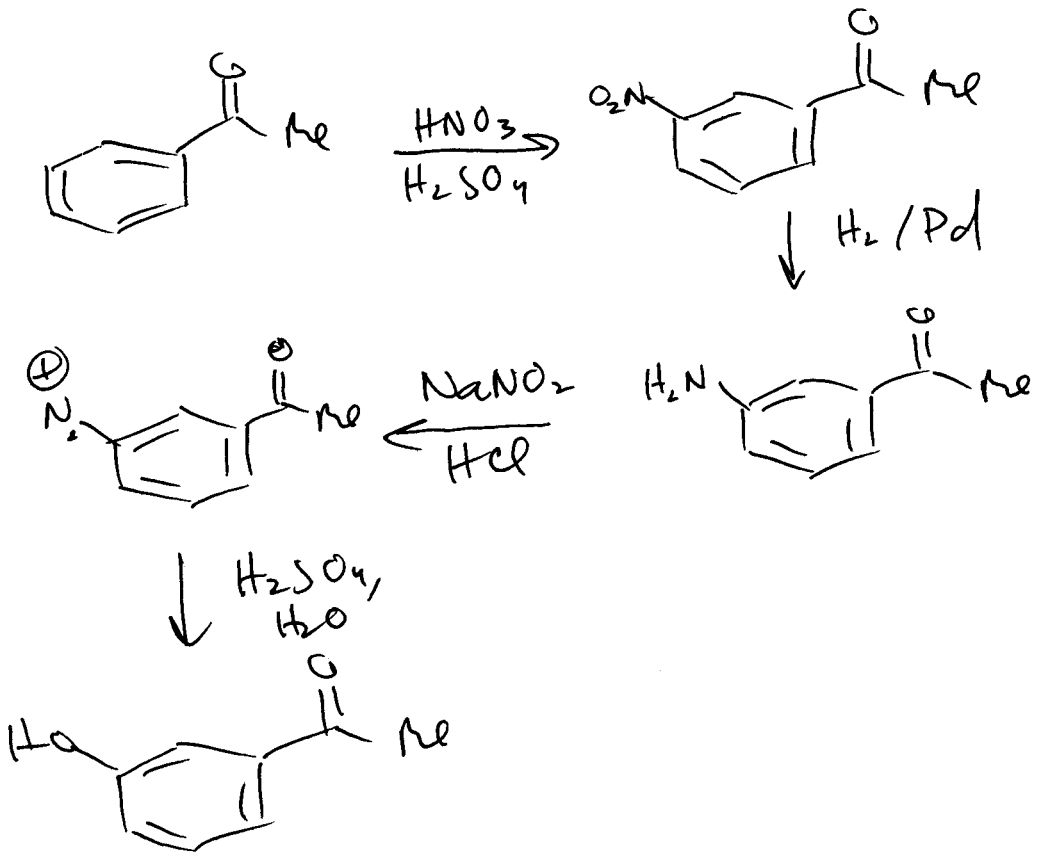
. there are also acceptable routes using acylation/reduction & Hofmann rearrangement.

Name Key

8. (11 points) Provide a synthesis that will *selectively* convert **A** to **B**. Show all of the key intermediates and furnish all of the important reagents. This is not a one-step process.



A **B**



Name Key