

KEY

Massachusetts Institute of Technology
Dr. Kimberly L. Berkowski

5.13, Fall 2006
Organic Chemistry II

PRACTICE EXAM #3

Hour exam #3 will be held on Wednesday, November 15, from 12:05-12:55.

Location:

If your last name begins with A-L, report to 54-100.

If your last name begins with M-Z, report to 2-190.

A 10 point deduction for reporting to the wrong room.

Books, notes, and calculators **will not** be allowed during the exam.

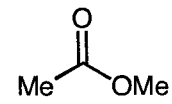
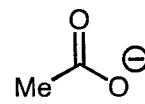
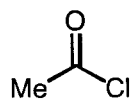
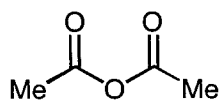
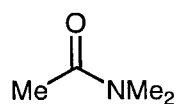
Molecular model kits **will** be allowed during the exam. You will be given a periodic table and blank pages.

Material Covered on Exam #3:

- Everything presented in lecture related to Amines, Carboxylic Acids, and Carboxylic Acid Derivatives
- Recitation and Drill Problems
- Problem Sets 5 and 6
- McMurry Chapters 20, 21, 24
- All 5.12 material.

The answer key will be posted on Monday

1. Rank the following acyl derivatives based on their reactivity as electrophiles toward hydroxide ion (1 = most reactive, 5 = least reactive).



4

2

1

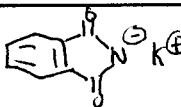
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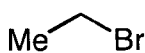
3

2. In the boxes, please provide the reagents for the illustrated transformations. More than one step may be required.

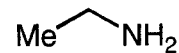
a)

1. NaN_3
 2. LiAlH_4 or
 3. H_2O

1.  K^+ or excess NH_3
 2. H_2NNH_2

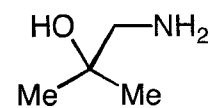
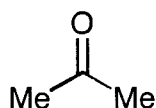


WITHOUT over-alkylation

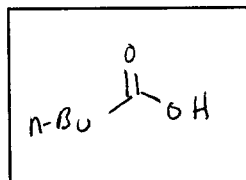
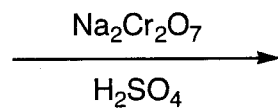
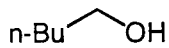
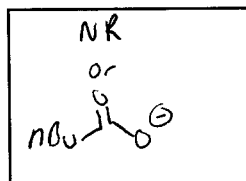
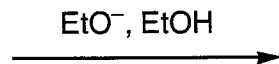
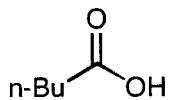
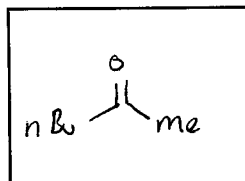
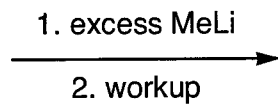
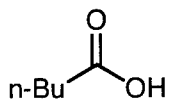
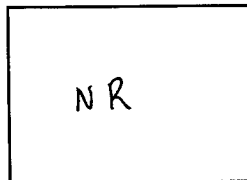
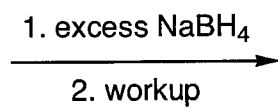
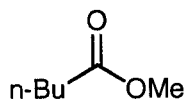
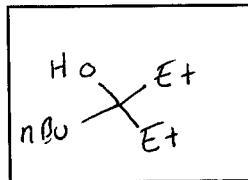
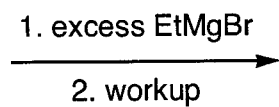
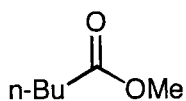
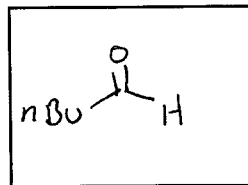
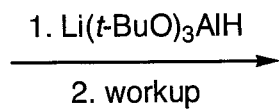
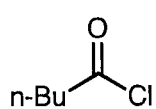


b)

1. HCN , cat. KCN
 2. LiAlH_4
 3. H_2O

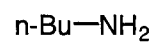
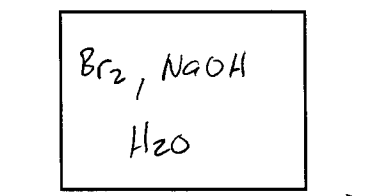
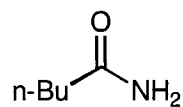


3. Please provide the requested products. If no reaction is expected, write "NR".

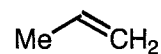
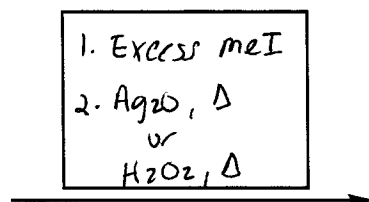
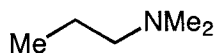


4. Please provide the requested reagents.

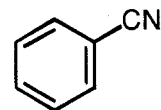
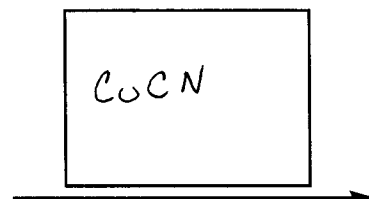
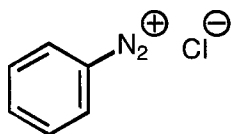
a)



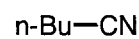
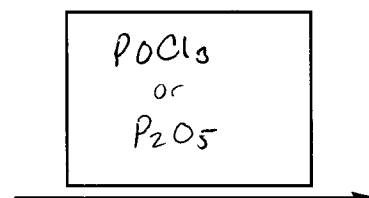
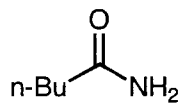
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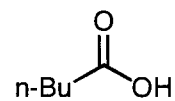
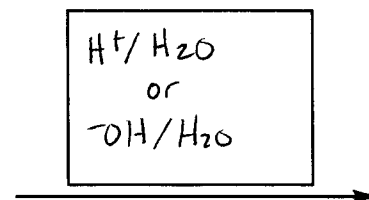
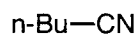
c)



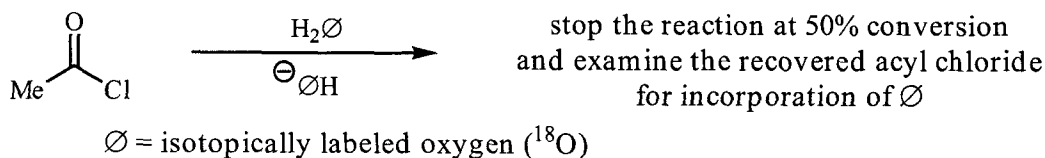
d)



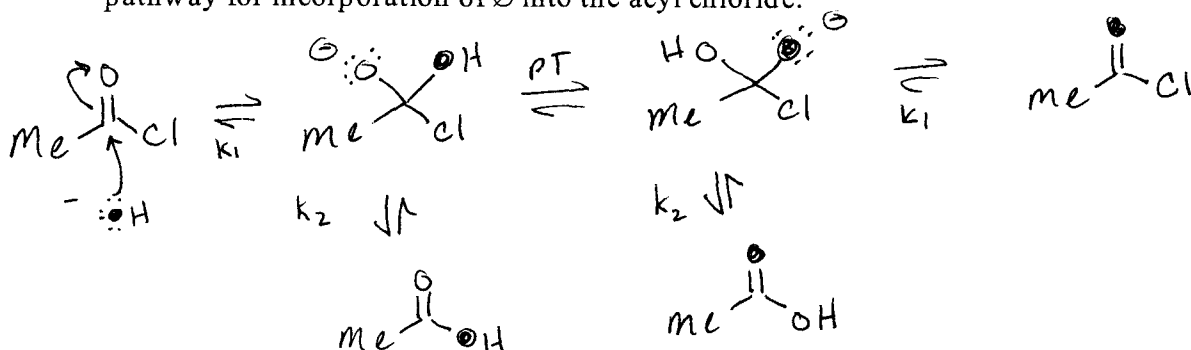
e)



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



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



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

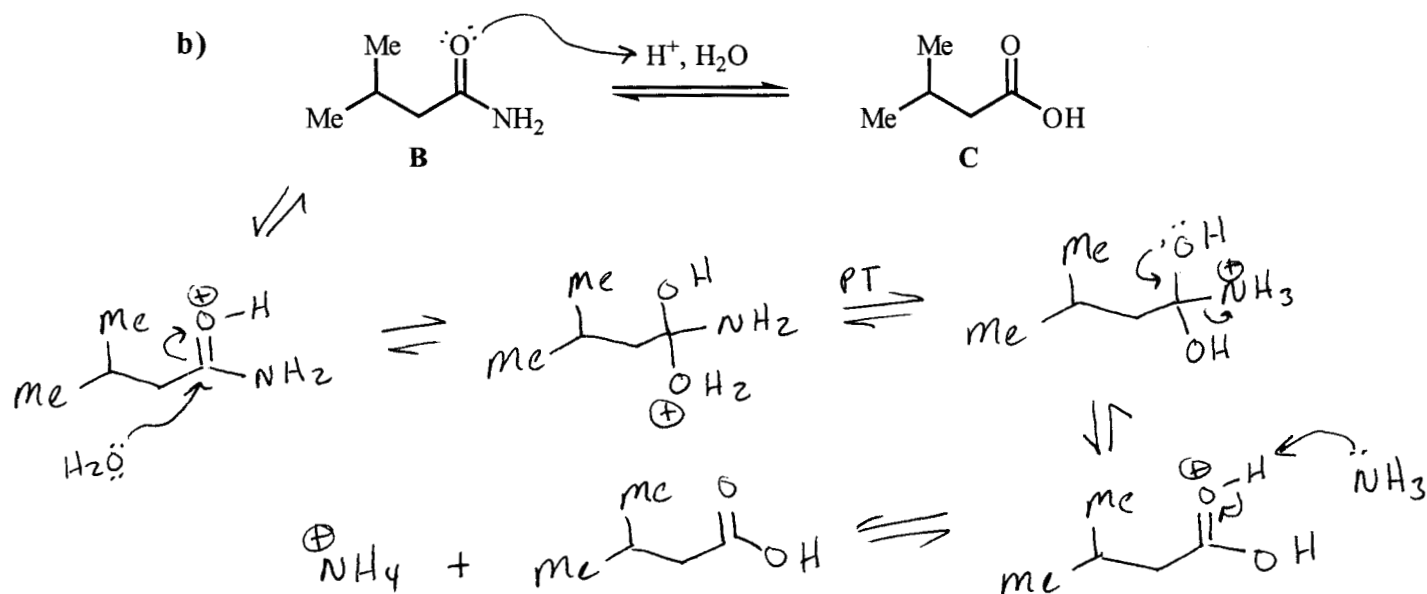
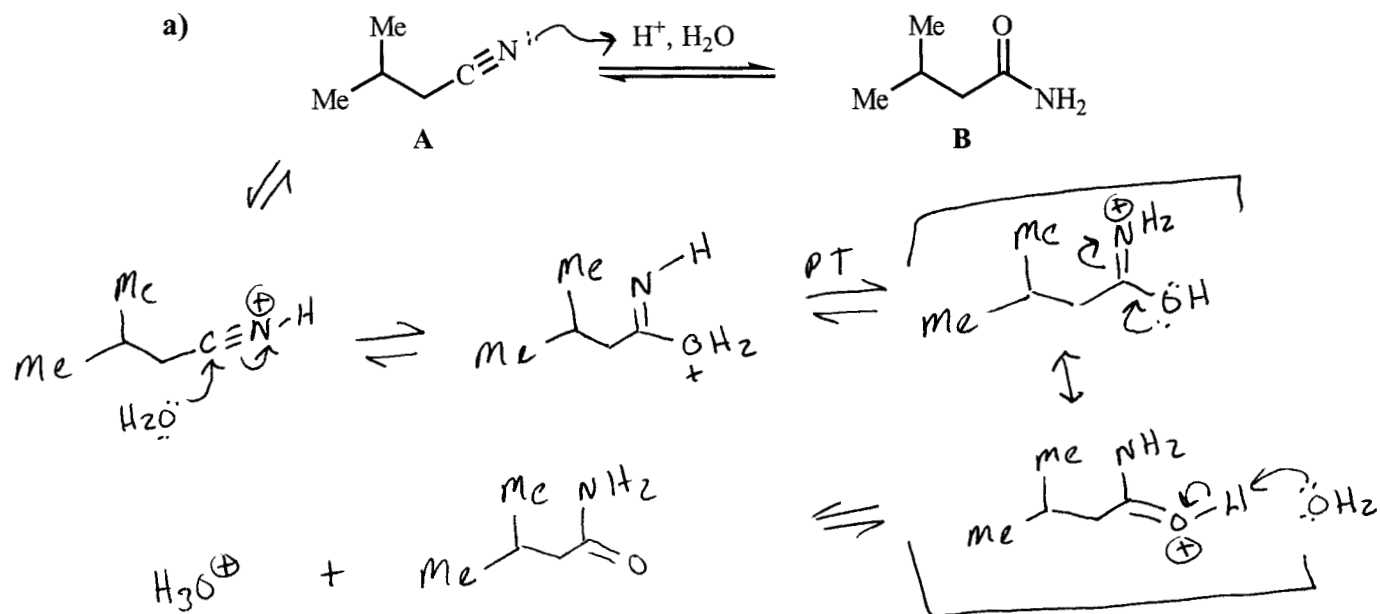
Very low incorporation of labeled Oxygen into acid chloride
 Cl^{\ominus} is a much better leaving group than OH^{\ominus}
 Hydrolysis will take place much faster than label incorporation
 $k_2 \gg k_1$

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. It is impossible to definitely prove a mechanism
 Incorporation of the label is consistent with both $\text{S}_{\text{N}}2$
 + addition elimination mechanisms

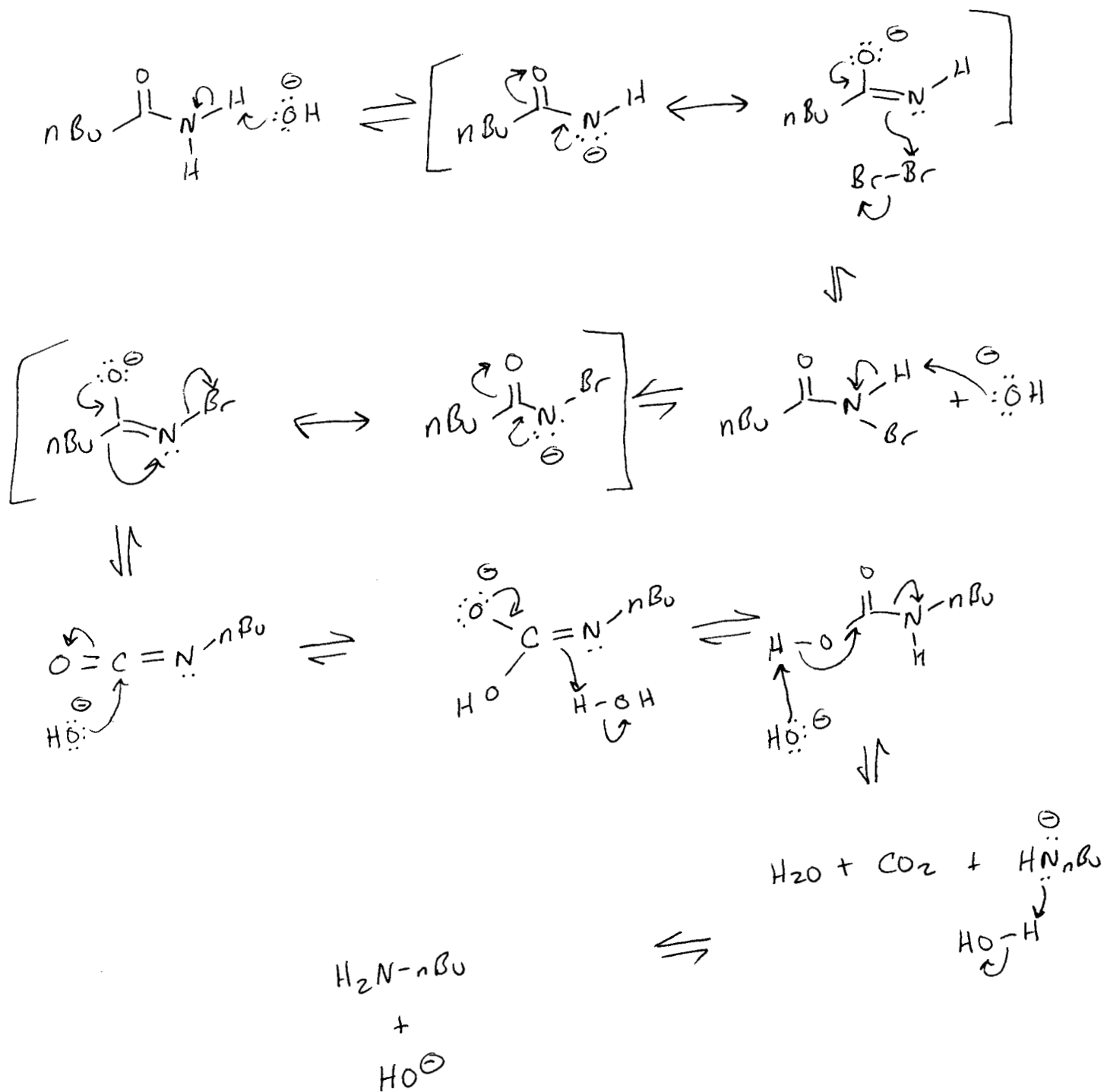
Name _____

6. (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.

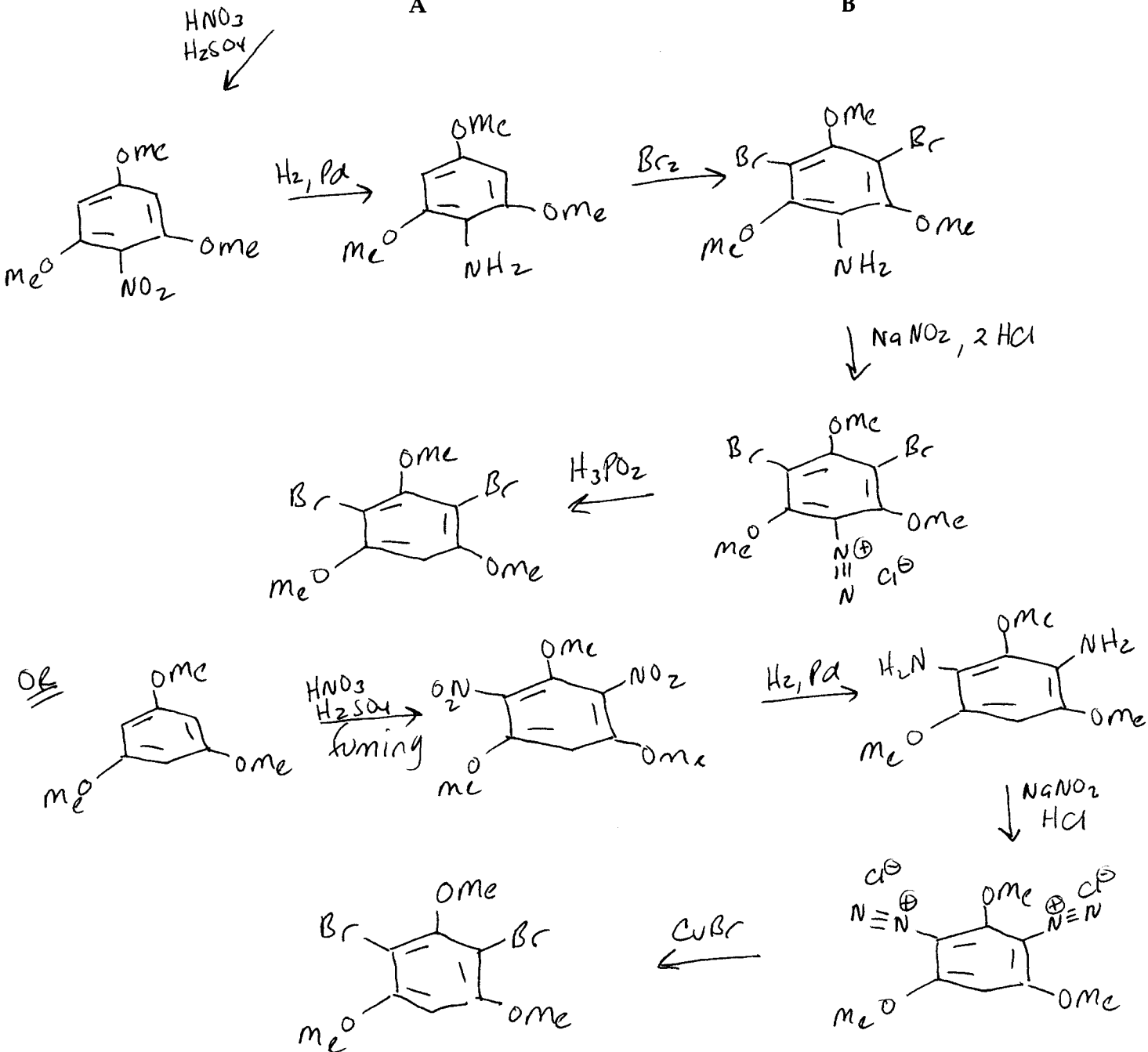
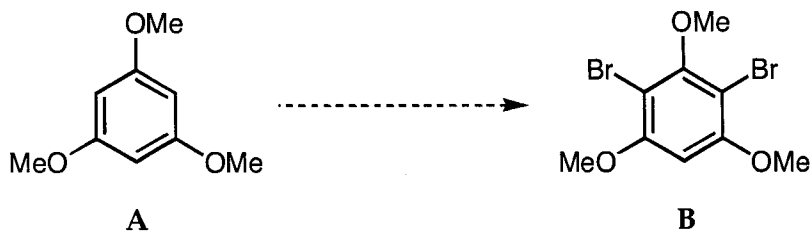


Name _____

7. Provide a mechanism for the Hofmann elimination. Please show all arrow pushing.



8. Provide a synthesis that will *selectively* convert A to B. Show all of the key intermediates, and furnish all of the important reagents.



9. Provide syntheses for the following compounds. All of the carbons in the target molecules should be derived from the allowed starting materials. You may use any common reagents.

