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.

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

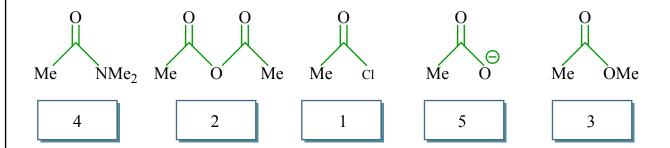
Molecular model kits will be allowed during the exam. You will be given a periodic table and blank pages.

Material Covered on Exam #3:

- Everything presented in lecture related to Amines, Carboxylic Acids, and Carboxylic Acid Derivatives
- Reaction 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).



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

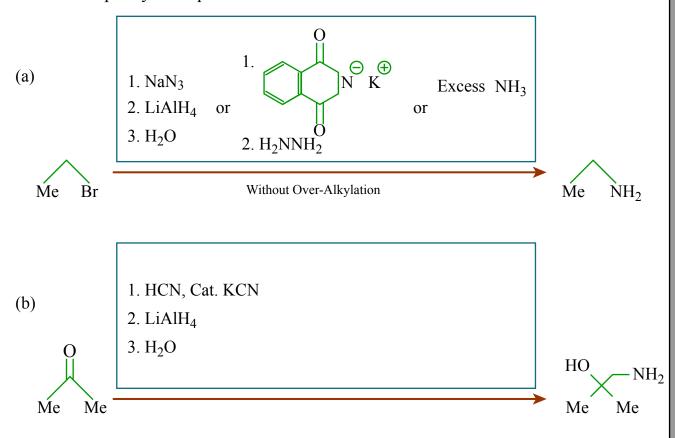


Figure by MIT OCW.

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

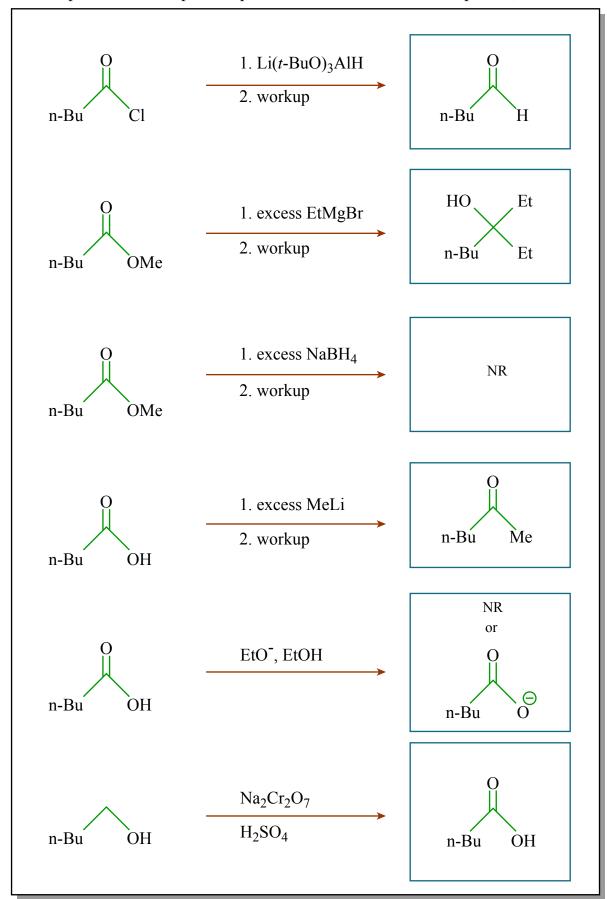


Figure by MIT OCW.

4. Please provide the requested reagents.

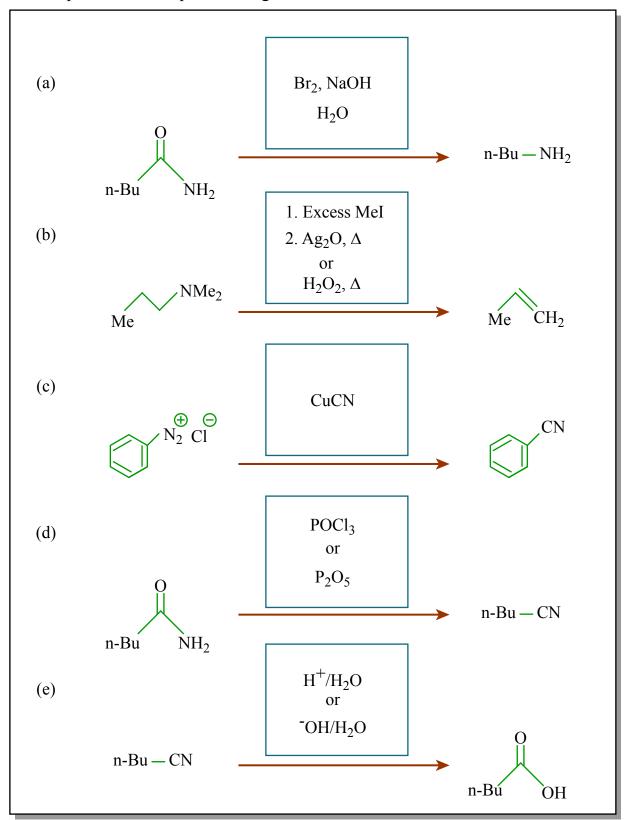


Figure by MIT OCW.

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

Stop the reaction at 50% conversion and examine the recovered acyl chloride for incorporation of
$$\emptyset$$

Me Cl
 \emptyset = isotopically labeled oxygen (^{18}O)

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

(b) What level of @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 is a much better leaving group than OH. Hydrolysis will take place much faster than label incorporation.

$$k_2 >> k_1$$

(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 S_{N2} and addition elimination mechanisms.

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.by MIT OCW.

(a)
$$Me$$
 NH_2 Me NH_2 NH_2 Me NH_2 NH_2 Me NH_2 Me NH_2 NH_2 Me NH_2 N

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

Figure by MIT OCW.

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

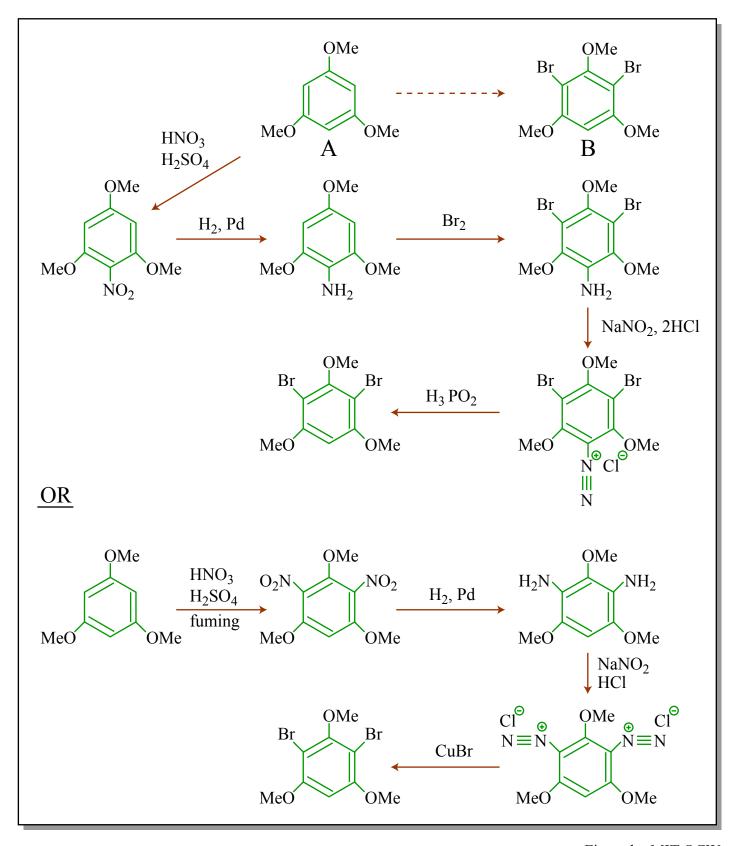


Figure by MIT OCW.

9. Provide synthesis 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.

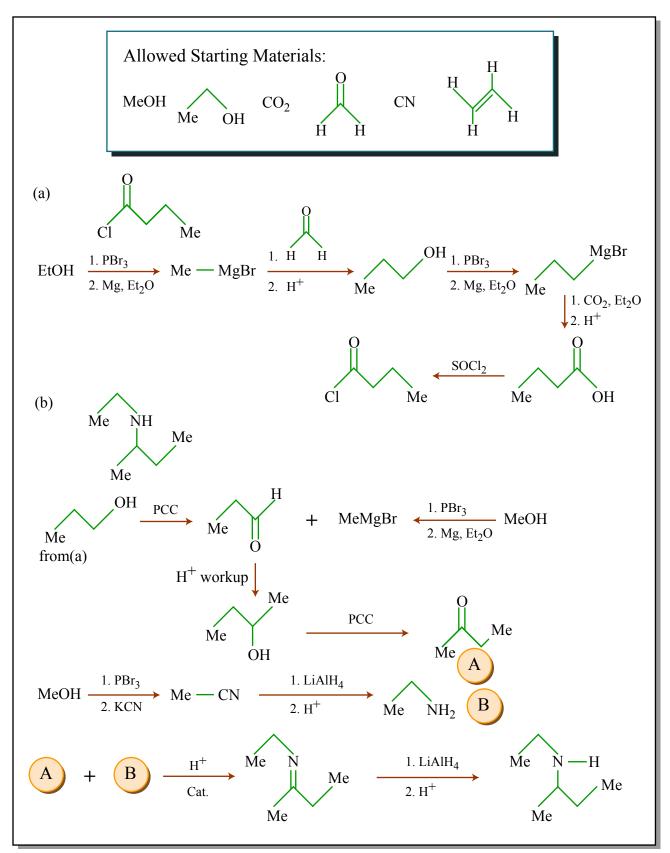


Figure by MIT OCW.