

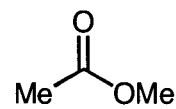
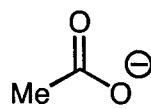
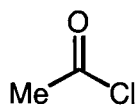
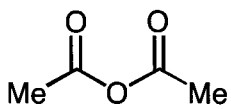
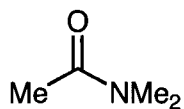
Key

**Practice Exam #3
5.13: Organic Chemistry II
Fall 2003**

- Midterm exam #3 will be held on Wednesday, November 12, from 12–1pm .
- Notes, books, and calculators will not be allowed in the exam.
- You will be free to use molecular models during the exam.
- You will be given a periodic table.
- The exam will cover reading (Ch. 19–21) and lecture material through Unit V (Wednesday, November 5).
- For best results, take this test as if it were your exam (without a key in 50 minutes!). That way, you'll know what areas to work on before you get to the real exam.

Practice, Practice, Practice!!!

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



4

2

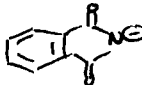
1

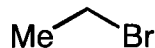
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3

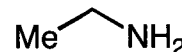
2. In the boxes, please provide the reagents for the illustrated transformations. More than one step may be required.

a) (three correct answers)

#1 - 1. NaN_3 2. LiAlH_4 3. workup
 #2 - 1.  2. H_2NNH_2
 #3 - excess NH_3

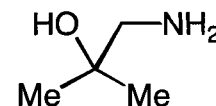
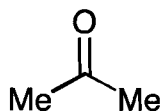


WITHOUT over-alkylation

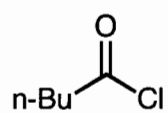


b)

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

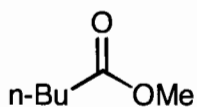
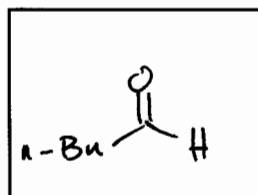


3. Please provide the requested products. If no reaction is expected, write "NR".



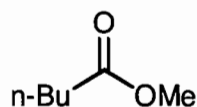
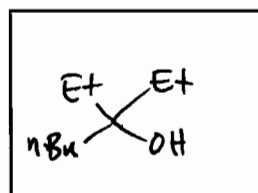
1. Li(t-BuO)3AlH

2. workup



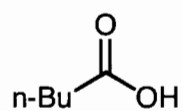
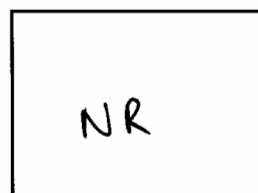
1. excess EtMgBr

2. workup



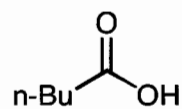
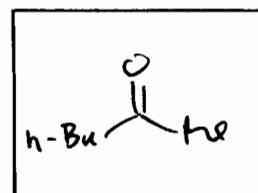
1. excess NaBH4

2. workup

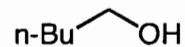
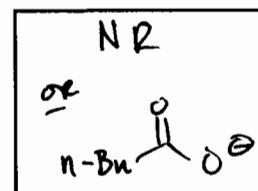


1. excess MeLi

2. workup

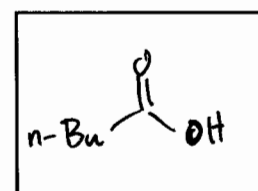


EtO^-, EtOH



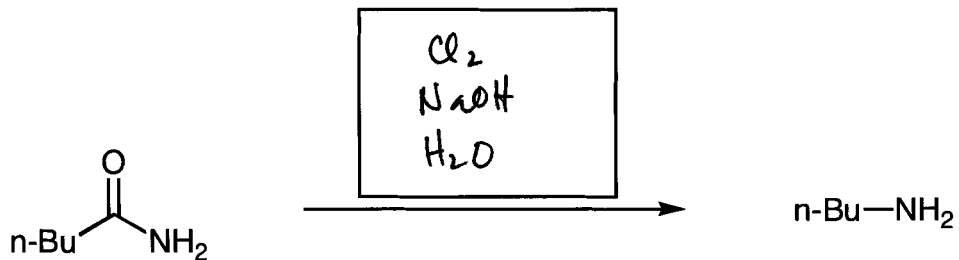
Na2Cr2O7

H2SO4

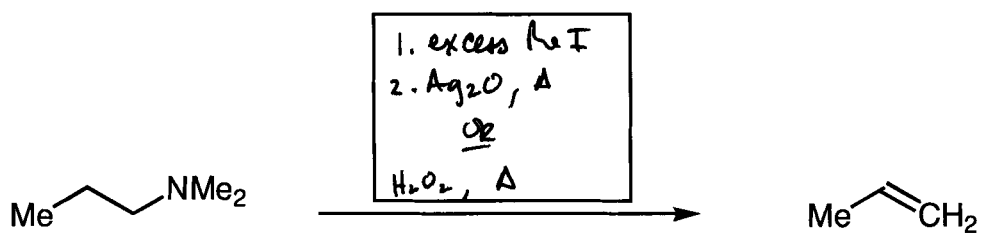


4. Please provide the requested reagents.

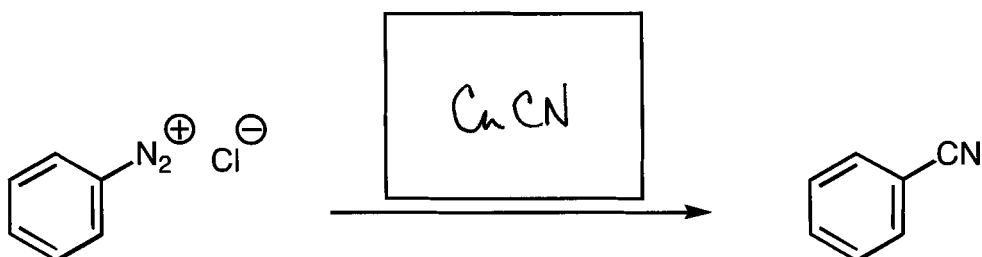
a)



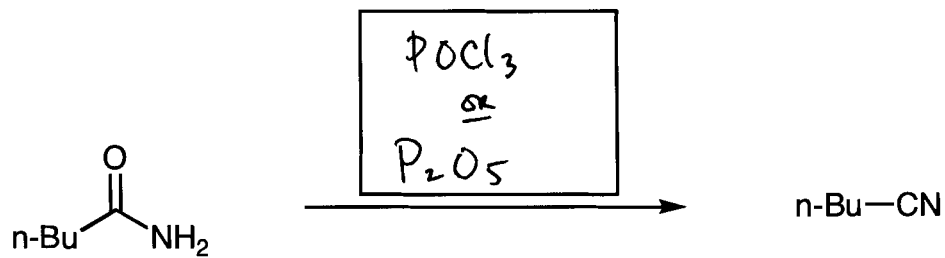
b)



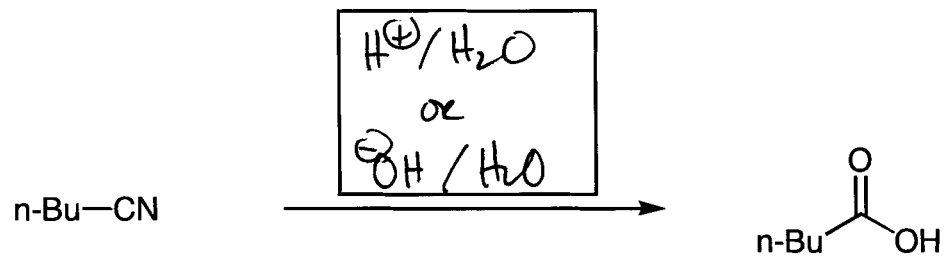
c)



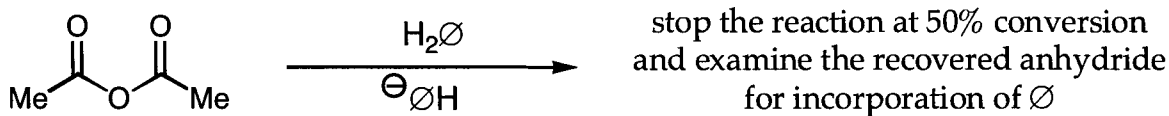
d)



e)

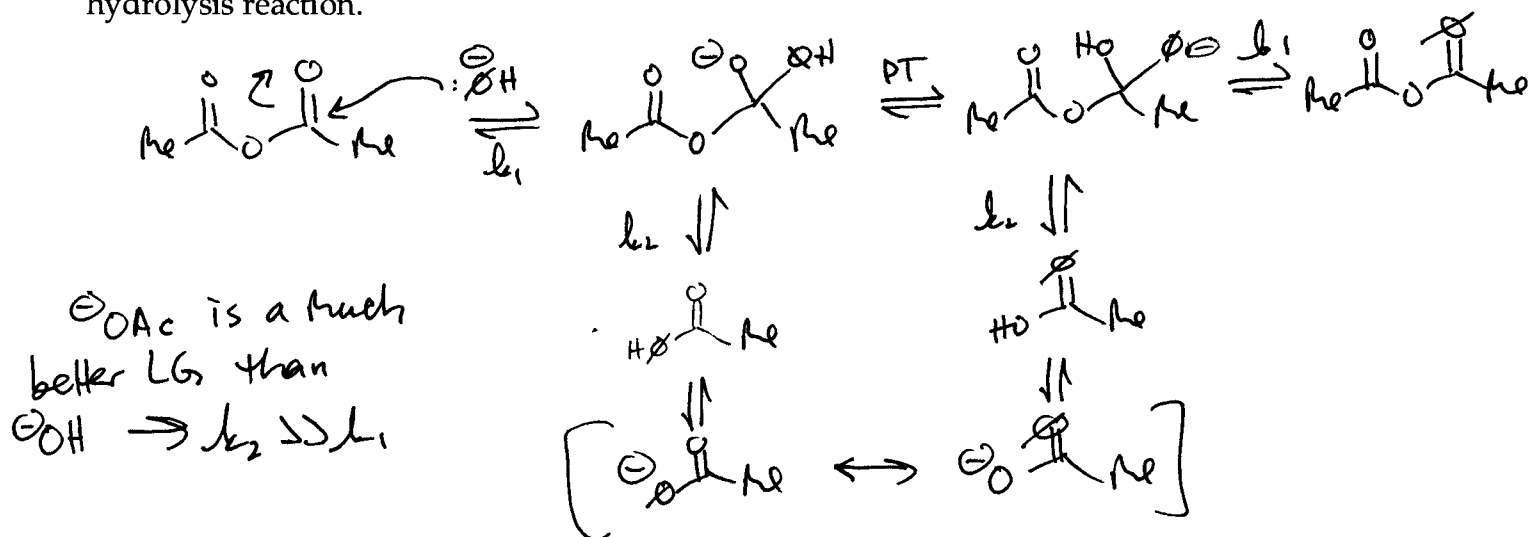


5. Consider the labeling experiment outlined below.:



$\text{O} =$ isotopically labeled oxygen

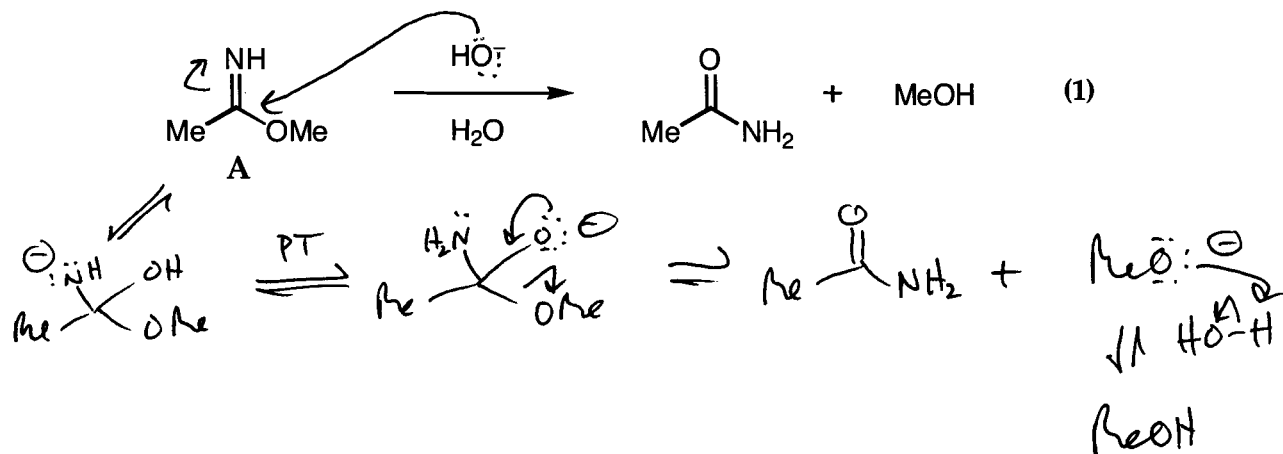
In analogy with the discussion in class regarding the labeling studies of acyl chlorides, esters, and amides, carefully explain what level ("high" or "low") of O incorporation you expect to observe in the recovered anhydride. Your answer should include the mechanism for this hydrolysis reaction.



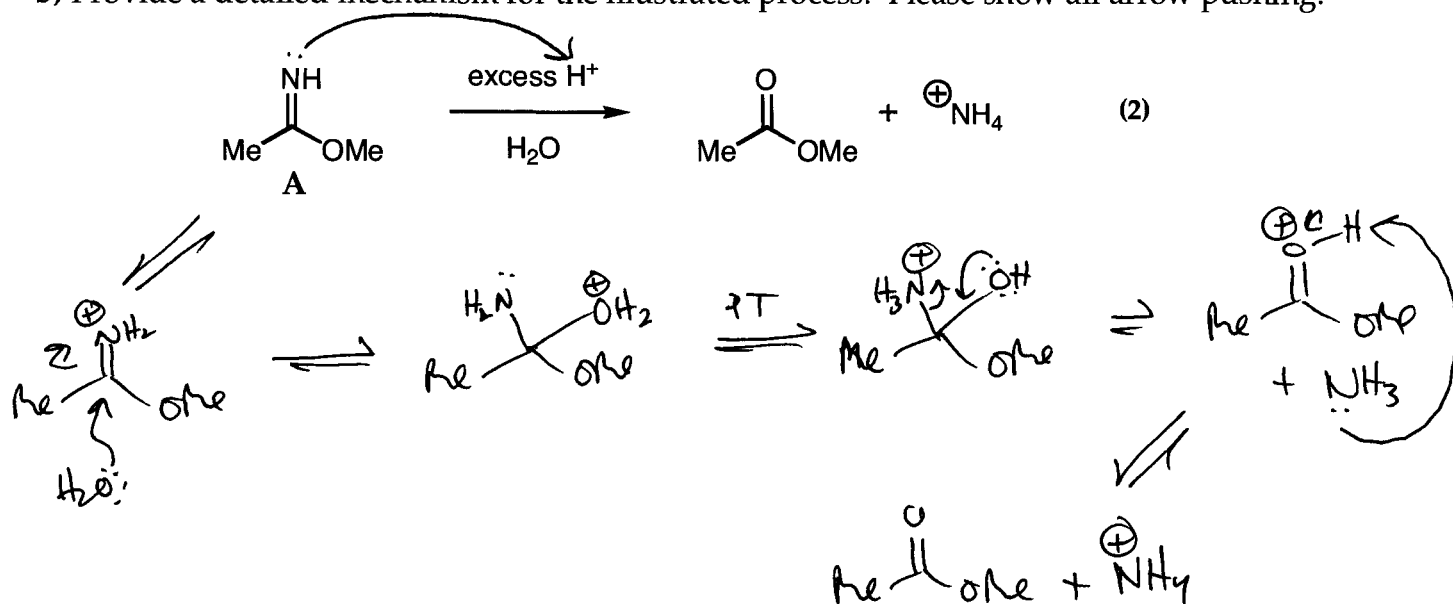
There should be low incorporation of the O label into the recovered anhydride. When the tetrahedral intermediate forms, it can either collapse to reform the anhydride or the acid. Formation of the acid is much faster because $\ominus\text{OAc}$ is a much better leaving group than $\ominus\text{OH}$. Very little of the intermediate reverts back to anhydride, so incorporation of the label is low.

6. Methyl acetimidate (A) is hydrolyzed in aqueous sodium hydroxide to give mainly acetamide and methanol (eq 1). In aqueous acid, A hydrolyzes to give primarily methyl acetate and ammonium ion (eq 2).

a) Provide a detailed mechanism for the illustrated process. Please show all arrow pushing.



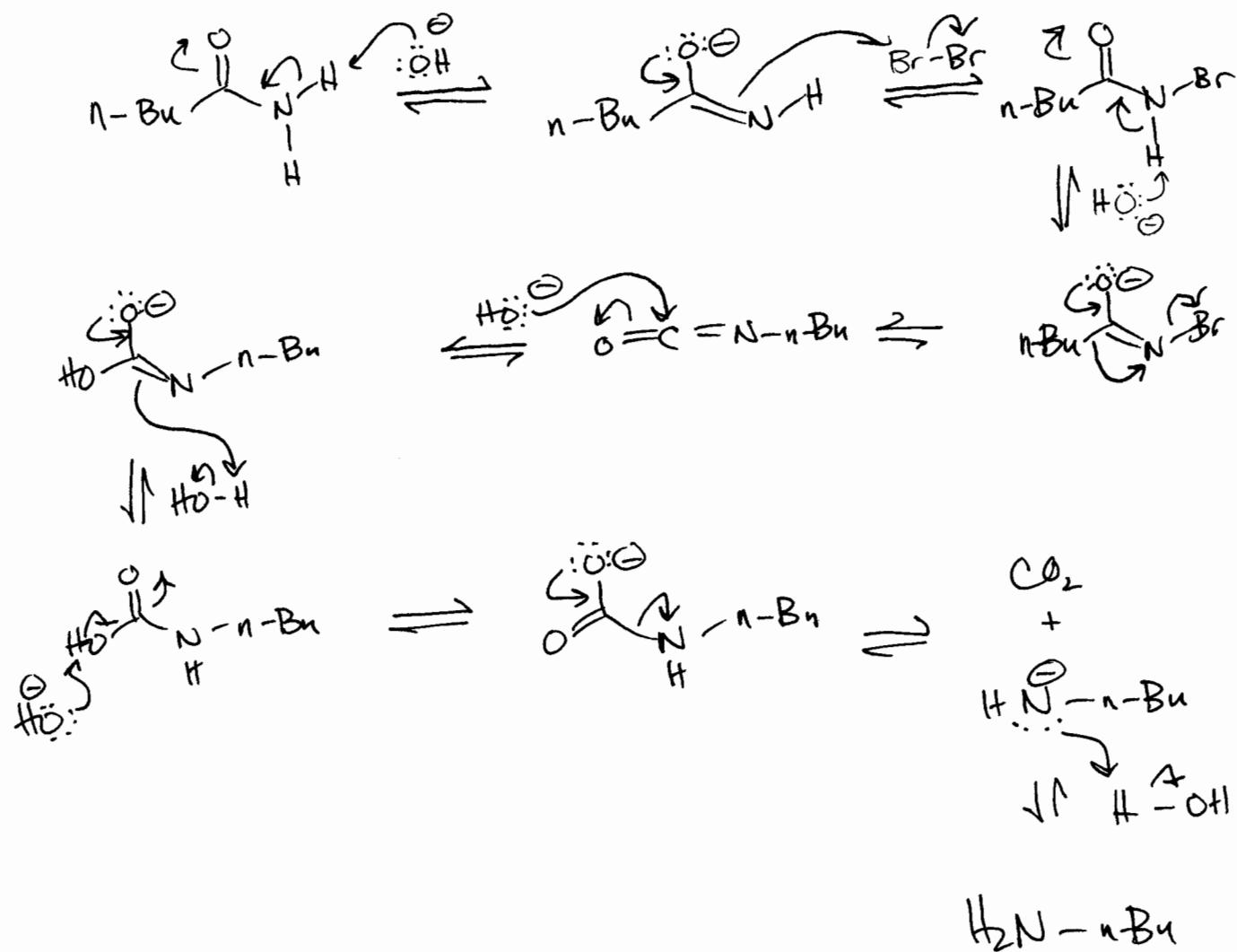
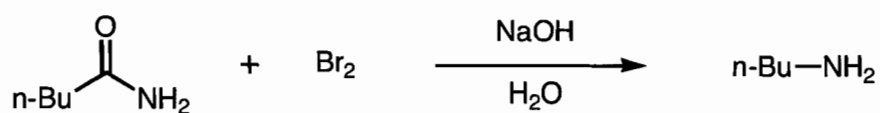
b) Provide a detailed mechanism for the illustrated process. Please show all arrow pushing.



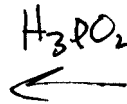
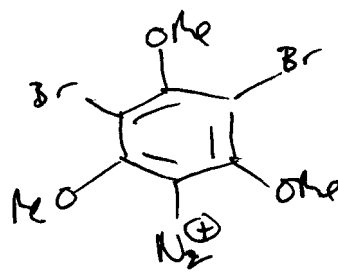
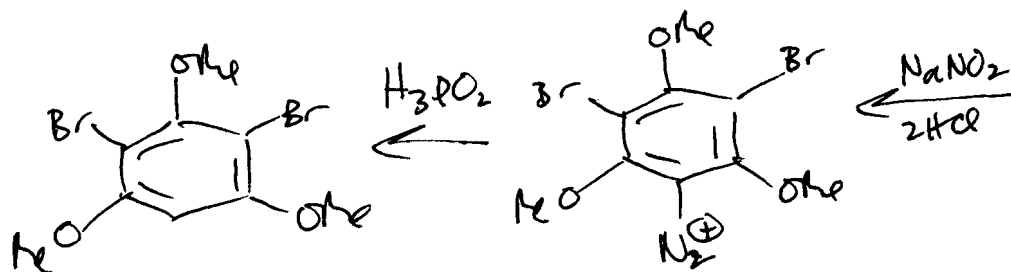
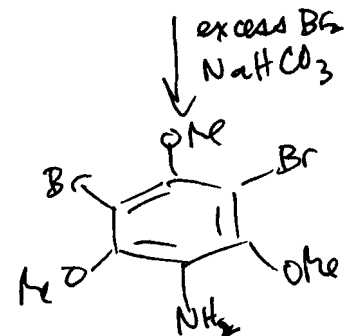
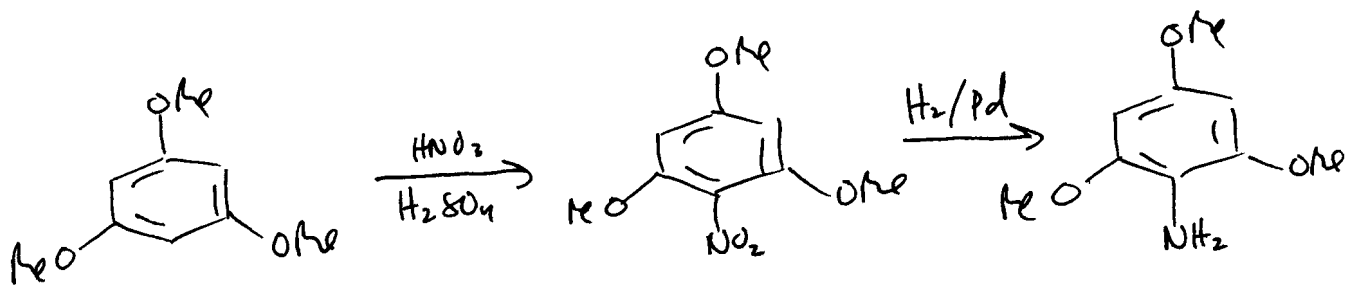
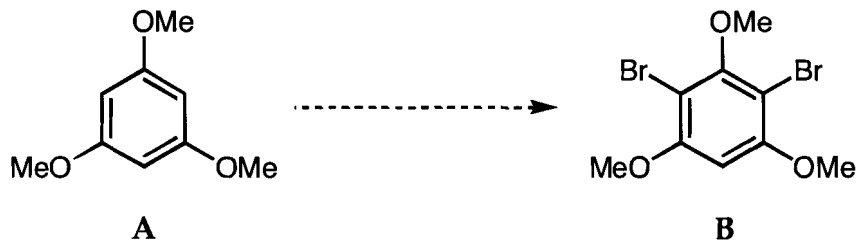
c) Briefly explain why the two reactions provide different products.

Under basic conditions, OH^- is a worse LG than O^- , so elimination occurs to give the amide. Under acidic conditions, acid/base equilibrium favors protonation of the nitrogen, making it a good LG. In addition, NH_4^+ is not nucleophilic, so formation of the ester is irreversible.

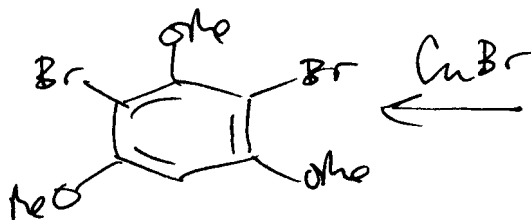
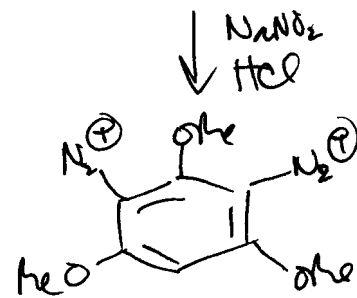
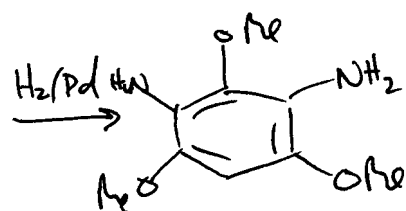
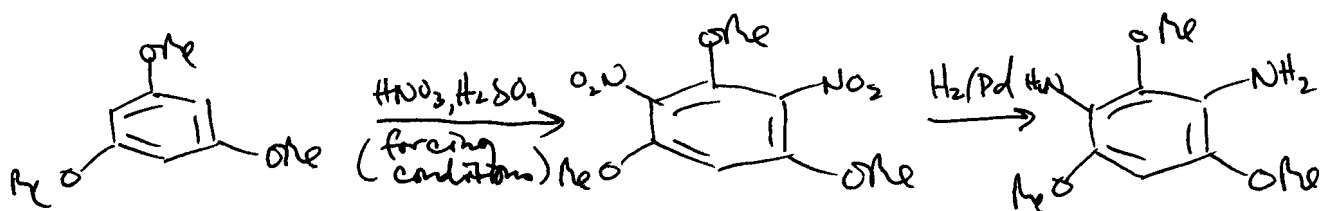
7. Provide a mechanism for the Hofmann elimination. Please show all arrow pushing.



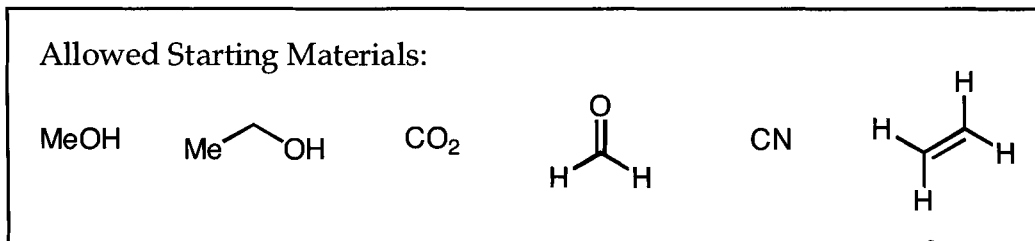
8. Provide a synthesis that will *selectively* convert A to B. Show all of the key intermediates, and furnish all of the important reagents.



OR



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.



You can put these together in a few different ways.

