

EXAM #3 EXTRA PROBLEMS

KEY

What to expect on Exam #3:

1. ~1 Labeling experiment
2. ~2 Mechanisms
3. ~2 Syntheses
4. ~5 transformations – supply missing product
5. ~5 transformations – supply missing reagents
6. ~3 General questions

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.

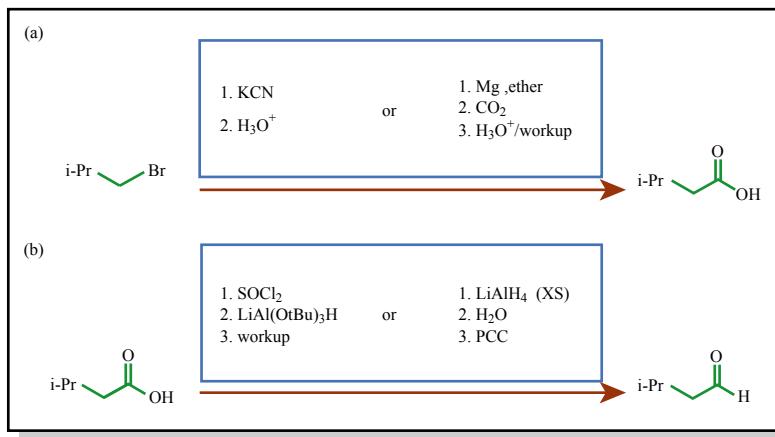


Figure by MIT OCW.

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

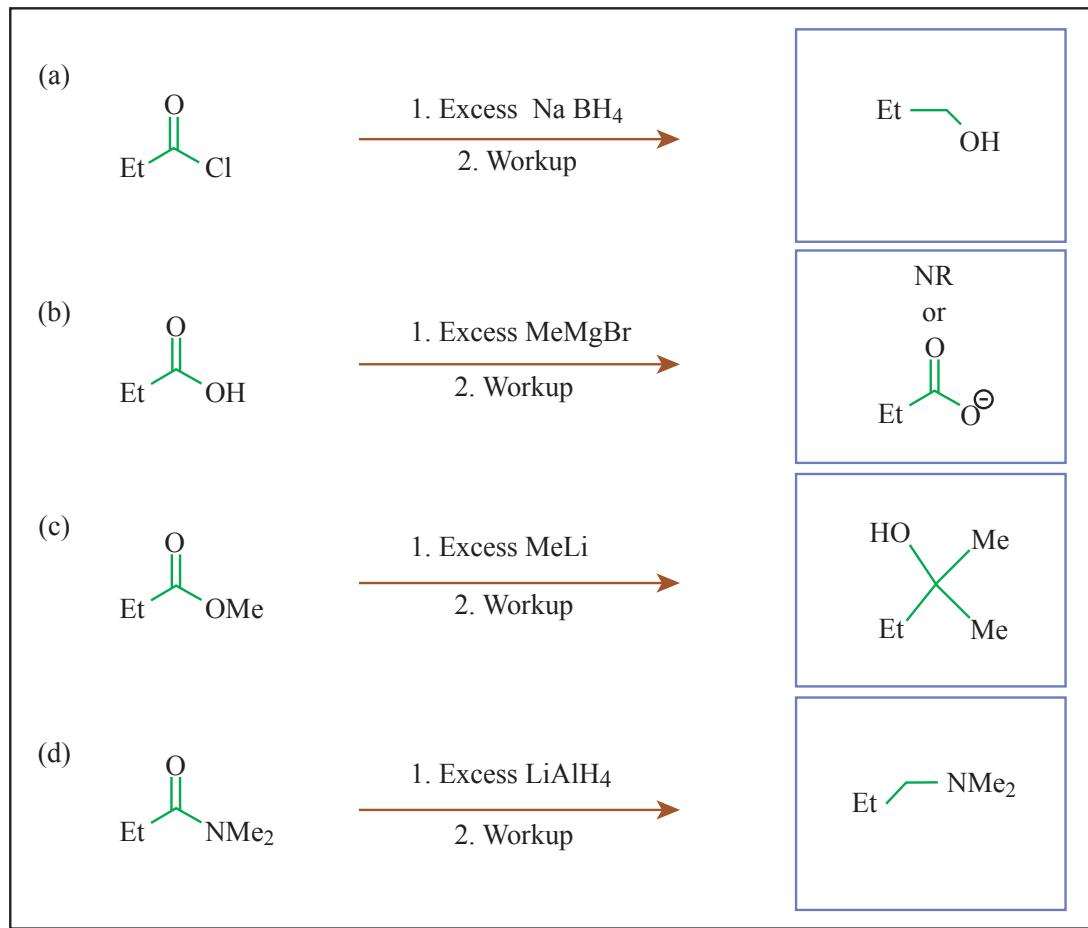
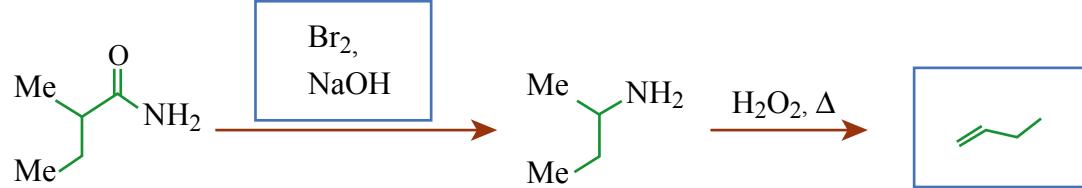


Figure by MIT OCW.

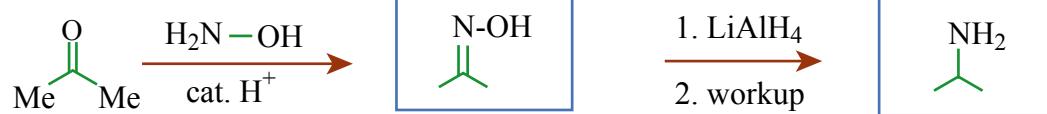
NAME _____

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

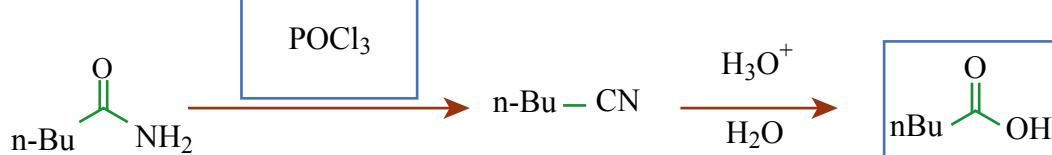
(a)



(b)



(c)



(d)

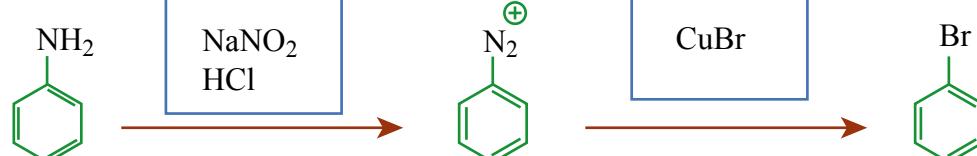


Figure by MIT OCW.

Name _____

4. (11 points) Please provide a detailed mechanism for the illustrated conversion of acetic acid (A) to acetyl chloride (B).

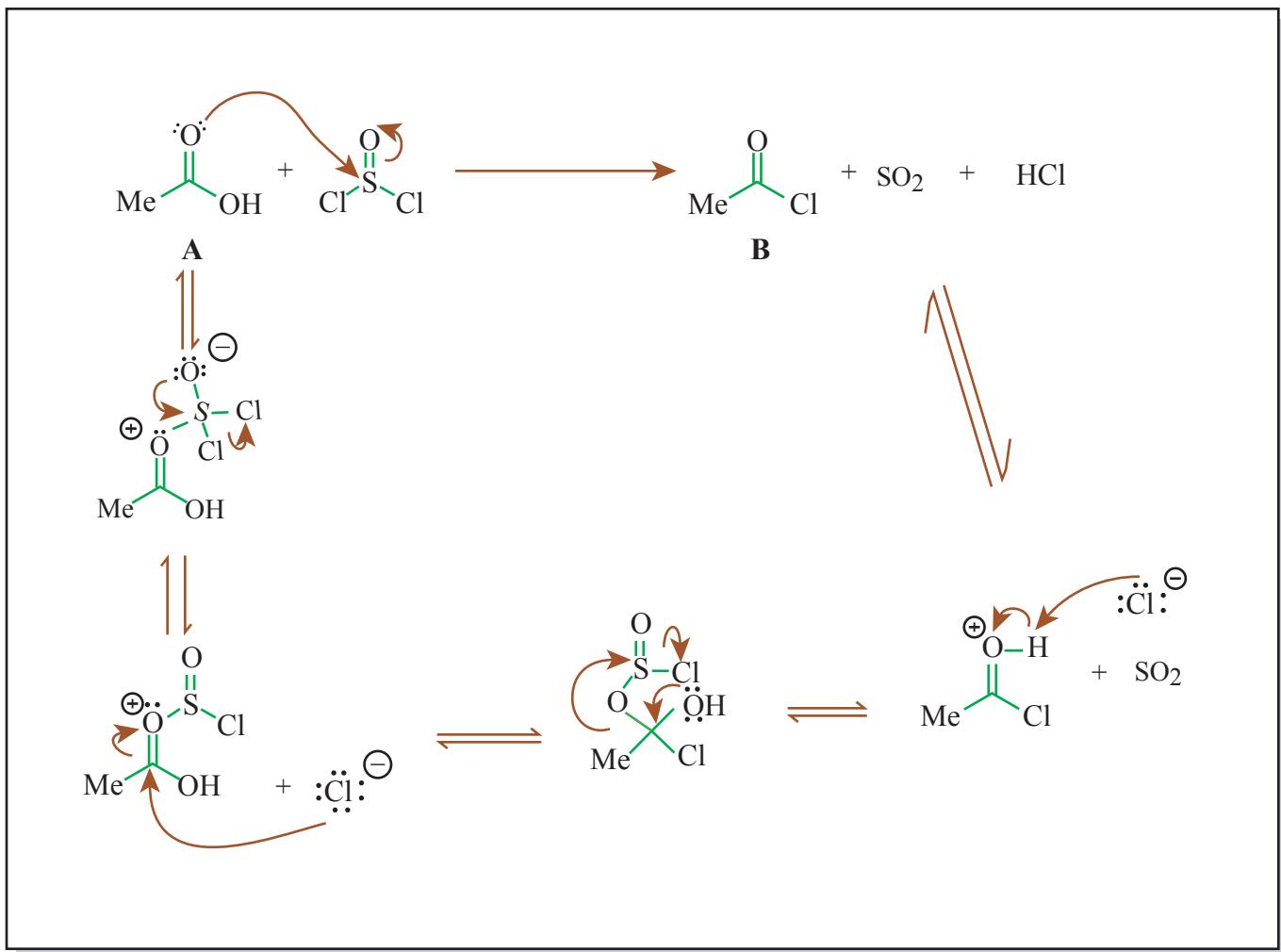


Figure by MIT OCW.

Name _____

5. (11 points each, 22 points total) Please provide syntheses for **only two of the three** indicated compounds. All the carbon atoms should be derived from the allowed starting materials. You may use any common reagents.

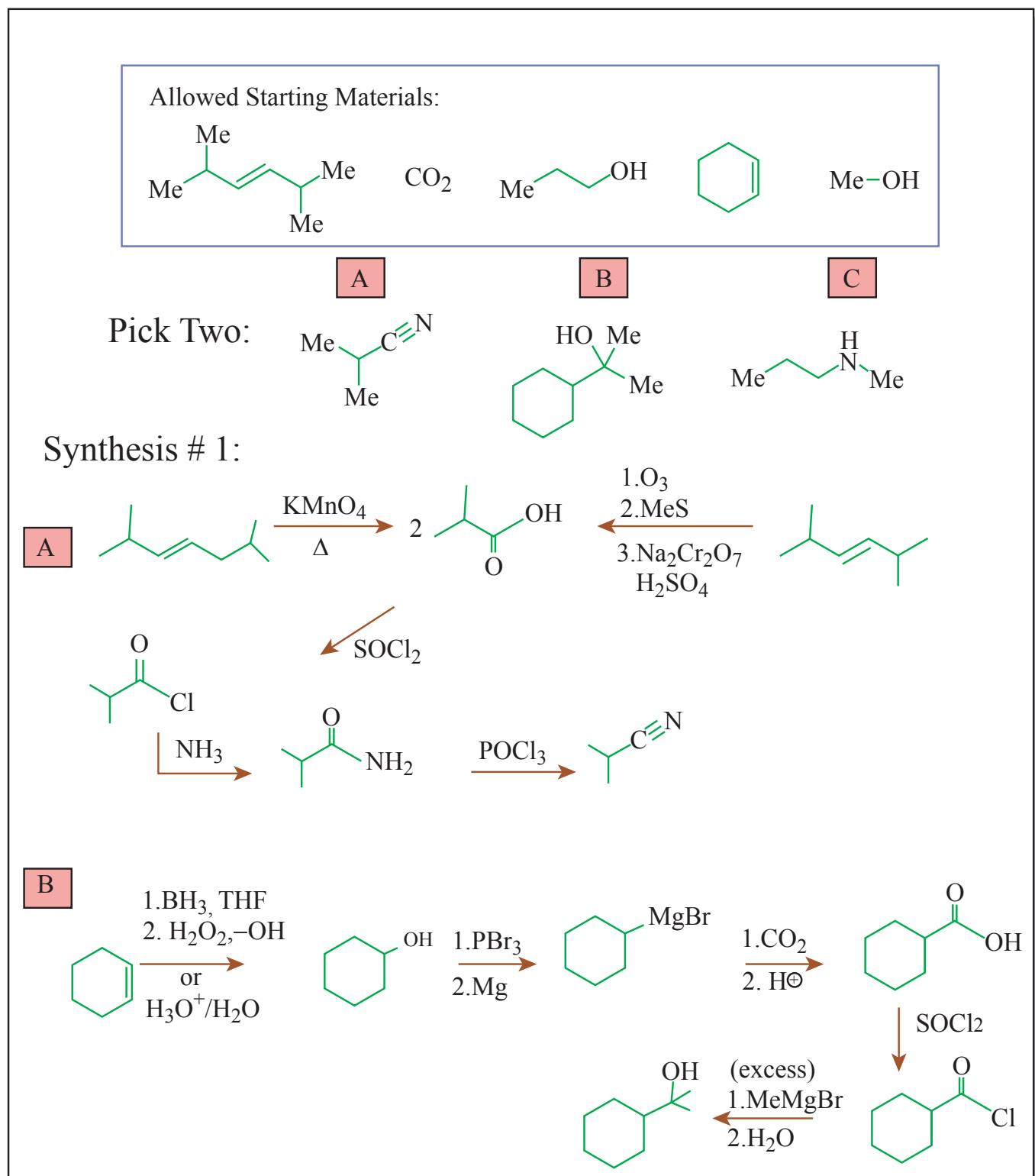


Figure by MIT OCW.

Name _____

5. (Continued)

Allowed Starting Materials:

Pick Two:

Synthesis #2:

Route 1: $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{or } \text{TsCl, Pyridine}]{\text{PBr}_3} \text{CH}_3\text{CH}_2\text{Br}$. Then $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow[\substack{1. \text{NaN}_3 \\ 2. \text{LiAlH}_4 \\ 3. \text{H}_3\text{O}^+ \\ \text{or XS NH}_3}]{2. \text{H}_2\text{NNH}_2} \text{CH}_3\text{CH}_2\text{NH}_2$.

Route 2: $\text{MeOH} \xrightarrow{\text{PCC}} \text{H}_2\text{C=O}$. Then $\text{H}_2\text{C=O} \xrightarrow[\text{Cat H}^+]{\text{CH}_3\text{CH}_2\text{NH}_2} \text{CH}_3\text{CH}_2\text{N}=\text{CH}_2$. Finally, $\text{CH}_3\text{CH}_2\text{N}=\text{CH}_2 \xrightarrow[\substack{1. \text{LiAlH}_4 \\ 2. \text{H}_2\text{O}}]{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{NH}_2$.

Figure by MIT OCW.

Name _____

6. (11 points) Provide a synthesis that will *selectively* convert **A** to **B**. Show all the key intermediates and furnish all the important reagents. This is not a one-step process.

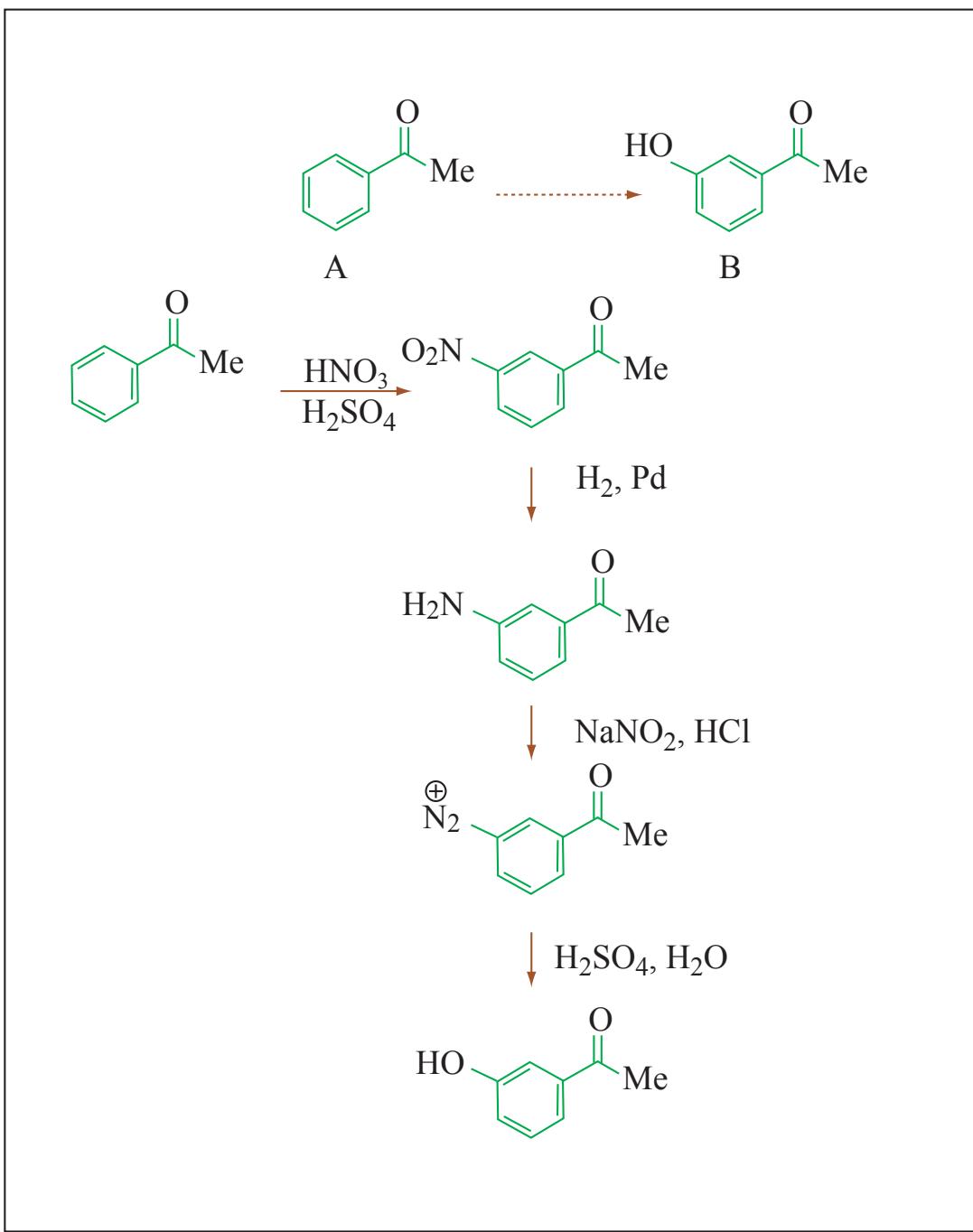


Figure by MIT OCW.

Name _____

7. 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.

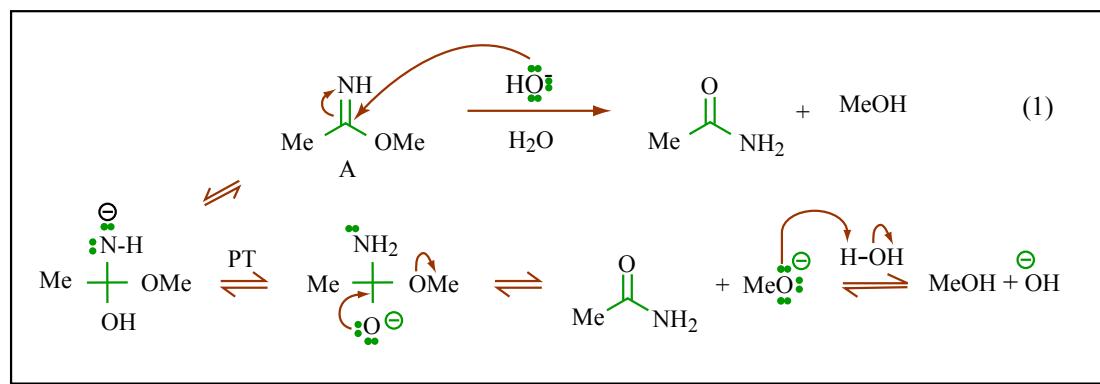


Figure by MIT OCW.

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

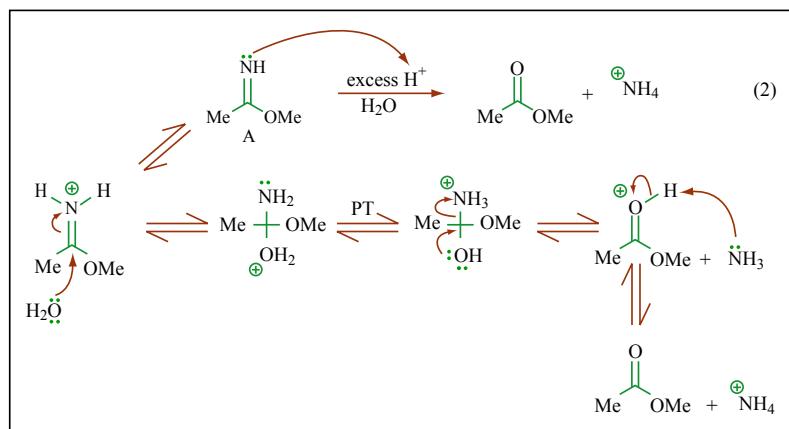


Figure by MIT OCW.

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

Basic conditions: NH_2^- worse L.G. than OMe^- . Elimination favors amide

Acidic conditions: Acid/base equilibrium favors protonation of nitrogen making it a good

L.G. Also, NH_4^+ is not nucleophilic + formation of ester is reversible

Figure by MIT OCW.

Massachusetts Institute of Technology

5.13: Organic Chemistry II

8. Synthesize the indicated compounds from the allowed starting materials shown below. All of the carbons of the target compounds should be derived from the allowed starting materials.

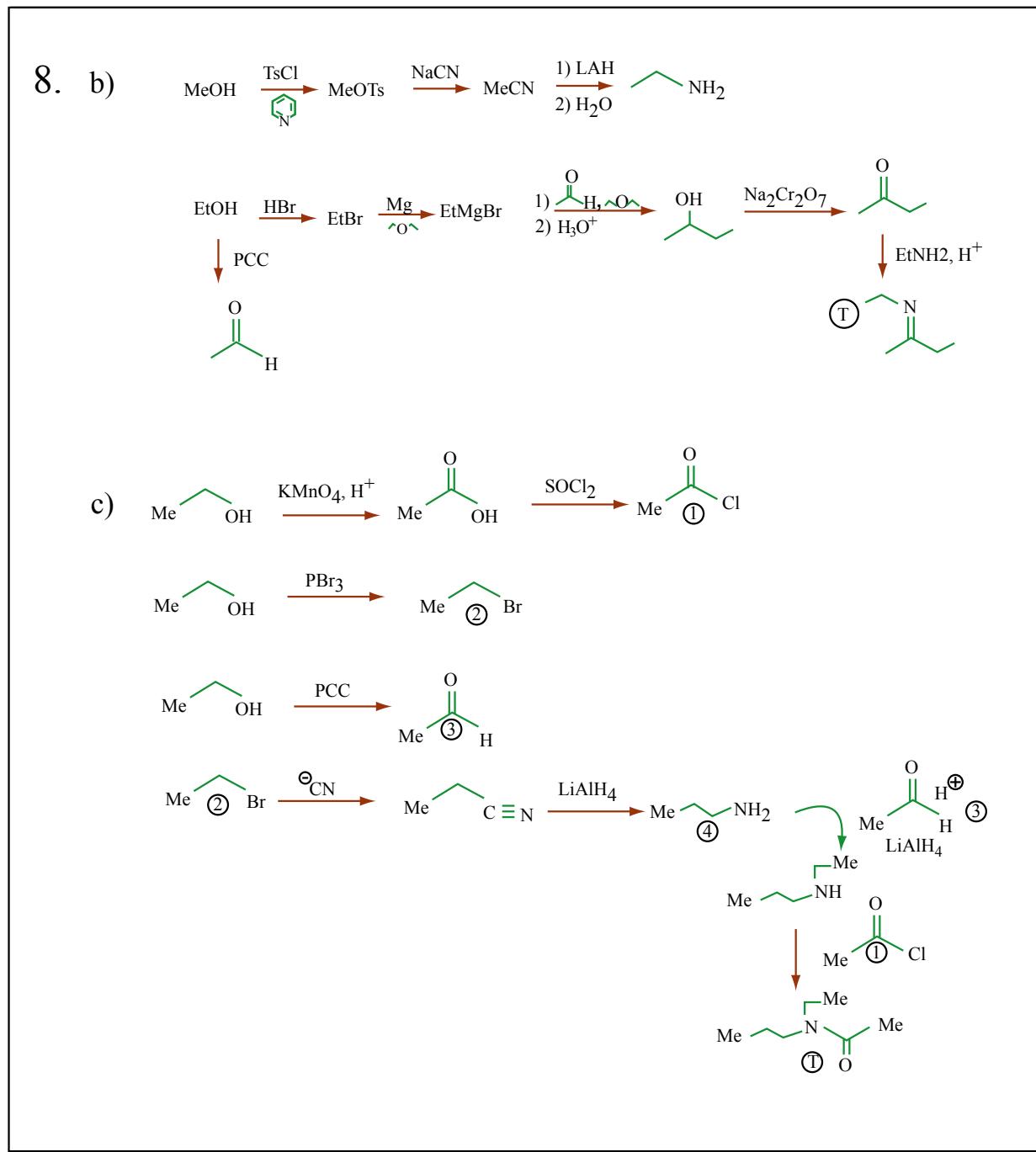


Figure by MIT OCW.

Massachusetts Institute of Technology

5.13: Organic Chemistry II

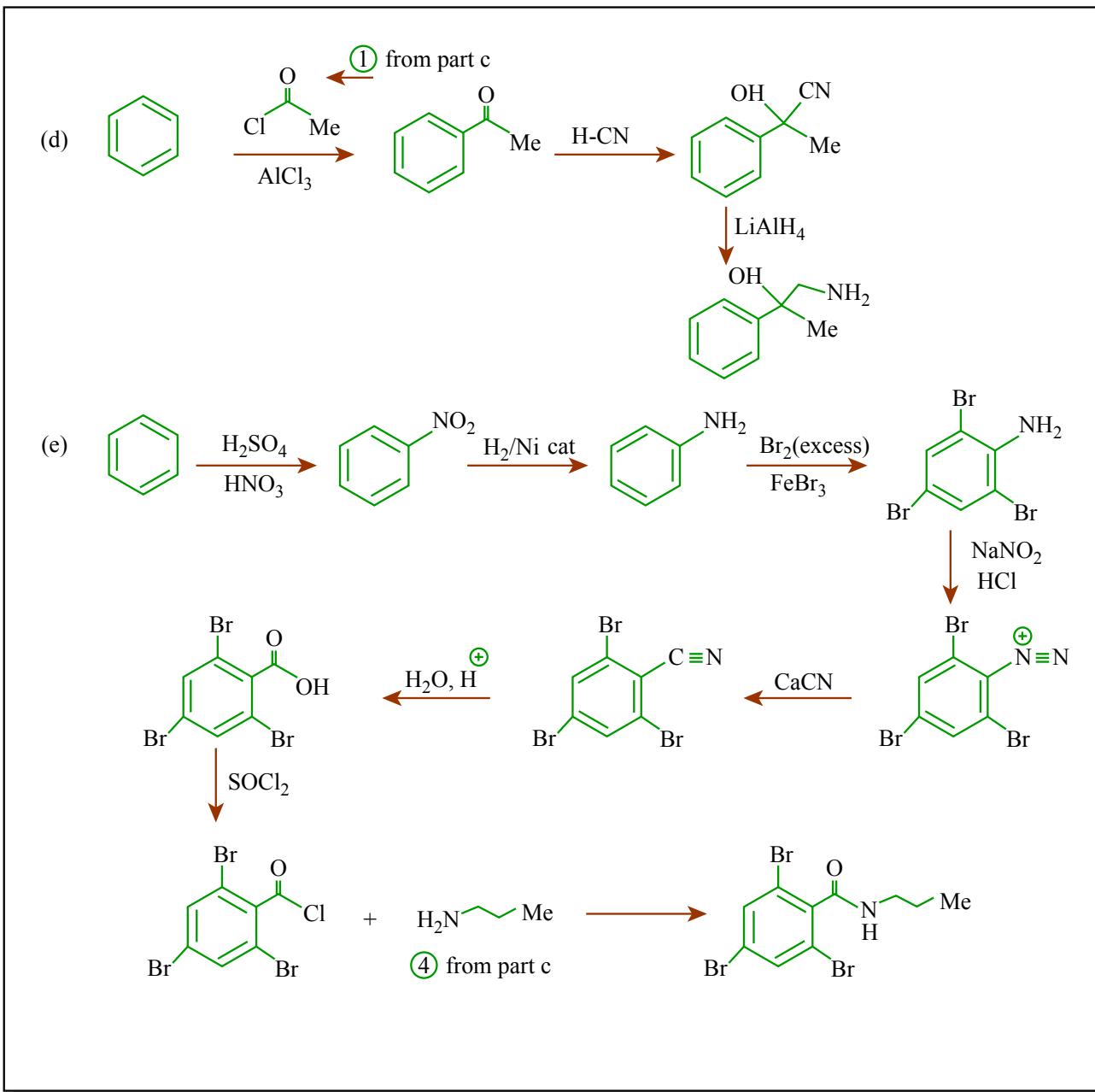


Figure by MIT OCW.

5.13: Organic Chemistry II

9. Provide the best stepwise mechanism for the illustrated process. Please show all arrow pushing.

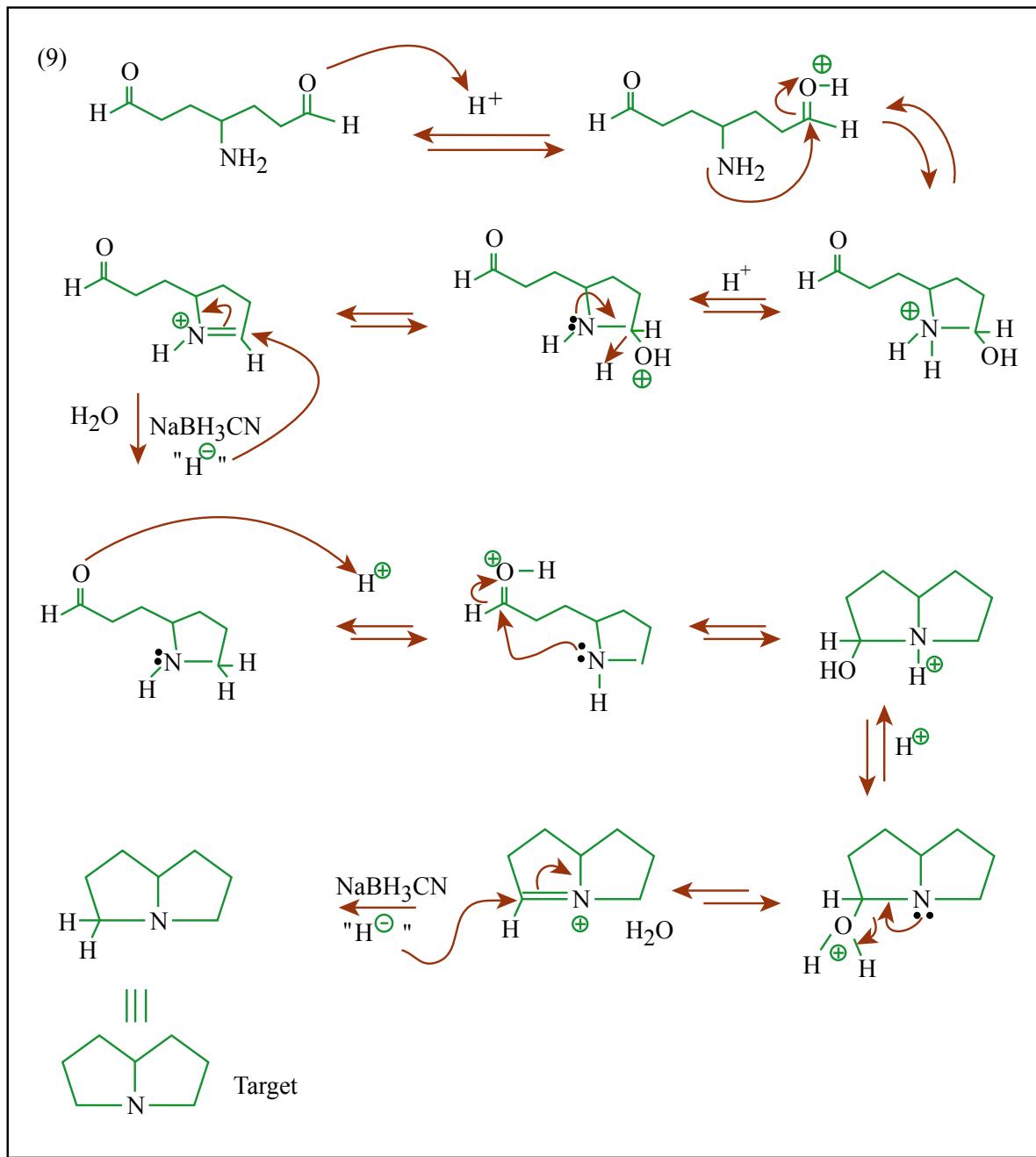


Figure by MIT OCW.

5.13: Organic Chemistry II

10. (a) Provide the best mechanism. Please show all arrow pushing.

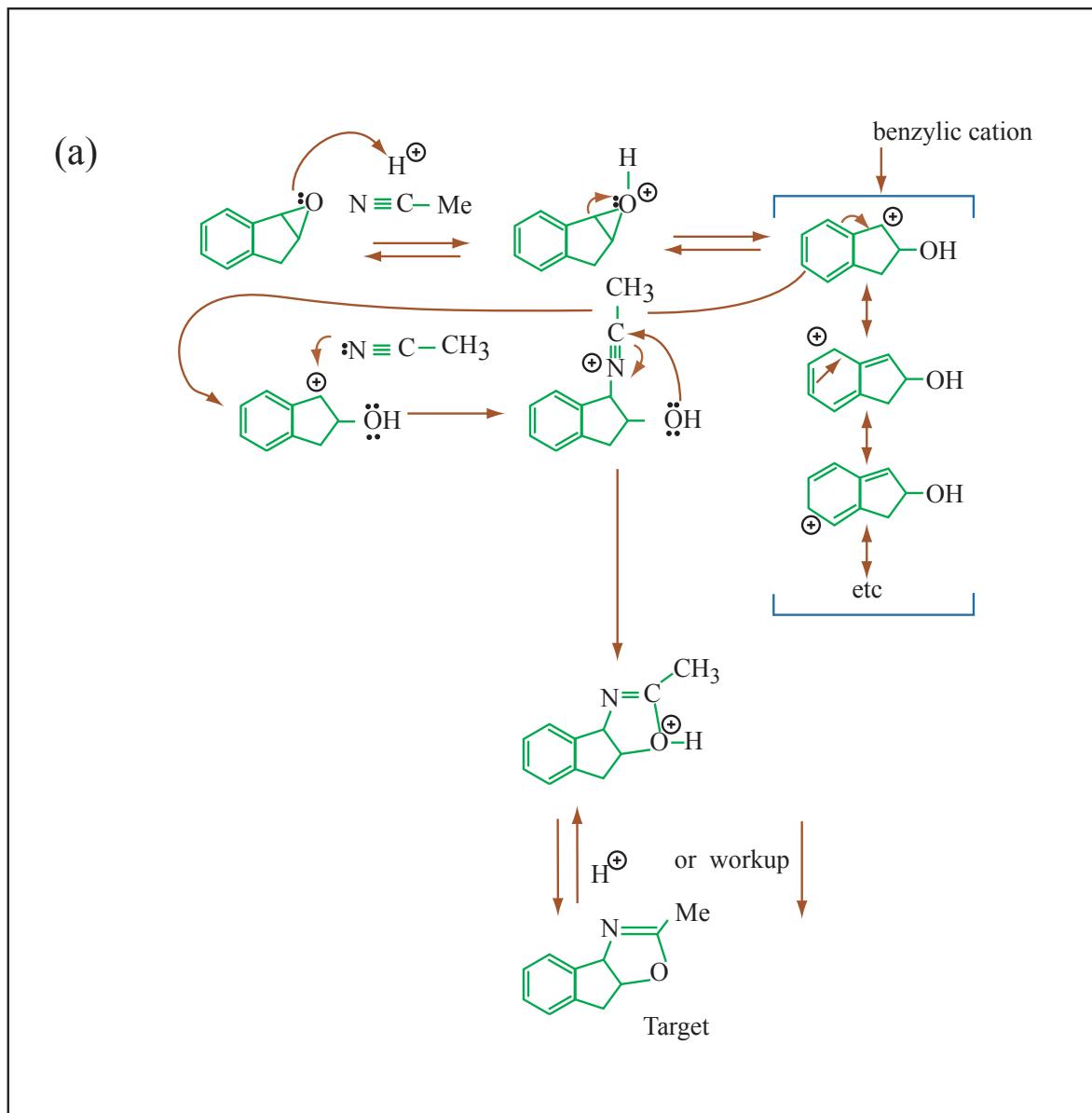


Figure by MIT OCW.

5.13: Organic Chemistry II

(b) Provide the best mechanism. Please show all arrow pushing.

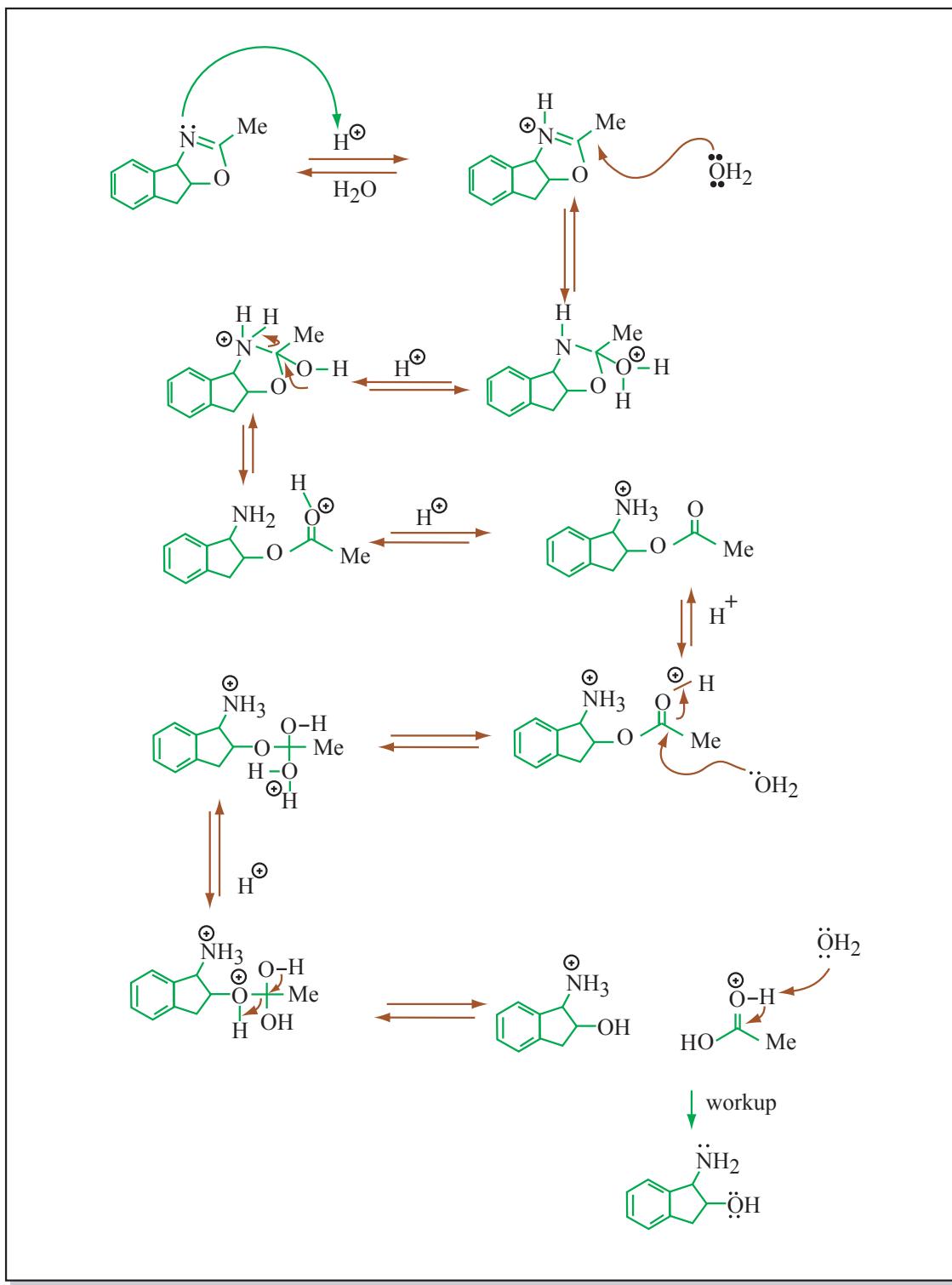


Figure by MIT OCW.

5.13: Organic Chemistry II

11. Consider the labeling experiments outlined below:

11. Start with the mechanisms:

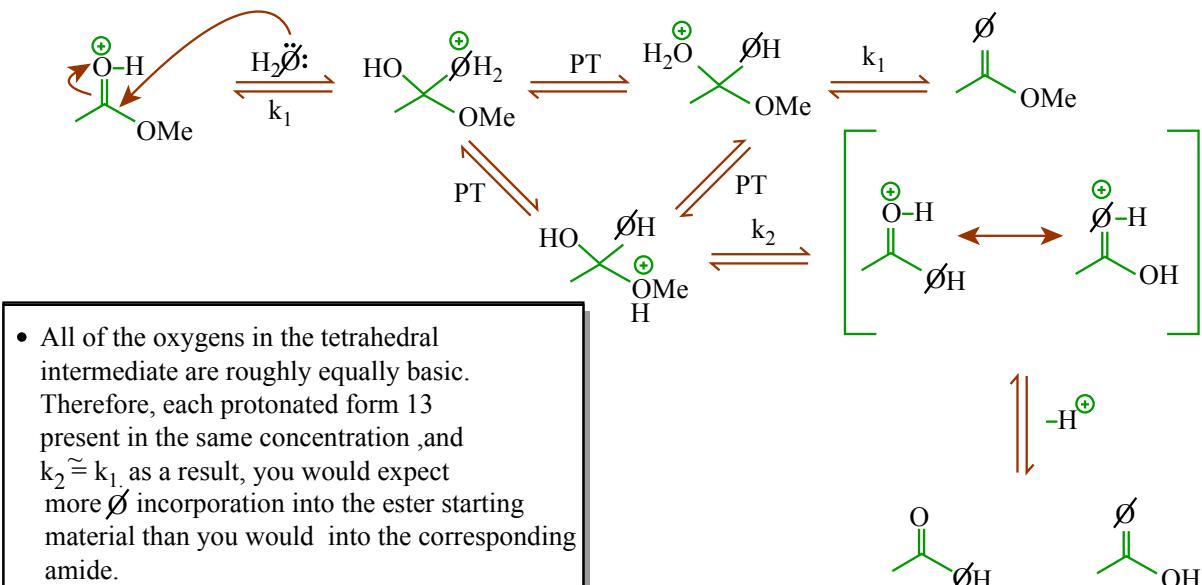
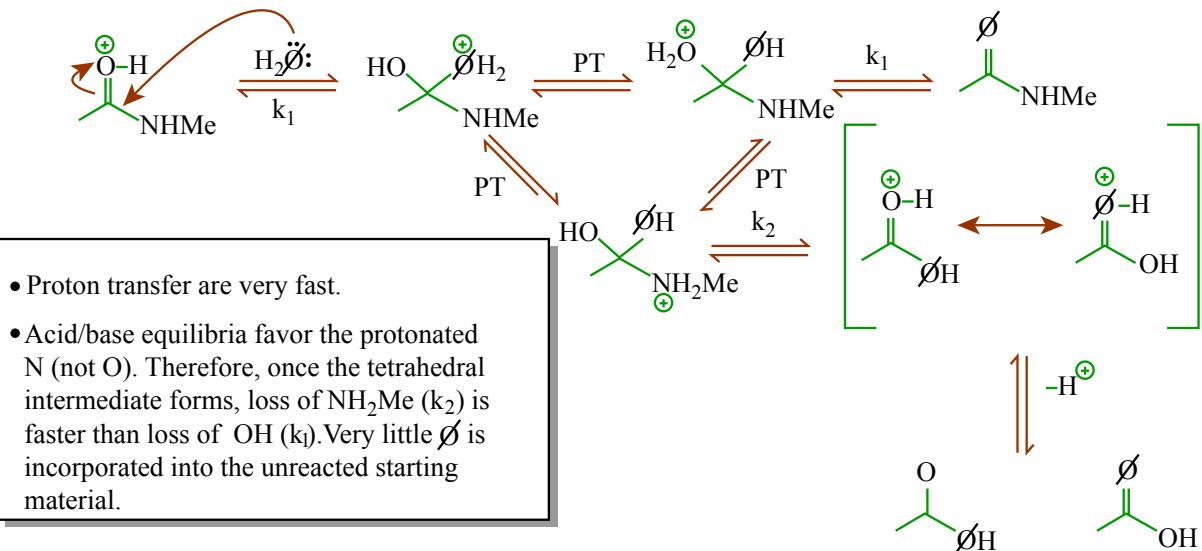


Figure by MIT OCW.

Name _____