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).

\[ \text{Me}^+\text{NMe}_2 \quad \text{Me}^\text{-} \text{O} \text{Me} \quad \text{Me}^\text{-} \text{Cl} \quad \text{Me}^\text{-} \text{O} \text{-} \quad \text{Me}^\text{-} \text{O} \text{Me} \]

\[
\begin{array}{cccc}
\square & \square & \square & \square \\
\end{array}
\]

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

a)

\[ \text{MeBr} \quad \text{MeNH}_2 \]

\[ \text{WITHOUT over-alkylation} \]

b)

\[ \text{MeOMe} \quad \text{MeOHNH}_2 \]
3. Please provide the requested products. If no reaction is expected, write "NR".

\[ \text{n-Bu}^+ \text{Cl} \xrightarrow{1. \text{Li(t-BuO)}_3\text{AlH}} \xrightarrow{2. \text{workup}} \]

\[ \text{n-Bu}^+ \text{OMe} \xrightarrow{1. \text{excess EtMgBr}} \xrightarrow{2. \text{workup}} \]

\[ \text{n-Bu}^+ \text{OMe} \xrightarrow{1. \text{excess NaBH}_4} \xrightarrow{2. \text{workup}} \]

\[ \text{n-Bu}^+ \text{OH} \xrightarrow{1. \text{excess MeLi}} \xrightarrow{2. \text{workup}} \]

\[ \text{n-Bu}^+ \text{OH} \xrightarrow{\text{EtO}^-, \text{EtOH}} \]

\[ \text{n-Bu}^+ \text{OH} \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4} \]
4. Please provide the requested reagents.

a) \( n\text{-Bu} \text{NH}_2 \) \( \rightarrow \) \( n\text{-Bu} \text{NH}_2 \)

b) \( \text{Me} \text{NMMe}_2 \) \( \rightarrow \) \( \text{Me} \text{CH}_2 \)

c) \( \text{Cl} \text{N}_2^+ \text{Cl}^- \) \( \rightarrow \) \( \text{CN} \text{N} \)

d) \( n\text{-Bu} \text{NH}_2 \) \( \rightarrow \) \( n\text{-Bu} \text{CN} \)

e) \( n\text{-Bu} \text{CN} \) \( \rightarrow \) \( n\text{-Bu} \text{COOH} \)
5. Consider the labeling experiment outlined below:

\[
\begin{align*}
\text{Me} & \quad \text{O} & \quad \text{O} & \quad \text{Me} \\
\quad & \quad \text{H}_2\text{O} & \quad \Theta & \quad \Theta\text{H} \\
\end{align*}
\]

stop the reaction at 50% conversion and examine the recovered anhydride for incorporation of \( \Theta \)

\( \Theta = \) 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 \( \Theta \) incorporation you expect to observe in the recovered anhydride. Your answer should include the mechanism for this hydrolysis reaction.
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.

\[
\begin{align*}
\text{NH}_2 & \quad \text{O} \\
\text{Me} & \quad \text{O} \\
\text{Me} \quad \text{H}_2\text{O} & \quad \text{NH}_2 \\
\text{Me} & \quad \text{O} \\
\text{Me} \quad \text{H}_2\text{O} & \quad \text{MeOH} \\
\end{align*}
\]

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

\[
\begin{align*}
\text{NH}_2 & \quad \text{O} \\
\text{Me} & \quad \text{O} \\
\text{Me} \quad \text{H}_2\text{O} & \quad \text{NH}_4 \\
\text{Me} & \quad \text{O} \\
\text{Me} \quad \text{H}_2\text{O} & \quad \text{NH}_4 \\
\end{align*}
\]

c) Briefly explain why the two reactions provide different products.
7. Provide a mechanism for the Hofmann elimination. Please show all arrow pushing.

\[
\text{n-Bu-CONH}_2 + \text{Br}_2 \xrightarrow{\text{NaOH}, \text{H}_2\text{O}} \text{n-Bu-\text{NH}_2}
\]
8. Provide a synthesis that will *selectively* convert A to B. Show all of the key intermediates, and furnish all of the important reagents.
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.

**Allowed Starting Materials:**

| MeOH | MeOH | CO₂ | H₂CO | CN | H₂C=CH₂ |

**a)**

![Image](image1.png)

**b)**

![Image](image2.png)