Organic Chemistry c3444y
2nd Hour Exam
Monday, Feb. 28, 2000
Prof. Leighton

Answer Key
1. Provide detailed mechanisms for the following transformations:
   a. (10 pts) (Just a simple mechanism, no long explanations needed here.)

   \[
   \begin{align*}
   \text{Cl} & \quad \text{CF}_3 \\
   \text{H}_2\text{N}^- & \quad \text{NO}_2 \\
   \text{K}^+ & \quad \text{NH}_2 \\
   \text{H}_2\text{N}^- & \quad \text{CF}_3 \\
   \text{H}_2\text{N}^- & \quad \text{NO}_2 \\
   \end{align*}
   \]

   \[S_{\text{NAr}} \text{ requires much less harsh conditions than the benzene mechanism. Therefore, if both are possible as is the case here, } S_{\text{NAr}} \text{ will win out.}\]

   b. (10 pts)

   \[
   \begin{align*}
   \text{OH} & \quad \text{H}^+ \\
   \text{H}^+ & \quad \text{MeOH} \\
   \text{H}^+ & \quad \text{MeOH} \\
   \text{MeOH} & \quad \text{H}^+ \\
   \end{align*}
   \]
2. Predict the major product of the following reactions:

a. (10 pts)

\[
\text{\begin{array}{c}
\text{\(\text{R} - \text{O} - \text{O} - \text{H}\)}
\end{array}}
\]

1. \(\text{R} - \text{O} - \text{O} - \text{H}\)
2. \(\text{LiAlH}_4\)
3. \(\text{H}_3\text{O}^+\)

\[
\text{HO-CH-Cyclopentane-HOH}
\]

b. (10 pts)

\[
\text{\begin{array}{c}
\text{\(\text{Br}\)}
\end{array}}
\]

1. \(\text{PPh}_3\)
2. \(\text{LDA (a base)}\)
3. \(\text{H-CO-Me}\)

\[
\text{Me-Cyclopentene-Me}
\]

c. (10 pts)

\[
\text{\begin{array}{c}
\text{\(\text{Me-CO-COOH} - \text{OH} - \text{OH}\)}
\end{array}}
\]

\(\text{H}^+\)

\[
\text{Me-Cyclic ether-Me}
\]
3. (10 pts) Given that the Wittig reaction produces cis alkenes preferentially, it would be useful to have a method for the conversion of cis alkenes to trans alkenes. One such method is shown below. In the first step the cis alkene is epoxidized with a peracid. In the second step, the epoxide is treated with PPh\(_3\).

Provide a mechanism for the second step and explain (briefly!) why a trans alkene is produced.

The first step is an S\(_\text{N}\)\(_2\) with stereochemical inversion. Upon rotation to close the oxaphosphatane ring, the R and R' groups end up trans, thus providing the trans alkene.
4. Provide the reagents necessary to accomplish the following transformations:

a. (8 pts)

\[
\text{Br} - \biggarrow[1. \text{NaNO}_2, \text{HCl} \atop 2. \text{CuBr}] \biggarrow \text{Br} \quad \text{Br}
\]

b. (8 pts)

\[
\text{R} \quad \text{H} \quad \text{O} \quad 1. \text{Me}_3\text{SiCN}, \text{BF}_3 \atop 2. \text{DIBAL, -78 °C} \atop 3. \text{H}_3\text{O}^+ \biggarrow \text{R} \quad \text{OH} \quad \text{CH}_2 \quad \text{O}
\]

c. (8 pts)

\[
\text{O} \quad \text{1. LiMe}_2\text{Cu} \atop 2. \text{H}_3\text{O}^+ \biggarrow \text{O} \quad \text{CH}_3
\]
5. Recall that 2-chloropyridine undergoes smooth $S_{N}Ar$ reactions:

\[
\begin{array}{c}
\text{Cl} \\
\downarrow
\end{array}
\text{Cl} \\
\downarrow
\begin{array}{c}
\text{OCH}_3 \\
\downarrow
\end{array}
\text{OCH}_3
\]

\[
\begin{array}{c}
\text{Cl} \\
\downarrow
\end{array}
\text{Cl} \\
\downarrow
\begin{array}{c}
\text{OCH}_3 \\
\downarrow
\end{array}
\text{OCH}_3
\]

- (8 pts) This reaction can occur because the intermediate anion that is generated enjoys special stability. Explain with structures what is the nature of this special stability.

\[
\begin{array}{c}
\text{Cl} \\
\downarrow
\end{array}
\text{Cl} \\
\downarrow
\begin{array}{c}
\text{OCH}_3 \\
\downarrow
\end{array}
\text{OCH}_3
\]

This is a particularly strong contributor, with the anion on the relatively electronegative nitrogen.

- (8 pts) Would you expect 2-chlorofuran to undergo smooth $S_{N}Ar$ reactions? (We will look at your work, but you must clearly write "yes" or "no.")

\[
\begin{array}{c}
\text{OCH}_3 \\
\downarrow
\end{array}
\text{Cl} \\
\downarrow
\begin{array}{c}
\text{Cl} \\
\downarrow
\end{array}
\text{OCH}_3
\]

No special stability for this anion. Thus we would not expect it to form.