51C Practice Problems 6  
Spring 2015

1. For the following set, write in the box a single compound letter which correctly completes the statement.

\[
\begin{align*}
&\text{A: } \text{CH}_3\text{C} = \text{O} \text{CH}_3 \\
&\text{B: } \text{CH}_3\text{CH}_3 \text{C} = \text{O} \\
&\text{C: } \text{CH}_3\text{CH}_3 \text{CO} \text{OH} \\
&\text{D: } \text{CH}_3\text{CH}_3 \text{CO} \text{OCH}_3
\end{align*}
\]

a) The least acidic compound?
b) The most acidic compound?
c) The compound expected to form the greatest percentage of enol isomer at equilibrium?
d) The compound not expected to form any enol isomer at equilibrium?

2. a) When acetaldehyde is placed in deuterated water (D$_2$O) with a trace of acid or base, the $\alpha$-hydrogens are replaced by deuteriums. Provide a mechanism for the acid catalyzed and base catalyzed reaction.

\[
\text{H}_3\text{C} = \text{O} \quad \xrightarrow{\text{D}_2\text{O}} \quad \text{H}_3\text{C} = \text{D} = \text{O}
\]

b) Explain why the aldehydic hydrogen (the hydrogen shown in bold) in acetaldehyde does not get replaced by deuterium.

3. Diels-Alder reaction of the following dieneophile forms an enol ether. Closely related to enols, an enol ether can be hydrolyzed to a ketone. The overall strategy provides a route to cyclohexanone rings. Provide a mechanism for hydrolysis of the following enol ether:

\[
\text{H}_3\text{C} = \text{CH}_{\text{NO}_2} \quad \xrightarrow{\Delta} \quad \text{H}_3\text{C} = \text{CH}_{\text{NO}_2} \quad \xrightarrow{\text{H}_3\text{O}^+ / \text{H}_2\text{O}} \quad \text{C,H,C,H}_2\text{NO}_2
\]

4. Provide a mechanism for the following two $\alpha$-bromination reactions.

\[
\begin{align*}
a. &\quad \text{Ph}\text{CH}_3\text{CO} \quad \xrightarrow{\text{Br}_2 / \text{H}_3\text{O}^+} \quad \text{PhCH}_2\text{Br} \\
b. &\quad \text{Ph}\text{CH}_3\text{CO} \quad \xrightarrow{\text{Br}_2 / \text{HO}^-} \quad \text{PhCO}^{-}
\end{align*}
\]
5. Predict the products or provide reagents for the following reactions:

\[
\begin{align*}
\text{Br} & \quad \text{NaCN} \\
\text{H}_3\text{O}^+ & \quad \Delta \\
\text{H}_2\text{O}, \text{H}_3\text{O}^+ & \quad \text{CH}_3\text{CH}_2\text{OH}, \text{H}_3\text{O}^+(\text{cat}) \\
\end{align*}
\]