WORKSHOP

Week 18

Aldehydes and Ketones: Synthesis and Nucleophilic Additions

1. a. Discuss the similarities and differences in the structures and reactivities of the double bonds of 2-methylpropene and 2-propanone.

   b. With part (a) in mind, account for the following observations. Identify the nucleophile and the electrophile for the first step of each reaction.

   \[
   \begin{align*}
   {\text{HCN}} & \quad \text{fast} \\
   {\text{HCN}} & \quad \text{No Reaction} \\
   \end{align*}
   \]

2. Write detailed electron-pushing mechanisms that explain the stated observations.

   a. The following reaction occurs rapidly at pH = 5 but fails at pH = 1.

   \[
   \text{acetone} + \text{phenylhydrazine} \quad \text{aq. solution} \quad \text{phenylhydrazine} \\
   \]

   b. The labeling of acetone with \(^{18}\text{O}\) is catalyzed by both acid and base.

   \[
   \begin{align*}
   \text{acetone} & \quad \text{H}_2\text{O}^{18}\text{O}^+ \quad \text{or} \\
   & \quad \text{HO}^- \\
   \end{align*}
   \]

   c. \[
   \text{glucose} \quad \text{H}_3\text{O}^+ \quad \text{H}_2\text{O} \quad \text{pH} \geq 7
   \]

   \[
   \text{no reaction} \\
   \text{CH} + \text{OH}_2\text{OH}
   \]
3. Propose structures for the lettered compounds.

a. Compound X, C\textsubscript{7}H\textsubscript{14}O\textsubscript{2}, gives a silver mirror when treated with Ag\((\text{NH}_3)\textsubscript{2}\text{H}^+\)/OH\(^-\). Treatment of the compound with Zn(Hg)/HCl produces 2-methylhexane. The IR spectrum exhibits strong absorption at 1710 cm\(^{-1}\) and two moderate absorptions between 2700 and 2800 cm\(^{-1}\). The \(^1\)H NMR spectrum shows a one-hydrogen doublet at \(\delta 9.70\) (\(J = 2\) Hz).

b. Compound A, C\textsubscript{9}H\textsubscript{12}O, was optically active, did not give a precipitate with 2,4-dinitrophenylhydrazine, showed a broad IR band at 3400 cm\(^{-1}\), and was readily oxidized to B, C\textsubscript{9}H\textsubscript{10}O, with aqueous chromic acid (H\textsubscript{2}CrO\textsubscript{4}) at room temperature. When A was refluxed with chromic acid, benzoic acid was obtained. Compound B showed strong IR absorption at 1670 cm\(^{-1}\) but none at 3400 cm\(^{-1}\) and reacted with 2,4-dinitrophenylhydrazine reagent to give C. When B was reacted with EtMgBr followed by aqueous workup, compound D was obtained. D did not react with chromic acid reagent at room temperature and showed an IR band at 3400 cm\(^{-1}\). B and D were optically inactive and could not be resolved.

4. Explain how to selectively carry out the following synthesis

\[
\text{K} \quad \text{CHO} \quad \text{HO} \quad \text{C}=\text{CH} \\
\text{H} \quad \text{CHO} \quad \text{H} \quad \text{CHO} \\
\text{(mixture of cis and trans)}
\]
5. Show how to carry out the specified chemical conversions using any necessary organic and inorganic reagents. More than one step may be required.