Problem Session Zsofi April 2014

Named Reactions:

Give reaction name and/or mechanism.

1. 

\[
\begin{align*}
\text{R}_2\text{C} & \quad \text{R}_2\text{S} \\
\text{O} & \quad \text{O} \\
\text{BH}_3\text{THF} & \quad \text{Me} \\
\rightarrow & \quad \text{OH} \\
\text{R}_1 & \quad \text{R}_5 \\
\end{align*}
\]

a) What is the origin of enantioselectivity? Draw a diagram.

2. 

\[
\begin{align*}
\text{R} & \quad \text{Cl} \\
\text{O} & \quad \text{SO}_2 \quad \text{R'} \\
\text{KOH} & \quad \text{H}_2\text{O, heat} \\
\rightarrow & \quad \text{R'} \\
\end{align*}
\]

a) What needs to be changed to yield the E-isomer?

b) Give the name and mechanism for a modification which includes \textit{in situ} halogenation.

3. 

\[
\begin{align*}
\text{R'} & \quad \text{N}_3 \\
\text{PPh}_3 & \quad \text{-N}_2 \\
\rightarrow & \quad \text{H}_2\text{O} \\
\text{R'} & \quad \text{NH}_2 \\
\end{align*}
\]

4. 

\[
\begin{align*}
\text{H}_2\text{C} = \text{CH}_2 & \quad \text{PdCl}_2 \text{ (cat)} \\
\text{CuCl}_2 \text{ (cat), O}_2, \text{H}_2\text{O} & \quad \text{O} \\
\rightarrow & \quad \text{H} \\
\end{align*}
\]

a) What is the name of the lab-scale modification to form ketones, and what are the reagents/catalysts?
NMR Problems:

Eight structure elucidation problems based on \(^1\)H nmr, \(^{13}\)C nmr and some infrared spectroscopic data are presented below. In each case, from the 15 formulas shown at the bottom of the page (A through O), select that one which best fits the evidence.

1. A C\(_5\)H\(_{12}\)O\(_2\) compound has strong infrared absorption at 3300 to 3400 cm\(^{-1}\). The \(^1\)H NMR spectrum has three singlets at \(\delta 0.9\), \(\delta 3.45\) and \(\delta 3.2\) ppm; relative areas 3:2:1. The \(^{13}\)C NMR spectrum shows three signals all at higher field than \(\delta 100\) ppm. Suggest a structure for this compound.

2. A C\(_4\)H\(_{6}\)O\(_2\) compound has a strong infrared absorption at 1150 cm\(^{-1}\), but no absorption at 3300 to 3400 cm\(^{-1}\). It's \(^1\)H NMR spectrum shows a singlet at \(\delta 3.55\) ppm. The \(^{13}\)C NMR spectrum shows one signal at \(\delta 66.5\) ppm. Suggest a structure for this compound.

3. A C\(_9\)H\(_{12}\)O compound has strong infrared absorption at 3300 to 3400 cm\(^{-1}\). The \(^{13}\)C NMR spectrum of this compound has six discrete signals. It's \(^1\)H NMR spectrum has three sets of lines: singlets at \(\delta 1.1\) (6H), 1.9 (1H) and 7.3 (5H) ppm. Suggest a structure for this compound.

4. A C\(_{10}\)H\(_{14}\) compound. The \(^1\)H NMR spectrum has two singlets at \(\delta 2.45\) and 7.0 ppm (ratio = 6:1). The \(^{13}\)C NMR spectrum shows three signals at \(\delta 132.9\), 130.5 and 18.9 ppm. Suggest a structure for this compound.

5. A C\(_8\)H\(_2\)N\(_2\) compound shows a sharp infrared absorption at 2230 cm\(^{-1}\). It's \(^1\)H NMR spectrum has a singlet at \(\delta 7.6\) ppm. The \(^{13}\)C NMR spectrum shows three signals at \(\delta 132\), 119 and 117 ppm. Suggest a structure for this compound.

6. A C\(_{14}\)H\(_{22}\) compound. The \(^1\)H NMR spectrum has two singlets at \(\delta 1.1\) and 7.25 ppm (ratio = 9:2). The \(^{13}\)C NMR spectrum shows four signals at \(\delta 147\), 125, 39.3 and 30.8 ppm. Suggest a structure for this compound.

7. A C\(_9\)H\(_{12}\)O\(_3\) compound has strong infrared absorption near 1100 cm\(^{-1}\). Its \(^1\)H NMR spectrum has sharp singlet peaks at \(\delta 3.6\) and 6.6 ppm (intensity ratio 3:1). Its \(^{13}\)C NMR spectrum shows three lines at \(\delta 165\), 115 and 55 ppm. Suggest a structure for this compound.

8. A C\(_9\)H\(_{18}\)O compound has a strong infrared absorption at 1710 cm\(^{-1}\). Its \(^1\)H NMR spectrum has a single sharp peak (a singlet) at \(\delta 1.2\) ppm. Its \(^{13}\)C NMR spectrum shows three lines at \(\delta 210\), 45 and 25 ppm. Suggest a structure for this compound.
(+)-Seimatopolide A is a 10-membered lactone isolated from the fungus Seimatosporium discosioides. Seimatopolides are shown to activate the \( \gamma \)-subtype peroxisome proliferator-activated receptors (PPAR-\( \gamma \)), which is an apparent pivotal process in the regulation of type 2 diabetes. Give the mechanism, and reagents or structure where appropriate for all steps.

**Total Synthesis**

Which enantiomer?