Chem 333, Exam 1
Professor Fox
FALL 2009

Your Name

1)  9 points
2)  9 points
3)  12 points
4)  22 points
5)  48 points
1. Calculate the chemical shifts for each of carbons in the following molecule. Place your answers on the line after the appropriate carbon atom. (9 points total)

You answers must match the correct answer within +/- 1 ppm

You may use the area below for scratch work, but it will not be graded

\[
\begin{align*}
C^a &= 128.5 \ (+19.6) \ (-1.0) = 147.1 \\
&\quad \quad ^1C - \text{NO}_2 \quad ^4C - \text{Br} \\
C^b &= C^c = 128.5 \ (-5.3) \ (+2.2) = 125.4 \\
&\quad \quad ^2C - \text{NO}_2 \quad ^3C - \text{Br} \\
C^d &= C^e = 128.5 \ (+0.9) \ (+3.4) = 132.8 \\
&\quad \quad ^3C - \text{NO}_2 \quad ^2C - \text{Br} \\
C^f &= 128.5 \ (+6.0) \ (-5.4) = 129.1 \\
&\quad \quad ^4C - \text{NO}_2 \quad ^1C - \text{Br}
\end{align*}
\]
2. Calculate the chemical shifts for each of protons in the following molecules. Place your answers on the line after the appropriate carbon atom. (9 points total)
Your answers must match the correct answer within +/- 1 ppm

\[
\begin{align*}
H^a & \quad 5.72 \quad \text{ppm} \\
H^b & \quad 5.96 \quad \text{ppm}
\end{align*}
\]

\[
\begin{align*}
H^c & \quad 6.66 \quad \text{ppm} \\
H^d & \quad 7.00 \quad \text{ppm}
\end{align*}
\]

You may use the area below for scratch work, but it will not be graded

\[
\begin{align*}
H^a &= 5.25 \quad (+0.44) \quad (+0.03) = 5.72 \\
&\quad \text{Gem} \quad \text{trans} \\
&\quad \text{ALKYL} \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
H^b &= 5.25 \quad (-0.29) \quad (+1.00) = 5.96 \\
&\quad \text{trans} \quad \text{gem} \\
&\quad \text{ALKYL} \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
H^c &= 5.25 \quad (+0.37) \quad (+1.04) = 6.66 \\
&\quad \text{CIS} \quad \text{Gem} \\
&\quad \text{Aromatic} \quad \text{Br}
\end{align*}
\]

\[
\begin{align*}
H^d &= 5.25 \quad (1.35) \quad (0.40) = 7.00 \\
&\quad \text{Gem} \quad \text{CIS} \\
&\quad \text{Aromatic} \quad \text{Br}
\end{align*}
\]
3. Match the following $^1$H NMR spectra with one of the following substances. Write your answer in the box along side the spectrum. (6 points each)

- **A**: $CH_3$-CH=CH-COOH
- **B**: $CH_3$-C=CH-COOH
- **C**: $CH_3$-C=CH-COOH
- **D**: $CH_3$-C=CH-COOH

**Spectrum A**
- 9.72 (t, $J = 2.1$ Hz, 1H)
- 2.36 (dd, $J = 7.1$, 2.1 Hz, 2H)
- 2.21 (m, 1H)
- 0.98 (d, $J = 6.7$ Hz, 6H)

**Spectrum F**
- 5.664 (m, 2H)
- 1.991 (m, 4H)
- 1.612 (m, 4H)
4. Elucidate the following structure based on the $^{13}$C NMR data

$\text{C}_6\text{H}_{11}\text{BrO}_2$

$^{13}\text{C NMR}$
173.4, s
51.5, q
33.1, t
32.9, t
32.0, t
23.5, t

a) Calculate the IHD: \[ \Box \] (1 point)

b) Show the substructure that is associated with the following $^{13}$C NMR resonances (7 points)

\[ \begin{array}{c}
\text{173.4, s} \\
\text{51.5, q}
\end{array} \]

\[ \begin{array}{c}
\text{CO} \\
\text{O} \\
\text{CH}_3
\end{array} \]

C) Draw the structure (14 points)
5. Elucidate the following structure based on the following $^1$H NMR and $^{13}$C NMR data:

<table>
<thead>
<tr>
<th>$^{13}$C NMR</th>
<th>$^1$H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>166.4, s</td>
<td>5.92, dd, J=7.9, 11.5 Hz, 1H</td>
</tr>
<tr>
<td>149.0, d</td>
<td>5.68, d, J=11.5 Hz, 1H</td>
</tr>
<tr>
<td>118.2, d</td>
<td>4.15, q, J=7.2 Hz, 2H</td>
</tr>
<tr>
<td>59.7, t</td>
<td>2.40, m, 1H</td>
</tr>
<tr>
<td>39.2, t</td>
<td>1.27, t, J=7.2 Hz, 3H</td>
</tr>
<tr>
<td>32.4, d</td>
<td>1.2-1.3, m, 4H</td>
</tr>
<tr>
<td>20.7, t</td>
<td>0.99, d, J=6.6 Hz, 3H</td>
</tr>
<tr>
<td>20.2, q</td>
<td>0.88, t, J=7.1 Hz, 3H</td>
</tr>
<tr>
<td>14.2, q</td>
<td></td>
</tr>
<tr>
<td>14.1, q</td>
<td>3/18 all H's on C</td>
</tr>
</tbody>
</table>

a) Calculate the IHD: $\underline{2}$ (1 point)

b) Show the substructure that is associated with the following $^{13}$C NMR resonances (5 points)

149.0, d
118.2, d

\[ \text{I, Z disubstituted alkene.} \]

c) Show the substructure that is associated with the following $^{13}$C NMR resonances (5 points)

166.4, s

\[ \text{A ketone.} \]
d) Show the substructure that is associated with the following $^1H$ NMR resonances (5 points)

4.15, q, $J=7.2$ Hz, 2H
1.27, t, $J=7.2$ Hz, 3H

![Structure image]

5.92, dd, $J=7.9$, 11.5 Hz, 1H
5.68, d, $J=11.5$ Hz, 1H

![Structure image]

f) Show your final structure (20 points)

![Final structure image]