Chem 30B Spring 2004

MIDTERM #2

(50 Min)

Weds May 26th

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

***DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO***

<table>
<thead>
<tr>
<th>Q1</th>
<th>/ 20</th>
<th>Q4</th>
<th>/ 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q2</td>
<td>/ 20</td>
<td>Q5</td>
<td>/ 30</td>
</tr>
<tr>
<td>Q3</td>
<td>/ 15</td>
<td>Bonus</td>
<td>/ 15</td>
</tr>
<tr>
<td></td>
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<td>Total</td>
<td>/ 100</td>
</tr>
</tbody>
</table>

"Marge, don’t discourage the boy! Weaseling out of things is important to learn. It’s what separates us from the animals … except the weasel." – Homer Simpson
1. Predict the number of signals you would expect to see in the 1H-decoupled 13C-NMR spectrum of each of the molecules shown below. (2 points each)
2. Some spectroscopic data for an unknown compound (A) are shown below. Use these data to answer the questions on the following page.

**IR Spectrum**

![IR Spectrum Image]

**Mass Spectrum**

![Mass Spectrum Image]

The base peak (100% intensity) is at \( m/z = 54 \). The peaks at \( m/z = 133, 134, 135, \) and \( 136 \), have the following relative intensities (49:2:48:2), respectively.

**1H-NMR Spectrum**

\[ \delta = 3.0 \text{ (triplet, integration = 1)}, \delta = 3.5 \text{ (triplet, integration = 1)} \text{ ppm} \]

**13C-NMR Spectrum**

\[ \delta = 22, 25, 117 \text{ ppm} \]
(a) What is the molecular formula of compound A? (3 points)

(b) What is the structure of compound A? (10 points)

(c) What is the precise structure of the fragment that gives rise to a peak at m/z = 93? (2 points)

(d) What is the precise structure of the fragment that gives rise to a peak at m/z = 95? (Your answer should differ from that given in part (c)) (2 points)

(e) What is the structure of the fragment that gives rise to the base peak at m/z = 54? (3 points)
3. Some spectroscopic data for an unknown compound (B) are shown below. Use these data to answer the questions on the following page.

**IR Spectrum**

**Mass Spectrum**

**13C-NMR Spectrum**
The relative integration of the peak groupings from left to right are 2:3:3

(a) What is the molecular formula of compound B? (3 points)

(b) What is the structure of compound B? (10 points)

(c) What is the structure of the fragment that gives rise to the base peak at \( m/z = 43 \)? (2 points)
4. Compounds C, D, and E are isomers with the molecular formula C₅H₁₁Br. The 1H-decoupled 13C-NMR spectrum of each compound is shown below, with the assignment from the DEPT spectrum shown above each peak (All peaks are shown, there are no peaks at ppm values > 100). In the boxes provided below, draw the structures of C, D, and E, based upon these spectra. (5 points each)
5. The diols shown below react with ketones (acetone in a and b; methyl ethyl ketone in c and d) to form cyclic ketals. In each case, draw the product of the reaction (F, G, and H), note: in d, two different diastereomeric products (J and K) are formed. In parts a and b, predict how many methyl signals will be observed in the 1H NMR spectra of compounds F and G, respectively. In compounds H, J, and K, what are the stereotopical relationships between the phenyl groups in each case. (3 points per box)

(a)
\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{Ph} & \quad \text{OH}
\end{align*}
\]
\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{H}^+ \text{cat}
\end{align*}
\]
\[
\begin{align*}
F & \quad \text{Number of methyl signals in 1H NMR spectrum of F?}
\end{align*}
\]

(b)
\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{Ph} & \quad \text{OH}
\end{align*}
\]
\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{H}^+ \text{cat}
\end{align*}
\]
\[
\begin{align*}
G & \quad \text{Number of methyl signals in 1H NMR spectrum of G?}
\end{align*}
\]

(c)
\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{Ph} & \quad \text{OH}
\end{align*}
\]
\[
\begin{align*}
\text{Me} & \quad \text{Et} \\
\text{H}^+ \text{cat}
\end{align*}
\]
\[
\begin{align*}
H & \quad \text{Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in H?}
\end{align*}
\]

(d)
\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{Ph} & \quad \text{OH}
\end{align*}
\]
\[
\begin{align*}
\text{Me} & \quad \text{Et} \\
\text{H}^+ \text{cat}
\end{align*}
\]
\[
\begin{align*}
J & \quad \text{Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in J?}
K & \quad \text{Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in K?}
\end{align*}
\]
6 (BONUS) At –100 °C, undecadeuteriocyclohexane (L) gives rise to two equal intensity signals in the 1H-NMR spectrum. In contrast, at room temperature, only one signal is observed in the 1H-NMR spectrum.

![Diagram of L](image)

(a) Draw the two different species (L₁ and L₂) that give rise to the signals at –100 °C (3 points each)

(b) Briefly explain why only one signal is observed in the 1H-NMR spectrum when it is recorded at room temperature (4 points)

7 (BONUS) Compound M has the molecular formula C₄H₆O₂. Only one peak is observed in the 1H-decoupled 13C-NMR spectrum, and only one singlet is observed in the 1H-NMR spectrum. Propose a structure for M. (5 points)
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