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***

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"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)

(a)  
(f)  
(b)  
(g)  
(c)  
(h)  
(d)  
(i)  
(e)  
(j)  

1  3  6  5  2  5  5  9  5
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

Mass Spectrum

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.

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

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

\[ \text{C}_3\text{H}_4\text{Br-N} \]

M+1 peak ~ 4% of N+, hence \( \frac{4}{1.1} = 3.6 \), so contains 3 C atoms

\[ 3\text{C} = 3 \times 12 = 36 \]
\[ 1\text{Br} = 1 \times 79 = 79 \]

\[ \text{M} = 115 \]
\[ 133 - 115 = 18 \]
\[ = 1\text{N and 4H} \]

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

\[ \text{Br-CH}_2\text{CH}_2\text{C}=\text{N} \]

Triplets in \(^1\text{H NMR}\)

\[ ^{13}\text{C} \delta = 117 \]

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

\[ \text{Br-CH}_2 \]

\[ 79 + 14 = 93 \]

Significant \( \text{M}+2 \) peak

(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)

\[ \text{Br-CH}_2 \]

\[ 81 + 14 = 95 \]

Significant \( \text{M}+2 \) peak

(e) What is the structure of the fragment that gives rise to the base peak at \( m/z = 54 \)? (3 points)

\[ \text{CH}_2\text{CH}_2\text{CN} \]

Contains no Br

\( \text{no significant M}+2 \) peak

\[ \text{C}=\text{N} + 2 \quad \text{Br} + 2 \quad \boxed{3 \text{CH}_2\text{CH}_2 + 2} \quad \boxed{\text{N} + 1} \]
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**

- νO-H
- νO-H
- C=O
- C=O

**Mass Spectrum**

- Base peak
- M⁺ at 88

**13C-NMR Spectrum**

- C=O
- Suggests
- \( \frac{O}{C=O} \)
- or
- \( C=O + C-O \)
1H-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)

\[
\text{C}_4\text{H}_8\text{O}_2 + 3
\]

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

\[
\text{CH}_3\text{CH}_2\text{O} - \text{CH}_3
\]

(c) What is the structure of the fragment that gives rise to the base peak at \(m/z = 43\)? (2 points)

\[
\text{V. Stable, in resonance with } \text{CH}_3-\text{C}═\text{O}
\]
4. Compounds C, D, and E are isomers with the molecular formula C_{5}H_{11}Br. 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)

C

\[ \text{CH}_{3} \quad \text{CH}_{2} \quad \text{CH}_{3} \]
\[ 100 \quad 75 \quad 50 \quad 25 \quad 0 \quad \delta (\text{ppm}) \]

D

\[ \text{CH}_{3} \quad \text{CH}_{2} \quad \text{CH}_{3} \]
\[ 100 \quad 75 \quad 50 \quad 25 \quad 0 \quad \delta (\text{ppm}) \]

E

\[ 3 \times \text{CH}_{2} \quad \text{CH}_{2} \quad \text{CH}_{3} \]
\[ 100 \quad 75 \quad 50 \quad 25 \quad 0 \quad \delta (\text{ppm}) \]

\[ \text{C} \quad \text{CH}_{3} \quad \text{CH}_{2} \quad \text{Br} \quad \text{CH}_{2} \quad \text{CH}_{2} \quad \text{Br} \quad \text{CH}_{3} \quad \text{CH}_{3} \]
\[ \text{C} \quad \text{CH}_{3} \quad \text{CH}_{2} \quad \text{Br} \quad \text{CH}_{2} \quad \text{CH}_{2} \quad \text{Br} \quad \text{CH}_{3} \quad \text{CH}_{3} \]

E

\[ 4 \times \text{CH}_{2} / 1 \times \text{CH}_{3} \]
all different
5. The diols shown below react with ketones (acetone in a and b; methyl ethyl ketone in c and d) to form cyclic ketal s. 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) 

\[
\begin{align*}
\text{Ph} & \text{H} \quad \text{OH} \\
\text{Ph} & \text{H} \quad \text{OH} \\
& \xrightarrow{\text{Me} \quad \text{Me}} \\
& \xrightarrow{\text{H}^+ \text{cat}} \\
\text{F} & \quad \text{Ph} \quad \text{Me} \quad \text{O} \quad \text{Me} \\
& \quad \text{Ph} \quad \text{H} \quad \text{Me} \\
\end{align*}
\]

Number of methyl signals in 1H NMR spectrum of F?

\[\text{ONE}\]

(b) 

\[
\begin{align*}
\text{Ph} & \text{H} \quad \text{OH} \\
\text{Ph} & \text{H} \quad \text{OH} \\
& \xrightarrow{\text{Me} \quad \text{Me}} \\
& \xrightarrow{\text{H}^+ \text{cat}} \\
\text{G} & \quad \text{Ph} \quad \text{Me} \quad \text{O} \quad \text{Me} \\
& \quad \text{Ph} \quad \text{H} \quad \text{Me} \\
\end{align*}
\]

Number of methyl signals in 1H NMR spectrum of G?

\[\text{TWO}\]

(c) 

\[
\begin{align*}
\text{Ph} & \text{H} \quad \text{OH} \\
\text{Ph} & \text{H} \quad \text{OH} \\
& \xrightarrow{\text{Me} \quad \text{Et}} \\
& \xrightarrow{\text{H}^+ \text{cat}} \\
\text{H} & \quad \text{Ph} \quad \text{Me} \quad \text{O} \quad \text{Et} \\
& \quad \text{Ph} \quad \text{H} \quad \text{Et} \\
\end{align*}
\]

Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in H?

\[\text{DIESTEREO-TOPI-CA}\]

(d) 

\[
\begin{align*}
\text{Ph} & \text{H} \quad \text{OH} \\
\text{Ph} & \text{H} \quad \text{OH} \\
& \xrightarrow{\text{Me} \quad \text{Et}} \\
& \xrightarrow{\text{H}^+ \text{cat}} \\
\text{J} & \quad \text{Ph} \quad \text{Me} \quad \text{O} \quad \text{Et} \\
& \quad \text{Ph} \quad \text{H} \quad \text{Et} \\
\text{K} & \quad \text{Ph} \quad \text{Me} \quad \text{O} \quad \text{Et} \\
& \quad \text{Ph} \quad \text{H} \quad \text{Me} \\
\end{align*}
\]

Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in J?

\[\text{ENANTIOTA-TOPI-CA}\]

Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in K?

\[\text{ENANTIOTA-TOPI-CA}\]
6 (BONUS) At \(-100^\circ\text{C}\), 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.

(a) Draw the two different species (L1 and L2) that give rise to the signals at \(-100^\circ\text{C}\) (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 \(\text{C}_4\text{H}_8\text{O}_2\). 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)