Organic Chemistry II (CHE 232-001)
Examination I
February 11, 2009

Name (Print legibly): __________ Key __________________________
(last) (first)

Student ID#: ____________________________________________

PLEASE observe the following:
You are allowed to have scratch paper (provided by me), and a simple
model set. **You do not need a calculator.** Please have your student ID
card present on your desk. Read through the entire exam before beginning
and start first on the problems that seem easiest to you. Please provide
clear and concise answers to the questions **in the area provided** or
the back of an exam page.

<table>
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<tr>
<th>Problem</th>
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TABLE OF ATOMIC WEIGHT MULTIPLES

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<table>
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<td>C=\text{C–H}, \text{O=C–H, C≡C–H}</td>
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<tr>
<td>X–C–H; X=O, N, S, Hal</td>
<td>2.5-4.5</td>
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<tr>
<td>C≡C–H, RX₂C–H</td>
<td>4.5-6.5</td>
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<td>ary1 H</td>
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<tr>
<td>alkyl N–H</td>
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<td>RCO₂H</td>
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1. (15 pts) How would each of the following pairs of compounds differ in their IR spectra? **Describe precisely the differences in IR data** of the two compounds that would allow you to unambiguously distinguish between them. Be thorough but brief (no more than two sentences).

(a)

The alkene will show a C=C stretch at 1650 cm\(^{-1}\) and a C\(^{sp2}\)-H stretch at 3000-3150 cm\(^{-1}\); each of these stretches will be absent in the IR spectrum for the alkyne, which will instead contain C≡C and C\(^{sp1}\)-H stretches at 2250 cm\(^{-1}\) and 3300 cm\(^{-1}\), respectively.

(b)

The carboxylic acid will show a strong and broad O-H absorption between 2500-3500 cm\(^{-1}\), which will be absent in the IR spectrum for the ester. It is also possible to distinguish the compounds by their carbonyl stretches: \(\nu\) (CO) for RCOOH = 1710 cm\(^{-1}\) while \(\nu\) (CO) for RCOOR = 1735-1745 cm\(^{-1}\).
(c) The IR spectrum of a molecule known to have structure A, B, or C is shown below. Which structure is most consistent with the spectrum? Briefly, explain your reasoning.

A ν (C≡N) stretch at 2250 cm⁻¹ will be present only in the IR spectrum for B.
2. (35 pts) **Describe precisely differences in the $^1$H NMR data of** each of the following pair of compounds that would allow you to unambiguously distinguish between them. In other words, **describe differences** that you expect to see in $^1$H NMR spectra of the two compounds that would allow you to distinguish between them. **Be brief** (no more than two sentences).

(a)

![diagram](https://via.placeholder.com/150)

**Difference:**
Assuming only 3-bond H-C-C-H coupling occurs, only compound A will show a singlet aromatic resonance (for $H_c$) in its $^1$H NMR spectrum ($H_a$ and $H_b$ will show as two doublets with $J = 7-12$ Hz). All of the aromatic resonances for B will at least show H-C-C-H coupling (7-12 Hz) and hence appear as two doublets and a doublet of doublets (which might be observed as a triplet if $J_{H_a-H_b} = J_{H_b-H_c}$).

If weak 4-bond coupling is observed, $H_c$ in A will show as doublet with $J = 1-2$ Hz.

(b)

![diagram](https://via.placeholder.com/150)

**Difference:**

The CH proton in C will show as a quartet (in the 4-5.5 ppm region) while the CH$_3$ group will show as a doublet. In contrast, two triplets (one around 2.5 ppm and the other around 3.0 PPM) will be observed in the $^1$H NMR spectrum for D.

Also, two non-aromatic resonances in 1:3 integral ratio will be observed for C and two non-aromatic resonances in 1:1 integral ratio will be observed for D.
(c) **Describe precisely the difference in the $^{13}\text{C}$ NMR data of the**
following pair of compounds that would allow you to unambiguously distinguish
between them.

\[
\begin{align*}
\text{G} & : \begin{array}{c}
\text{C} \\
\text{H}_3
\end{array} & \text{H}_3C
\begin{array}{c}
\text{C} \\
\text{H}_3
\end{array}
\text{C} \\
\text{H}_3
\text{G} \\
\text{H}_3C
\begin{array}{c}
\text{C} \\
\text{H}_3
\end{array}
\text{H}_3C
\end{align*}
\]

Difference:
The carbon atoms exist in four different chemical environments in G while the
carbon atoms exist in three different chemical environments in H. Hence G will show four total $^{13}\text{C}$ resonances while H will show 3.

(d) An unknown compound has the molecular formula $\text{C}_9\text{H}_{11}\text{Br}$. Its $^1\text{H}$ NMR spectrum shows the following absorptions:
7.1 ppm, singlet, 2H;
2.3 ppm, singlet, 6H;
2.2 ppm, singlet, 3H.

Draw the structure of the compound. **Briefly**, explain your reasoning.

See Ace Assignment Chapter 13 and 14 – Spectroscopy, problem 16.
(e) A molecule known to have structure A, B, C, or D shows the following absorptions in its $^1$H NMR spectrum:

- 2.32 ppm, multiplet, 2H;
- 3.68 ppm, triplet, 2H;
- 3.95 ppm, singlet, 1H;
- 5.75-6.35 ppm, multiplet, 2H.

Its mass spectrum shows $M^+$ and $[M+2]^+$ peaks in a 3:1 ratio. Which structure is most consistent with the given data? 

Briefly, explain your reasoning.

M$^+$ and $[M+2]^+$ peaks in a 3:1 ratio rules out compounds that contain a Br atom.

- 2.32 ppm, multiplet, 2H; CH$_2$ next to the double bond
- 3.68 ppm, triplet, 2H; CH$_2$ next to OH group
- 3.95 ppm, singlet, 1H; OH proton
- 5.75-6.35 ppm, multiplet, 2H; alkene protons
3. (12 pts) Draw a detailed mechanism for bromination of ethyl phenylacetate (1) with NBS. Explain the origin of the selectivity for formation of 2.

\[ \begin{align*}
\text{INITIATION} \\
\text{NBS} &\quad \text{Br} \\
\text{CCl}_4 &\quad \text{C} \\
\text{CCl}_4 &\quad \text{O} \\
\text{CCl}_4 &\quad \text{O} \\
\end{align*} \]

\[ \begin{align*}
\text{PROPAGATION} \\
\text{Br} &\quad \text{Br} \\
\text{O} &\quad \text{O} \\
\text{O} &\quad \text{O} \\
\end{align*} \]

\[ \begin{align*}
\text{TERMINATION} \\
\text{Br} &\quad \text{Br} \\
\text{O} &\quad \text{O} \\
\text{O} &\quad \text{O} \\
\end{align*} \]
4. (26 pts) Draw the major product of each of the following reactions.

(i) \[
\begin{align*}
\text{ cyclohexane } & \quad \xrightarrow{\text{Br}_2, \text{hv}} \\
& \quad \text{Br} \\
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \xrightarrow{\text{HBr}, \text{ROOR}} \\
& \quad \text{CH}_3\text{Br}
\end{align*}
\]

(iii) \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 & \quad \xrightarrow{\text{HBr}} \\
& \quad \text{Br}
\end{align*}
\]

(iv) \[
\begin{align*}
\text{CH}_3\text{CH} & \quad \xrightarrow{\text{NBS}, \Delta, \text{ROOR}} \\
& \quad \text{Br}
\end{align*}
\]

(vi) see radical reactions assignment, question 8

Provide the reagents required for the following conversions. Write the required reagents in the box above each reaction arrow.

(vi, 6pts) \[
\begin{align*}
\text{cyclopentane} & \quad \xrightarrow{\text{NBS, hv, }\Delta, \text{ or ROOR}} \\
& \quad \xrightarrow{\text{Br}_2} \\
& \quad \text{Br}
\end{align*}
\]
5. (12 pts) Which of the two structures A and B (below) is more reasonable for a compound that has the spectral data given below? Briefly explain how the given data is consistent with the structure you picked.

(a) The compound has an $M^+$ ion at 85 amu. There is no $[M+2]^+$ peak.
(b) The only IR absorbances in the interpretable region are at 3340 and 2900 cm$^{-1}$.
(c) The $^{13}$C NMR spectrum shows three resonances at $\delta$ 40, 30, and 25.
(d) The $^1$H NMR shows three resonances at $\delta$ 2.7 (m, 4H), 1.5 (m, 6H), and a broad peak at about 5.0 (1H) that changes its position with concentration and temperature.

The low resolution MS and $^{13}$C NMR data provided does not allow structures A and B to be unambiguously distinguished. The IR absorbance at 3340 cm$^{-1}$ is consistent with structure A since it should show only one N-H absorbance peak. That structure A is more reasonable is confirmed by the $^1$H NMR data assignment below:

![Diagram of Structures A and B]

$^{a}$CH$_2$ = 2.7 ppm (m, 4H)
$^{b}$CH$_2$ and $^{c}$CH$_2$ = 1.5 ppm (m, 6H)
N–H = 5.0 ppm (1H)

The broad peak at about 5.0 changes its position with concentration and temperature due to changes in the amount of hydrogen bonding it is involved in, confirming that it is the amine proton.