FINAL EXAMINATION

Chemistry 3B
Professor K. Peter C. Vollhardt
May 20, 1998

Name:

(Print first name before second! Use capital letters)

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

111  Jong, Kimmy  ______  311  Chan, Gina  ______
112  Yun, Shine Sun  ______  312  Chiu, Anita  ______
113  Toochnida, Tab  ______  313  Lemieux, George  ______
211  Cho, Joanne  ______  411  Upasani, Sayli  ______
212  Ong, Angeline  ______  412  Ong, Angeline  ______
213  Yu, Jerry  ______  413  Mar-Tang, Roger  ______
301  Chan, Gina  ______  511  Wu, Jack  ______
302  Goon, Scarlett  ______  512  Cho, Joanne  ______
303  Wasser, Ian  ______  601  Lecture Only  ______
Making up an I Grade  ______

(If you are, please indicate the semester in which you took previous Chem 3B)

Please write the answer you wish to be graded in the spaces provided. Do scratch work on the back of the pages. This test should have 20 pages. Check to make sure that you have received a complete exam. A good piece of advice: read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases, it is better to be pedantic in accuracy! Grades will be posted 9 am, Monday, May 25, outside 320 Latimer Hall (Lab B). Good luck and have a good summer!

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I. [30 Points] Write detailed mechanisms for the hydrolyses of methyl acetate in acid (a) and base (b).

(a) \[
\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COH} + \text{CH}_3\text{OH}
\]

(b) \[
\text{CH}_3\text{COCH}_3 + \text{Na}^+ \cdot \text{OH}^{-} \rightarrow \text{CH}_3\text{CO}^-\text{Na}^+ + \text{CH}_3\text{OH}
\]
II. [100 Points; (a) - (j) 5 Points each, (k) - (o) 10 Points each] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

(a)  \[ \text{CH}_3\text{OH} \quad \text{CH}_3\text{SO}_3\text{H} \]

(b) \[ \text{O} \quad \text{CH} \]

(c) \[ \Delta \]

(d) \[ \text{C}_6\text{H}_5\text{O} \]

(e) \[ \text{Cl} \]

(f)  \[ \text{H}^+, \text{CH}_3\text{OH} \]
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(g) 
\[ \text{R} - 
\text{C} = \text{O} \rightarrow \text{CH}_3 \text{NH} \rightarrow \text{CH}_3 \text{NH} \]

(h) 
\[ \text{CH}_3 \text{CH}_2 \text{C} = \text{O} + \text{R} \rightarrow \text{CH}_3 \text{CH} = \text{CH}_2 \rightarrow \text{R} + \text{R} \]

(i) 
\[ \text{CH}_3 \text{NH}_2 \rightarrow \text{R} \]

(j) 
\[ \text{R} + \text{R} \rightarrow \text{R} \quad \text{OH, H}_2\text{O} \rightarrow \text{R} \]

(k) 
\[ \text{NO}_2 \quad \text{CH}_3 \rightarrow \text{R} \quad \text{CN} \rightarrow \text{R} \]

(l) 
\[ \text{CH}_3 \text{C} = \text{O} \rightarrow \text{R} \rightarrow \text{CH}_3 \text{C} \]

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(m) 
\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\begin{array}{c}
1. \text{PBr}_3 \\
2. \text{NaCN} \\
3. \text{MgBr} \\
4. \text{H}^+, \text{H}_2\text{O}
\end{array}} \]

(n) 
\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2
\]
\[
\xrightarrow{\begin{array}{c}
1. \Delta \\
2. 
\end{array}} \]
\[
\text{CH}_3\text{COCH}_3
\]

13C NMR: \( \delta = 53.6, 74.6, 152.3 \) ppm

(o) 
\[
\text{C}_6\text{H}_{12} \xrightarrow{\begin{array}{c}
1. \text{Br}_2, \text{hv} \\
2. \\
3. \text{CO}_2 \\
4. \\
5. \text{CH}_3\text{NH}_2
\end{array}} \]
\[
\text{CH}_3\text{CONHCH}_3
\]
III. [90 Points] Treatment of lactone A with HBr in ethanol gave a new compound B.

\[
\begin{align*}
\text{A} & \xrightarrow{\text{HBr, CH}_3\text{CH}_2\text{OH}} \text{B} \\
\end{align*}
\]

Its spectral data are depicted below.

(a) What is B? (Draw in the box provided.)

\[
\begin{align*}
\text{C} & \quad \text{B} \\
\end{align*}
\]

(b) Interpret the spectral information as requested in the spaces provided.
1. IR spectrum of B

Assign the following peaks to their respective (vibrating) bonds:

Peak at 2900 cm\(^{-1}\) due to

Peak at 1700 cm\(^{-1}\) due to
Assign the signals in the boxes provided. (Hints: 1. Br exists as two isotopes 79 and 81, in a 1:1 ratio. 2. Think McLafferty rearrangements and α-cleavages.)
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\[ m/z \ 194, 196 \ (1:1) \]

\[ m/z \ 166, 168 \ (1:1) \]

\[ m/z \ 149, 151 \ (1:1) \]

\[ m/z \ 121, 123 \ (1:1) \]

\[ m/z \ 88 \]
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3. $^1$H NMR Spectrum of B

Draw your suggestion for B in the box below and label the hydrogens A, B, C, D, E giving rise to the correspondingly labeled (below the signals) peaks in the spectrum.
4. $^{13}$C NMR spectrum of B

Note that there are six signals (see chemical shift table in the insert).

Draw your suggestion for B in the box below and label the carbons A, B, C, D, E, F giving rise to the correspondingly labeled (above the signals) peaks in the spectrum.
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(c) Write a mechanism for the formation of B.
IV. [60 Points] Write detailed mechanisms to explain the following observations.

\[ \text{(a)} \quad \text{Reactions: } H^+, H_2O, \Delta \rightarrow \text{Product} + 2 \text{CO}_2 + \text{NH}_3 \]
(b) \[
\begin{align*}
\text{CH}_3\text{CH} & \xrightarrow{\text{NaOH, } \text{H}_2\text{O}} \text{CH}_3\text{CH}=\text{CHCH} \\
\end{align*}
\]
1. \( \text{LiAlD}_4 \)
2. \( H^+, H_2O \) (work up)
V. [60 Points] Provide a reasonable synthetic route from starting material to product. Note: several steps are required and there may be more than one solution to the problem. You may use any additional organic or organometallic reagents, containing four carbons or less, to effect your conversions.

(a) \[
\begin{align*}
\text{starting material} & \rightarrow \\
\text{product} & \\
\end{align*}
\]
(b) \[ \text{C}_{6}\text{H}_{6} \rightarrow \text{C}_{6}\text{H}_{4}
\text{ClCH}_{2}\text{NH}_{2}\n\text{CH}_{2}\text{NH}_{2} \]
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\[
\begin{array}{c}
\text{H}_3\text{N}^+ + \text{COO}^- \\
\end{array}
\]
VI. [60 Points]

(a) Mark with an arrow, e.g. \( \text{\includegraphics{aromatic-molecule.png}} \), the site of preferential electrophilic attack in the following molecules.

\[ \text{CH}_3\text{OCH}_3 \quad \text{CH}_3\text{O-} \text{Thio} \quad \text{CH}_3\text{O-} \text{Thio} \]

(b) The ketopentose A gives only one compound on reduction with \( \text{NaBH}_4 \) (draw in the box below). Explain. Is the product optically active? (circle the correct answer)

\[ \text{HO} \quad \text{H} \quad \text{OH} \quad \text{CH}_2\text{OH} \quad \text{NaBH}_4 \]

Product
optically active: yes \( \square \); no \( \square \)

(c) Among the following compounds, circle the ones which are aromatic.

\[ \text{\includegraphics{aromatic-compounds.png}} \]

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