EXAMINATION 1

Chemistry 3B
Professor K. Peter C. Vollhardt
February 24, 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 Toodhinda, 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 14 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! Good Luck!

I. ________ (30 Points)

II. ________ (50 Points)

III. ________ (50 Points)

IV. ________ (40 Points)

V. ________ (30 Points)

TOTAL (200 Points)
I. [30 Points] 1-Methoxy-4-nitrobenzene undergoes preferential electrophilic attack by \( E^+ \) to give only one of the two products shown.

\[
\begin{array}{c}
\text{OCH}_3 \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{NO}_2
\end{array}
\xrightarrow{E^+ \text{ or } -H^+}
\begin{array}{c}
\text{OCH}_3 \\
\text{E} \\
\text{NO}_2
\end{array}
\quad \text{or} \quad 
\begin{array}{c}
\text{OCH}_3 \\
\text{E} \\
\text{NO}_2
\end{array}
\]

(a) Which one? Mark the box below your choice.

(b) Write the resonance forms of the intermediate formed on attack of \( E^+ \) at:

C-2:

Four resonance forms

C-3:

Three resonance forms

(c) Circle (in your answer above) the most strongly contributing resonance form of the attack at C-2 and the least contributing counterpart of attack at C-3.
II. [50 Points] 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 \textit{not} part of any answer.

(a) \[ \text{Thermodynamic product} \]

(b) A dinitrobenzene

(c) \[ \text{A hexatriene isomer of product} \]

(d) \[ \text{DH} \]
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(e) \chem{\text{Na}^+ \text{NH}_2} \rightarrow \chem{\text{Cyclohexene}}

13C NMR: 10 lines

(f) \chem{\text{Cl}_2 \text{C}_6 \text{H}_4 \text{OCH}_3} \rightarrow \chem{\text{SO}_3 \cdot \text{H}_2\text{SO}_4}

13C NMR: 6 lines

(g) \chem{\text{IR: } \nu = 3500 \text{ cm}^{-1}}

13C NMR: 3 lines

(h) 1. \chem{\text{CH}_3\text{CCH}_3 \text{Cl, AlCl}_3}

2. \chem{\text{Cyclohexene}} \rightarrow \chem{\text{Cyclohexene}}

You can write the conditions for a one-step conversion in 2. (as indicated by the simple box) or a two step sequence (if you can’t remember the one-step procedure).
(i) An aldehyde + A second aldehyde $\xrightarrow{\text{OH, H}_2\text{O}}$ \[ \text{phenylpropionaldehyde} \]

(j) \[ \text{CH}_3\text{I} \]

1. $\text{P(C}_6\text{H}_5\text{)}_3$
2. $\text{CH}_3\text{Li}$
3. $\xrightarrow{\text{}}$
III. [50 Points] Treatment of acetone with phenylmagnesium bromide gave, in addition to the desired alcohol, a small amount of compound A, as shown:

\[ \text{MgBr} + \text{CH}_3\text{CCH}_3 \rightarrow \text{H}^+\text{H}_2\text{O} \rightarrow \text{A} \text{ (minor product)} \]

Its spectral data are depicted below.

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

b. Interpret the spectral information as requested in the spaces provided.
There are two characteristic areas in which peaks occur and one in which a peak is noticeably absent (considering the starting materials). Specify and assign to stretching frequencies (for example, "peak present at 900 cm\(^{-1}\), due to Mg-C stretch"
--- I made this up) the

peak present at

, due to

peak absent at

, due to absence of
2. \(^1H\) NMR SPECTRUM

Draw your suggestion for A and label the hydrogens A, B, C, D giving rise to the correspondingly labeled signals in the spectrum.
3. $^{13}$C NMR Spectrum

$\delta = 25.8, 112.4, 125.9, 127.9, 128.0, 141.6, 143.1$ ppm.

How does this spectrum confirm your structural assignment of A?

4. UV Spectrum

How does this spectrum confirm your structural assignment of A?
IV. [40 Points] Write detailed mechanisms to explain the following observations.
(b) \[ \text{Δ, polar solvent} \]

\[
\begin{align*}
\text{O} & \quad \text{S} \quad \text{CF}_3 \\
\text{O} & \quad \text{S} \quad \text{CF}_3 \\
\text{O} & \quad \text{S} \quad \text{CF}_3 \\
\end{align*}
\]

\[ \text{F}_3\text{CSO}_3\text{H} \]

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(c) \[ \text{enantiomerically pure} \] \rightarrow \text{racemate}
V. (30 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 to effect your conversions.

(a) Ibuprofen (Advil) from benzene:

\[
\text{Benzene} \quad \xrightarrow{\text{reaction}} \quad \text{Ibuprofen}
\]
Phenyl benzoate from 3-pentanone and 1,3-butadiene.