EXAMINATION I

Chemistry 3B
Professor K. Peter C. Vollhardt
February 21, 1995

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.

101  Paikoff, Sari
102  Panomitros, Demetra
111  Herrmann, Paul
112  Mayberry, Kit
113  Bunn, Barry
211  Herrmann, Paul
212  Jalisatgi, Sathish
213  Chen, Melissa
301  Backes, Brad
302  Gonzales, Hector
311  Liu, Guangcheng
312  Yang, Jerry
313  Gonzales, Hector
411  Yang, Kelly
412  Panomitros, Demetra
413  Siesel, Brian
511  Fuller, Joanna
512  Frost, Mareia
513  Tsai, Sheryl
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)
II. _________ (50)
III. _________ (60)
IV. _________ (30)
V. _________ (30)
TOTAL (200)
I. [30 Points] Name (IUPAC) or draw, as appropriate, the following molecules, including their stereochemistry.

a. 

b.  
cis-2-Ethenyl-3-methyl-cyclohexanone

c. 


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 not part of any answer.

a. 

\[ \text{+} \quad \text{N-Br} \]

b. 

\[ \text{HNO}_3, \text{H}_2\text{SO}_4 \]
c. 

\[ \text{[Chemical reaction diagram]} \]

d. 

\[ \text{[Chemical reaction diagram]} \]

e. 

\[ \text{[Chemical reaction diagram]} \]

IR: \( v = 3350, 1690 \text{ cm}^{-1} \)
III. [60 Points] Treatment of benzenol with CO and conc. HCl (a source of HCCl) in the presence of AlCl₃, followed by work-up with ethanol, gave compound A. Its IR and NMR spectra are depicted below; the UV spectrum shows a peak at λmax 290 nm.

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

b. Interpret the spectral data as requested in the spaces provided.
1. IR Spectrum

There is a characteristic peak present and (considering the starting material) a characteristic peak absent in the spectrum. Specify and assign to stretching frequencies:

Peak present at \[ \text{due to} \]

Peak absent at \[ \text{due to} \]
2. $^{13}$C NMR Spectrum

![NMR Spectrum Diagram]

Note: in this spectrum, the relative peak heights can be used as a measure of relative abundance, with the exception of the small peaks at 129.5 and 164.0 which are due to two quaternary carbons.

Draw your suggestion for A and label the carbon atoms, A, B, C, etc., giving rise to the corresponding signals in the spectrum.
3. $^1$H NMR Spectrum

Note: the J values for the peaks at $\delta = 1.50$ and 4.15 ppm are 8 Hz, for those at 7.05 and 7.90 they are 9 Hz. Draw your suggestion for A and label the hydrogens A, B, C, D, and E giving rise to the corresponding signals in the spectrum.
c. Suggest a plausible mechanism for the formation of A.
IV. [30 Points] Write detailed mechanisms to explain the following observations.

a. 

\[
\text{CF}_3\text{CHO} + \text{O}_\text{O} \xrightarrow{\text{H}^+} \text{O}_\text{O} + \text{CH}_3\text{CH}
\]

Why does the equilibrium lie to the right? Explain.
b. The phenyl substituent is an ortho-para director in electrophilic aromatic substitutions. Show why this is so for the monobromination of biphenyl (\chem{\text{\begin{tikzpicture}[baseline] \draw (0,0) ellipse (0.2 and 0.3); \draw (0.5,0) ellipse (0.2 and 0.3); \draw (0,0) -- (0.5,0); \end{tikzpicture}}}).
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.
Hint: work backwards (reverse Diels-Alder reaction)! Work forwards (electrocyclic reaction)! Use a protecting group as part of your scheme.

"Don't worry, Howard. The big questions are multiple choice."