FINAL EXAMINATION

Chemistry 3A
Professor K. Peter C. Vollhardt
December 11, 1995

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

111 Tewell, Craig _______ 331 Bruchez, Marcel _______
121 Caylor, Chris _______ 341 Werkema, Evan _______
131 Nitschke, Jonathan _______ 351 Sweeney, Zachary _______
141 deForest, Sarah _______ 361 Chan, Eugene _______
151 Wanandi, Paulus _______ 411 Barchas, Eric _______
161 Laszlo, Chloe _______ 421 Gray, Nathanael _______
211 Robblee, John _______ 431 Gobran, Hala _______
221 Staunton, Joanna _______ 441 Dysard, Jeff _______
231 Cave, John _______ 511 Furlanetto, Michael _______
311 Fulton, Robin _______ 521 Andryski, Scott _______
321 Golden, Jeff _______ 531 Bise, Ryan _______
Making-up an I grade _______ 541 Kotz, Kenneth _______

(If you are, please indicate which semester you previously took Chem 3A _______

Please write the answer you want graded in the space provided. Do scratch work on the back of the pages. This test should have 21 numbered 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 on Friday, December 15, outside 305 Latimer Hall (Lab Q). Good Luck!

DO NOT WRITE IN THIS SPACE

I. _________ (30)
   IVa. _________
   IVb. _________
   IVc. _________

II. _________ (90)
   III. _________ (30)
   IV. _________ (60)

V. _________ (50) Subtotal _________
   VI. _________ (60)
   VII. _________ (60)

Total _________ (400)
I. [30 Points]

Provide the IUPAC name or draw the structure, as appropriate, of the following molecules. Remember the priority of functional groups in choosing names, indicate the correct stereochemistry (e.g. R, S, and E, Z), and do not forget about the alphabetical ordering of substituents!

a. 

b. 1-(2-Propenyl)cyclohexanol

c. 1, 5, 9-Cyclododecatriyne
II. [90 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.

\[
\text{CH}_4 + \text{F}_2 + \text{Br}_2 \xrightarrow{\text{hv}} \text{a monohalomethane}
\]

b.

\[
\begin{align*}
\text{Br} & \\
 & \quad \xrightarrow{} \quad \text{S}^+(\text{CH}_3)_2\text{Br}^-
\end{align*}
\]

c.

\[
\text{Ketone} \xrightarrow{} \text{OH} \quad \xrightarrow{} \text{Haloalkane}
\]
d.

\[
\begin{align*}
\text{Cl} & \quad \text{H} \\
\text{H} & \quad \text{CH}_2\text{CH}_3 \\
\text{H} & \quad \text{CH}_3
\end{align*}
\]

\[\text{Li}^+ \cdot \text{N(CH(CH}_3)_2\text{)}_2 \rightarrow \]

\[
\begin{align*}
\text{Li}^+ \cdot \text{N(CH(CH}_3)_2\text{)}_2 \\
\text{H}_3\text{C} & \quad \text{C} - \text{SO}_2\text{Cl} \\
\text{NaCN} & \rightarrow \text{CN}
\end{align*}
\]

C\text{}_5\text{H}_{12}\text{O}

\[\tilde{\nu} = 3350 \text{ cm}^{-1}\]

e.

f.

\[
\begin{align*}
\text{OH} & \rightarrow \text{H}^+, \text{H}_2\text{O} \\
\text{HS} & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

IR: no peak at 3350 cm\(^{-1}\)

g.

1. 

2. 

\[
\begin{align*}
\text{Cyclane} & \rightarrow \text{Cyclane} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_3
\end{align*}
\]

IR: no peak at 3350 cm\(^{-1}\)
h. 

\[ \text{H}_2\text{C} = \equiv \text{CH}_3 \]

1. Na, NH\textsubscript{3} (liq)
2. Br\textsubscript{2}, CH\textsubscript{3}OH

i. 

1. 
2. 
3. 

\[ \text{CH}_3 \]

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

j. 

\[ \text{C}_8\text{H}_{12} : \quad ^1\text{H NMR} \delta = 5.54 \text{ (m, 4 H)} \]
\[ 2.11 \text{ (m, 8H) ppm} \]
\[ ^13\text{C NMR} \delta = 128.5, 28.5 \text{ ppm} \]

k. 

1. 
2. 

\[ \text{Hex} \Rightarrow \text{Oct} \]
l.  

\[ \text{Hexyne} \rightarrow \text{BH}_3 \rightarrow \text{H}_2\text{O}_2,\text{OH} \rightarrow \text{Product} \]

m.  

\[ \text{(CH}_3\text{)}_3\text{CH} \rightarrow \text{CH}_3\text{CCH}_2\text{OH} \]

n.  

\[ \text{Butyne} \rightarrow \text{Product} \]

o.  

\[ \text{OH} \rightarrow \text{HCl} \rightarrow \text{Product} \]

C₅H₅Cl:  
\[ ^1\text{H NMR} \delta = 4.00 \text{ (m, 1 H), 1.0 - 2.0 (m, 8 H) ppm} \]
\[ ^1\text{H NMR} \delta = 59, 43, 26 \text{ ppm} \]
III. [30 Points]

Treatment of ethane with bromotrichloromethane in the presence of light results in bromoethane and trichloromethane (chloroform).

\[ \text{CH}_3\text{CH}_3 + \text{BrCCl}_3 \xrightarrow{\text{hv}, 20^\circ \text{C}} \text{CH}_3\text{CH}_2\text{Br} + \text{HCCl}_3 \quad \Delta H^\circ = -12 \text{ kcal mol}^{-1} \]

a. Write the two propagation steps for the radical chain reaction:

Step 1

Step 2

b. Given the \( \Delta H^\circ \) of the reaction and the following data, calculate the bromine-carbon bond strength in BrCCl₃.

\[
\begin{align*}
\text{DH}^\circ: & \quad \text{CH}_3\text{CH}_2 - \overset{\cdot}{\text{H}} & \quad 98 \text{ kcal mole}^{-1} \\
& \quad \text{CH}_3\text{CH}_2 - \overset{\cdot}{\text{Br}} & \quad 68 \text{ kcal mole}^{-1} \\
& \quad \text{Cl}_2\text{C} - \overset{\cdot}{\text{H}} & \quad 96 \text{ kcal mole}^{-1} \\
\end{align*}
\]

\[\text{DH}^\circ(\text{Br} - \overset{\cdot}{\text{CCl}}_3) : \]
c. The dependence of rate on temperature is given by the Arrhenius equation:
\[ k = A e^{-\frac{E_a}{RT}} \]. Will this reaction speed up, slow down, or proceed at the same rate at 50° C? Explain your answer.

<table>
<thead>
<tr>
<th>Speed up</th>
<th>Slow down</th>
<th>Proceed at the same rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Circle one)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Explain:

IV. [60 Points]
Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques.

a.
b. \[
\text{cyclohexene} + \text{Br}_2 \xrightarrow{\Delta} \text{cyclohexene oxide} + 2\text{HBr}
\]

c. \[
\text{cyclopentene} + \text{HBr} \xrightarrow{\text{ROOR}} \text{cyclopentene with Br}
\]
V. [50 Points]
Catalytic hydrogenation of A with Lindlar's catalyst (i.e. deactivated Pd) gave several compounds, one of which, B, gave rise to the spectra depicted below.

\[
\begin{align*}
A & \xrightarrow{\text{H}_2, \text{Pd (deactivated)}} B \\
\text{C}_{10}\text{H}_{16}\text{O}_2 &
\end{align*}
\]

a. Write the structure of B in the box above.
b. Interpret the spectral data as requested in the spaces provided.

1. IR Spectrum

Considering the oxygen functionality present in A, the product B could be an alcohol. Confirm or rule out this possibility:

Hydroxy peak is:

present / absent at
(circle correct statement)

Considering the double bonds present in A, the product B could be an alkene. Confirm or rule out this possibility:

\( \tilde{v} \text{C}_{\text{sp}^2}-\text{H} \) is:

present / absent at
(circle correct statement)
2. $^{13}$C NMR Spectrum

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

Note: $\delta = 5.63$ (quintet, $J = 4$ Hz), 4.22 (triplet, $J = 4$ Hz)

Draw your suggestion for B in the box and label the hydrogens A, B, C giving rise to the corresponding signals in the spectrum.
VI. [60 Points]
Show synthetic connections (reagents, intermediates; no mechanisms!) between the following starting materials and the final products. Note: several steps are required in each case; there may be several solutions to each problem, but you should use only one; it is best to work backwards (retrosynthetically), to enable you to dissect the products into less complex precursors; in addition to the starting structure, you may use any organic and organometallic reagents containing four carbons or less.

a.
VII. [80 Points]
Mark the answer in each of the following multiple choice problems that you deem most correct.

a. The number of resonance structures for the cyclopentadienyl anion, $\text{C}_5\text{H}_5^-$, is:
   
   ____ one
   ____ two
   ____ three
   ____ five

b. Beryllium hydride in ether solvents ($\text{R}_2\text{O}$) forms ether addition products of the type: $\text{H}_2\text{Be(OR}_2)_2$. In these compounds, Be is hybridized as:
   
   ____ $\text{sp}$
   ____ $\text{sp}^2$
   ____ $\text{sp}^3$
   ____ not hybridized
c. Consider the following potential energy diagram.

Reaction coordinate

Indicate which reaction sequence conforms best with the diagram.

- A  \[\text{fast}\] B  \[\text{slow}\] C
- A  \[\text{slow}\] B  \[\text{fast}\] C
- A  \[\text{slow}\] B  \[\text{fast}\] C
- C  \[\text{fast}\] B  \[\text{slow}\] A

d. The \(^1\)H NMR spectrum of 1,1-dibromo-1,2-dichloroethane at -130°C reveals the presence of the rotamer A by the observation of two doublets for the two hydrogens:

![A molecule with two Br and two Cl](image)

On warming to room temperature, the onset of "free rotation" will change this pattern to a:

- singlet
- doublet
- two singlets
- doublet of doublets
e. Consider the following conformational equilibrium and the $\Delta G^0$ values for axial-equatorial conversion of the given group in substituted cyclohexane:

\[ \Delta G^{\text{axial} \rightarrow \text{equatorial}, \text{ kcal mol}^{-1}}: \]

- HO : -0.9 kcal mole\(^{-1}\)
- Br : -0.6 kcal mole\(^{-1}\)
- (CH\(_3\))\(_2\)CH : -2.2 kcal mole\(^{-1}\)

A is more stable than B by 0.7 kcal mole\(^{-1}\)
A is less stable than B by 0.7 kcal mole\(^{-1}\)
A is more stable than B by 2.2 kcal mole\(^{-1}\)
A is more stable than B by 1.9 kcal mole\(^{-1}\)

f. The optically pure starting sulfonate has a specific rotation $[\alpha]$ which is monitored as it reacts with F\(^-\) by second order kinetics.

\[ \text{O} \quad \text{H} \quad \text{H} \quad + \text{F}^- \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad + \text{CH}_3\text{SO}_3^- \]

$[\alpha]$ goes to zero faster than the rate of disappearance of starting sulfonate
$[\alpha]$ goes to zero at the same rate as starting sulfonate disappears
$[\alpha]$ changes but never goes to zero as the reaction goes to completion
$[\alpha]$ stays unchanged
g. In each pair of acids shown below, circle the stronger one:

1) HCN vs. CCH₃

2) CH₃CH₂OH vs. ClCH₂CH₂OH

3) CH₃NH₂ vs. CH₃NH₃

4) H₂S vs. H₂O

h. Considering what you know about the relative bond strength of C-H versus C-D, estimate the \( \tilde{\nu}_{C-D} \) relative to \( \tilde{\nu}_{C-H} \):

- \( \tilde{\nu}_{C-H} = \frac{1}{2} \tilde{\nu}_{C-D} \)
- about the same
- \( \tilde{\nu}_{C-D} > \tilde{\nu}_{C-H} \)
- \( \tilde{\nu}_{C-D} < \tilde{\nu}_{C-H} \)

i. Consider the following oxidation and all the possible products.

\[
\text{CH₃COOH} \xrightarrow{\text{1 equivalent}} \quad \text{A} + \text{B} + \text{C}
\]

What will be the observed product distribution?

- only A
- A:B:C = 1:1:1
- only B
- A:B:C = 1:1:2
j. For the indicated hydrogen in compound A, what will be the expected $^1$H NMR pattern:

- singlet
- doublet

triplet, because the two hydrogens at C-3 are equivalent

doublet of doublets

---

Hospitals to avoid

* THE END *

Merry Christmas!