Your Name: ____________________________

PLEASE CIRCLE YOUR SECTION NUMBER/NAME OF TA

101/Matthew Marx  301/Whitney Smith  I  (40 pts) ________
102/Bruce Ellsworth  311/Adam Matzger  II  (30 pts) ________
111/Jim Krom  312/Drew Thompson  III  (15 pts) ________
112/Jason Martin  411/Stephen Mills  IV  (30 pts) ________
211/Corey Liu  412/Sun Yeoul Lee  V  (30 pts) ________
212/Chad Peterson  511/Traci Hopkins  VI  (30 pts) ________

VII (15 pts) ________
VIII (35 pts) ________
IX (30 pts) ________
X (20 pts) ________
XI (15 pts) ________
XII (20 pts) ________
XIII (30 pts) ________
XIV (30 pts) ________
XV (30 pts) ________
Total (400 pts) ________

AT THE BEGINNING:

This exam has FIFTEEN pages; make sure that you have them all. Please write your answers in the boxes provided. We will only grade the answers that are in the boxes; please do your scratch work on the backs of the pages.

Chemistry 3B  Fall, 1992  Final Examination  19 December 1992  Paul A. Bartlett

Periodic Table of the Elements

He  Ne

H  Li  Be  B  C  N  O  F  Ne

Na  Mg  Al  Si  P  S  Cl  Ar

K  Ca  Sc  Ti  V  Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr

Rb  Sr  Y  Zr  Nb  Mo  Tc  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I  Xe

Cs  Ba  La  Hf  Ta  W  Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  At  Rn

Fr  Ra  Ac

Ce  Pr  Nd  Pm  Sm  Eu  Gd  Tb  Dy  Ho  Er  Tm  Yb  Lu

Th  Pa  U  Np  Pu  Am  Cm  Bk  Cf  Es  Fm  Md  No  Lr
I. (40 points)

Show how to synthesize 5-hepten-2-one in an efficient manner. You do not have to control the stereochemistry of the double bond. The carbon atoms in your product must come from ethanol, acetaldehyde, and/or acetic acid; you may use any other reagents. Although there are many ways to do this synthesis, the best answer will include an aldol condensation and a Claisen condensation.
II. (30 points)

Rank the following compounds in order of decreasing acidity.

A

\[
\text{OH}
\]

B

\[
\text{H}_3\text{N}\text{CO}_2\text{H}
\]

C

\[
\text{CO}_2\text{H}
\]

D

\[
\text{CH}_3\text{OPOH}_2\text{OH}
\]

E

\[
\text{C}
\]

F

\[
\text{CH}_3^+\text{NH}_2\text{CH}_3
\]

G

\[
\text{NH}_2
\]

H

\[
\text{H-Br}
\]

III. (15 points)

A. What element in the periodic table has the following electronic configuration?

\[1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7\]

B. What is the complete description of the electronic configuration of element 43, assuming that the orbitals are filled according to the aufbau principle?
IV. (30 points)

In the presence of NaOH/H₂O, isopropyl acetate is hydrolyzed to acetate and isopropyl alcohol.

\[
\text{CH}_3\text{C} = \text{O} \quad \xrightarrow{\text{NaOH}} \quad \text{CH}_3\text{C}O^- \text{Na}^+ + \text{HO}^{-}\]

A. Show the stepwise mechanism for this reaction.

B. If the reaction is carried out in $^{18}$O-labeled water ($H_2^{18}$O = "H₂'O"), some of the acetate ion that is formed has TWO $^{18}$O atoms in it.
Show the sequence of steps that accounts for this result.
V. (30 points)

\[
\begin{align*}
\text{D-arabinose} & \\
\text{L-lyxose} & \\
\end{align*}
\]

For parts A, B, and C below, the choices are: "the same", "enantiomers" or "diastereomers".

A. The two sugars above are

B. Each sugar is treated with NaBH₄; the products from these reactions are

C. Each sugar is subjected to the Ruff degradation procedure; the products from these reactions are

D. Write the structure of an isomeric sugar that gives the same product as D-arabinose on Ruff degradation.

E. What is the name of this sugar?
VI. (30 points)

A. The interconversion of the two anomers of 2-deoxyribose is accelerated by base. Write a step-wise mechanism for this isomerization.

B. The interconversion of the two anomers of methyl 2-deoxyribose is **NOT** catalyzed by base; it requires acid instead. Show the step-wise mechanism for the acid-catalyzed isomerization.
VII. (15 points)

Grandisol, the boll weevil sex attractant, is biosynthesized from geraniol (which, in spite of its name, is a primary component of rose oil).

A. Circle the isoprene units in grandisol.

B. Write a mechanism that might account for the formation of grandisol from geraniol.
VIII. (35 points)

Write the structures of the organic compounds in each solution at each step of the following sequences. Pay attention to the ionization states! If there is no organic compound in a particular solution, write "nothing".

A.

B.
IX. (30 points)

Starting with Na$^{14}$CN or Na$_2^{14}$CO$_3$ ($\xrightarrow{H^+}^{14}$CO$_2$) as the source of $^{14}$C, along with any other reagent or starting material, show how to synthesize the following labeled amines.

A.

B.
X. (20 points)
An octapeptide has been isolated from the venom of a rare snake in the Amazon rainforest. The analytical instrument that Sean Connery used in “Medicine Man” is broken, but you have narrowed down the sequences to the four possibilities below.

Sequence 1

Sequence 2

Sequence 3

Sequence 4

Name the first 6 amino acids in this sequence.

Treatment of the octapeptide with chymotrypsin gives a tetrapeptide, a tripeptide, and a free amino acid, while trypsin gives a pentapeptide, a dipeptide, and a free amino acid.

A. Which of the four sequences above is/are consistent with this information?  

B. What test would you apply to the octapeptide to distinguish between these possibilities? Describe what reagent(s) you would use and what you would look for.
XI. (15 points)

The reaction of 1,3-butadiene with methyl acrylate (Reaction 1) is a typical example of a Diels-Alder reaction:

\[
\text{Reaction 1} \quad \begin{array}{c}
\text{CH}_2=CH-CH_2-CH=CH_2 + \text{CH}_2=CH-\text{CO}_2\text{CH}_3 \\
\to \quad \text{CH}_2=CH-\text{CO}_2\text{CH}_3 \quad \text{CH}_2=CH-\text{CO}_2\text{CH}_3
\end{array}
\]

This reaction can also be carried out with substituted analogs of the diene component (Reactions 2 and 3).

\[
\text{Reaction 2} \quad \begin{array}{c}
\text{CH}_2=CH-CH_2-CH=CH_2 + \text{CH}_2=CH-\text{CO}_2\text{CH}_3 \\
\to \quad \text{CH}_2\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3
\end{array}
\]

\[
\text{Reaction 3} \quad \begin{array}{c}
\text{CH}_2=CH-\text{CH}=\text{CH}-\text{CH}_3 + \text{CH}_2=CH-\text{CO}_2\text{CH}_3 \\
\to \quad \text{C}_6\text{H}_5\text{CO}_2\text{CH}_3
\end{array}
\]

A. Do you expect Reaction 2 to be faster or slower than Reaction 1? Give a brief explanation of your choice.

B. Do you expect Reaction 3 to be faster or slower than Reaction 1? Give a brief explanation of your choice.
XII. (20 points)

Predict the major products of each of the following reactions.

\[
\text{This is tricky!}
\]

\[
\begin{align*}
&\text{CH}_3\text{O} \quad \text{CH}_3\text{O} \\
&\text{H}_2\text{SO}_4 \\
&\text{H}_2\text{SO}_4 \\
&\text{SO}_3 \\
&\text{H}_2\text{SO}_4 \\
&\text{FeBr}_3
\end{align*}
\]
XIII. (30 points)
Show how to prepare the following compounds, using benzoic acid or toluene as starting materials.
XIV. (30 points)

Predict the properties of the following compounds or elements. Check one box for each of the four categories.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Type</th>
<th>In Water</th>
<th>Color</th>
<th>State at 25°C, 1 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃Cl₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂PcCl₆</td>
<td></td>
<td>Leave</td>
<td></td>
<td>blank</td>
</tr>
<tr>
<td>BaCl₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
XV. (30 points)

The isolation of the cyclobutadienyl iron carbonyl complex, depicted below, was a landmark in organometallic chemistry, since it represented the first compound with a "cyclobutadiene" group. This complex is uncharged.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{Fe(CO)}_n \\
\text{H} & \quad \text{H}
\end{align*}
\]

A. How many CO groups are required to fulfill the 18-electron rule? ____

(Note: All the \(\pi\)-electrons of the cyclobutadiene complex are involved in bonding to the metal.)

B. Several schemes can be written to account for the stable bonding arrangement in this compound. What oxidation state would you assign to the metal atom if the organic ligand \((C_4H_4)\) has aromatic character? ____

C. Justify your answer by providing an account of the electronic structure of this complex by filling in the boxes below.

<table>
<thead>
<tr>
<th>Charge on each unit</th>
<th>Number of electrons contributed to valence shell of metal</th>
<th>Contribution to the net charge of the complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cyclobutadiene]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{n}) CO</td>
<td>18</td>
<td>Total charge</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Total electrons} & = 18 \\
\text{Total charge} & = 0
\end{align*}
\]