Chemistry 110a
FOURTH EXAM
November 7, 2014

Name (print)______________________________

Bookman's tip: Freeze-dry your organic knowledge. That way, it'll last forever.

(From Seinfeld episode 22 "The Library" written by Larry David. Detective Bookman is a jaded NY library cop)

BOOKMAN: You don't have any instant coffee?
JERRY: Well, I don't normally--
BOOKMAN: Who doesn't have instant coffee?
JERRY: I don't.
BOOKMAN: You buy a jar of Folger's Crystals, you put it in the cupboard, you forget about it. Then later on when you need it, it's there. It lasts forever. It's freeze-dried. Freeze-dried Crystals.
JERRY: Really? I'll have to remember that.
JERRY: Yes, and I returned it in 1971.
BOOKMAN: Yeah, '71. That was my first year on the job. Bad year for libraries. Bad year for America. Hippies burning library cards, Abbie Hoffman telling everybody to steal books. I don't judge a man by the length of his hair or the kind of music he listens to. Rock was never my bag. But you put on a pair of shoes when you walk into the New York Public Library, fella.

Note: Your exam should consist of 6 pages including the cover page and grade tabulation sheet. Skim the entire exam and solve the easiest problems first. Exams not returned at the end of the period will not be graded.

PLEASE DO NOT OPEN THIS EXAM UNTIL YOU ARE INSTRUCTED TO DO SO.
1. Propose a structure consistent with the following data. 5 pts

2. Compound S (C₈H₁₆) reacts with one mole of bromine to form a compound with molecular formula C₈H₁₆Br₂. The broadband proton-decoupled ¹³C spectrum of S is shown below; carbon types are labelled as C, CH, CH₂, or CH₃. Cleavage of S with ozone produces 2 products, one of which is acetone. Propose a structure for S. 10 pts

3. Propose a structure for the following compound on the basis of its ¹H NMR and mass spectral data. 15 pts

- **¹H NMR data**
  - δ 0.91 ppm (doublet, 6H)
  - δ 1.1 ppm (triplet, 3H)
  - δ 1.41 ppm (quartet, 2H)
  - δ 1.81 ppm (nonet, 1H)
  - δ 3.37 ppm (triplet, 2H)
  - δ 3.5 ppm (quartet, 2H)

- **Mass spectral data**
  - M⁺ = 116 (100%)
  - M⁺1 = 117 (7.7%)
4. Give the structures of the products (if any) expected from the reaction of the alkene (in the box) with the following reagents. **Indicate the stereochemical outcome with clearly drawn structures, if applicable.** 4 pts ea

- a. HBr
- b. Br₂ / H₂O
- c. CH₂I₂, Zn-Cu
- d. OsO₄ (1 equiv.), H₂S work-up
- e. O₃; then Zn
- f. KMnO₄ (hot and alkaline)

5. Propose reagent(s) that would provide the compounds shown below. Mechanisms not required. 4 pts ea

- [Diagram of reaction with HBr and Br₂ / H₂O]
- [Diagram of reaction with CH₂I₂, Zn-Cu]
- [Diagram of reaction with OsO₄ (1 equiv.), H₂S work-up]
- [Diagram of reaction with O₃; then Zn]
- [Diagram of reaction with KMnO₄ (hot and alkaline)]
7. Assign a structure that is consistent with the following spectral data. 10 pts

\[
\begin{align*}
\delta & 1.32 \text{ ppm (doublet, 6H)} \\
\delta & 2.34 \text{ ppm (singlet, 3H)} \\
\delta & 5.24 \text{ ppm (heptet-7 lines, 1H)} \\
\delta & 7.30 \text{ ppm (triplet, 1H)} \\
\delta & 7.43 \text{ ppm (doublet, 1H)} \\
\delta & 7.78 \text{ ppm (singlet, 1H)} \\
\delta & 7.88 \text{ ppm (doublet, 1H)} \\
\end{align*}
\]

\[C_{11}H_{14}O_2\]

8. The 'n+1' rule is an oft-used tool for solving NMR spectra. What is the origin of the rule? How would you explain it to a first-year science student? **No essays!** All you need to provide is a diagram or two and simple annotations--similar to what your chalkboard would look like when you are finished with your explanation. 10 pts

9. We saw the following result on one of our lecture handouts. How do you rationalize the origin of and differences in regioselectivity for BH\textsubscript{3} vs. 9-BBN? Analyze the key transition state structure & annotate lightly. **No essays!** 10 pts

\[
\begin{align*}
\text{1. BH}_3 \text{ or 9-BBN} & \\
\text{2. H}_2\text{O}_2/\text{NaOH} & \\
\end{align*}
\]

\[
\begin{align*}
\text{BH}_3: & \quad 6\% \quad 94\% \\
9\text{-BBN:} & \quad 0.1\% \quad 99.9\% \\
\end{align*}
\]
Figure 2-1.
Chemical shifts of $^1$H nuclei in organic compounds.

Figure 2-2.
Chemical shifts of $^{13}$C nuclei in organic compounds.
<table>
<thead>
<tr>
<th>Element</th>
<th>Most Common Isotope</th>
<th>Natural Abundance of Other Isotopes (Based on 100 Atoms of Most Common Isotope)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>$^{12}$C</td>
<td>$^{13}$C 1.11</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$^{1}$H</td>
<td>$^{2}$H 0.016</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}$N</td>
<td>$^{15}$N 0.38</td>
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<tr>
<td>Oxygen</td>
<td>$^{16}$O</td>
<td>$^{17}$O 0.04 $^{18}$O 0.20</td>
</tr>
<tr>
<td>Fluorine</td>
<td>$^{19}$F</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>$^{28}$Si</td>
<td>$^{29}$Si 5.10 $^{30}$Si 3.35</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>$^{31}$P</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}$S</td>
<td>$^{33}$S 0.78 $^{34}$S 4.40</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}$Cl</td>
<td>$^{37}$Cl 32.5</td>
</tr>
<tr>
<td>Bromine</td>
<td>$^{79}$Br</td>
<td>$^{81}$Br 98.0</td>
</tr>
<tr>
<td>Iodine</td>
<td>$^{127}$I</td>
<td></td>
</tr>
</tbody>
</table>