Chemistry 110a
FOURTH EXAM
November 5, 2010

Name (print)______________________________

Note: Your exam should consist of 6 pages including the cover page, appendix materials, 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 OPEN AND CLOSE THIS EXAM WHEN YOU ARE INSTRUCTED TO DO SO.

INDIVIDUALS WHO DO NOT COMPLY WITH THESE INSTRUCTIONS WILL RECEIVE A 15 PT DEDUCTION.
1. When 3,3-dimethyl-2-butanol is treated with concentrated HI, a rearrangement takes place. Which alkyl iodide would you expect from the reaction? Show the arrow-pushing mechanism by which it is formed. 10 pts

2. Write an arrow-pushing mechanism to explain the following reaction. 10 pts

\[
\text{Br}_2 \quad \text{pH} = 8.5 \quad \text{(buffered)}
\]

\[
\begin{align*}
\text{O} \quad \text{Br} & \quad \text{O} \\
\text{OH} & \quad \text{Br}
\end{align*}
\]

3. Propose a structure for the following compound (C₆H₁₄O) on the basis of its \(^1\)H NMR data. 10 pts
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.**

a. Hg(OAc)$_2$/H$_2$O, then NaBD$_4$

b. Br$_2$ dilute in H$_2$O

c. CH$_2$I$_2$/Zn-Cu

d. OsO$_4$ (1 equiv.), H$_2$S work-up

e. O$_3$; then Zn

5. Explain, using structures and a diagram of your own choosing, how the Hammond-Leffler postulate can be used
to explain the Markovnikov addition of HBr to an alkene. 10 pts

6. Write separate chemical equations showing two ways how an M+1 peak of m/z = 17 can arise in a mass spectral
analysis of methane. Which of the two is more likely? 6 pts
7. Assign a structure that is consistent with the following spectral data. 10 pts

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

\( \text{C}_{11}\text{H}_{14}\text{O}_2 \)

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? \textbf{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 BH₃ vs. 9-BBN? Analyze the key transition state structure & annotate lightly. \textbf{No essays!} 10 pts
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 9.3  Principal Stable Isotopes of Common Elements

<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>100 $^{13}$C 1.11</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$^{1}$H</td>
<td>100 $^{2}$H 0.016</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}$N</td>
<td>100 $^{15}$N 0.38</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}$O</td>
<td>100 $^{17}$O 0.04 $^{18}$O 0.20</td>
</tr>
<tr>
<td>Fluorine</td>
<td>$^{19}$F</td>
<td>100</td>
</tr>
<tr>
<td>Silicon</td>
<td>$^{28}$Si</td>
<td>100 $^{29}$Si 5.10 $^{30}$Si 3.35</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>$^{31}$P</td>
<td>100</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}$S</td>
<td>100 $^{33}$S 0.78 $^{34}$S 4.40</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}$Cl</td>
<td>100 $^{37}$Cl 32.5</td>
</tr>
<tr>
<td>Bromine</td>
<td>$^{79}$Br</td>
<td>100 $^{81}$Br 98.0</td>
</tr>
<tr>
<td>Iodine</td>
<td>$^{127}$I</td>
<td>100</td>
</tr>
</tbody>
</table>