Chemistry 333

Examination #3

July 14, 2006                                                                             Professor Charonnat

Name: _____________________________

Be certain that your examination has nine (9) pages including this one.

Put your name on each page of this examination booklet.

By putting your name on this examination booklet you agree to abide by California State University, Northridge policies of academic honesty and integrity.

Molecular models are allowed for this examination. All electronic devices, including calculators, are unnecessary and are not allowed.
1. (25 points)

Draw the structure of the expected major organic product for each of the following five (5) questions. Clearly specify stereochemistry, if relevant.

A. 

\[
\begin{array}{c}
\text{Br} \\
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\xrightarrow{(\text{H}_3\text{CCH}_2)_2\text{CuLi}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{CH}_3
\end{array}
\]

B. 

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{I}_2 \\
\end{array}
\xrightarrow{\text{CH}_2\text{I}_2}
\xrightarrow{\text{Zn/Cu}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{CH}_3
\end{array}
\]

C. 

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{CH}_3
\end{array}
\xrightarrow{\text{HBr}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{CH}_3
\end{array}
\]

D. 

\[
\begin{array}{c}
\text{O} \\
\text{H}_3\text{C} \\
\end{array}
\xrightarrow{\text{a.) PhMgBr}}
\xrightarrow{\text{b.) H}_2\text{O}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{CH}_3
\end{array}
\]

E. 

\[
\begin{array}{c}
\text{I} \\
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{NaCN}}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C}_\text{H}_2\text{CH}_3
\end{array}
\]
2. (25 points)

Circle the number that corresponds to the correct answer for each of the following five (5) questions.

A. If a carbon resonance appears in both DEPT 90 and DEPT 135 spectra, then the carbon is a
   1. quaternary carbon
   2. methine carbon
   3. methylene carbon
   4. methyl carbon

B. The mass spectrum of an organic compound has molecular ions at $m/z = 184$ and 186, with a relative-abundance ratio of 3:1, respectively. The compound contains
   1. nitrogen
   2. chlorine
   3. bromine
   4. sulfur

C. Which technique can be used to determine molecular formulas directly?
   1. infrared spectroscopy
   2. $^1$H NMR spectroscopy
   3. low-resolution mass spectrometry
   4. high-resolution mass spectrometry

D. Which type of electromagnetic radiation is used for NMR spectroscopy?
   1. radio wave
   2. microwave
   3. visible
   4. infrared

E. Under normal conditions (with trace acid present), the $^1$H NMR multiplicity of the C-3 proton of (R)-2-methylhexan-3-ol is a
   1. doublet of triplets
   2. quartet
   3. doublet of doublet of doublets
3. (20 points)

Devise a synthesis of the unsaturated sulfide 1 from the terminal alkyne 2, any inorganic reagents and any organic compounds that contain three carbons or less. Write specific reagents and denote each step carefully. Show all stable, synthetic intermediate compounds. (N.B. Do not draw mechanisms!)

4. (10 points)

Use IUPAC nomenclature to write the systematic name of the following alkyne.
5. (20 points)

The product from the following reaction shows infrared absorptions at 1451 cm\(^{-1}\), 1500 cm\(^{-1}\), 1583 cm\(^{-1}\), 1600 cm\(^{-1}\), 1710 cm\(^{-1}\), 2720 cm\(^{-1}\), 2820 cm\(^{-1}\), 3025 cm\(^{-1}\) and a number of weak resonances in the 2870-2950 cm\(^{-1}\) range. Draw the structure of the product. Use the infrared spectroscopic evidence to support your answer. Make clear assignments of all absorptions to explain your reasoning. (An IR correlation table is included separately.)

\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{a.) DMSO} & \quad \text{Cl} & \quad \text{Cl} \\
\text{b.) Et}_3\text{N} & \quad \text{?}
\end{align*}
\]

infrared assignments:

<table>
<thead>
<tr>
<th>absorption (cm(^{-1}))</th>
<th>assignment</th>
</tr>
</thead>
</table>


6. (25 points)

Draw the major organic product that is formed from the following reaction. The $^1$H NMR spectrum of the product is shown below. The labels next to each of the resonances signify the integrals and multiplicities observed in the spectrum ($s =$ singlet, $d =$ doublet, $t =$ triplet, $dsept =$ doublet of septets). Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning. (A $^1$H NMR correlation table is included separately.)

![Diagram of reaction and NMR spectrum]

A) BH$_3$ · THF  
B) aq. NaOH  H$_2$O$_2$

**NMR Spectrum:**
- 3.19 (s, 1H)
- 2.0 1.91 (t, 2H)
- 1.01 (dsept, 12H)
- D$_2$O exchangeable

**Explanation:**

Based on the NMR spectrum, the compound contains a singlet at 3.19 ppm, indicating a methyl group. The doublet at 2.0 ppm corresponds to a methylene group. The multiplet at 1.01 ppm is a doublet of septets, suggesting a tertiary methyl group. The D$_2$O exchangeable signal indicates the presence of a hydroxyl group.

The reaction can be deduced as follows:

- The BH$_3$ · THF reagent likely adds to the alkene, forming an enamine intermediate.
- The subsequent reaction with aq. NaOH and H$_2$O$_2$ leads to the formation of the observed product.

**Assignment:**

- 3.19 ppm: Me$_3$SiH (methyl group)
- 2.0 ppm: CH$_2$ (methylene group)
- 1.01 ppm: CH$_3$ (tertiary methyl group)

**Conclusion:**

The major organic product formed from the reaction is a compound with the following structure:

![Diagram of proposed product structure]

This structure is consistent with the observed NMR spectrum and reaction conditions.
6. (continued)

$^1$H NMR assignments:

<table>
<thead>
<tr>
<th>chemical shift (ppm)</th>
<th>assignment</th>
<th>explanation of multiplicity</th>
</tr>
</thead>
</table>

Name: ______________________
7. (25 points)

Draw the major organic product that is formed from the following reaction. The broadband proton-decoupled $^{13}$C NMR spectrum of the product is shown below. The labels next to each of the resonances signify the multiplicities observed in the corresponding off-resonance proton-decoupled $^{13}$C NMR spectrum (d = doublet, t = triplet, q = quartet). Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning. (A $^{13}$C NMR correlation table is included separately.)
\[ ^{13}\text{C NMR assignments:} \]

<table>
<thead>
<tr>
<th>chemical shift (ppm)</th>
<th>assignment</th>
<th>explanation of multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>/25</td>
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<tr>
<td>3</td>
<td>/20</td>
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Total: /150

Congratulations!