Chemistry 334

Examination #1

October 1, 2002                                                                 Professor Charonnat

Name: _____________________________

Be certain that your examination has seven (7) 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. 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. \[
\begin{align*}
\text{H}_2\text{C} & \text{CH}_2 \\
\text{H}_2\text{C} & \text{CH}_2
\end{align*}
\]

B. \[
\begin{align*}
\text{H}_3\text{C} & \text{CH}_3 \\
\text{H}_3\text{C} & \text{CH}_3
\end{align*}
\]

C. \[
\begin{align*}
\text{H}_3\text{C} & \text{CH}_3 \\
\text{H}_3\text{C} & \text{CH}_3
\end{align*}
\]

D. \[
\begin{align*}
\text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph}
\end{align*}
\]
2. (25 points)

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

A. The alkene, trans,trans-2,5-octadiene, is:
   1. an isolated diene
   2. a conjugated diene
   3. a cumulated diene

B. When trans-1,3-pentadiene and methyl acrylate (H₂C=CHCO₂CH₃) are heated together
   1. the endo cycloaddition product is formed predominantly
   2. the exo cycloaddition product is formed predominantly
   3. a 1:1 mixture of the endo and exo cycloaddition products is formed

C. Sulfides can be oxidized to:
   1. alcohols
   2. thiols
   3. sulfoxides

D. The reaction of ethylbenzene with lithium metal and tert-butyl alcohol in anhydrous ammonia yields a:
   1. cyclohexene derivative
   2. 1,3-cyclohexadiene derivative
   3. 1,4-cyclohexadiene derivative

E. Benzylic halides are very reactive S_N2 substrates due to:
   1. resonance stabilization of the starting material
   2. resonance stabilization of the transition state
   3. resonance stabilization of the product
3. (10 points)

Use IUPAC nomenclature to write the systematic name of the following sulfide.

![Structure of the sulfide]

4. (20 points)

Draw the mechanism of the following reaction, using the curved-arrow notation to indicate the reorganization of electron density. Show all intermediates and denote all unshared electrons, formal charges and countercharges where appropriate. Draw all important resonance contributors for intermediates.

![Mechanism of the reaction]
5. (20 points).

A compound is known to be a trimethylbenzene derivative. The broadband proton-decoupled \(^{13}\text{C}\) NMR spectrum of this compound is shown below. The \(^{13}\text{C}\) NMR multiplicities (s = singlet, d = doublet, q = quartet) noted are the multiplicities in the corresponding off-resonance proton-decoupled \(^{13}\text{C}\) NMR spectrum. On the next page, draw all the possible trimethylbenzene isomers and use the \(^{13}\text{C}\) spectrum to identify the correct structure. Put a star next to this structure. Clearly assign all the resonances of the \(^{13}\text{C}\) NMR spectrum to support your answer. Explain concisely why the other isomers can be ruled out, due to the spectroscopic data. (A \(^{13}\text{C}\) NMR correlation table is included on page 7.)
5. (continued)

Possible isomers:

$^{13}$C NMR assignments:

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

Reasoning:

Congratulations!

<table>
<thead>
<tr>
<th></th>
<th>/25</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Total: /100
### SELECTED $^{13}$C NMR CORRELATIONS

<table>
<thead>
<tr>
<th>structural type</th>
<th>chemical shift range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopropyl</td>
<td>- 10 - 10</td>
</tr>
<tr>
<td>$-\text{CH}_3$ (saturated)</td>
<td>10 - 30</td>
</tr>
<tr>
<td>$-\text{CH}_2$ (saturated)</td>
<td>10 - 55</td>
</tr>
<tr>
<td>$-\text{CH}$ (saturated)</td>
<td>25 - 55</td>
</tr>
<tr>
<td>$-\text{C}$ (saturated)</td>
<td>30 - 55</td>
</tr>
<tr>
<td>$-\text{C}^-\text{I}$</td>
<td>- 10 - 45</td>
</tr>
<tr>
<td>$-\text{C}^-\text{Br}$</td>
<td>25 - 65</td>
</tr>
<tr>
<td>$-\text{C}^-\text{Cl}$</td>
<td>35 - 80</td>
</tr>
<tr>
<td>$\overset{\text{O}}{\text{C}}\text{=C}$</td>
<td>20 - 50</td>
</tr>
<tr>
<td>$-\text{C}^-\text{N}$</td>
<td>30 - 70</td>
</tr>
<tr>
<td>$-\text{C}^-\text{O}$</td>
<td>40 - 80</td>
</tr>
<tr>
<td>$-\text{C}^-\text{C}$</td>
<td>65 - 85</td>
</tr>
<tr>
<td>$\overset{\text{C}^-\text{C}}{\text{C}}$</td>
<td>100 - 150</td>
</tr>
<tr>
<td>$-\text{C}^-\text{N}$</td>
<td>110 - 125</td>
</tr>
<tr>
<td>ArH</td>
<td>110 - 160</td>
</tr>
<tr>
<td>$\overset{\text{O}}{\text{C}}\text{=C}^-\text{OH} \quad \overset{\text{O}}{\text{C}}\text{=C}^-\text{X}$</td>
<td>155 - 185</td>
</tr>
<tr>
<td>$\overset{\text{O}}{\text{C}}\text{=C}^-\text{H} \quad \overset{\text{O}}{\text{C}}\text{=C}^-\text{C}$</td>
<td>190 - 210</td>
</tr>
</tbody>
</table>