Chemistry 333

Examination #1

June 18, 2004

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 specific reagent(s) necessary to effect the transformation shown for each of the following five (5) questions. Specify relative stoichiometry, if relevant.

A.

\[
\begin{align*}
\text{Br} & \quad \text{CH}_3 \\
& \quad \text{Br} \\
\rightarrow & \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

B.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
\rightarrow & \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

C.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} \\
& \quad \text{Br} \\
\rightarrow & \quad \text{Li} \\
& \quad \text{Li} \\
\end{align*}
\]

D.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\rightarrow & \quad \text{Br} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

E.

\[
\begin{align*}
\text{Li} & \quad \text{Li} \\
\rightarrow & \quad \text{CuLi} \\
\end{align*}
\]
2. (30 points)

Circle the number that corresponds to the correct answer for each of the following six (6) questions.

A. Alkanes are:
   1. unsaturated aromatic hydrocarbons
   2. saturated aromatic hydrocarbons
   3. saturated aliphatic hydrocarbons

B. Decreased entropy:
   1. is energetically favorable
   2. is energetically unfavorable
   3. has no effect on the energy of a system

C. Bond homolysis affords:
   1. cations
   2. anions
   3. radicals

D. 2-Methylpentane and n-hexane are:
   1. conformational isomers
   2. structural isomers
   3. identical

E. Eclipsed and staggered propane are:
   1. conformational isomers
   2. structural isomers
   3. identical

F. Which of the following species is the most stable radical?

1. 
   
2. 
   
3. 

3. (20 points)

Draw reaction-energy diagrams (graphs of reaction progress versus potential energy) for both of the following two (2) reactions. Label the curves with the following: starting material (sm), transition states (ts\_X), intermediates (int\_X), product (p), activation energies (Ea\_X) and overall standard heat of reaction (\(\Delta H^0\)).

A. an overall endothermic, three-step reaction with a rate-determining third step

```
\begin{center}
\begin{tikzpicture}
    \draw (0,0) -- (6,0); % reaction progress axis
    \draw (0,-2) -- (0,2); % potential energy axis
    \draw (0,0) -- (0,-2); % reaction progress
    \draw (6,0) -- (6,-2); % reaction progress
    \node at (3,1) {potential energy};
    \node at (3,-1.5) {reaction progress};
\end{tikzpicture}
\end{center}
```

B. a two-step reaction with a late transition state in the first step, and an early transition state in the second step

```
\begin{center}
\begin{tikzpicture}
    \draw (0,0) -- (6,0); % reaction progress axis
    \draw (0,-2) -- (0,2); % potential energy axis
    \draw (0,0) -- (0,-2); % reaction progress
    \draw (6,0) -- (6,-2); % reaction progress
    \node at (3,1) {potential energy};
    \node at (3,-1.5) {reaction progress};
\end{tikzpicture}
\end{center}
```

4. (10 points)

Draw Lewis structures for both of the following two (2) compounds. Show all covalent bonds and nonzero formal charges clearly.

A. CO\textsubscript{2}

```
\begin{center}
\begin{tikzpicture}
    \node at (0,0) {C};
    \node at (1,0) {O};
    \node at (1,-1) {O};
    \draw (0,0) -- (1,0); % CO bond
    \draw (0,0) -- (1,-1); % CO bond
    \draw (1,0) -- (1,-1); % CO bond
\end{tikzpicture}
\end{center}
```

B. Na\textsubscript{2}SO\textsubscript{4}

```
\begin{center}
\begin{tikzpicture}
    \node at (0,0) {Na};
    \node at (1,0) {Na};
    \node at (2,0) {S};
    \node at (3,0) {O};
    \node at (3,-1) {O};
    \node at (3,-2) {O};
    \draw (0,0) -- (1,0); % Na bond
    \draw (1,0) -- (2,0); % Na bond
    \draw (2,0) -- (3,0); % Na bond
    \draw (2,0) -- (3,-1); % S-O bond
    \draw (2,0) -- (3,-2); % S-O bond
    \draw (3,0) -- (3,-1); % O-S bond
    \draw (3,0) -- (3,-2); % O-S bond
\end{tikzpicture}
\end{center}
```
5. (20 points)

Use IUPAC nomenclature to write the systematic names for both of the following two (2) alkanes.

A. 

\[
\begin{align*}
&\text{CH}_3 \\
&\text{CHCH}_2\text{CH}_3 \\
&(\text{H}_3\text{C})_2\text{CHCH}_2\text{CH}_2\text{CHCH}_2\text{CH}_3
\end{align*}
\]

B. 

\[
\begin{align*}
&\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH(CH}_3)_2 \\
&\text{CH}_2\text{CHCH}_2\text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]

6. (25 points)

Draw the two possible chair conformations of the following disubstituted cyclohexane. Denote all 1,3-diaxial interactions for both conformations. Calculate the total strain energy for each conformation. Put a star next to the more stable conformation. Finally, determine the approximate ratio of the two conformations at 298 K. (See the tables on page 7.)
7. (10 points)

Draw all of the important resonance structures for the following cation.

\[ \text{Cation Image} \]

8. (10 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 lone pairs, charges and countercharges.

\[ \text{Reaction Image} \]

**Congratulations!**

1. /25
2. /30
3. /20
4. /10
5. /20
6. /25
7. /10
8. /10
Total: /150
**Calculated Equilibrium Values at T = 298 K**

<table>
<thead>
<tr>
<th>energy difference (kcal/mol)</th>
<th>% more stable isomer</th>
<th>% less stable isomer</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>50</td>
<td>50</td>
<td>1.00</td>
</tr>
<tr>
<td>0.119</td>
<td>55</td>
<td>45</td>
<td>1.22</td>
</tr>
<tr>
<td>0.240</td>
<td>60</td>
<td>40</td>
<td>1.50</td>
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<tr>
<td>0.367</td>
<td>65</td>
<td>35</td>
<td>1.86</td>
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<tr>
<td>0.502</td>
<td>70</td>
<td>30</td>
<td>2.33</td>
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<tr>
<td>0.651</td>
<td>75</td>
<td>25</td>
<td>3.00</td>
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<tr>
<td>0.821</td>
<td>80</td>
<td>20</td>
<td>4.00</td>
</tr>
<tr>
<td>1.028</td>
<td>85</td>
<td>15</td>
<td>5.67</td>
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<tr>
<td>1.302</td>
<td>90</td>
<td>10</td>
<td>9.00</td>
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<tr>
<td>1.745</td>
<td>95</td>
<td>5</td>
<td>19.0</td>
</tr>
<tr>
<td>2.723</td>
<td>99</td>
<td>1</td>
<td>99.0</td>
</tr>
<tr>
<td>4.092</td>
<td>99.9</td>
<td>0.1</td>
<td>999</td>
</tr>
</tbody>
</table>

Axial Y

Equatorial Y

<table>
<thead>
<tr>
<th>substituent Y</th>
<th>1,3-diaxial interaction (kcal/mol)</th>
<th>total steric strain due to two H-Y 1,3-diaxial interactions (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-F</td>
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<td>0.24</td>
</tr>
<tr>
<td>-Cl</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>-Br</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>-OH</td>
<td>0.50</td>
<td>1.0</td>
</tr>
<tr>
<td>-CH₃</td>
<td>0.90</td>
<td>1.8</td>
</tr>
<tr>
<td>-CH₂CH₃</td>
<td>0.95</td>
<td>1.9</td>
</tr>
<tr>
<td>-CH(CH₃)₂</td>
<td>1.1</td>
<td>2.2</td>
</tr>
<tr>
<td>-C(CH₃)₃</td>
<td>2.7</td>
<td>5.4</td>
</tr>
<tr>
<td>-Ph</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>-CO₂H</td>
<td>0.70</td>
<td>1.4</td>
</tr>
<tr>
<td>-CN</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>