Chem 51A

Final Exam

December 5, 2005, 8-10 am

This exam is closed-book. No notes are permitted. Molecular models, electronic calculators, and rulers are permitted.

DO NOT OPEN YOUR EXAMS UNTIL INSTRUCTED TO DO SO!

Note: All exams will be photocopied prior to being returned. In the event of a grading error, please submit the original exam along with a note explaining the grading error. Do not mark on or alter the exam in any way. Any marks or alteration may be taken as evidence of academic dishonesty and may result in a failing grade in the class and a letter in the student's file.

<table>
<thead>
<tr>
<th>Problem</th>
<th>Possible Points</th>
<th>Score</th>
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<tr>
<td>1</td>
<td>24</td>
<td>_____</td>
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<tr>
<td>2</td>
<td>18</td>
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<td>3</td>
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<td>8</td>
<td>20</td>
<td>_____</td>
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<td><strong>Total</strong></td>
<td><strong>140</strong></td>
<td>_____</td>
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1. For each of the following reactions, write the missing reactant, reagent, or product in the box. Clearly indicate the stereochemistry, if relevant. If no reaction occurs, please indicate this. (24 points)
2. Propose short syntheses of the following compounds, beginning only with compounds containing *six carbon atoms or fewer* and any organic or inorganic reagents that you require. (18 points)

(Hint: Consider reactions that you have learned that form C–O bonds.)
3. Consider the electrophilic addition of HBr to conjugated diene A, in which two isomeric products, C and D, form by way of common intermediate B. (18 points)

\[
\begin{array}{cccc}
\text{A} & \xrightarrow{\text{HBr (1 equivalent)}} & \text{B} & \rightarrow \text{C} + \text{D} \\
\end{array}
\]

a. On the reaction coordinate diagram below indicate position of A, B, C and D. (Hint: more substituted alkenes are more thermodynamically stable).

![Reaction Coordinate Diagram]

b. Indicate the positions of transition states E, F, and G on the reaction coordinate diagram.

![Transition States Diagram]

c. Which product forms faster? _______

Explain based on the diagram. ________________________________________________________
______________________________________________________________________________
______________________________________________________________________________
4. Consider the various stereoisomers of 3,4-hexanediol (18 points).

![3,4-hexanediol](image)

**a.** Draw the \( R,R \) enantiomer: \((3R,4R)-3,4\)-hexanediol.

**b.** Draw a molecule that has the same melting point and boiling point as the \((3R,4R)-3,4\)-hexanediol but has equal and opposite optical rotation.

**c.** Draw a diastereomer of 3,4-hexanediol that lacks optical activity.

**d.** Draw a constitutional isomer of 3,4-hexanediol.

**e.** What is the optical rotation of a mixture of equal parts of \((3R,4R)-3,4\)-hexanediol and \((3S,4S)-3,4\)-hexanediol? ________________

What do we call such a mixture?____________________

**f.** If the specific rotation of \((3R,4R)-3,4\)-hexanediol is +10 degrees, what is percentage of each enantiomer in a mixture of \((3R,4R)-3,4\)-hexanediol and \((3S,4S)-3,4\)-hexanediol with a specific rotation of -5 degrees?

_________% \((3R,4R)-3,4\)-hexanediol and _________% \((3S,4S)-3,4\)-hexanediol
5. (18 points)

a. Make drawings of the two chair conformers of (1R,2S)-2-methylcyclohexanol that clearly illustrate the chair conformation and clearly show the position of all hydrogen atoms on the ring.

\[
\begin{align*}
\text{CH}_3 & \quad \text{OH} \\
\text{(1R,2S)-2-methylcyclohexanol} & \\
\end{align*}
\]

one conformer (A)  

another conformer (B)

b. Make molecular models of these two conformers using your Darling (Molecular Visions) Molecular Models. Use a ruler to measure the distance between the methyl carbon and alcohol oxygen atoms in each of the two models.

What is the distance between the methyl carbon and alcohol oxygen atoms in conformer A, in centimeters?  _________

What is the distance between the methyl carbon and alcohol oxygen atoms in conformer B, in centimeters?  _________

c. The Darling (Molecular Visions) Molecular Models are constructed on a scale of 5.08 cm to the angstrom.

What is the distance between the methyl carbon and alcohol oxygen atoms in conformer A, in angstroms?  _________
6. Consider the hydrogenation of cis-2-butene that has the hydrogen isotope deuterium (D) at the 2- and 3-positions. (12 points)

a. Indicate the product on the template provided by filling in the blanks. Be sure to include the relative stereochemistry.

\[
\begin{array}{c}
\text{D} \\
\text{H} \\
\text{C} = \text{C} \\
\text{H}_3 \text{C} \\
\text{CH}_3
\end{array}
\xrightarrow{\text{H}_2, \text{Pd/C}}
\begin{array}{c}
\text{Cf}_3 \\
\text{Cf}_3
\end{array}
\]

b. Draw Newman projections of the product from the above reaction. (Note that the steric properties of deuterium are similar to those of hydrogen.)

conformation depicted in the above template
lowest energy conformer
2nd lowest energy conformer

7. (12 points)

a. Circle the more important (major) resonance structure in each pair and explain briefly why it is the major structure.

\[
\begin{array}{c}
\overset{\cdot}{\text{O}} \\
\text{C} = \text{C} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

\[
\begin{array}{c}
\overset{\cdot}{\text{O}} \\
\text{C} = \text{C} \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

b. Circle the more stable structure in each pair and explain briefly why it is more stable.

\[
\begin{array}{c}
\overset{\cdot}{\text{H}} \\
\text{C} = \text{C} \\
\text{H}_3 \text{C}
\end{array}
\]

\[
\begin{array}{c}
\overset{\cdot}{\text{H}} \\
\text{C} = \text{C} \\
\text{H}_3 \text{C}
\end{array}
\]

\[
\begin{array}{c}
\overset{\cdot}{\text{H}} \\
\text{C} = \text{C} \\
\text{H}_3 \text{C}
\end{array}
\]

\[
\begin{array}{c}
\overset{\cdot}{\text{H}} \\
\text{C} = \text{C} \\
\text{H}_3 \text{C}
\end{array}
\]
8. The cyclization of linear polyenes containing 10, 15, 20, etc. carbon atoms into compounds containing rings is key to the biosynthesis of terpenes, a class of natural products that includes limonene (a major sweet-smelling oil in citrus peel) and cholesterol. Using the template shown below, write a curved-arrow mechanism for the acid-catalyzed formation of terpene α-terpineol from the linear diene nerol, which is found in juniper oil. Make sure to show all lone pairs of electrons and all formal charges. (20 points)