### Problems

<table>
<thead>
<tr>
<th>Problems</th>
<th>Points</th>
<th>Credit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Functional Group Nomenclature (1 large structure)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>2. Types of Isomers, Degrees of Unsaturation or common nomenclature</td>
<td>25</td>
<td></td>
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<tr>
<td>terms</td>
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<tr>
<td>3. Cyclohexane Conformations, 2 substituents, Newman Projections</td>
<td>30</td>
<td></td>
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<tr>
<td>5. Stereochemical Analysis</td>
<td>30</td>
<td></td>
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<tr>
<td>6. 3D Structure, Hybridization, Angles, Shapes</td>
<td>30</td>
<td></td>
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<tr>
<td>7. Forces of Interaction and Physical Properties</td>
<td>24</td>
<td></td>
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<tr>
<td>8. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge</td>
<td>35</td>
<td></td>
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<tr>
<td>9. $S_N$/$E$ Mechanisms, with all of the details</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>10. Various Reactions, predict the products (20 reactions)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>11. $S_N1$ and $E1$ mechanisms</td>
<td>20</td>
<td></td>
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<tr>
<td>12. Fill in all mechanistic details, curved arrows, lone pairs, formal charge, in acid or in base</td>
<td>20</td>
<td></td>
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<tr>
<td>13. Free Radical Reactions – Predict the products, write a mechanism and calculate $\Delta H$ of steps</td>
<td>25</td>
<td></td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>372</strong></td>
<td></td>
</tr>
</tbody>
</table>

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

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*What sculpture is to a block of marble, education is to the soul.*

*Joseph Addison*
1. Provide an acceptable name for the following molecule. (30 pts)

![Molecule Diagram]

2. Match the arrows with the terms. Some arrows may be associated with more than one term. (25 pts)

1. vinyl  
2. allyl  
3. propargyl  
4. phenyl  
5. benzyl  
6. primary amine  
7. sec-butyl  
8. t-butyl  
9. neopentyl  
10. quarternary  
11. isopropyl  
12. isobutyl  
13. methyl  
14. methylene  
15. methine  
16. primary  
17. secondary  
18. tertiary  
19. quaternary ammonium ion  
20. tertiary amine  
21. secondary amine
3. Draw all possible chair conformations of cis-1-ethenyl-4-ethynyl cyclohexane. Make C1 the left most carbon and number towards the front. Show all axial and equatorial groups in the first chair. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the more stable conformation using the C1→C6 and C3→C4 bonds sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a ethenyl group is 1.7 kcal/mole and 0.5 kcal for a ethynl group and a ethynyl/phenyl gauche interaction is 1.0 kcal/mole, what is the difference in energy between the chair conformations? What are the relative percents of each conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes. (30 pts)
4. Use a Newman projection of the C3→C4 bond of 2-methyl-4-phenylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Using those energy values, calculate ratio of the most stable to the least stable conformations. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (30 pts)

![2D structure](image)

**Approximate Eclipsing Energy Values (kcal/mole)**

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Me</th>
<th>Et</th>
<th>i-Pr</th>
<th>t-Bu</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.0</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>3.0</td>
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<td>Me</td>
<td>1.4</td>
<td>2.5</td>
<td>2.7</td>
<td>3.0</td>
<td>8.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Et</td>
<td>1.5</td>
<td>2.7</td>
<td>3.3</td>
<td>4.5</td>
<td>10.0</td>
<td>3.8</td>
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<td>i-Pr</td>
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<td>4.5</td>
<td>7.8</td>
<td>13.0</td>
<td>8.1</td>
</tr>
<tr>
<td>t-Bu</td>
<td>3.0</td>
<td>8.5</td>
<td>10.0</td>
<td>13.0</td>
<td>13.5</td>
<td>8.3</td>
</tr>
<tr>
<td>Ph</td>
<td>1.7</td>
<td>3.3</td>
<td>3.8</td>
<td>8.1</td>
<td>13.5</td>
<td>8.3</td>
</tr>
</tbody>
</table>

**Approximate Gauche Energy Values (kcal/mole)**

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Me</th>
<th>Et</th>
<th>i-Pr</th>
<th>t-Bu</th>
<th>Ph</th>
</tr>
</thead>
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<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Me</td>
<td>0</td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
<td>2.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Et</td>
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<td>0.9</td>
<td>1.1</td>
<td>1.6</td>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
<td>i-Pr</td>
<td>0.2</td>
<td>1.1</td>
<td>1.6</td>
<td>2.0</td>
<td>4.1</td>
<td>2.1</td>
</tr>
<tr>
<td>t-Bu</td>
<td>0.5</td>
<td>2.7</td>
<td>3.0</td>
<td>4.1</td>
<td>8.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Ph</td>
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<td>1.4</td>
<td>1.5</td>
<td>2.1</td>
<td>3.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\[
K = 10^{-\frac{\Delta G}{2.3RT}}
\]

\[
R = 2 \text{ cal/mol-K, } T = 300 \text{ K}
\]
5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (30 pts)

![Fischer projections]

a. Which is not an isomer with the others? A B C D E
b. Which are meso? A B C D E
c. Which are optically active? A B C D E
d. Which pairs are identical? AB AC AD AE BC BD BE CD CE DE
e. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE
f. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE
g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BC BD BE CD CE DE

h. Draw any stereoisomers of pentane-2,3-diamine as Fischer projections, which are not shown above. If there are none, indicate this.

j. The structure of a steroid, amarasterol was recently isolated from a microorganism, cyathula capitata. Circle all chiral centers. How many stereoisomers are possible from the stereogenic centers shown? (Org. Lett. May 13, 2014, ASAP article)

![Steroid structure]

Maximum possible stereoisomers = _____________

The complete formula is C_{29}H_{50}O_4

What is the degree of unsaturation?
6. Fill in the missing lone pairs and formal charge on the first 2D structure. Assume ALL nonhydrogen atoms have full octets, unless a positive charge is shown. Draw three additional 2D resonance structures of the given structure using proper resonance curved arrows. Which structure is best (=1), second best, etc. and why? Draw a 3D structure for the given resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms. (30 pts)

\[
\begin{array}{cccc}
1 & 2 & 5 & 6 \\
\downarrow & \downarrow & \downarrow & \downarrow \\
N & C & C & C \\
\uparrow & \uparrow & \uparrow & \uparrow \\
3 & \text{CH}_3 & H & 4 \\
\text{C} & H & \text{C} & \text{C} & \text{O} \\
\end{array}
\]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shape</th>
<th>Hybridization</th>
<th>Bond Angles</th>
<th>#\sigma bonds</th>
<th>#\pi bonds</th>
<th># lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>2</td>
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<td>3</td>
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<tr>
<td>4</td>
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<td></td>
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<tr>
<td>5</td>
<td></td>
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<td></td>
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<tr>
<td>6</td>
<td></td>
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</tr>
</tbody>
</table>
7. a. The structures of vitamin A and vitamin C are shown below. If they are taken in large daily amounts one is toxic and one is not. Explain why this observation is reasonable? (8 pts)

![Vitamin A and Vitamin C structures](image)

b. The melting points and boiling points for the following two compounds are: -57°C, 101°C, 106°C and 126°C. Match those temperatures with the structures below and provide a possible explanation for the differences. (8 pts)

![Temperatures and Structures](image)

c. Provide an explanation for why NaCl is soluble in water, but not soluble in hexane. Use structures. (8 pts)
8. Using arrow-pushing mechanisms, write the expected products from the following reactions and indicate whether the equilibrium lies to the “right” or to the “left”. Also, very briefly explain your reasoning. (35 pts)

a) 

\[
\begin{align*}
\text{O}^- & \quad \text{N}^+ \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

b) 

\[
\begin{align*}
\text{H} & \quad \text{N}^- \\
\text{H} & \quad \text{N}^- \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

c) 

\[
\begin{align*}
\text{H} & \quad \text{N}^- \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

d) 

\[
\begin{align*}
\text{H} & \quad \text{O}^- \\
\text{H} & \quad \text{O}^- \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

e) 

\[
\begin{align*}
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

f) 

\[
\begin{align*}
\text{H} & \quad \text{N}^- \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

g) 

\[
\begin{align*}
\text{H} & \quad \text{C}^- \\
\text{H} & \quad \text{C}^- \\
\text{H} & \quad \text{N}^- \\
\text{H} & \quad \text{N}^-
\end{align*}
\]
9. Use (3S,4R)-3-bromo-4-deuteriohexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. Do not consider carbocation rearrangement possibilities. You can abbreviate (simplify) parts of the molecule that are not part of a reaction. (43 pts)

a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)

2D structure

3D structure

(3S,4R)-3-bromo-4-deuteriohexane

b. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (7 pts)

c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (13 pts)
d. Show the $S_N$ reaction (what kind?). You can use one intermediate to show all possible mechanistic $S_N$ possibilities. Indicate absolute configuration(s) of the $C_\alpha$ center in your product(s). (10 pts)

![Mechanism diagram]

Indicate absolute configuration(s) of the $C_\alpha$ center in your product(s).

E or Z

Configuration in product

e. Redraw the intermediate used in 8d above to show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism and just draw the additional possible products. (10 pts)

![Mechanism diagram]

Indicate if E, Z or neither.

E or Z
10. Indicate the major product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (30 pts)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
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<tbody>
<tr>
<td>a.</td>
<td></td>
</tr>
<tr>
<td>b.</td>
<td></td>
</tr>
<tr>
<td>c.</td>
<td></td>
</tr>
<tr>
<td>d.</td>
<td></td>
</tr>
<tr>
<td>e.</td>
<td></td>
</tr>
<tr>
<td>f.</td>
<td></td>
</tr>
<tr>
<td>g.</td>
<td></td>
</tr>
<tr>
<td>h.</td>
<td></td>
</tr>
<tr>
<td>i.</td>
<td></td>
</tr>
<tr>
<td>j.</td>
<td></td>
</tr>
<tr>
<td>k.</td>
<td></td>
</tr>
<tr>
<td>l.</td>
<td></td>
</tr>
<tr>
<td>m.</td>
<td></td>
</tr>
<tr>
<td>n.</td>
<td></td>
</tr>
<tr>
<td>o.</td>
<td></td>
</tr>
<tr>
<td>p.</td>
<td></td>
</tr>
<tr>
<td>q.</td>
<td></td>
</tr>
<tr>
<td>r.</td>
<td></td>
</tr>
<tr>
<td>s.</td>
<td></td>
</tr>
<tr>
<td>t.</td>
<td></td>
</tr>
</tbody>
</table>
11. Provide a complete arrow-pushing mechanism for the following transformations. (20 pts)

![Chemical structures](image)

12. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformations, one in acid and one in base. Assume all nonhydrogen atoms have full octets unless a positive charge is written by the atom. (20 pts)

![Chemical structures](image)
13. a. Show all possible products when 2-methylpentane is brominated with Br₂/hv? Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp³ C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (10 pts)

b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrows, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. To make a bond is positive energy and to make a bond is negative bond energy. (15 pts)

\[ \begin{array}{c|c}
\text{Br} & 46 \\
\text{H} & 87 \\
\hline
\text{Me C-H} & 105 \\
\text{1° C-H} & 98 \\
\text{2° C-H} & 95 \\
\text{3° C-H} & 92 \\
\hline
\text{Me C-Br} & 70 \\
\text{1° C-Br} & 68 \\
\text{2° C-Br} & 68 \\
\text{3° C-Br} & 67 \\
\end{array} \]

Don't be pushed around by the fears in your mind. Be led by the dreams in your heart. – Roy Bennett