<table>
<thead>
<tr>
<th>Problems</th>
<th>Points</th>
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<tbody>
<tr>
<td>1. Functional Group Nomenclature (1 large structure)</td>
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<td>2. Types of Isomers, Degrees of Unsaturation</td>
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<td>3. Cyclohexane Conformations, 2 substituents, Newman Projections,</td>
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<td>Relative Energies</td>
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<td>4. Newman Projections, Conformational Energies, $K_{eq}$ Calculation</td>
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<td>5. Stereochemical Analysis</td>
<td>30</td>
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<tr>
<td>6. 2D Resonance Structures, 3D Structure, Hybridization, Angles, Shapes</td>
<td>30</td>
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<td>7. Lewis Structures, Resonance, Formal Charge</td>
<td>18</td>
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<td>8. Quantitative Acid/Base Equation, Identify Conjugate Acid and Base and</td>
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<tr>
<td>Calculate $K_{eq}$, Supply Curved Arrows.</td>
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<td>9. Acid / Base Chemistry, Explanation, Curved Arrows, Formal Charge,</td>
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<td>Qualitative Equilibrium (7)</td>
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<td>10. $S_n/E$ 3D Mechanisms, with all of the details, Templates Provided</td>
<td>43</td>
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<td>11. Various Reactions, predict the products (20 reactions)</td>
<td>30</td>
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<td>12. Fill in all mechanistic details, curved arrows, lone pairs, formal charge,</td>
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<td>13. SN/E Mechanism, Carbocation Reactions</td>
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<td>Much, Stereochemistry and Provide a Mechanism For Major Product</td>
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<td>Total</td>
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Premidterm material = 188
Postmidterm material = 188

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.

"The limits of the impossible can only be defined by going beyond them…into the impossible." – Arthur Clark
1. Provide an acceptable name for the following molecule. (30 pts)

![Molecule Diagram]

1-benzyl-2R-mercapto-6-(2-methoxycarbonyl-4-hexylcyclopentyl)-7-(5-amido-6-ethylcycloocta-2E,4E-dienyl)-10-chloroundec-9E-en-4-ynyl 2R-hydroxy-3-phenyl-4-(2-methylbutoxy)-5,12-dioxo-6-cyano-9S-amino-10-formyl-11R-nitrododec-3Z-en-7-ynoate

2. Use the formula C₅H₁₀FNO to draw examples for each type of isomerism indicated. This will require that you draw at least two structures to show these differences. What is the degree of unsaturation? (25 pts)

\[
\text{C}_5\text{H}_{10}\text{FNO} \quad 2(5) + 2 + 1 = 13 = \text{saturated number} \\
-11 = \text{actual number} \\
\text{unsaturation} = \frac{2}{2} = \text{1st unsaturation}
\]

<table>
<thead>
<tr>
<th>Skeletal Isomers</th>
<th>Positional Isomers</th>
<th>Functional Group Isomers</th>
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</thead>
<tbody>
<tr>
<td><img src="image1" alt="Skeletal Isomer 1" /></td>
<td><img src="image2" alt="Positional Isomer 1" /></td>
<td><img src="image3" alt="Functional Group Isomer 1" /></td>
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<tr>
<td><img src="image4" alt="Skeletal Isomer 2" /></td>
<td><img src="image5" alt="Positional Isomer 2" /></td>
<td><img src="image6" alt="Functional Group Isomer 2" /></td>
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</tbody>
</table>

Conformational Isomers

- ![Conformational Isomer 1](image7)
- ![Conformational Isomer 2](image8)

Enantiomers

- ![Enantiomer 1](image9)
- ![Enantiomer 2](image10)

Diastereomers

- ![Diastereomer 1](image11)
- ![Diastereomer 2](image12)
3. Draw all possible chair conformations of trans-1-isopropyl-2-methylcyclohexane. Make the left most ring carbon C1 and number towards the front. Show all axial and equatorial groups in the first chair. Draw the more stable conformation first. Provide a reason for your answer. Draw a Newman projection of the least stable conformation using the C2→C1 and C4→C5 bonds to sight along. Point out any substituent gauche interactions shown in your Newman projection. If the axial energy of an isopropyl group is 2.1 kcal/mole and the axial energy of an methyl group is 1.7 kcal/mole and a isopropyl/methyl gauche interaction is 1.1 kcal/mole, what is the ratio of the two conformations at equilibrium? Show your work. Sketch an energy diagram that shows how the energy changes (lower to higher) with the conformational changes and estimate the ratio of the two conformations at equilibrium. (30 pts)

a. Newman projection

b. Newman projection (C2→C1 and C4→C5) – least stable, point out any gauche interactions with the substituent(s)

c. Energy diagram (lower to higher) and relative percents (K_{eq} = ?) (5 pts)

d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq}. (Assume R = 2 cal/mol-K and T = 300 K.) Use energy values provided in the box. Show your work. (5 pts)
4. Use a Newman projection of the C4→C3 bond of 2,2,5-trimethyl-3-ethylhexane 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. Calculate a ratio of least stable to most stable based on ∆H values. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (25 pts)

2D structure (3 pts)

Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

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<tr>
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Approximate Gauche Energy Values (kcal/mole)
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Newman projections:

least stable

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most stable

Triangles: V 4@C3

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Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

2D Structure

2,2,5-trimethyl-3-ethylhexane

Approximate Gauche Energy Values (kcal/mole)
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Et

t-Bu

H

i-Pr

Ph

Br

H

Me

Et

i-Pr

t-Bu

2D Structure

2,2,5-trimethyl-3-ethylhexane
5. Use the following set of Fischer projections to 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](image)

a. Which are optically active? A B C D E
b. Which are meso? A B C D E

c. Which is not an isomer with the others? A B C D E

d. Which pairs are enantiomers? AB AC AE BC BD BE CE DE

e. Which pairs are identical? AB AC AD AE BD BE CE DE

f. Which pairs are diastereomers? AB AC AD AE BD BE CD CE DE

g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BD BE CD CE DE

h. Draw any stereoisomers of 2,4-diamino-3-fluorohexane as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)

![Additional Fischer projections](image)

i. Taxol was isolated from the slow growing Pacific Yew tree in 1971 and developed into an important anti-cancer drug grown in cell cultures. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)

![Taxol / Paclitaxel](image)

Number chiral centers = 11

Possible stereoisomers = 2^{11} = 2048
6. Draw two additional “better” 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets except for + carbon. Add in any necessary lone pairs and use proper curved arrows. Which structure(s) is(are) best 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 in the given structure. (30 pts)

![Resonance Structures](image)

<table>
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<tr>
<th>Atom</th>
<th>Shape</th>
<th>Hybridization</th>
<th>Bond Angles</th>
<th>#σ bonds</th>
<th># π bonds</th>
<th># lone pairs</th>
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7. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent. (18 pts)

- The second resonance structure is better because it has full octets and it quenches formal charge.
- The second resonance structure is better because it moves the negative charge from nitrogen to the more electronegative oxygen.
- The second resonance structure is better because it has full octets and it quenches formal charge.

8. Only the reactant acid and base are drawn below. Decide which is which and draw a mechanism to show formation of the conjugate base and acid. The two acids have pK_a's of 15 and 12 (K_a values are 10^{-15} and 10^{-12}). Match the K_a values with the proper acid, write a K_{equilibrium} expression and calculate a quantitative K_{equilibrium} value for the reaction. Show your work. Provide an explanation for your value of K_{equilibrium}. (15 pts)

\[
K_{\text{equilibrium}} = \frac{K_a (\text{CH}_3\text{OH})}{K_a (\text{CH}_3\text{OOH})} = \frac{K_a = 10^{-15}}{K_a = 10^{-12}} = 10^{-3}
\]

The equilibrium is favored to the left because of the inductive withdrawing effect of the second oxygen atom, which helps to stabilize the negative charge. There is no resonance effect here.

b. Use the above K_a values to estimate a K_a for the following acid. Very briefly explain your reasoning. (5 pts)

\[
K_a = 10^{-15}
\]

We can estimate a K_a value between the two given acids. N is inductively electron withdrawing relative to carbon, but not as electronegative as oxygen, so the inductive withdrawing effect of N helps stabilize the anion more than carbon but not as much as oxygen.
9. 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. The left side is favored because the anion charge is more delocalized on the larger phosphorous than nitrogen (same Z_{eff}).

b. The right side is favored because the cation charge is more delocalized on 3 nitrogen atoms than 2 nitrogen atoms.

c. The left side is favored because the anion charge is more delocalized on two oxygen atoms than one oxygen.

d. The right side is favored because the anion charge is stabilized by the inductive withdrawing effect of the 3 fluorine atoms.

e. The left side is favored because the cation charge is more stable with resonance donation from a nitrogen than from an oxygen.

f. The left side is favored because the anion is more stabilized in a more electronegative sp orbital (50% s) than in an sp^{2} orbital (33% s).

g. The right side is favored because the anion is more stabilized without the inductive donating effect of 3 methyl groups.
10. Use (2S,3R)-3-bromo-2-deuterioheptane 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)

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

Backside attack = inversion of configuration.

2Z (with deuterium)

configuration in product

c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (13 pts)
rotate "D" anti

C_β-D is anti to C_α-Br

lose H_a from other side

C_β-H is anti to C_α-Br

rotate H_b anit and lose H_b from other side

C_β-H_b is anti to C_α-Br
d. Show the SN reaction (what kind?). You can use one intermediate to show all possible mechanistic SN possibilities. Indicate absolute configuration(s) of the C_α center in your product(s). (10 pts)

![SN Reaction Diagram]

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

![E Reaction Diagram]
11. Indicate the major product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralization conditions) (30 pts)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td><img src="image1.png" alt="Product" /></td>
</tr>
<tr>
<td>b.</td>
<td><img src="image2.png" alt="Product" /></td>
</tr>
<tr>
<td>c.</td>
<td><img src="image3.png" alt="Product" /></td>
</tr>
<tr>
<td>d.</td>
<td><img src="image4.png" alt="Product" /></td>
</tr>
<tr>
<td>e.</td>
<td><img src="image5.png" alt="Product" /></td>
</tr>
<tr>
<td>f.</td>
<td><img src="image6.png" alt="Product" /></td>
</tr>
<tr>
<td>g.</td>
<td><img src="image7.png" alt="Product" /></td>
</tr>
<tr>
<td>h.</td>
<td><img src="image8.png" alt="Product" /></td>
</tr>
<tr>
<td>i.</td>
<td><img src="image9.png" alt="Product" /></td>
</tr>
<tr>
<td>j.</td>
<td><img src="image10.png" alt="Product" /></td>
</tr>
<tr>
<td>k.</td>
<td><img src="image11.png" alt="Product" /></td>
</tr>
<tr>
<td>l.</td>
<td><img src="image12.png" alt="Product" /></td>
</tr>
<tr>
<td>m.</td>
<td><img src="image13.png" alt="Product" /></td>
</tr>
<tr>
<td>n.</td>
<td><img src="image14.png" alt="Product" /></td>
</tr>
<tr>
<td>o.</td>
<td><img src="image15.png" alt="Product" /></td>
</tr>
<tr>
<td>p.</td>
<td><img src="image16.png" alt="Product" /></td>
</tr>
<tr>
<td>q.</td>
<td><img src="image17.png" alt="Product" /></td>
</tr>
<tr>
<td>r.</td>
<td><img src="image18.png" alt="Product" /></td>
</tr>
<tr>
<td>s.</td>
<td><img src="image19.png" alt="Product" /></td>
</tr>
<tr>
<td>t.</td>
<td><img src="image20.png" alt="Product" /></td>
</tr>
</tbody>
</table>
12. Provide all missing arrow-pushing mechanistic details (curved arrows, lone pairs and formal charge) to explain the following transformation. Assume all nonhydrogen atoms have full octets unless a positive charge is written by a carbon atom. (20 pts)

a.

\[
\text{resonance}
\]

\[
\begin{align*}
&\text{H}_3C\text{C}^\text{\delta-}\text{O}^+ \quad \text{H}_3C\text{C}^\text{\delta-} \quad \text{resonance} \quad \text{H}_3C\text{C}^\text{\delta-}\text{O}^+ \\
\end{align*}
\]

\[
\text{2. workup}
\]

\[
\text{resonance}
\]

\[
\begin{align*}
&\text{H}_3C\text{C}^\text{\delta-}\text{O}^+ \quad \text{H}_3C\text{C}^\text{\delta-} \quad \text{resonance} \quad \text{H}_3C\text{C}^\text{\delta-}\text{O}^+ \\
\end{align*}
\]

\[
\text{3. workup}
\]

\[
\text{resonance}
\]

\[
\begin{align*}
&\text{H}_3C\text{C}^\text{\delta-}\text{O}^+ \quad \text{H}_3C\text{C}^\text{\delta-} \quad \text{resonance} \quad \text{H}_3C\text{C}^\text{\delta-}\text{O}^+ \\
\end{align*}
\]

13. Provide a complete arrow-pushing mechanism for the following transformations (lone pairs, formal charge and curved arrows). (15 pts)

\[
\begin{align*}
&\text{R + S} \quad \text{O}^+ \quad \text{R + S} \quad \text{O}^+ \quad \text{R + S} \\
\end{align*}
\]

\[
\begin{align*}
&\text{2° carbocation rearrangement} \quad \text{add nucleophile} \quad \text{op & bottom} \\
\end{align*}
\]

\[
\begin{align*}
&\text{3° carbocation (more stable)} \quad \text{3° carbocation and resonance (even more stable)} \\
\end{align*}
\]

\[
\begin{align*}
&\text{E1} \quad \text{lose Cβ-H} \\
\end{align*}
\]
14. a. Show all possible products when 2S-bromopentane is chlorinated with Cl₂/hv? Indicate the approximate relative amounts (RA) of each product formed if the relative rates of reaction of a chlorine atom with an sp³ C-H bond are: primary = 1, secondary = 4, tertiary = 5 and C-H on a carbon with bromine = 15. Identify any stereoisomers as enantiomers, diastereomers or meso structures. Show 3D stereochemistry clearly at any chiral centers. (15 pts)

\[
\text{relative amounts } = RA = (\text{number of C-H}) \times (\text{relative reactivity})
\]

\[
\begin{align*}
\text{RA} &= (3) \times (1) = 3 \\
\text{enantiomers} \\
\text{RA} &= (1) \times (15) = 15 \\
\text{diastereomers} \\
\text{RA} &= (1) \times (4) = 4 \\
\text{RA} &= (1) \times (4) = 4 \\
\text{diastereomers} \\
\text{RA} &= (3) \times (1) = 3
\end{align*}
\]

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 \( \Delta H \) for each step of your mechanism using the given bond energies. To break a bond is positive energy and to make a bond is negative bond energy. (15 pts)

\[
\begin{align*}
\text{1. initiation} & \quad \text{Cl-Cl} \quad 58 \\
\text{H-Cl} & \quad 103 \\
\text{Me C-H} & \quad 105 \\
\text{1° C-H} & \quad 98 \\
\text{2° C-H} & \quad 95 \\
\text{3° C-H} & \quad 92 \\
\text{Br-C-H} & \quad 90 \\
\text{Me -Cl} & \quad 85 \\
\text{1° C-Cl} & \quad 81 \\
\text{2° C-Cl} & \quad 81 \\
\text{3° C-Cl} & \quad 81 \\
\text{Br-C-Cl} & \quad 79
\end{align*}
\]

1. initiation

\[
\begin{align*}
\Delta H &= \text{Cl-Cl} \quad 58 \\
\Delta H &= \text{H-Cl} \quad 103 \\
\Delta H &= \text{Me C-H} \quad 105 \\
\Delta H &= \text{1° C-H} \quad 98 \\
\Delta H &= \text{2° C-H} \quad 95 \\
\Delta H &= \text{3° C-H} \quad 92 \\
\Delta H &= \text{Br-C-H} \quad 90 \\
\Delta H &= \text{Me -Cl} \quad 85 \\
\Delta H &= \text{1° C-Cl} \quad 81 \\
\Delta H &= \text{2° C-Cl} \quad 81 \\
\Delta H &= \text{3° C-Cl} \quad 81 \\
\Delta H &= \text{Br-C-Cl} \quad 79
\end{align*}
\]

2a. propagation

\[
\begin{align*}
\Delta H &= \text{Cl} \quad +58 \\
\Delta H &= \text{Br} \quad +90 \\
\Delta H &= \text{H} \quad -103 \\
\Delta H &= \text{Br} \quad -21
\end{align*}
\]

2b. propagation

\[
\begin{align*}
\Delta H &= \text{Cl} \quad +58 \\
\Delta H &= \text{Br} \quad -79
\end{align*}
\]

3. termination = combination of 2 radicals to shut down chain reaction

\[
\Delta H = \text{R} \quad -81
\]