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. Only write answers in the space provided.

The best preparation for tomorrow is doing your best today.  H. Jackson Brown
3. Draw all possible chair conformations of trans-1,4-dibutyl-3-phenylcyclohexane. Draw C1 at the leftmost side and number C2 towards the front. Show all axial and equatorial groups. Draw the most stable conformation first. Provide a reason for your choice. Based on the Newman projection, explain the relative stability of the conformations. The energy of each conformation is 3.5 kcal/mol and 2.9 kcal/mol for a phenyl group. The gauche energy of phenyl/c-butyl is listed in the table on the next page, if necessary. What is the difference in energy between the chair conformations? Show your work. Sketch an energy diagram that shows how the energy changes with the conformational changes. (25 pts)

4. Use a Newman projection of the C3→C4 bond of 2-methyl-4-phenylhexane. 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. What are the relative percents of each conformation? Plot the changes in energy in the graph provided. Hence draw a 2D structure first and "bold" the bond viewed in your Newman projection, then decide your line of sight. (25 pts)

<table>
<thead>
<tr>
<th>Approximate Relative Energy (kcal/mol)</th>
<th>Approximate Gauche Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Me</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>Me</td>
<td>1.1</td>
</tr>
<tr>
<td>Et</td>
<td>2.1</td>
</tr>
<tr>
<td>i-Pr</td>
<td>3.2</td>
</tr>
<tr>
<td>t-Bu</td>
<td>5.1</td>
</tr>
<tr>
<td>Ph</td>
<td>7.2</td>
</tr>
</tbody>
</table>

2D structure

Most stable conformation

**K = 10**

<table>
<thead>
<tr>
<th>ΔPE</th>
<th>ΔPE</th>
<th>ΔPE</th>
<th>ΔPE</th>
<th>ΔPE</th>
<th>ΔPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>5.2</td>
<td>3.0</td>
<td>10.7</td>
<td>4.0</td>
<td>6.8</td>
</tr>
</tbody>
</table>

**K = 10**

**K = 10**

**K = 10**
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. (25 pts)

![Fischer projections image]

- Which are optically active? A B C D E
- Which are none? A B C D E
- Which is not an isomer with the others? A B C D E
- Which pairs are enantiomers? AB AD AE BD BE CD CE DE
- Which pairs are identical? AB AC AD AE
- Which pairs are diastereomers? AB AC AD AE
- Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE

b. Draw any additional stereoisomers of 2,4-dihydroxyhexane as Fischer projections. If there are none, indicate this. (5 pts)

![Additional stereoisomers image]

6. Draw two additional "better" 2D resonance structures of the given structure. Which structure is best and why?

- Draw a 3D structure for the best 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)

![Resonance structures image]

- Use given structure A to fill in this table.

<table>
<thead>
<tr>
<th>Atom Shape</th>
<th>Hybridization</th>
<th>Bond Angles</th>
<th>#s bonds</th>
<th>#π bonds</th>
<th># lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 trigonal planar</td>
<td>sp²</td>
<td>120°</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2 trigonal planar</td>
<td>sp²</td>
<td>120°</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3 linear</td>
<td>sp</td>
<td>180°</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4 linear</td>
<td>sp</td>
<td>180°</td>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>5 trigonal planar</td>
<td>sp²</td>
<td>120°</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>6 tetrahedral</td>
<td>sp³</td>
<td>109°</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- A recent Organic Letters paper presented an approach for making 'ladder ethers' found in toxins common among dinoflagellate algae that cause toxic red tides (Org. Lett., p.774, 2015). Circle all chiral centers and any other stereochanical features, and calculate the maximum number of stereoisomers possible. (5 pts)

![Stereochemistry image]

Number of stereogenic centers = 8
Maximum number of stereoisomers = \( 2^8 = 256 \)
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? (10 pts)

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. (10 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". Very briefly explain your reasoning. If resonance is important, show this. (42 pts)
9. Use (2S,3R)-2-bromo-3-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)

b. Show the $S_N$ reaction (what kind?), indicate the absolute configuration(s) of the C$_a$ 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$_a$ center in your product(s). (10 pts)

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 for those two atoms and just draw the additional possible products. (10 pts)

all E2 = anti C$_{E}^{+}$/C$_{E}^{°}$Br
10. Indicate the major product in the following reactions. Indicate stereochemistry if part of the reaction. Do NOT show mechanisms. (WK = workup = neutralize conditions) (45 pts)

Arrows are added to give hints about mech. They are NOT required.

11. Using the given formula, \( C_5H_9Br \), draw an isomer which satisfies each given statement. Do not use any given isomer more than one time. If stereochemistry is important make sure you draw your structure so that its three-dimensional nature is clearly indicated. Point out the feature of your structure that makes it consistent with the given statement. How many degrees of unsaturation are there? (show work) (20 pts)

degree of unsaturation = \( \frac{16 - 10}{2} = 3 \) (2 pts)

- a. Undergoes E2 reaction, but not S_{n}2 reaction in HO^-OH. Show a possible mechanism. (4 pts)
- b. Does not react by S_{n}2 or E1 reaction. (2 pts)
- c. Can reasonably react by all four mechanisms (E1c, E2, S_{n}2, E1). (2 pts)
- d. Undergoes fast S_{n}2 reaction with H_2O. Show the product(s). (4 pts)
- e. Undergoes fast S_{n}2 reaction with HO^-OH. Show the product(s). (4 pts)
- f. Write a possible product(s) from part d. (2 pts)