CEM 351, Fall 2007
Midterm Exam 1
Friday, September 28, 2007
1:50 – 2:40 p.m.
Room 138, Chemistry

Name (print) L. T. N. Swers
Signature
Student # Section Number (2 pts extra credit)

Grade?

1. (20 pts.)
2. (20 pts.)
3. (20 pts.)
4. (20 pts.)
5. (20 pts.)
6. (20 pts.)

TOTAL (100 pts.)

Score

Note: Answer any 5 questions for a total score of 100 pts. Be sure to look over all the questions first before beginning the exam, and indicate which five questions are to be graded by checking the corresponding box.

<table>
<thead>
<tr>
<th>Recitation</th>
<th>Day and Time</th>
<th>Instructors:</th>
<th>Room</th>
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</thead>
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<tr>
<td>1.</td>
<td>T 9:10-10:00 a.m.</td>
<td>Alex Predeus</td>
<td>85</td>
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<tr>
<td>2.</td>
<td>M 10:20-11:10 a.m.</td>
<td>Alex Predeus</td>
<td>281</td>
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<td>3.</td>
<td>T 10:20-11:10 a.m.</td>
<td>Karrie Manes</td>
<td>85</td>
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<td>4.</td>
<td>Th 10:20-11:10 a.m.</td>
<td>Kostas Rampalokos</td>
<td>287</td>
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<td>5.</td>
<td>T 10:20-11:10 a.m.</td>
<td>Alex Predeus</td>
<td>283</td>
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<td>6.</td>
<td>T 11:30-12:20 p.m.</td>
<td>Kostas Rampalakos</td>
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<td>7.</td>
<td>Th 11:30 - 12:20</td>
<td>Kostas Rampalakos</td>
<td>85</td>
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<td>8.</td>
<td>M 4:10-5:00 p.m.</td>
<td>Karrie Manes</td>
<td>110</td>
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<td>9.</td>
<td>W 4:10-5:00 p.m.</td>
<td>Karrie Manes</td>
<td>110</td>
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</table>
1. (20 pts)
   (a) (3 pts each) Form acceptable Lewis structures for the following uncharged compounds by adding the necessary nonbonding electrons and multiple bonds:

   ![Carbon Dioxide](image)
   ![Formamide](image)

   (b) (3 pts each) Assign formal charges as necessary to the atoms in the following Lewis structures.

   ![Bicarbonate](image)
   ![Glycine (an amino acid)](image)

   (c) (4 pts) A full description of bicarbonate (above) requires two main resonance structures. The one you completed was one; draw the other one:

   ![Bicarbonate resonance structure](image)

   (d) (4 pts) Shown below is another commonly published representation of Glycine. Is this a valid resonance structure of the version in (b)? Please circle your answer and explain.

   ![Glycine representation](image)

   **Yes**

   **No**

   **Explanation:** Resonance structures are related only by moving electrons/bonds around, not atoms. This structure has atoms in different places than the one above; instead of the charged $\text{H}_2\text{N}^+$ and $-\text{COO}^-$ groups as above, it has $\text{H}_2\text{N}$ and $-\text{COOH}$, both neutral groups.
2. (20 pts) Consider the five Newman projections below.

(a) (2 pts) All of these diagrams depict compounds of formula __C₅H₁₂_________.

(b) (4 pts) Structure __E__ represents a compound different from the other four. This compound’s IUPAC name is ____________2,2-dimethylpropane_________.

(c) (2 pts) The other four depict (IUPAC name): ____________2-methylbutane_________.

Of the four in (c),…

(d) (2 pts) …which two structures represent staggered conformations? __B__ and __D__.

(e) (2 pts) …which two structures represent energy maxima (high points) on the torsional potential energy surface? __A__ and __C__.

(f) (4 pts) For two of the above structures there are additional conformations of equal energy. Which ones are they? __B__ and __C__. Draw their same-energy conformations by completing the Newman projections, labeled __F__ and __G__ below.

(g) (4 pts) In the box below, take structure __A__ to be at 0° and sketch the rotational potential energy diagram, placing structures __A-G__ (except for the misfit) in your picture.
3. (20 pts)
   (a) (12 pts) Draw structures to represent the following IUPAC names

   (i) 2-chloro-2-fluoroethanol

   ![Structure of 2-chloro-2-fluoroethanol]

   (ii) 1,1,2-trimethylcyclopentane

   ![Structure of 1,1,2-trimethylcyclopentane]

   (iii) 3,3-diethylpentane

   ![Structure of 3,3-diethylpentane]

   (b) (2 pts) Which of the compounds in (a) has no dipole? Please circle your answer

   (i) (ii) [iii]

   Note: based on symmetry, compound ii’s dipole is small but finite.

   (c) (3 pts) Why don’t we have to give a number to show the hydroxy group position in compound (i), a substituted alcohol?

   Explanation: With only two carbons to choose from, the –OH group defines the numbering.

   (d) (3 pts) Why don’t we have to indicate cis or trans in describing (ii), a cycloalkane?

   Explanation: With two methyls at C-1, the “top” and “bottom” face substituents are the same, so “cis” or “trans” are meaningless to describe the compound (though one could refer to the cis- and trans- methyls relative to the methyl at C-2).
4. (20 pts) Structural analysis by spectroscopy
(a) (3 pts each) For each pair of compounds in the grid below, propose a spectroscopic method to tell them apart, and explain what you would look for with the suggested method.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Method &amp; Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MS of left cpd would see easy losses of t-Bu (57) but much less of CH₃ (15), whereas CH₃, CH₃CH₂O losses dominate for cpd at right. ¹H NMR would see left cpd as three singlets, right at singlet + ethyl pattern.</td>
</tr>
<tr>
<td>B</td>
<td>IR of right cpd would show carbonyl (C=O) and CH3 bands missing in left case. ¹H NMR of left cpd would be three multiplets integrating to 2:4:4, right cpd = ethyl pattern.</td>
</tr>
<tr>
<td>C</td>
<td>UV-vis spectrum of conjugated diene at right would absorb at ca. 225-230 nm; left cpd’s isolated alkenes would be &lt;190 nm and weak. ¹H NMR &amp; IR would show left’s terminal alkenes. IR would show right’s methyl groups.</td>
</tr>
<tr>
<td>D</td>
<td>Chemical shifts in ¹H or especially ¹³C NMR would distinguish—Cl is more electronegative than Br. C-Hal stretch in IR would also work, but they’re weak bands. And MS obviously would be different—different elements.</td>
</tr>
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</table>

(b) (8 pts) Below are ¹H NMR and IR spectra for some MSU students’ favorite substance of abuse (ethanol). Please identify the key features that confirm this structure—i.e., assign the three NMR peaks to the sites in the molecule, explain their splitting patterns, and predict their respective integrals. Similarly, identify at least three features of the IR spectrum that support the structural assignment.

(Images of ¹H NMR and IR spectra showing key features.)

(Note: this peak is in C=O region, but too broad; impurity?)
5. Consider the following equilibrium constant values (from Bruice, Table 2.10, p. 112) for interconversions between the two chair conformations of substituted cyclohexanes.

<table>
<thead>
<tr>
<th>R</th>
<th>K(eq/ax)</th>
<th>ΔG(eq/ax) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>CH₃</td>
<td>18</td>
<td>1.7</td>
</tr>
<tr>
<td>CH₂CH₃</td>
<td>21</td>
<td>1.8</td>
</tr>
<tr>
<td>CH(CH₃)₂</td>
<td>35</td>
<td>2.1</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>4800</td>
<td>5.0</td>
</tr>
</tbody>
</table>

a. (3 pts) In which structure above is R axial? (Circle your choice):  A  

b. (6 pts) Use the templates below to construct Newman projections of the three ethyl rotation energy minima as viewed down the CH₃CH₂–CH(CH₂)₅ (i.e. ethyl-cyclohexyl) bond in ethylcyclohexane (the cyclohexane ring is already shown).

![Newman projections of ethyl rotation energy minima](image)

Higher
Lower

Higher
Lower

Higher
Lower

![Higher and Lower projections](image)

c. (6 pts) Rank the three conformations in part (b) higher or lower in energy (two are the same) by circling the correct word for each.

d. (5 pts) The equilibrium constants in part (a) translate into the energy differences shown at right (from the relationship ΔG = -RTln K; ΔG = “Gibbs free energy difference”). Along the way from R = CH₃ to R = C(CH₃)₃, the methyl, ethyl, and isopropyl groups have axial-equatorial ΔG values (1.7, 1.8, 2.1) within 0.4 kcal/mol—hardly different. But the next jump, to the t-butyl group, raises the ΔG up to 5 kcal/mol! Explain, using careful drawings on the templates below and a few carefully chosen words, why this last methyl replacement makes a difference so much bigger than the others. (Hint: how would the conformations you produced in part (b) be affected by chair-chair flipping of the cyclohexane part?)

![Energy difference and explanation](image)
6. (20 pts) More on structural analyses based on spectroscopies:

(a) (8 pts) For each compound below, circle and label (with a, b, c… as in the example at right) the groups of equivalent ^1^H sites. If it’s helpful, feel free to add H’s as appropriate to the structures.

(i) 
(ii) 
(iii) 
(iv) 

(b) (6 pts) Only one of the above compounds would show simple singlets (i.e. unsplit peaks) in its ^1^H NMR spectrum. Redraw the compound and point out the site(s) responsible.

(c) (6 pts) Compounds (iii) and (iv) in part (a) are isomers. Could you tell them apart by IR spectroscopy? How? Identify at least two spectroscopic differences you could easily see. (Assume the strained cyclopropane ring doesn’t do anything special.)

Cyclopropanol (same as (b) answer) should show:
(a) Alcohol bands:
   a. broad OH stretch ca. 3600-3300 cm^-1
   b. C-O stretch near 1300-1000 cm^-1
(b) Methyl group bending bands:
   a. 1385-1365 along with general C-H 1450-1420