Chemistry 211
Exam 1
Fall 2015
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1) There are a total of 16 questions
2) Counting this cover sheet, there are a total of 7 pages- check to ensure you have all 7.
3) All 7 pages must be turned in for grading.
4) Use the backside of preceding pages for scratch paper.
8) *Any cheating will result in the dismissal from class with an "F" grade.*
9) Please put your name or initial on each page
10) You must sign below to receive a grade on this exam.

I have read and understand the above instructions for this exam.

Signature ________________________________

Page 1               Cover page
Page 2               _____/12
Page 3               _____/24
Page 4               _____/25
Page 5               _____/18
Page 6               _____/14
Page 7               _____/11

Total               _____/104
1. (20) Multiple Choice. Please write your answers in the boxes provided on the right.

a) Shown below is the reaction of acetylene with hydrogen. This reaction is a(n) __________

A) oxidation  B) reduction  C) double replacement  D) impossible  E) none of these

b) Which statement is correct concerning the relative stabilities of the two conformations, 1 and 2, below:

A) 1 is more stable than 2.
B) 2 is more stable than 1.
C) 1 and 2 are equally stable.
D) 1 and 2 are not equal in stability, but the preferred conformation cannot be determined by inspection.

B

C) Predict which of the following constitutional isomers of C₅H₁₀ would have the highest heat of combustion? least Stable one...

A) methylcyclobutane  B) cyclopentane  C) cis-1,2-dimethylcyclopropane  D) trans-1,2-dimethylcyclopropane

C

d) Identify the two atoms anti to the bromine.

A) the equatorial H's on C-2 and C-6.
B) the axial H's on C-2 and C-6.
C) C-2 and C-6.
D) C-3 and C-5.
E) none of these

D

e) Which isomer of 1-tert-butyl-3-ethyl-5-methylcyclohexane below is thermodynamically the most stable?

A

f) The IUPAC name of the following compound is:

A) cis-1,2-dimethylcyclohexane  B) trans-1,2-dimethylcyclohexane  C) cis-1,3-dimethylcyclohexane  D) trans-1,3-dimethylcyclohexane  E) none of these

A
g) What is the IUPAC name of the following bicyclicalkane?

- A) bicyclo[6.3.0]heptane
- B) bicyclo[4.2.0]hexane
- C) bicyclo[4.1.0]hexane
- D) bicyclo[4.1.0]heptane

Answer: D

h) The sawhorse drawing of butane below is:

- A) a gauche conformation
- B) an anti conformation
- C) the least stable eclipsed conformation
- D) the most stable eclipsed conformation
- e) none of these

Answer: A

i) Arrange the following compounds in order of increasing heat of combustion.

- (1) pentane
- (2) hexane
- (3) isopentane

Answer: E

j) A mixture containing the following compounds is placed on an alumina column and chromatography is done with a ethyl acetate solvent. In what order will they elute from the column?

- (1) chlorocyclohexane
- (2) phenol
- (3) diisopropyl ether

Answer: F

2. (8) Determine if the molecules below are a) chiral b) meso and achiral or c) achiral with no stereocenters.

- (2R,3S)-2,3-dichlorobutane

3. (8) Assign the absolute configurations in each of the compounds shown below.
4. (12) What is the relationship between the following pairs of structures?
A) identical B) conformers C) structural isomers D) enantiomers E) diastereomers F) not isomers

5. (3) Mark the following as true or false statements
A. Diastereomers can be distinguished by their melting point or other physical properties. T
B. Enantiomers have the same boiling point. T
C. Enantiomers have the same density. F

6. (6) Fill in the following table with respect to the indicated compound.
a) Indicate the oxidation number for each carbon
b) Indicate the hybridization for each carbon.
c) Indicate the formal charge for each heteroatom.

<table>
<thead>
<tr>
<th>Carbon #</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation #</td>
<td>+1</td>
<td>3+</td>
<td>2</td>
</tr>
<tr>
<td>Hybridization</td>
<td>$sp^2$</td>
<td>$sp^2$</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>Heteroatom</td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Formal Charge</td>
<td>-1</td>
<td>0</td>
<td>+1</td>
</tr>
</tbody>
</table>

7. (4) Circle the most acidic proton(s) in each structure.
8. (5) Draw the most stable conformer of the following, show all of the attached hydrogens, and indicate whether each alkyl substituent is axial or equatorial.

trans-1-ethyl-4-methyl cyclohexane

9. (4) Provide the correct IUPAC name for the following compound.

2-cyclohexyl-3-methyl octane

10. (4) Draw the correct structure for (3S,4S)-3,4-dibromocyclohexanone.

11. (5) Draw the Newman projection at the C2-C3 bond of the following molecule in the indicated conformation and indicate the dihedral angle between the two methyl groups.

Dihedral angle 60°
12. (8) For the following: draw the most stable resonance structure for each, and draw arrows to show electron flow. Be sure to include the formal charges if they are present. Explain why the structure you've drawn is more stable than the structure provided.

(a)

Explanation:

There is no charge separation in the more stable one unlike the less stable one.

(b)

Explanation:

The more stable structure has a negative charge on a more electron-negative position.

13. (6) The anti conformation of 1,2 dichloroethane is more stable than the gauche by about 0.8 Kcal/mol at room temperature (25°C). Since there are no degrees of freedom, ΔS = 0

a) Calculate the equilibrium constant, K_{eq}, for the interconversion from the gauche to anti conformer.

R = 1.987 cal/mol K

\[ \Delta G = -RT \ln K_{eq} \]

\[ c > \frac{\Delta H}{RT} = K_{eq} \]

\[ K_{eq} = e^{\frac{0.8 \text{ Kcal/mol}}{298 \text{ K}}} \]

\[ K_{eq} = 3.86 \]

b) Calculate the relative % of anti and gauche conformers at room temperature (25°C)

\[ K_{eq} = \frac{[\text{Anti}]}{[\text{Gauche}]} \]

\[ \% \text{ Anti} = \frac{[\text{Anti}]}{\text{[Anti]} + [\text{Gauche}]} = \frac{46}{46 + 6} = \frac{46}{52} = \frac{23}{26} \]

\[ 80 \text{ % anti} \quad 20 \text{ % gauche} \]
14. (5) Rank the following compounds according to increasing positive character of the carbon atom.

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>CH₃Cl</th>
<th>CH₃NH₂</th>
<th>CH₃Li</th>
<th>CH₃OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Li⁺</td>
<td>C</td>
<td>close</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>+</td>
<td></td>
<td>close</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>+</td>
<td></td>
<td>close</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>+</td>
<td></td>
<td>close</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>+</td>
<td></td>
<td>close</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Least + < A < B < C < E

Most +

15. (3) What is% concentration of a mixture of 2-butanol if the observed rotation is 22.4° and the specific rotation of the pure S isomer is 72.8°?

\[
\frac{22.4°}{72.8°} \times 100\% = 30.177\% \text{ ee}
\]

\[
\frac{34.6\% S + 30.8\% S}{65.4\%} = 34.6R < 34.6S
\]

\[
\frac{69.2 = 34.6R + 34.6S}{2} = 34.6 \% R = 65.4 \% S
\]

16. (3) Consider a solution that contains 81.0% R isomer and 19.0% S isomer. If the observed specific rotation of the mixture is -84.0°, what is the specific rotation of the pure R isomer?

\[
\frac{81\% R - 19\% R + S}{62\% R \text{ in excess of } S} \times 100 = 62\% ee
\]

\[
\frac{x}{100} = \% ee
\]

\[
\frac{x}{6\% ee} \times 100 = [\alpha]
\]

\[
-84.0° \left( \frac{100 R + S}{62 R} \right) = -135°
\]