FINAL EXAMINATION
Organic Chemistry, Chem 220
9 A.M.; Saturday, December 11, 2010

NAME (print): ______________________________________________________________

TA:_____________________ Section Day:_____________ Section Time:______________

Take a few moments to look over the exam. Do problems first with which you are most comfortable. Important points and unknowns are in **bold** type. Do all **preliminary** work on the worksheets. The worksheets will not be graded. The exam is the length of two hour exams with an additional one hour for review. **STOP** writing when you are asked to do so. Put your name on the **cover sheet and subsequent pages** (except for Work Sheets) where indicated. **No calculators or electronic devices.** A Periodic Table and Bond Dissociation Energy table are on page 15. Isotope abundance and A-values tables are on page 16.

**REMEMBER:** Neatness is to your advantage.

**Have a GREAT winter break!**

1. Spectroscopy/Structure (25 pts) _________

2. Reactions I (32 pts; 4 of 5) _________

3. Potpourri (40 pts; 8 of 10) _________

4. Synthesis (25 pts.) _________

5. Thermochemistry (25 pts.) _________

6. Reactions II (30 pts., 6 of 8) _________

7. Kinetics/Thermodynamics (20 pts.) _________

8. Mechanisms (25 pts.) _________

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Total (222 pts)

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**Note:** The final exam is worth 160 points toward the final grade. The grade shown above will be multiplied by 0.72 to obtain the adjusted score (222 x 0.72 = 160).
1. **Spectroscopy/Structure**: (25 pts.) Achiral compound A (M$^+$ = 112; Degrees of Unsaturation = 2) is inert to aqueous chromic acid and its infrared spectrum displays a strong absorption at 1717 cm$^{-1}$. Compound A reacts with one equivalent of Grignard reagent B (RMgBr) to form a mixture of achiral diastereomers C and C', each of whose mass spectrum displays a molecular ion at M$^+$ = 128. Compound C is more stable than compound C'. Compounds C and C', together or separately, react readily with catalytic H$_2$SO$_4$ by an E1 mechanism to give two isomers [(±)-D (major) and achiral E (minor)]. Ozonolysis and dimethyl sulfide reduction of compound (±)-D provides F, which upon reduction with LiAlH$_4$ gives G, 3-methylheptan-1,6-diol. Exposure of E to excess hot aqueous KMnO$_4$ gives rise to compounds A and H. What are the structures of A – H? **Show your reasoning.** [Hint: Work backwards from G.]
2. **Reactions I:** (4 x 8 pts. = 32 pts.) **Do 4 of 5.** Provide structures for the unknown compounds. Be explicit about stereochemistry, optical activity, racemates, etc. No mechanisms required! **If you do more than four problems, cross out (with a large X through the solution) the one that you do not want graded.**

**a)**

\[ \begin{align*}
A & \xrightarrow{HBr} B \xrightarrow{aq. KOH} C (C_5H_{12}O) \\
 & \xrightarrow{aq. H_2Cr_2O_7} D (C_6H_{10}O) \\
 & \xrightarrow{cat. OsO_4, HIO_4} E \xrightarrow{aq. H_2Cr_2O_7} F (C_3) + G (C_2) \\
\text{room temp.} & \xrightarrow{H_2O} \\
\end{align*} \]

**b)**

\[ \begin{align*}
A (C_8H_{14}) & \xrightarrow{aq. KMnO_4} B \xrightarrow{cold, alkaline} C \xrightarrow{aq. KMnO_4} D (meso) \\
 & \xrightarrow{aq. KMnO_4} E \\
F & \xrightarrow{Br_2} G \xrightarrow{Br_2} H \text{ (meso - C}_6\text{H}_{16}\text{Br}_2) \\
\end{align*} \]

**c)**

\[ \begin{align*}
\text{1) TsCl, pyridine} & \xrightarrow{1) BH_3} 2) \text{aq. NaOH} \xrightarrow{1) BH_3} 2) \text{aq. NaOHH} \xrightarrow{1) BH_3} 2) \text{aq. NaOHH} \xrightarrow{1) BH_3} 2) \text{aq. NaOHH} \\
C & \xrightarrow{1) BH_3} 2) \text{aq. NaOHH} \xrightarrow{1) BH_3} 2) \text{aq. NaOHH} \xrightarrow{1) BH_3} 2) \text{aq. NaOHH} \\
\end{align*} \]

...continued
d) 

1) NaNH₂, 150°C

A → B → C → D → E

2) H₂O

NaNH₂, 150°C

E → 3-octanone and 4-octanone

cat. HgSO₄

aq. H₂SO₄

E

H₂

Lindlar's catalyst

4) HBr

ROOR

E

F

e) 

A (C₆H₁₄O₂) → H₂SO₄ → B (C₆H₁₂O)

cat. OsO₄

H₂O₂

C (C₆H₁₂)

H₂SO₄

OH

NaBH₄

A (C₆H₁₄O₂)
3. **Potpourri:** (8 x 5 pts. = 40 pts.) Do 8 of 10 problems. **If you do more than eight problems, cross out (with a large X through the solution) the ones that you do not want graded.**

i) a) **Circle** the greatest number of compound(s) that are at the same oxidation level. b) Place a **square** around those functional groups that have sp$^2$ hybridization.

![Chemical structures](image)

ii) **Circle** the mass spectral pattern that is typical of the ion CHCl$_2^+$? **Explain briefly** and provide relative intensities.

![Mass spectra](image)

iii) Testosterone C$_{19}$H$_2$O$_2$ contains four rings, one secondary alcohol, one ketone and one double bond. What is the molecular formula of this steroid? **Show work.**

iv) The specific rotation of (S,S)-tartaric acid is $[\alpha] = -12^\circ$. What is the percentage of each enantiomer in a mixture of the two enantiomers that has $[\alpha] = +2^\circ$. **Show work.**

…continued
v) **Circle** the terms that apply to E2 eliminations.

orbital overlap  rehybridization  isotope effect

intermediate  kinetically controlled

vi) \((E)-(3R,6S)-3,6\text{-dimethyl-4-octene (1)}\) is a meso compound yet it does not have a plane of symmetry. What makes it meso? [**Hint:** Think of one of the two reasons why meso-tartaric acid is actually meso.]

![Chemical Structure](image)

\(1\)

vii) Provide a **diagram and an equation** that relates bond dissociation energy and heat of formation for a generic alkane, \(R-H\).

…continued
viii) The bonds (shown as line bonds) in each of the following functional groups absorb energy in the infrared region. **Number** the structures on the lines in order of increasing vibrational frequency (1 = lowest; 5 = highest).

\[
\begin{align*}
\text{O} & \quad \text{RCOR} \\
\text{R-Br} & \\
\text{O} & \quad \text{RCNH}_2 \\
\text{RO-H} & \\
\text{O} & \quad \text{RCl}
\end{align*}
\]

ix) In the free radical chlorination of (S)-1-chloro-2-methylbutane to form dichloropentanes, **draw** the dichloride(s) that is no longer optically active. Give a **ONE WORD** explanation why it is no longer optically active.

x) **Circle** the bases that are protonated by 1-butyne.

\[
\begin{align*}
\text{KNH}_2 & \\
\text{RMgCl} & \\
\text{CH}_3\text{ONa} & \\
\text{NH}_3 & \\
\text{LiOH}
\end{align*}
\]
4. **Synthesis:** (25 pts.) Design a synthesis of 2,5-dimethylhexan-2-ol (1) using 2-methyl-2-bromopropane (C₄H₉Br) as your **only** source of carbon. All other reagents are available to you. No mechanisms are required.

\[
\text{\begin{center}
\includegraphics[width=0.2\textwidth]{image.png}
\end{center}}
\]
5. **Thermochemistry**: (25 pts.) Determine the heat of formation of chlorocyclooctane prepared by the free radical chlorination of cyclooctane. Provide the two propagation steps and the overall reaction for this process. **Place the reactants and products in the appropriate boxes.** Compute the heats of each reaction using the data in the BDE Table (pg. 15) and the following data: $\Delta H_f^\circ (\text{HCl}) = -22.1 \text{ kcal/mol}$; $\Delta H_f^\circ (\text{cyclooctane}) = -29.7 \text{ kcal/mol}$. **Show work.**

**Propagation step 1**

\[ \ \ \ \ \ \ \ \ \ \text{reactants} \quad \rightarrow \quad \text{products} \ \ \ \ \ \ \ \ \ \quad \ \ \ \text{kcal/mol} \]

**Propagation step 2**

\[ \ \ \ \ \ \ \ \ \ \text{reactants} \quad \rightarrow \quad \text{products} \ \ \ \ \ \ \ \ \ \quad \ \ \ \text{kcal/mol} \]

**Overall reaction**

\[ \ \ \ \ \ \ \ \ \ \text{reactants} \quad \rightarrow \quad \text{products} \ \ \ \ \ \ \ \ \ \quad \ \ \ \text{kcal/mol} \]
6. **Reactions II**: (30 pts.) **Do 6 of 8.** Provide structures for the unknown compounds or provide reagents. Be explicit about stereochemistry, optical activity, racemates, etc. No mechanisms required! **If you do more than 6 problems, cross out (with a large X through the solution) the one(s) that you do not want graded.**

a) ![Structure](image)

b) (R)- ![Structure](image)

![Structure](image)

c) ![Structure](image)

d) ![Structure](image)
e) \[
\begin{align*}
\text{CHO} & \quad \text{reagents?} \\
\text{O} & \quad \text{OH} \\
\text{CO}_2\text{CH}_3 & \quad \text{OH} \\
\end{align*}
\]

f) \[
\begin{align*}
\text{reagents?} \\
& \quad \text{Cl}
\end{align*}
\]

g) \[
\begin{align*}
\text{(±)-} & \quad \text{reagents?} \\
\text{(no } S_\text{N}2) & \quad \text{(±)-}
\end{align*}
\]

h) \[
\begin{align*}
\text{(S)-CH}_3\text{CH}_2\text{CH}_2\text{CHDBr} & \quad 1 \text{ equiv. aq. KOH} \\
& \quad 1 \text{ equiv. thiophenol}
\end{align*}
\]
7. **Kinetics/Thermodynamics:** (20 pts.) Do 2 of 4. Keep your answer short and to the point! If you do more than two problems, cross out (with a large X through the solution) the one(s) that you do not want graded.

a) What is the structure of A and why? Is the reaction kinetically or thermodynamically-controlled? Why? **Be concise.**

![Structure of A](image)

b) The E2 reaction of 2-bromobutane with strong base (kinetically-controlled) **does not** give the same distribution of butenes (there are three of them) that is obtained by acid-catalyzed dehydration of 2-butanol (thermodynamically-controlled). **Explain briefly.**

…continued
c) The formation of cyclohexene from 1,7-octadiene in the presence of Grubbs’ catalyst (Ru=CHPh) and Fischer esterification illustrate two different techniques for shifting unfavorable, equilibria. Explain briefly.

d) In acyclic compounds and flexible ring compounds, why is anti-periplanar (180° dihedral angle) favored over syn-periplanar (0° dihedral angle) in E2 elimination?
8. **Mechanisms:** (25 pts) Provide a mechanism using the curved arrow formalism for **one** of the following reactions. **If you do more than one problem, cross out (with a large X through the solution(s) of the one(s) that you do not want graded).**

a) Swern oxidation of 2-deuterio-2-butanol
b) The conversion of 3-hexyne to \((E)\)-3-hexene
c) The conversion of 3-hexyne to 3-hexanone in the presence of HgSO₄
d) ozonolysis of cyclohexene
### Bond Dissociation Energies (kcal/mol)

\[(X-Y \rightarrow X^+ + Y^-)\]

\[\Delta H^\circ_{\text{RH}} = \Delta H^\circ_{\text{R}}(R) + \Delta H^\circ_{\text{H}}(H) - \Delta H^\circ_{\text{RH}}(RH)\]

Note: These values are the ones used principally in Wade's text. We will use these values. Newer values have been determined by Blanksby and Ellison, Acc. Chem. Res. 2003, 36, 255. The Ellison paper is [here](http://classes.yale.edu/chem220/STUDY AIDS/thermo/BDE.html) in pdf format. For a discussion of heats of reaction, BDEs and heats of formation, click here.

#### C-H Bonds

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$-H</td>
<td>94</td>
</tr>
<tr>
<td>CH$_2$CH$_2$-H</td>
<td>90</td>
</tr>
<tr>
<td>CH$_3$CH$_2$-CH$_3$</td>
<td>71</td>
</tr>
<tr>
<td>CH$_3$C=CH$_2$-H</td>
<td>87</td>
</tr>
<tr>
<td>PHCH$_2$-H</td>
<td>85</td>
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<tr>
<td>CH$_2$=CH$_2$-H</td>
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#### C-C Bonds

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<th>Energy (kcal/mol)</th>
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<tbody>
<tr>
<td>CH$_3$-CH$_3$</td>
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<tr>
<td>CH$_2$CH$_2$-CH$_3$</td>
<td>84</td>
</tr>
<tr>
<td>CH$_3$CH$_2$-CH$_2$-CH$_3$</td>
<td>82</td>
</tr>
<tr>
<td>CH$_3$CH$_2$-CH$_2$CH$_3$</td>
<td>81</td>
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#### C-Cl Bonds

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<td>CH$_3$-Cl</td>
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<td>CH$_2$Cl$_2$-Cl</td>
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<td>(CH$_3$)$_2$CH-Cl</td>
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<tr>
<td>(CH$_3$)$_2$C-Cl</td>
<td>80</td>
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#### C-Br Bonds

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<th>Energy (kcal/mol)</th>
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<tbody>
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<td>CH$_3$-Br</td>
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<tr>
<td>CH$_2$Br$_2$-Br</td>
<td>68</td>
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<tr>
<td>(CH$_3$)$_2$Br-Br</td>
<td>68</td>
</tr>
<tr>
<td>(CH$_3$)$_2$C-Br</td>
<td>68</td>
</tr>
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</table>

#### C-I Bonds

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<thead>
<tr>
<th>Bond Type</th>
<th>Energy (kcal/mol)</th>
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<tbody>
<tr>
<td>CH$_3$-I</td>
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<tr>
<td>CH$_2$I$_2$-I</td>
<td>63</td>
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<tr>
<td>(CH$_3$)$_2$I-CH</td>
<td>63</td>
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<tr>
<td>(CH$_3$)$_2$I-C</td>
<td>60</td>
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#### H-X and X-X Bonds

<table>
<thead>
<tr>
<th>Bond Type</th>
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<tbody>
<tr>
<td>H-F</td>
<td>93</td>
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<tr>
<td>H-Cl</td>
<td>88</td>
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<td>H-Br</td>
<td>80</td>
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<tr>
<td>H-Br</td>
<td>71</td>
</tr>
<tr>
<td>H-Cl</td>
<td>85</td>
</tr>
<tr>
<td>H-Br</td>
<td>66</td>
</tr>
<tr>
<td>H-Cl</td>
<td>51</td>
</tr>
</tbody>
</table>

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* Lanthanide series
* Actinide series
### Natural Abundance of Common Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$^1\text{H} = 99.985%$, $^2\text{H} = 0.015%$</td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{12}\text{C} = 98.90%$, $^{13}\text{C} = 1.10%$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}\text{N} = 99.63%$, $^{15}\text{N} = 0.37%$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}\text{O} = 99.762%$, $^{17}\text{O} = 0.038%$, $^{18}\text{O} = 0.200%$</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}\text{S} = 95.02%$, $^{33}\text{S} = 0.75%$, $^{34}\text{S} = 4.21%$, $^{36}\text{S} = 0.02%$</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}\text{Cl} = 75.77%$, $^{37}\text{Cl} = 24.23%$</td>
</tr>
<tr>
<td>Bromine</td>
<td>$^{79}\text{Br} = 50.69%$, $^{81}\text{Br} = 49.31%$</td>
</tr>
</tbody>
</table>

### $\Delta V$ Values

Energy Differences Between Equatorial and Axial Monosubstituted Cyclohexanes

![Equatorial and Axial Conformations](image)

<table>
<thead>
<tr>
<th>X Group</th>
<th>$\Delta G^\circ$ (axial-equatorial) [kcal/mole]</th>
<th>$\Delta G^\circ$ (axial-equatorial) [kJ/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CN</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>-F</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>-Cl</td>
<td>0.5</td>
<td>2.1</td>
</tr>
<tr>
<td>-Br</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>-CHO</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>-OH</td>
<td>1.0</td>
<td>4.1</td>
</tr>
<tr>
<td>-COOH</td>
<td>1.4</td>
<td>5.9</td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>1.8</td>
<td>7.6</td>
</tr>
<tr>
<td>CH$_2$$CH_3$</td>
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<td>7.9</td>
</tr>
<tr>
<td>CH(CH$_3$)$_2$</td>
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<td>8.8</td>
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<tr>
<td>C(CH$_3$)$_3$</td>
<td>5.4</td>
<td>23</td>
</tr>
<tr>
<td>CO$_2$CH$_3$</td>
<td>1.2</td>
<td>5.0</td>
</tr>
<tr>
<td>-CCH</td>
<td>0.4</td>
<td>1.7</td>
</tr>
<tr>
<td>-SiH$_3$</td>
<td>1.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Si(CH$_3$)$_3$</td>
<td>2.5</td>
<td>10.5</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_3$</td>
<td>1.0</td>
<td>4.2</td>
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<tr>
<td>-CeH$_5$</td>
<td>2.8</td>
<td>11.7</td>
</tr>
<tr>
<td>-N$_3$</td>
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<tr>
<td>-OCH$_3$</td>
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<td>2.5</td>
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</table>