Organic Chemistry 1 – CHM 2210
Exam 4 (December 10, 2001)

Name (print): _________________________
Signature: _________________________
Student ID Number: _________________________

There are 12 multiple choice problems (4 points each) on this exam. Record the answers to the multiple choice questions on THIS PAGE. There are also 5 short answer questions and one bonus question (problem 17). Please make sure that your curved arrow mechanisms are drawn to precisely indicate the movement of electrons. You will be graded out of 100 points.

1 _____  7 _____
2 _____  8 _____
3 _____  9 _____
4 _____ 10 _____
5 _____ 11 _____
6 _____ 12 _____

“All our science, measured against reality, is primitive and childlike – and yet it is the most precious thing we have”

Albert Einstein
1. An unknown alkene with the formula C\textsubscript{7}H\textsubscript{12} undergoes oxidation in the presence of hot basic KMnO\textsubscript{4} to yield only the following product. What was this alkene?

\[ \text{C}_7\text{H}_{12} \xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}, \text{HO}^-, \text{heat}} \text{product} \]

a) cyclohexene  

b) 1-methylcyclohexene  

c) 1-heptene  

d) none of the above

2. Give the correct structure of the product resulting from the following reaction?

\[ \text{product} \xrightarrow{\text{HBr} \text{(2 equivalents)}} \]

a) A  

b) B  

c) C  

d) D

3. A shielded proton will absorb energy and convert to the $\beta$-spin state at higher external field strengths relative to a proton without its electronic shell.  

a) This statement is false  

b) This statement is true  

c) The statement could be either true or false depending on the spectrometer frequency

4. Both homotopic and enantiotopic hydrogens give only one chemical shift in $^1$H NMR.  

a) This statement is false  

b) This statement is true  

c) The statement could be either true or false depending on the spectrometer frequency

5. How many signals would you expect to find in the $^1$HNMR spectrum of trans-1,2-dimethylcyclopropane (disregard signal splitting)?

a) 2  

b) 3  

c) 4  

d) 5  

e) 10
6. In a $^1$HNMR spectrum, the indicated proton would appear as a _______.
   a) singlet
   b) doublet
   c) triplet
   d) quartet

7. The most intense peak in the mass spectrum of 2,2-dimethylbutane occurs at $m/z$ 57. What carbocation does this peak represent?
   a) ethyl cation
   b) tert-butyl cation
   c) methyl cation
   d) 2-methylbutyl cation
   e) none of the above

8. What product would you expect from the acid-catalyzed hydration of 2-methyl-1-butene?
   a) no reaction
   b) 1-methyl-1-butanol
   c) 2-methyl-2-butanol
   d) 2-methyl-1-butanol

9. What would be the appropriate starting material for the synthesis of isopropyl alcohol using the oxymercuration-demercuration reactions?
   a) 2-chloropropane
   b) propene
   c) propane
   d) 2-methyl-propene

10. What would be the appropriate starting material for the synthesis of propyl alcohol using the hydroboration-oxidation reactions?
    a) 1,2-propane diol
    b) propene
    c) propane
    d) 2-methyl-propene

11. A primary alcohol becomes a good electrophile when it is…
    a) treated with p-toluenesulfonyl chloride (tosyl chloride)
    b) converted to its conjugate base (alkoxide)
    c) treated with iodic acid (HI)
    d) both a and c
12. Grignard reagents (RMgX) react with formaldehyde (CH₂O) to give…
   a) secondary alcohols
   b) epoxides
   c) tertiary alcohols
   d) primary alcohols

13. (10 pts) Outline two methods for preparing 2-methoxypentane by a Williamson synthesis. Explain which is the better method and why.

14. (14 pts) Provide the curved arrow mechanism and the structure of the product(s) which results from the following epoxidation/acid-catalyzed hydrolysis reaction sequence. If more than one product is obtained, indicate their relationship to each other (diastereomer, enantiomer, and etc.).
15. (bonus question, 8 pts) Provide a curved arrow mechanism and the structure of the product which results in the reaction below.

\[
\text{OH} + \text{HO}^\text{\textcircled{O}}\text{Cr}^\text{\textcircled{OH}}\rightarrow
\]

16. (14 pts) Proton H_a in 1,1-Dibromo-2,2-dichloroethane (see below) is split into two peaks (a doublet) by H_b. Briefly (<100 words) explain the principle of NMR signal splitting arising from spin-spin coupling. Specifically, how does H_b split H_a in the magnetic field? Include in your discussion, \( \alpha \) and \( \beta \)-states and the coupling constant \( J_{ab} \).

17. (14 pts) Propose a structure for a compound that gives the following spectroscopic data. To obtain full credit you must show how you arrived at the answer from the data (see tables on following page).

Three important peaks in the mass spectrum (m/z): 120, 105 (base peak), 77

In the \(^1\text{H NMR}: \) Several peaks in the range 7.6-7.2 ppm (5 protons)
A septet at 2.95 ppm (1 proton)
A doublet at 1.29 pm (6 protons)
### Summary of IR Stretching Frequencies

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Functional Group</th>
<th>Comments</th>
<th>Type of Proton</th>
<th>(\delta) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300</td>
<td>alcohol</td>
<td>O-H</td>
<td>Primary alkyl</td>
<td>0.8 – 1.0</td>
</tr>
<tr>
<td></td>
<td>amine, amide</td>
<td>N-H</td>
<td>Secondary alkyl</td>
<td>1.2 – 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tertiary alkyl</td>
<td>1.4 – 1.7</td>
</tr>
<tr>
<td>3000</td>
<td>alkyne</td>
<td>sp(^3)C-H</td>
<td>Allylic</td>
<td>1.6 – 1.9</td>
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<tr>
<td></td>
<td>alkane</td>
<td>sp(^3)C-H</td>
<td>Ketone ((\alpha)-proton)</td>
<td>2.1 – 2.6</td>
</tr>
<tr>
<td></td>
<td>acid</td>
<td>O-H</td>
<td>Acetylenic</td>
<td>2.5 – 3.1</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Ether</td>
<td>3.3 – 3.9</td>
</tr>
<tr>
<td>2200</td>
<td>alkyne</td>
<td>C=C</td>
<td>Alcohol ((\alpha)-proton)</td>
<td>3.3 – 4.0</td>
</tr>
<tr>
<td></td>
<td>nitrile</td>
<td>C=N</td>
<td>Alkyl bromide</td>
<td>3.4 – 3.6</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Alkyl chloride</td>
<td>3.6 – 3.8</td>
</tr>
<tr>
<td>1700 (very strong)</td>
<td>carbonyl</td>
<td>C=O</td>
<td>Alkene</td>
<td>5.0 – 6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>esters higher (1800 cm(^{-1}))</td>
<td>Aromatic</td>
<td>6 – 9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>amides lower (see below)</td>
<td>Aldehyde</td>
<td>9.5 – 10.5</td>
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<tr>
<td></td>
<td></td>
<td>strong absorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1650</td>
<td>alkene</td>
<td>C=C</td>
<td>aromatic lower (1600 cm(^{-1}))</td>
<td>6 – 9</td>
</tr>
<tr>
<td></td>
<td>amide</td>
<td>C=O</td>
<td>strong absorption</td>
<td></td>
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