CHEM 203

Final Exam
December 15, 2010

Your name:

ANSWERS

This a closed-notes, closed-book exam

You may use your set of molecular models

This test contains 15 pages

Time: 2h 30 min

1. ______ / 16
2. ______ / 15
3. ______ / 24
4. ______ / 35
5. ______ / 36
6. ______ / 36
7. ______ / 40
8. ______ / 48

TOTAL ______ / 250 = ______ / 100

This exam counts for 45% of your CHEM 203 final grade
1. (16 pts.) Indicate the approximate pKa's for the Bronsted dissociation of the proton in boldface in the following molecules (write your answers in the appropriate boxes)

| Molecule          | pKa   
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>50</td>
</tr>
<tr>
<td>TH</td>
<td>-3</td>
</tr>
<tr>
<td>NH</td>
<td>35</td>
</tr>
<tr>
<td>H–Br</td>
<td>-8</td>
</tr>
<tr>
<td>CH₃–C≡C–H</td>
<td>25</td>
</tr>
<tr>
<td>H–OSO₂CF₃</td>
<td>-10</td>
</tr>
<tr>
<td>H–H</td>
<td>40</td>
</tr>
<tr>
<td>CH₃–CH₂–O–H</td>
<td>17</td>
</tr>
</tbody>
</table>

2. (15 pts.) Write a detailed mechanism to account for the observation that treatment of compound A with ozone, but without the usual Zn/H⁺ step, furnishes a 1 : 1 mixture of products B and C:

HO–CH=CH–CH=CH–CH(=O)–OH  \( \xrightarrow{O_3 \text{ no Zn/H}^+} \)  \( \text{1 : 1 ratio} \)
B \( \text{and} \) C

\[ \begin{align*}
\text{HO–CH=CH–CH=CH–CH(=O)–OH} & \quad \xrightarrow{O_3 \text{ no Zn/H}^+} \quad \text{HO–CH=CH–CH(=O)–OH} \\
& \quad \xrightarrow{\pm H^+} \quad \text{B} \\
\text{HO–CH=CH–CH(=O)–OH} & \quad \xrightarrow{O_3 \text{ no Zn/H}^+} \quad \text{HO–CH=CH–CH–C(O)=O} \\
& \quad \xrightarrow{\pm H^+} \quad \text{C}
\end{align*} \]
3. (24 pts.) Draw:

a. Accurate mechanisms for an example of $S_N2$ reaction and an example of $S_N1$ reaction:

$S_N2$:

(b) A chemical equation showing an example of Williamson reaction (without mechanism):

(c) A chemical equation showing an example of Wittig reaction (without mechanism):
d. A chiral Schiff base:

![Schiff base structure](image)

*(other answers possible)*

e. An achiral epoxide that will react with aq. H₂SO₄ to form a chiral diol:

![Epoxide structure](image)

*(other answers possible)*

f. An olefin containing at least than 3 C atoms that will produce the same diol when treated either with OsO₄ followed by aq. NaHSO₃, or with MCPBA followed by aq. H₂SO₄.

![Olefin structure](image)

*(other answers possible)*

g. An alcohol containing at least 4 C atoms that is likely to undergo dehydration without rearrangement and one also containing at least 4 C atoms that is likely to undergo rearrangement during dehydration (write your answers in the appropriate boxes):

<table>
<thead>
<tr>
<th>Not likely to rearrange</th>
<th>Likely to rearrange</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Alcohol structure" /></td>
<td><img src="image" alt="Alcohol structure" /></td>
</tr>
</tbody>
</table>

*(other answers possible) (other answers possible)*

h. An alcohol that forms the same product when treated either with PCC or with the Jones reagent, and one that forms one product when treated with PCC, but a different product when treated with the Jones reagent (write your answers in the appropriate boxes):

<table>
<thead>
<tr>
<th>Gives the same product</th>
<th>Gives two different products</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Alcohol structure" /></td>
<td><img src="image" alt="Alcohol structure" /></td>
</tr>
</tbody>
</table>

*(other answers possible) (other answers possible)*
4. (35 pts.) The $^1$H NMR spectrum of an alkane, $A$, exhibited only a singlet at 0.9 ppm. Treatment of $A$ with Cl$_2$ / hv afforded a monochloro derivative, $B$, which upon reaction with metallic Mg followed by formaldehyde, H-CHO, produced compound $C$. The IR spectrum of $C$ displayed a strong, broad absorption at 3340 cm$^{-1}$. The $^1$H NMR spectrum of $C$ is shown below. Reaction of $C$ with H$_2$SO$_4$ at 160 °C yielded compound $D$. When substance $D$ was treated with OsO$_4$ followed by aqueous NaHSO$_3$, compound $E$ emerged. Furthermore, ozonolysis of $D$ followed by Zn/H$^+$ produced only $F$, which upon treatment with NaBH$_4$ furnished $G$. The $^1$H NMR spectra of $E$ and $G$ are also provided below. Deduce the structures of compounds $A$ – $G$ and write your answers in the appropriate boxes.
H NMR spectrum of A

H NMR spectrum of C

IR spectrum of E

^1H NMR spectrum of E
IR spectrum of F

$^1$H NMR spectrum of F

IR spectrum of G

$^1$H NMR spectrum of G
5. (36 pts.) Indicate which among compounds a-j produce the spectra shown below:

- ![Spectra of Compound j](image1)
  - These are the spectra of compound: **j**
- ![Spectra of Compound f](image2)
  - These are the spectra of compound: **f**
these are the spectra of compound: \( C \)

these are the spectra of compound: \( H \)
6. (36 pts.) Draw the structure of the major product expected from each of the following reactions. If no overall change is predicted, answer "NO REACTION." **Important:** where appropriate, molecules must be drawn with the correct configuration.

a. \[ \text{pentane} \]
   1. HBr, rad. init.
   2. CH\textsubscript{3}–C\textequiv–Na
   then mild H\textsubscript{3}O\textsuperscript{+}
   3. Na. NH\textsubscript{3}(\text{aq})

b. \[ \text{propan-2-ol} \]
   1. H\textsubscript{2}SO\textsubscript{4}, heat
   2. O\textsubscript{3}, then
   Zn / H\textsuperscript{+}
   3. NaBH\textsubscript{4}, then
   mild H\textsubscript{3}O\textsuperscript{+}

c. \[ \text{propene} \]
   1. OsO\textsubscript{4}, then
   aq. NaHSO\textsubscript{3}
   2. acetone, cat.
   H\textsubscript{2}SO\textsubscript{4}, 60 °C,
   removal of H\textsubscript{2}O

\[ \text{(or enantiomer)} \]

d. \[ \text{propene} \]
   1. BH\textsubscript{3}, then
   H\textsubscript{2}O\textsubscript{2}, aq. NaOH
   2. PCC
   3. HC\equivC–Na
   then mild H\textsubscript{3}O\textsuperscript{+}

\[ \text{OH} \]

e. \[ \text{cyclohexene} \]
   1. NBS, rad. initiator
   2. Mg
   3. H-CHO, then
   mild H\textsubscript{3}O\textsuperscript{+}

\[ \text{OH} \]

f. \[ \text{phenyltrimethylsilane} \]
   1. OK
   2. MCPBA
   3. CH\textsubscript{3}MgBr,
   CuBr, then
   mild H\textsubscript{3}O\textsuperscript{+}

\[ \text{(or enantiomer)} \]
7. (40 pts.) Indicate all the reagents, catalysts, etc., in the correct order, that are necessary to induce the transformations shown below. List such reagents above / below the reaction arrows. If a product does not appear to be available from the substrate shown by any method known to you, write "INACCESSIBLE" on the reaction arrow.

a. \( \begin{array}{c}
\text{a.} \\
\text{b.} \\
\text{c.} \\
\end{array} \)

b. \( \begin{array}{c}
\text{1. H}_2, \text{Lindlar [or Na / NH}_3\text{[liq]} \]
\text{2. H}_2\text{O, H}_2\text{SO}_4 \text{(or hydroboration)}
\text{3. PCC (or Jones)}
\end{array} \)

c. \( \begin{array}{c}
\text{1. H}_2\text{SO}_4, \text{heat}
\text{2. BH}_3, \text{then}
\text{H}_2\text{O}_2, \text{aq. NaOH}
\end{array} \)

d. \( \begin{array}{c}
\text{1. H}_2, \text{Lindlar [or Na / NH}_3\text{[liq]} \]
\text{2. PCC}
\text{3. CH}_3\text{MgBr}
\text{4. PBr}_3
\text{5. BH}_3, \text{then H}_2\text{O}_2, \text{aq. NaOH}
\text{6. NaH}
\end{array} \)

e. \( \begin{array}{c}
\text{1. PBr}_3
\text{2. NaN}_3
\end{array} \)

f. \( \begin{array}{c}
\text{1. TsCl, pyridine}
\text{2. NaN}_3
\end{array} \)

h. \( \begin{array}{c}
\text{1. LiAlH}_4
\text{2. PCC}
\text{3. Ph}_3\text{P}=\text{CH}_2
\end{array} \)
8. (48 pts.) Propose a good synthesis of the molecules shown below using only methanol, NaCN, acetylene and ethylene oxide (see below) as the sources of carbon atoms. Intermediates / products obtained during an earlier sequence may be employed in a subsequent procedure, without showing their preparation again. Assume the availability of all necessary reagents (such as bases, acids, BH₃, Mg, TsCl, PCC, PBr₃, MCPBA, etc.).

Important: 
Note: answers other than the ones given below are possible
i. aqueous workups at the end of each reaction are understood and need not to be shown.
ii. It is not necessary to write mechanisms

\[
\begin{align*}
\text{CH}_3\text{OH} & \quad \text{H-} \quad \text{C-acetylene} \\
\text{methanol} & \quad \text{acetylene} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C-} & \quad \text{H}_2\text{O} \quad \text{ethylene oxide}
\end{align*}
\]
c. \( \text{CH}_3\text{O}-\text{CH}_2-\text{CH}(-\text{CHO}) \) → PCC → \( \text{CH}_3\text{O}-\text{CH}_2-\text{CH}(\text{CHOH}) \) → 1. BH\(_3\) → \( \text{CH}_3\text{O}-\text{CH}_2-\text{CH}(-\text{CH}_2) \) → 2. \( \text{H}_2\text{O}_2\) → aq. NaOH → NaH → CH\(_3\)I (part a.)

(d). \( \text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH} \) → cat. H\(_2\text{SO}_4\) → heat, – H\(_2\text{O}\) → \( \text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{CH}_3 \) → 1. OsO\(_4\) → 2. aq. NaHSO\(_3\) → \( \text{CH}_3\text{O}-\text{CH}_3 \) (part c.)
e.  
\[
\text{COOH} \xrightarrow{\text{Jones}} \text{OH} \xrightarrow{\text{Na}} \text{NH}_3 \text{ (liq)} \xrightarrow{1. \ NaNH_2} \text{OH} \xrightarrow{2.} \text{OH}
\]

(part a.)

\[
\text{(part c.)}
\]

f.  
\[
\text{H}_2 \xrightarrow{\text{Pd}} \text{OH} \xrightarrow{\text{H}_2} \text{OH} \xrightarrow{\text{PCC}} \text{OH} \xrightarrow{\text{Mg}} \text{Br}
\]

(part b.)
### Characteristic Infrared Absorptions of Common Functional Groups

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Bond</th>
<th>Frequency Range (cm(^{-1}))</th>
<th>Functional Group</th>
<th>Bond</th>
<th>Frequency Range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>O–H</td>
<td>3400 – 3650 (s, broad)</td>
<td>Nitrile</td>
<td>C≡N</td>
<td>2210 – 2280 (w – m)</td>
</tr>
<tr>
<td></td>
<td>C–O</td>
<td>1050 – 1150 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ether</td>
<td>C–O</td>
<td>1000 – 1260</td>
<td>Carboxylic acid</td>
<td>O–H</td>
<td>2500-3100 (s, broad)</td>
</tr>
<tr>
<td>Amine</td>
<td>N–H</td>
<td>3300 – 3350 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkane</td>
<td>C–H</td>
<td>2850 – 2950 (m – s)</td>
<td>Acyl halide</td>
<td>C=O</td>
<td>1770 – 1820 (s)</td>
</tr>
<tr>
<td>Alkene</td>
<td>≡C–H</td>
<td>3020 – 3100 (m)</td>
<td>Acid anhydride</td>
<td>C=O</td>
<td>1740 – 1790 (s)</td>
</tr>
<tr>
<td></td>
<td>C=C</td>
<td>1640 – 1680 (m)</td>
<td></td>
<td></td>
<td>1800 – 1850 (s)</td>
</tr>
<tr>
<td>Alkyne</td>
<td>≡C≡H</td>
<td>3270 – 3330 (s)</td>
<td>Amide</td>
<td>C=O</td>
<td>1630 – 1700 (s)</td>
</tr>
<tr>
<td></td>
<td>C≡C</td>
<td>2100 – 2260 (w – m)</td>
<td>Aldehyde, ketone</td>
<td>C=O</td>
<td>1680 – 1730 (s)</td>
</tr>
</tbody>
</table>

### Characteristic Proton (\(^1\)H) NMR Chemical Shifts

<table>
<thead>
<tr>
<th>Type of Hydrogen</th>
<th>Structure</th>
<th>Chemical Shift δ (ppm)</th>
<th>Type of Hydrogen</th>
<th>Structure</th>
<th>Chemical Shift δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>(CH(_3))(_3)Si</td>
<td>0.00</td>
<td>Amines</td>
<td>(\text{N–C–H})</td>
<td>2.3 – 3.0</td>
</tr>
<tr>
<td>Alkane, primary</td>
<td>-CH(_3)</td>
<td>0.7 – 1.3</td>
<td>Alcohol, ether</td>
<td>(\text{O–C–H})</td>
<td>3.3 – 4.0</td>
</tr>
<tr>
<td>Alkane, secondary</td>
<td>-CH(_2)-</td>
<td>1.2 – 1.4</td>
<td>Ester</td>
<td>(\text{O–C–O–C–H})</td>
<td>3.7 – 4.8</td>
</tr>
<tr>
<td>Alkane, tertiary</td>
<td>(\text{C–H})</td>
<td>1.4 – 1.7</td>
<td>Olefinic</td>
<td>(\text{C=C–H})</td>
<td>5.0 – 6.5</td>
</tr>
<tr>
<td>Allylic, primary</td>
<td>C=C-CH(_3)</td>
<td>1.6 – 1.9</td>
<td>Aromatic</td>
<td>Ar–H</td>
<td>6.5 – 8.0</td>
</tr>
<tr>
<td>Methyl carbonyl</td>
<td>(\text{O–C–CH}_{3})</td>
<td>2.1 – 2.5</td>
<td>Aldehyde</td>
<td>(\text{O–C–H})</td>
<td>9.7 – 10.0</td>
</tr>
<tr>
<td>Aromatic methyl</td>
<td>Ar–CH(_3)</td>
<td>2.5 – 2.7</td>
<td>Amine</td>
<td>(-\text{NH}_{2})</td>
<td>1 – 5, variable</td>
</tr>
<tr>
<td>Alkyne</td>
<td>(\text{C–H})</td>
<td>2.5 – 2.7</td>
<td>Alcohol</td>
<td>(-\text{OH})</td>
<td>1 – 5, variable</td>
</tr>
<tr>
<td>Alkyl halide ((X = Cl, Br, I))</td>
<td>(\text{H–C–X})</td>
<td>2.5 – 4.5</td>
<td>Carboxylic acid</td>
<td>(-\text{COOH})</td>
<td>11.0 – 12.0</td>
</tr>
</tbody>
</table>