CHEM 203

Final Exam
December 18, 2013

Your name:

ANSWERS

This a closed-notes, closed-book exam

You may use your set of molecular models

This test consists of 10 pages

Time: 2h 30 min

1. _______ / 20
2. _______ / 20
3. _______ / 30
4. _______ / 30
5. _______ / 30
6. _______ / 40
7. _______ / 40
8. _______ / 40

TOTAL _______ / 250 = _______ / 100

This exam counts for 37.5% of your CHEM 203 grade
1. (20 pts.) The reagents shown below have not been discussed in class, but they are structurally related to reagents that have been covered in CHEM 203. On the basis of structural analogy, indicate the probable use of each of them (write your answers in the boxes):

```
<table>
<thead>
<tr>
<th></th>
<th>probably used as/or:</th>
<th>probably used as/or:</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>![Reagent Image] (OH)</td>
<td>![Reagent Image] (OH)</td>
</tr>
<tr>
<td></td>
<td>radical inhibitor</td>
<td>conversion of prim. / sec.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>alcohols into alkyl iodides</td>
</tr>
<tr>
<td>b.</td>
<td>![Reagent Image] (HO)</td>
<td>![Reagent Image] (HO)</td>
</tr>
<tr>
<td></td>
<td>epoxidation of alkenes</td>
<td>radical initiator</td>
</tr>
</tbody>
</table>
```

2. (20 pts) Check the appropriate box to indicate whether the following statements are true or false:

- a. An aqueous solution of $\text{H}_2\text{CrO}_4$ and $\text{H}_2\text{SO}_4$ oxidizes primary alcohols to aldehydes and secondary alcohols to ketones
- b. An alkene will form the same epoxide upon treatment with either $\text{Br}_2$ and $\text{H}_2\text{O}$ followed by base, or with MCPBA
- c. Rearrangements may occur during $\text{S}_\text{N}1$ reactions, but not during $\text{S}_\text{N}2$ reactions
- d. Rearrangements may occur during $\text{E}_2$ reactions, but not during $\text{E}_1$ reactions
- e. Carbocations may add to alkenes
- f. Radicals do not rearrange by the 1,2-shift mechanism typical of carbocations
- g. A C–Si bond provides more effective hyperconjugative stabilization than a C–C bond
- h. A bromohydrin is easily converted into a Grignard reagent upon reaction with metallic Mg
- i. An acetal is a special type of ether
- j. The Fischer-Kiliani synthesis of monosaccharide involves the addition of H–CN to an aldehyde
3. (30 pts.) Check the appropriate boxes to indicate whether:

a. The following carbohydrates belong to the D or the L series:

```
D- [ ] L- [✓]
D- [✓] L- [ ]
D- [✓] L- [■]
D- [✓] L- [✓]
D- [✓] L- [✓]
```

b. The following carbohydrates possess the α- or the β-anomeric configuration:

```
α- [✓] β- [■]
α- [■] β- [✓]
α- [■] β- [✓]
α- [■] β- [✓]
```

c. The following derivatives of glucose are reducing or nonreducing:

```
Reducing [ ] Nonreducing [✓]
Reducing [✓] Nonreducing [ ]
Reducing [■] Nonreducing [✓]
Reducing [✓] Nonreducing [ ]
Reducing [✓] Nonreducing [✓]
```
4. (30 pts) In the appropriate box, draw the structure of:

(a) A carbocation that forms as the major product of protonation of an alkene and that is likely to undergo rearrangement, and one that also forms as the major product of protonation of an alkene, but that is not likely to undergo rearrangement:

likely to rearrange

unlikely to rearrange

(b) A trans-alkene that gives a chiral product upon reaction with Cl₂ and a trans-alkene that gives an achiral product upon reaction with Cl₂:

gives a chiral product

gives an achiral product

(c) An alkyl halide that is likely to undergo substitution by the Sₙ2 mechanism, and one that is likely to undergo substitution by the Sₙ1 mechanism:

reacts by Sₙ2

reacts by Sₙ1
d. An alkene that is a good substrate for allylic bromination, and one that is a poor substrate for the same reaction:

<table>
<thead>
<tr>
<th>Good Substrate</th>
<th>Poor Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Diagram" /></td>
<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>Only 1 mono-bromo isomer can form</td>
<td>Multiple mono-bromo isomers can form</td>
</tr>
</tbody>
</table>

e. An alkyne containing at least 3 carbon atoms, that produces an achiral diol when treated with H₂ and Lindlar catalyst, followed by OsO₄ and then aqueous NaHSO₃, or when treated with Na in liquid NH₃, followed by MCPBA and then aqueous H₂SO₄, and an alkyne also containing at least 3 carbon atoms that produces a chiral diol when treated under the same conditions:

<table>
<thead>
<tr>
<th>Produces an Achiral Diol</th>
<th>Produces a Chiral Diol</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
</tbody>
</table>

f. An alcohol that gives the same product when treated either with PCC or with the Jones reagent, and one that gives two different products under the same conditions:

<table>
<thead>
<tr>
<th>Gives the Same Product</th>
<th>Gives Two Different Products</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5" alt="Diagram" /></td>
<td><img src="image6" alt="Diagram" /></td>
</tr>
</tbody>
</table>
5. (30 pts) Write accurate mechanisms for the following known reactions:

a. 

b. 

c. 
6. (40 pts.) Draw the structure of the major product expected from the following reactions (write your answer in the boxes). If no change is predicted, answer "NO REACTION."

a. \[
\begin{align*}
&\text{1. NaBH}_4, \text{ then} \\
&\quad \text{mild H}_3\text{O}^+ \\
&\text{2. Br}_2 \\
&\text{3. }\text{OK}
\end{align*}
\]

b. \[
\begin{align*}
&\text{1. HBr, rad.} \\
&\quad \text{initiator} \\
&\text{2. NaN}_3 \\
&\text{3. Zn, H}^+
\end{align*}
\]

c. \[
\begin{align*}
&\text{1. BH}_3, \text{ then} \\
&\quad \text{H}_2\text{O}_2, \text{ aq. NaOH} \\
&\text{2. PBr}_3 \\
&\text{3. Mg} \\
&\text{4. CO}_2, \text{ then} \\
&\quad \text{mild H}_3\text{O}^+
\end{align*}
\]

d. \[
\begin{align*}
&\text{1. Cl}_2, \text{ hv} \\
&\text{2. }\text{OK} \\
&\text{3. MCPBA} \\
&\text{4. }\text{Na}^+ \text{ then mild H}_3\text{O}^+
\end{align*}
\]

e. \[
\begin{align*}
&\text{1. O}_3, \text{ then} \\
&\quad \text{Zn, H}^+ \\
&\text{2. CH}_3\text{MgBr} \\
&\text{3. H}_2\text{SO}_4, 160 ^\circ\text{C} \\
&\text{4. Br}_2 \text{ and H}_2\text{O} \\
&\text{5. NaH}
\end{align*}
\]
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. **NOTE**: aqueous workups are understood and do not need to be shown.

a. \[
\begin{align*}
\text{OH} & \quad \xrightarrow{1. \text{ TsCl, pyridine}} \quad \text{SCH}_3 \\
& \quad \xrightarrow{2. \text{ CH}_3\text{SNa}} \quad \text{CH}_3
\end{align*}
\]

1. Cl₂, hv  
2. tert-BuOK  
3. MCPBA

b. \[
\begin{align*}
\text{H} & \quad \xrightarrow{1. \text{ Cl}_2, \text{ hv}} \quad \text{OCH}_3 \\
& \quad \xrightarrow{2. \text{ tert-BuOK}} \quad \text{OCH}_3
\end{align*}
\]

1.  
2. tert-BuOK  
3. MCPBA  
4. aq. H₂SO₄  
5. NaH, CH₃I

c. \[
\begin{align*}
\quad & \quad \xrightarrow{1. \text{ MCPBA}} \quad \text{NH}_2 \\
& \quad \xrightarrow{2. \text{ CH}_3\text{ONa}} \quad \text{OCH}_3 \\
& \quad \xrightarrow{3. \text{ TsCl, pyridine}} \quad \text{CH}_3
\end{align*}
\]

1.  
2. CH₃ONa  
3. TsCl, pyridine  
4. NaN₃  
5. Zn, H⁺

d. \[
\begin{align*}
\text{H} & \quad \xrightarrow{1. \text{ H}_2, \text{ Lindlar}} \quad \text{O} \\
& \quad \xrightarrow{2. \text{ BH}_3} \quad \text{O}
\end{align*}
\]

1. H₂, Lindlar  
2. BH₃  
3. H₂O₂, aq. NaOH  
4. PCC

e. \[
\begin{align*}
\text{H} & \quad \xrightarrow{1. \text{ NBS, hv}} \quad \text{CH}_3 \\
& \quad \xrightarrow{2. \text{ CH}_3\text{Li, CuBr}} \quad \text{CH}_3\text{Li}
\end{align*}
\]

1. NBS, hv  
2. CH₃Li, CuBr  
3. NBS, hv  
4. H-C≡C–Na⁺  
5. Cl₂, hv  
6. tert-BuOK

f. \[
\begin{align*}
\text{H} & \quad \xrightarrow{1. \text{ Cl}_2, \text{ hv}} \quad \text{O} \\
& \quad \xrightarrow{2. \text{ tert-BuOK}} \quad \text{O}
\end{align*}
\]

1. Cl₂, hv  
2. tert-BuOK  
3. O₃, then Zn / H⁺  
4. NaBH₄  
5. TsCl, pyridine  
6. Na₂S

g. \[
\begin{align*}
\text{OH} & \quad \xrightarrow{1. \text{ PBr}_3} \quad \text{O} \\
& \quad \xrightarrow{2. \text{ CH}_3\text{COO}^-\text{Na}^+} \quad \text{OH}
\end{align*}
\]

1.  
2. CH₃-COO⁻ Na⁺  
3. H₂, Lindlar catalyst  
4. MCPBA  
5. NaH, CH₃I  
6. Na₂S

h. \[
\begin{align*}
\text{CH} & \quad \xrightarrow{1. \text{ H-C≡C–Na}^+} \quad \text{OH} \\
& \quad \xrightarrow{2. \text{ H}_2, \text{ Lindlar catalyst}} \quad \text{OH}
\end{align*}
\]

1. H-C≡C–Na⁺  
2. H₂, Lindlar catalyst  
3. MCPBA  
4. NaN₃ followed by Zn / H⁺
8. (40 pts.) Propose a good synthesis of the molecules shown below using **only methanol, 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. Assume the availability of all necessary reagents (such as bases, acids, BH₃, Mg, TsCl, PCC, PBr₃, MCPBA, etc.).

methanol: CH₃OH  
acetylene: H−C≡C−H  
ethylene oxide: \( \text{O} \) \( \text{H}_2\text{C=CH}_2 \)

**Important:**

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.
c. \[
\text{CH}_2\text{=CH}_2 \stackrel{\text{OsO}_4, \text{then aq. } \text{NaHSO}_3}{\longrightarrow} \text{H}_2 \text{O} \quad \text{CH}_3\text{OH} + \quad \text{PCC} \quad \text{OCH}_3
\]

part b.

\[
\text{HBr} \quad \text{Br} \quad \text{Mg} \quad \text{MgBr} \quad \text{CuBr}
\]

\[
\text{H}_2\text{SO}_4, - \text{H}_2\text{O} \quad \text{CH}_3\text{OH} + \quad \text{H}_2\text{SO}_4 \quad \text{PCC} \quad \text{H}_2\text{O} \quad \text{PCC}
\]

Happy Holidays!