CHE 326 Final Exam Form 1
May 16, 2013

Questions 1 - 18 are 5 point multiple choice questions. Questions 19-28 are short answer questions worth 5 - 12 points each as indicated.
Hydroformylation is a reaction that converts an alkene to an aldehyde via the catalytic addition of one mole each of \( \text{H}_2 \) and \( \text{CO} \). Often Rh catalysts are used.

\[
\text{CO, H}_2 \xrightarrow{\text{RhH(CO)P}_2} \text{HCHO}
\]

A proposed catalytic mechanism for this reaction is shown below. Use it to answer the next two questions.

1. In the following chart which choice has the electron counts correct?

<table>
<thead>
<tr>
<th></th>
<th>Compound (X)</th>
<th>Compound (Y)</th>
<th>Compound (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>B</td>
<td>14</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>C</td>
<td>16</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>D</td>
<td>16</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>E</td>
<td>16</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>F</td>
<td>16</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

2. Which of the following statements about reaction types is correct?

<table>
<thead>
<tr>
<th></th>
<th>Step (i)</th>
<th>Step (ii)</th>
<th>Step (iii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>oxidative addition</td>
<td>reductive elimination</td>
<td>ligand association</td>
</tr>
<tr>
<td>B</td>
<td>oxidative addition</td>
<td>ligand insertion</td>
<td>ligand association</td>
</tr>
<tr>
<td>C</td>
<td>oxidative addition</td>
<td>oxidative addition</td>
<td>ligand association</td>
</tr>
<tr>
<td>D</td>
<td>ligand association</td>
<td>ligand association</td>
<td>oxidative addition</td>
</tr>
<tr>
<td>E</td>
<td>ligand association</td>
<td>oxidative addition</td>
<td>reductive elimination</td>
</tr>
<tr>
<td>F</td>
<td>ligand association</td>
<td>ligand insertion</td>
<td>oxidative addition</td>
</tr>
</tbody>
</table>
3. Predict the major product of the following reaction.

\[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array} \text{\footnotesize{+ enantiomers}} \\
A \quad \quad B \quad \quad C \quad \quad D \quad \quad E \quad \quad F
\]

4. Predict the major monobromination product of the following reaction.

\[
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} \\
A \quad \quad B \quad \quad C \quad \quad D \quad \quad E \quad \quad F
\]

5. Which of the following phenols is the most acidic?

\[
\begin{array}{c}
\text{OH} \\
\text{O} \cdot \text{CH}_3 \\
\text{C} \\
\text{O} \cdot \text{CO} \cdot \text{CH}_3 \\
\text{H}_3 \text{N} \cdot \text{CO} \cdot \text{CH}_3 \\
\text{A} \quad \quad B \quad \quad C \quad \quad D \quad \quad E \quad \quad F
\end{array}
\]
6. When benzene is protonated the resulting ion is the cyclohexadienyl cation. Which of the following MOs is the best representation of the HOMO of this cation?

![Diagram of MO representations]

7. Predict the major product of the following reaction sequence.

![Diagram of reaction sequence]

A  B  C
D  E  F
8. Which of the following reactions sequences would not give an aldehyde as a major product?

A. \( \text{CH}_3\text{COOH} \xrightarrow{\text{DIBAL-H}, 2, \text{H}_2\text{O}} \text{CH}_3\text{CHO} \)

B. \( \text{CH}_3\text{COOH} \xrightarrow{\text{SOCl}_2, \text{LiAlH(O-iBu)}_3, 2, \text{H}_2\text{O}} \text{CH}_3\text{CHO} \)

C. \( \text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4, \text{PCC}, 2, \text{H}_2\text{O}} \text{CH}_3\text{CHO} \)

D. \( \text{CH}_3\text{CN} \xrightarrow{\text{DIBAL-H}, 2, \text{H}_2\text{O}} \text{CH}_3\text{CHO} \)

E. \( \text{CH}_3\text{CN} \xrightarrow{\text{LiAlH}_4, 2, \text{H}_2\text{O}} \text{CH}_3\text{CHO} \)

F. \( \text{CH}_3\text{CN} \xrightarrow{1. \text{O}_3, 2. \text{Me}_2\text{S}} \text{CH}_3\text{CHO} \)

9. Predict the major product of the following reaction sequence.

\( \frac{\text{PhCOO} \cdot \text{EtO}_2}{\text{NaH}} \xrightarrow{\text{DIBAL-H}, 2. \text{H}_2\text{O}} \frac{\text{PhCHO}}{\text{(PhH)}_3\text{P} \rightarrow} \)

A.

B.

C.

D.

E.

F.
10. Choose the most probable set of substrates that would be used in the biosynthetic pathway for the following polyketide.

1. One **W**, five **Y**, and one **Z**
2. One **X** and six **Y**
3. One **Y** and six **X**
4. One **Z** and six **Y**
5. One **W**, one **X** and five **Y**
6. One **X**, five **Y** and one **Z**

11. Predict the major product of the following reaction sequence.

\[ \text{Cl}_2/\text{AlCl}_3 \rightarrow 1. \text{Fe, HCl} \rightarrow 2. \text{NaOH} \rightarrow \text{Br}_2/\text{FeBr}_3 \rightarrow \text{NaOH} \rightarrow \text{H}_2\text{SO}_4, \text{NaNO}_2 \rightarrow \text{H}_3\text{PO}_2 \rightarrow \]

\[ \text{A} \quad \text{B} \quad \text{C} \quad \text{D} \quad \text{E} \quad \text{F} \]

12. Predict the major product of the following reaction sequence.

\[ \text{O} \quad \text{O} \quad + \quad \text{O} \quad \rightarrow \]

\[ \text{A} \quad \text{B} \quad \text{C} \quad \text{D} \quad \text{E} \quad \text{F} \]
13. Predict the major product of the following reaction sequence.

\[
\begin{align*}
\text{X} & \quad \text{Y} \\
\text{HBr} & \quad \text{Pd cat, base} \\
& \quad \text{Z}
\end{align*}
\]

\[
\begin{align*}
A & \quad B & \quad C \\
D & \quad E & \quad F
\end{align*}
\]

14. Predict the major product of the following reaction sequence.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} & \quad \text{NaOH} & \quad -\text{H}_2\text{O} & \quad \text{H}_2/\text{Pd}
\end{align*}
\]

\[
\begin{align*}
A & \quad B & \quad C \\
D & \quad E & \quad F
\end{align*}
\]
15. According to Hückel’s Rule, which of the following molecules is anti-aromatic?

\[ \text{\begin{array}{c}
\text{A} \\
\text{B} \\
\text{C} \\
\text{D} \\
\text{E} \\
\text{F}
\end{array}} \]

16. Predict the major product of the following reaction sequence.

\[ \text{\begin{array}{c}
\text{OH} \\
\text{Cl} \\
\text{NET}_3 \\
\text{1. LDA} \\
\text{heat} \\
\text{H}_2\text{O}
\end{array}} \]

\[ \text{\begin{array}{c}
\text{A} \\
\text{B} \\
\text{C} \\
\text{D} \\
\text{E} \\
\text{F}
\end{array}} \]

17. Identify the most acidic hydrogen in the compound shown below.

\[ \text{\begin{array}{c}
\text{A} \\
\text{B} \\
\text{C} \\
\text{D}
\end{array}} \]
18. Laminaribiose is a disaccharide of glucose. Deduce the structure of laminaribiose from the following information.

i. Laminaribiose is hydrolyzed by β-glucose enzymes, but not by α-glucose enzymes.

ii. Methylation of laminaribiose followed by hydrolysis yield the two glucose derivatives shown below.
Use the chart above to answer the following two questions. Put the letter identifying each compound into the corresponding blank.

19. Identify the following two sugars. (10 pts)

20. Suppose you had a mixture of two D-aldohexoses, compound J and compound K. You carried out the following tests to identify them. Identify the two sugars. (10 pts)
   
i. Ruff degradation of compounds J and K both gave the same pentose.
   
   ii. Nitric acid oxidation of the pentose from step i. gave a chiral aldaric acid.
   
   iii. NaBH₄ reduction of compound J gave an achiral alditol.
   
   iv. NaBH₄ reduction of compound K gave a chiral alditol.

21. Identify compounds A and B in the following reaction sequence. (10 pts)
22. Identify the main product $\mathbf{M}$ of the following reaction sequence. (6 pts)

\[
\begin{align*}
\text{O} & \quad \text{1. NaOEt} \quad \text{O} \\
\text{C} & \quad \rightarrow \quad \text{C} \\
\text{C} & \quad \rightarrow \quad \text{Br} \\
\text{Br} & \quad \rightarrow \quad \text{Br} \\
\text{C} & \quad \rightarrow \quad \text{HCl, heat} \\
\text{C} & \quad \rightarrow \quad \text{M}
\end{align*}
\]

23. Identify the main product $\mathbf{L}$ of the following reaction sequence. (5 pts)

\[
\begin{align*}
\text{OH} & \quad \text{Br} \\
\text{C} & \quad \rightarrow \quad \text{NaN}_3 \\
\text{C} & \quad \rightarrow \quad \text{LiAlH}_4 \\
\text{C} & \quad \rightarrow \quad \text{POC} \\
\text{C} & \quad \rightarrow \quad \text{NaBH}_3\text{CN} \\
\text{C} & \quad \rightarrow \quad \mathbf{L}
\end{align*}
\]

24. Draw a curved arrow mechanism for the biosynthesis of cryptomeridiol from farnesyl diphosphate. (12 pts)

\[
\begin{align*}
\text{O} & \quad \text{OPP} \\
\text{C} & \quad \rightarrow \quad \text{cryptomeridiol}
\end{align*}
\]

25. Draw a curved arrow mechanism for the following transformation. (12 pts)

\[
\begin{align*}
\text{O} & \quad \rightarrow \quad \text{NaOH} \\
\text{C} & \quad \rightarrow \quad \text{NaO} \\
\text{C} & \quad \rightarrow \quad \text{C}
\end{align*}
\]
26. **Selegiline** is a drug used for the treatment of Parkinson’s disease. Propose a synthesis starting with benzene and other carbon containing compounds of *three carbons* or less. (12 pts)

![Selegiline Structure]

Ambergris is formed in the intestines of the blue sperm whale. It is used as a perfume agent. One minor component is the compound **δ-Ambrinol**. The compound **δ-Ambrinol** has been synthesized via an intramolecular Diels Alder reaction.

![δ-Ambrinol Structure]

27. Draw the open chain precursor of the Diels Alder reaction. (5 pts)

28. Complete the **δ-Ambrinol** synthesis by showing how the open chain precursor can be prepared from carbon containing compounds of *four carbons* or less. (8 pts)