Midterm Examination | Answer Key
Thursday, February 20, 2014

Name: ________________________________

Student ID: __________________________

GSI: ________________________________

(1) ____________ 16 points
(2) ____________ 16 points
(3) ____________ 20 points
(4) ____________ 16 points
(5) ____________ 12 points
(6) ____________ 10 points
(7) ____________ 10 points

Total ____________ 100 points

YOUR EXAM SHOULD HAVE 17 PAGES

NOTE 1: PLEASE START BY WRITING YOUR NAME AND STUDENT ID ON THE COVER PAGE AND YOUR INITIALS ON THE TOP RIGHT OF EACH OF THE OTHER PAGES.

NOTE 2: PLEASE WRITE ALL ANSWERS IN THE SPACES PROVIDED. ONLY THESE WILL BE GRADED. IF YOU NEED MORE SPACE USE THE THREE SCRATCH PAPERS PROVIDED ON PAGE 15-17.

NOTE 3: PLEASE WRITE AND DRAW CLEARLY.
1) (16 points) Draw the major 1,2- and 1,4-addition products of the following reactions? For each reaction indicate the kinetic and the thermodynamic products.

(a) 
\[
\begin{align*}
\ce{CH2=CH-CH=CH2 + HCl &-> ClCH=CH-CH=CH2} \\
\text{kinetic} & \quad \text{thermodynamic}
\end{align*}
\]

(b) 
\[
\begin{align*}
\ce{C6H5CH=CH2 + Cl2 &-> ClC6H4CH=CHCl} \\
\text{kinetic} & \quad \text{thermodynamic}
\end{align*}
\]

(c) 
\[
\begin{align*}
\ce{C2H4 + HCl &-> ClCH2CH3} \\
\text{kinetic} & \quad \text{thermodynamic}
\end{align*}
\]

(d) 
\[
\begin{align*}
\ce{C10H15 + HBr &-> BrC10H14} \\
\text{kinetic} & \quad \text{thermodynamic}
\end{align*}
\]
2) (16 points) Suggest a reaction mechanism for each of the following reactions that accounts for both products. Use clear arrow pushing and draw all intermediates, and resonance structures. Indicate the minor and major product.

(a) 

\[
\text{Cl} \xrightarrow{\text{H}_2\text{O, acetone, reflux}} \xrightarrow{\text{OH}} \xrightarrow{\text{OH}} + \xrightarrow{\text{OH}} + \text{HCl}
\]
(b) \[ \text{HBr, H}_2\text{SO}_4 \quad 60 \, ^\circ\text{C} \]

\[
\begin{align*}
\text{HO} & \quad \text{H}^+ \\
\text{C=C} & \quad \text{H}_2\text{O} \\
\text{Br} & \quad \text{H}^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Br} \\
\text{C=C} & \quad \text{C=C} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Br} \\
\text{C=C} & \quad \text{C=C} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Br} \\
\text{C=C} & \quad \text{C=C} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Br} \\
\text{C=C} & \quad \text{C=C} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

minor

major
3) (20 points) Draw all the products formed in the following Diels-Alder reactions. Clearly indicate the stereochemistry in the products. If a racemic mixture of products is formed you only need to draw one enantiomer. Indicate the racemic mixture with a “(+/−)” sign.

(a)

\[ \text{Diels-Alder} \]

\[ \text{products} \]

\[ \text{reaction} \]

\[ \text{products} \]
(b) Diels-Alder reaction:

\[
\text{Keto} + \text{Alkene} \xrightarrow{\text{Diels-Alder}} \text{Product}
\]
(c) \[
\text{Br} \quad + \quad \text{C} \quad \rightarrow \quad \text{KNH}_2 \quad \rightarrow \quad \text{C}_{11}\text{H}_{10}\text{O}
\]
(d) Diels-Alder reaction

\[
\text{a bicyclic product}
\]

exo products not required for credit
4) (16 points) Using the Hückel rules determine whether each of the following compounds is aromatic, antiaromatic, or non-aromatic. Explain your choice in less than 20 words.

(a) ![Diagram of a compound with NO₂ group]

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Planar</th>
<th>Conjugated</th>
<th>$6\pi \rightarrow 4n+2\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

(b) ![Diagram of two N atoms connected by a bond]

<table>
<thead>
<tr>
<th>Non-aromatic</th>
<th>Planar</th>
<th>Not Conjugated: N atom is sp³ hybridized</th>
<th>4nπ antiaromaticity avoided</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Yes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) ![Diagram of a compound with a positive charge]

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Planar</th>
<th>Conjugated</th>
<th>$6\pi \rightarrow 4n+2\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

(d) ![Diagram of a compound with N=S bond]

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Planar</th>
<th>Conjugated</th>
<th>$6\pi \rightarrow 4n+2\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>
5) (12 points) Predict the major products of the following reactions.

(a)  
\[
\text{Ph-SMe} + \text{H}_2\text{SO}_4 \xrightarrow{\text{HNO}_3} 2 \text{ major monosubstitution products}
\]

(b)  
\[
\text{Ph-NO}_2 + \text{NCH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} 1 \text{ major product}
\]
(c) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 \rightarrow 2$ products resulting from electrophilic aromatic substitutions
6) (10 points) Identify the products of the following reactions. Draw a detailed curved arrow mechanism that leads to the major product. Clearly indicate resonance structures, and charges in the intermediates.

(a) Mechanism:
(b) Mechanism:

Product:

Mechanism:

hint: * is a strong acid that is soluble in organic solvents
7) (10 points) Propose a reasonable synthesis of 3-ethylbenzonitrile starting from benzene and any other inorganic or organic reagent with two or less carbon atoms.

![Synthesis diagram]

3-ethylbenzonitrile
Scratch Paper:
Scratch Paper: