NAME:

There are 6 questions on this exam. You may use molecular models, but no other material may be used. A periodic table is provided at the end of the exam. The exam is over at 11:15 AM.
<table>
<thead>
<tr>
<th>Question</th>
<th>Points</th>
<th>Possible</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>29</td>
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<td>4</td>
<td></td>
<td>84</td>
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<tr>
<td>5</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>250</td>
</tr>
</tbody>
</table>
1. Rank the following compounds in the trend requested. (15 points each)
   a. Rank by reactivity in an electrophilic aromatic substitution reaction. The compound which will react the fastest with \( \text{Br}_2/\text{FeBr}_3 \) is 1, while the compound which will react the slowest is 5.

   ![Chemical Structures](image1.png)

   ![Chemical Structures](image2.png)

   ![Chemical Structures](image3.png)

   ![Chemical Structures](image4.png)

   ![Chemical Structures](image5.png)

   ![Chemical Structures](image6.png)

   ![Chemical Structures](image7.png)

   ![Chemical Structures](image8.png)

   ![Chemical Structures](image9.png)

   ![Chemical Structures](image10.png)

   b. Rank by \( \lambda_{\text{max}} \) in a UV-Vis experiment. The compound which has the longest wavelength (largest \( \lambda_{\text{max}} \)) is 1, while the compound with the shortest wavelength is 5.

   ![Chemical Structures](image11.png)

   ![Chemical Structures](image12.png)

   ![Chemical Structures](image13.png)

   ![Chemical Structures](image14.png)

   ![Chemical Structures](image15.png)

   ![Chemical Structures](image16.png)

   ![Chemical Structures](image17.png)

   ![Chemical Structures](image18.png)

   ![Chemical Structures](image19.png)

   ![Chemical Structures](image20.png)

   c. Rank by acidity. The most acidic compound is 1, while the least acidic compound is 5.

   ![Chemical Structures](image21.png)

   ![Chemical Structures](image22.png)

   ![Chemical Structures](image23.png)

   ![Chemical Structures](image24.png)

   ![Chemical Structures](image25.png)

   ![Chemical Structures](image26.png)
2. Consider the molecule histamine shown below. This molecule causes numerous physiological responses that require many people to take "antihistamine" drugs. There are three nitrogen atoms in histamine labeled N1, N2 and N3.

\[
\begin{array}{c}
\text{H}_2\text{N-} \\
\text{N} \equiv \text{NH} \\
\text{N} \equiv \text{NH} \\
\end{array}
\]

a. (6) What is the hybridization of each N atom?

<table>
<thead>
<tr>
<th>N1</th>
<th>N2</th>
<th>N3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. (6) In which orbital is the lone pair of electrons located for each nitrogen atom?

<table>
<thead>
<tr>
<th>N1</th>
<th>N2</th>
<th>N3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

c. (8) Which nitrogen is hardest to protonate? Why?
3. Draw the arenium ion formed for the preferred product when meta-nitrotoluene reacts with Br₂/FeBr₃. Include all resonance structures for this arenium ion. (12 points)

![Chemical Structure]

b.(5) Circle the resonance form that is lowest in energy.

c.(4) Write “highest” under the resonance form that is highest in energy.

d.(8) Should ortho- or meta-nitrotoluene react faster under these conditions? Why?
4. Indicate the preferred product for the following reactions. (7 points each)

a. 
\[
\begin{align*}
&\text{HNO}_3, \text{H}_2\text{SO}_4 \\
&\text{(1 equiv.)}
\end{align*}
\]

b. 
\[
\begin{align*}
&\text{Br}_2, \text{FeBr}_3
\end{align*}
\]

c. 
\[
\begin{align*}
&\text{Br}_2, \text{FeBr}_3
\end{align*}
\]

d. 
\[
\begin{align*}
&\text{AlCl}_3
\end{align*}
\]

e. 
\[
\begin{align*}
&\text{AlCl}_3
\end{align*}
\]

f. 
\[
\begin{align*}
&\text{Na, NH}_3(\text{l}), \text{CH}_3\text{OH} \\
&1) \text{CH}_3\text{CO}_2\text{H} (1 \text{ equiv.})
\end{align*}
\]
g. ![chemical structure] \[\text{H}^+, \text{CH}_3\text{OH}\]

h. ![chemical structure] \[\text{HBr}, \Delta\]

i. ![chemical structure] \[\text{HBr, 1 equiv.}\Delta\]

j. ![chemical structure] \[\text{CN}\]

k. ![chemical structure] \[\text{CHO}\]

l. ![chemical structure] \[\text{NO}_2\]
5. Indicate how to synthesize the following compounds starting with benzene. You can use any other reagents you desire, but you must start with benzene. Assume all electrophilic aromatic substitution reactions with an ortho, para director yield only the para product. Indicate the structure for each step in the synthesis. (15 points each)

a. 

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{Br} \\
\text{Cl} & 
\end{align*}
\]

b. 

\[
\begin{align*}
\text{NO}_2 & \quad \text{Br} \\
\text{H}_3 & 
\end{align*}
\]
6.(42) When benzene was reacted with 1-chloropropane and aluminum trichloride under a given set of conditions, the major product (labeled A below) gave the $^1$H NMR shown on the following page (with relative integration shown). When A was reacted with nitric acid and sulfuric acid, compound B was obtained. When compound B was reacted with bromine and iron tribromide, compound C was obtained. Draw the products for compounds A, B and C.

![Diagram](https://via.placeholder.com/150)

Compound A → A → B → C

b. When the second and third steps in the reaction scheme above were reversed, a different product D was obtained. Draw the structure for product D.

![Diagram](https://via.placeholder.com/150)

Compound D

c. When the steps were run under the reverse order as in the initial sequence (step 3 first, then step 2 and finally step 1), draw the product obtained (E, F and G) after each step.

![Diagram](https://via.placeholder.com/150)

Compound E → E → F → G

Compound E → F → G
$^1$H NMR for compound A