Conjugation, Aromaticity, Electrophilic Aromatic Substitution

1. Provide Either the Name or the Structure for the Following Chemicals. (6 points) (3 minutes)

a. Furan

b. p-nitrobenzoic acid

c.

2. For the following substituents, classify each as 1) electron-donating or electron-withdrawing ["D" or "W"], 2) as activating or deactivating ["Act" or "Deact"], and as 3) ortho-para directing or meta directing ["o/p" or "m"]. (6 points) (2 minutes)

- OCH₃
- CCH₂CH₃
- CH₃
- Cl
3. Rank the reactivity (rates!) of the following sets of molecules toward the reagents shown, 1 being most reactive, 2 being middle, and 3 being least reactive. (10 points) (6 minutes)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molecules Being Compared</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. H₂, Pt</td>
<td><img src="image1" alt="Molecule 1" /> <img src="image2" alt="Molecule 2" /> <img src="image3" alt="Molecule 3" /></td>
</tr>
<tr>
<td>b. H⁺, H₂O (SN₁/E₁)</td>
<td><img src="image4" alt="Molecule 4" /> <img src="image5" alt="Molecule 5" /> <img src="image6" alt="Molecule 6" /></td>
</tr>
<tr>
<td>c.</td>
<td><img src="image7" alt="Molecule 7" /> <img src="image8" alt="Molecule 8" /> <img src="image9" alt="Molecule 9" /></td>
</tr>
<tr>
<td>d. HNO₃, H₂SO₄</td>
<td><img src="image10" alt="Molecule 10" /> <img src="image11" alt="Molecule 11" /> <img src="image12" alt="Molecule 12" /></td>
</tr>
<tr>
<td>f. NaOMe (SN₂ reactivity)</td>
<td><img src="image13" alt="Molecule 13" /> <img src="image14" alt="Molecule 14" /> <img src="image15" alt="Molecule 15" /></td>
</tr>
</tbody>
</table>
4. Draw the major product for each of the following reactions. (3 points each, 21 total, 7 minutes)

a. \[
\begin{align*}
\text{Cl}_2, \text{AlCl}_3
\end{align*}
\]

b. \[
\begin{align*}
\text{SO}_3, \text{H}_2\text{SO}_4 \\
\text{HNO}_3, \text{H}_2\text{SO}_4 \\
\text{H}_2\text{O}, \text{H}_2\text{SO}_4
\end{align*}
\]

c. \[
\begin{align*}
\text{HNO}_3, \text{H}_2\text{SO}_4 \\
\text{Fe, HCl}
\end{align*}
\]

d. \[
\begin{align*}
\text{Br}_2, \text{hv} \\
\text{NaOMe}
\end{align*}
\]

e. \[
\begin{align*}
\text{Cl}_2, \text{FeCl}_3
\end{align*}
\]

f. \[
\begin{align*}
\text{Mg, ether} \\
\text{Br}
\end{align*}
\]

Not Test Responsible for this problem.

g. \[
\begin{align*}
\text{heat}
\end{align*}
\]
5. Provide reagents for the following transformations. (5 points each, 10 total, 6 minutes)

a. \[
\begin{array}{c}
\text{CH}_3 \\
\text{C}_6\text{H}_5 \\
\end{array} \rightarrow \begin{array}{c}
\text{CO}_2\text{H} \\
\text{Cl} \\
\end{array}
\]

b. \[
\text{C}_6\text{H}_6 \rightarrow \begin{array}{c}
\text{NH}_2 \\
\end{array}
\]

6. Draw the diene and dienophile from which the following Diels-Alder products would have come. (3 points each, 6 total, 2 minutes)

a. \[
\begin{array}{c}
\text{Me}_2\text{N} \\
\text{CN} \\
\text{C}_6\text{H}_6 \\
\end{array} \rightarrow \begin{array}{c}
\text{Me}_2\text{N} \\
\text{CN} \\
\end{array}
\]

b. \[
\begin{array}{c}
\text{MeO} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{C}_6\text{H}_6 \\
\end{array} \rightarrow \begin{array}{c}
\text{MeO} \\
\text{H} \\
\text{O} \\
\text{O} \\
\end{array}
\]
7.  a. Draw the mechanism for the formation of the major product shown, and identify the "slow" step in the reaction. (6 points, 5 minutes)

\[
\begin{align*}
\text{MeO} & \quad + \quad \text{Cl} \quad \rightarrow \quad \text{AlCl}_3 \\
\text{MeO} & \quad \text{MeO} & \quad \text{O} \\
\end{align*}
\]

b. Draw all 4 resonance structures for the cation intermediate in the above reaction, and circle the most important contributor. (4 points)
8. Draw the major product or products that would result from the following reaction, and write either "chiral" or "achiral" and "optically active" or "racemic" by each product. Draw a mechanism for the reaction, and identify the "slow" step in the reaction. (8 points, 5 min)

\[
\text{+ 1.0 HBr } \rightarrow 
\]

9. Provide a synthesis for the following molecule, using benzene and anything else you like. "Backwards syntheses" are fine, so long as you draw the reagents! (7 points, 5 min)
10. Circle the aromatic molecules: (6 points) (3 minutes)

11. The molecule below has 3 different nitrogens. For each of the nitrogens, classify the hybridization of the nitrogen atom, the hybridization of the nitrogen's lone pair, and whether the basicity of the nitrogen is "normal" or "low". (6 points, 2 min)

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>Lone-Pair</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybridization</td>
<td>Hybridization</td>
<td>Basicity</td>
</tr>
<tr>
<td>N&lt;sub&gt;a&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N&lt;sub&gt;b&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N&lt;sub&gt;c&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

12. Outline the energies of the \( \pi \) molecular orbitals of cyclobutadiene (use a Frost diagram), indicate which are occupied by electrons, and indicate whether the molecule is "unusually stable" or not. (4 points, 1 min)

**Not Test Responsible for this problem.**

Nonbonding Line