1. Friedel-Crafts alkylations may be carried out using an alkene and an acid catalyst. Provide a detailed mechanism for the following reaction.

```
\[
\text{BF}_3 + \text{H}_2\text{O} + \text{BF}_3 \rightarrow \text{BF}_3\text{OH}^+ \rightarrow \text{BF}_3\text{OH} + \text{BF}_3\text{H}^+ \rightarrow \text{BF}_3\text{OH} + \text{BF}_3\text{H}^+ \rightarrow \text{BF}_3\text{OH} + \text{BF}_3\text{H}^+ \rightarrow \text{BF}_3\text{OH} + \text{BF}_3\text{H}^+
\]
```

2. Rank the following compounds in each group in the order of their reactivity to electrophilic substitution. (Draw structures for each.)

<table>
<thead>
<tr>
<th>Group</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>chlorobenzene, phenol, toluene, p-xylene</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>b)</td>
<td>ethylbenzene, phenol, chlorobenzene, benzenesulfonic acid</td>
</tr>
<tr>
<td></td>
<td>CH$_2$CH$_3$</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>c)</td>
<td>anisole, aniline, benzoic acid, t-butylbenzene</td>
</tr>
<tr>
<td></td>
<td>OMe</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

3. Draw all the intermediates (including resonance forms) for the bromination of anisole (Ph-OCH$_3$). Which intermediate(s) is(are) most favored and explain why using your resonance forms.

The ortho and para substitution intermediates are favored since each has an extra resonance form (K and L) that are especially stable, since all Cs and O have octets. The meta isomer does not have a similar resonance form, making it less stable and less favored.
4. Draw the structure of the major product(s) expected in the electrophilic chlorination of the following substances. If more than one major product is expected, state the relative amounts of each.

   a) o-nitroanisole
   \[ \begin{align*}
   &\text{o-nitroanisole} \\
   &\text{Cl}_2 + \text{FeCl}_3 \\
   &\text{H}_2\text{C} - \text{O} + \text{Cl} - \text{O}_2\text{N} - \text{CH}_3 \\
   &\sim 40:60
   \end{align*} \]

   b) 2,6-dichlorophenol
   \[ \begin{align*}
   &\text{2,6-dichlorophenol} \\
   &\text{Cl}_2 + \text{FeCl}_3 \\
   &\text{Cl} - \text{O} - \text{H} + \text{Cl} - \text{O}_2\text{N} - \text{Cl} \\
   &\text{Cl}
   \end{align*} \]

   c) p-bromobenzenesulfonic acid
   \[ \begin{align*}
   &\text{p-bromobenzenesulfonic acid} \\
   &\text{Cl}_2 + \text{FeCl}_3 \\
   &\text{SO}_3\text{H} - \text{Br} + \text{Br} \\
   &\text{Br} - \text{SO}_3\text{H} - \text{Br}
   \end{align*} \]

   d) o-xylene
   \[ \begin{align*}
   &\text{o-xylene} \\
   &\text{Cl}_2 + \text{FeCl}_3 \\
   &\text{H}_3\text{C} - \text{Cl} + \text{Cl} \\
   &\text{H}_3\text{C} - \text{Cl}
   \end{align*} \]

5. Starting with either benzene or toluene as your only source of aromatic compounds, how would you synthesize these substances? Assume that you can separate ortho and para isomers.

   a) p-bromobenzoic acid
   \[ \begin{align*}
   &\text{p-bromobenzoic acid} \\
   &\text{Br}_2 + \text{FeBr}_3 \\
   &\text{CH}_3
   \end{align*} \]

   b) m-nitrobenzoic acid
   \[ \begin{align*}
   &\text{m-nitrobenzoic acid} \\
   &\text{Br}_2 + \text{FeBr}_3 \\
   &\text{KMnO}_4/\text{NaOH} \quad \text{Hot} \\
   &\text{Br}
   \end{align*} \]

   c) 4-bromo-2-nitrotoluene
   \[ \begin{align*}
   &\text{4-bromo-2-nitrotoluene} \\
   &\text{Br}_2 + \text{FeBr}_3 \\
   &\text{HNO}_3 \quad \text{H}_2\text{SO}_4 \\
   &\text{Br}
   \end{align*} \]

   d) p-butyltoluene (remember direct alkylation will not work)
   \[ \begin{align*}
   &\text{p-butyltoluene} \\
   &\text{CH}_2 - \text{C} - \text{CH}_2\text{CH}_2\text{CH}_3 \\
   &\text{Cl} - \text{C} - \text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{AlCl}_3 \\
   &\text{H}_2\text{C} - \text{C} - \text{O} \quad \text{H}_2/\text{Pd} \quad \text{ethanol} \\
   &\text{H}_2\text{C} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
6. a) At what position and on what ring would you expect nitration to occur in the following substance. The left ring would react faster at the positions marked a and b. a would probably be the major product.

b) Draw the structure of the dinitro-product expected from further nitration of the product in a.

![Nitration Reaction](image)

The presence of the nitro group on the left ring would deactivate it enough that the next substitution would occur in the right ring which does not have the nitro.

7. Prepare the following compound starting from chlorobenzene. Be aware of the limitations of the Friedel-Crafts alkylation when considering possible pathways.

![Preparation Reaction](image)

8. Provide the structures of all the organic products expected in the following reactions. When mixtures of products are expected, indicate the relative amounts of each.

Provide a mechanism for each reaction.

![Reaction Mechanisms](image)
Problems #3

9. Provide the structures of all the organic products expected in the following reactions. When mixtures of products are expected, indicate the relative amounts of each.

a) \[ \text{HBr/peroxides} \]  
\[ \text{HBr/no peroxides} \]

b)  
1. KMnO₄/OH-/heat
2. H⁺

10. The following reaction sequence will not work effectively for the transformation shown. Explain why it will not work and predict what will actually take place.

Both the methyl and the acetyl group are oxidized by permanganate.