1. (4 points) The following reaction gives two major products.

\[ \text{Br} \quad \text{Br} \quad 1 \text{ eq } \text{HBr} \]

\[ X \quad Y \]

a. Use the following answers to describe the kinetic and thermodynamic products.
   A) X is the thermodynamic product and Y is the kinetic product.
   B) Y is the thermodynamic product and X is the kinetic product.
   C) X is both the thermodynamic and kinetic product and Y is formed in a side reaction.
   D) Y is both the thermodynamic and kinetic product and X is formed in a side reaction.
   E) It is impossible to tell from the information given.

b. Which product above will be the major product at 16°C?
   A) X  B) Y  C) It is impossible to tell  D) There is only one product

2. (5 points) Draw the molecular orbital diagram for 1,3,5-hexatriene, indicate the type of bonding (bonding or antibonding), and indicate the HOMO and LUMO.

3. (3 points) Circle the more acidic compound below and briefly explain why you made that choice.
4. (3 points) One complete resonance form for the s-cis configuration of 2,5-dimethyl-2,4-hexadiene is given in the central figure below. Two incomplete structures are given on either side of the molecule. Complete the given structures including non-bonding electrons and formal charges. Circle the structure that is the major resonance contributor. X out the structure that contributes the least to the resonance hybrid.

![Resonance Structure](image)

1. (3 points) For the structure below, determine the total number of π electrons and the number of π electrons delocalized in the ring. Indicate whether the compound is aromatic, nonaromatic, or antiaromatic. Assume the structure is planar.

<table>
<thead>
<tr>
<th>Questions</th>
<th>answers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of π electrons:</td>
<td></td>
</tr>
<tr>
<td>Number of π electrons delocalized in the ring.</td>
<td></td>
</tr>
<tr>
<td>The compound is aromatic nonaromatic antiaromatic.</td>
<td></td>
</tr>
</tbody>
</table>

2. (3 points) Circle the reaction that occurs at a faster rate and briefly explain why.

\[
\begin{align*}
\text{Br} & \quad \text{H}_3\text{O}^+ \\
\text{H} & \quad \text{NaOH}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad + \text{HBr} \\
\text{Na}^+ \text{CH}^- & \quad + \text{H}_2\text{O}
\end{align*}
\]
3. (9 points) Draw a Frost diagram for each of these compounds. Decide whether each is nonaromatic, aromatic or would be antiaromatic if planar. Explain why you chose your answers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cycloheptatriene</th>
<th>cycloheptatrienyl</th>
<th>Cycloheptatrienide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frost diagram</td>
<td><img src="image1" alt="Cycloheptatriene" /></td>
<td><img src="image2" alt="Cycloheptatrienyl" /></td>
<td><img src="image3" alt="Cycloheptatrienide" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aromatic?</th>
<th></th>
<th></th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Explanation:</th>
<th></th>
<th></th>
</tr>
</thead>
</table>

4. (7 points) Mark each of the following as true or false.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Dienes and alkenes are much more stable than benzene rings.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Addition reactions on benzene destroy the integrity of the benzene ring.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c. Benzene and its derivatives tend to undergo electrophilic aromatic substitution reactions.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d. Benzene and its derivatives undergo a type of substitution reaction in which a hydrogen atom is replaced by a nucleophile.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e. In aromatic substitution reactions the stable aromatic benzene ring remains throughout the mechanism.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f. Substitution reactions have energies of activation that are very high.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g. Benzene and its derivatives tend to undergo electrophilic aromatic addition reactions.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. (2 points) Write the rate equation for electrophilic aromatic substitution.
6. (12 points) Substituents on an aromatic ring can have several effects on electrophilic aromatic substitution reactions. Substituents can activate or deactivate the ring to substitution, donate or withdraw electrons inductively, donate or withdraw electrons through resonance, and direct substitution either to the ortho/para or to the meta positions. From the following lists, select the substituents that have the indicated property. The substituents are written as -XY, where X is the atom directly bound to the aromatic ring. Write an X in each box which describes the indicated substituents.

<table>
<thead>
<tr>
<th>Substituents:</th>
<th>-OH</th>
<th>-Br</th>
<th>-NHOCH₃</th>
<th>-COOH</th>
<th>-SO₃H</th>
<th>-NH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activates of the ring towards substitution.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Withdraws electrons through resonance.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Directs Ortho/para-substitution.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Will not react in a Freidel Crafts acylation reaction.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Is basic in water.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Is acidic in water.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7. (6 points) (3 points) Draw the mechanism for the reaction between benzene and the nitronium ion (NO₂⁺) to form nitrobenzene.
8. (6 points) Draw the structure of major product for the following Diels–Alder reaction, specify the stereochemistry via wedge-and-dash bonds.

\[ \text{Cyclopentadiene} + \text{Cyclopentadiene} \rightarrow \text{Diaddition Product} \]

9. (6 points) The following are the CMR spectra of the two major products of the reaction between toluene and iron (II) chloride with chlorine. Identify each of the compounds in the spectra.

a. 

b. 

1. (3 points) Provide the major product expected for the following series of reactions. Omit byproducts. Ignore stereochemistry.

\[ \text{Cyclohexene} \xrightarrow{\text{hv}} \text{Cyclohexene} \xrightarrow{\text{NBS}} \text{NBS adduct} \xrightarrow{\text{CH}_3\text{CO}K^+} \text{CH}_3\text{COH} \]
10. (9 points) Each of the following reactions produces two major products. Circle the one that is formed in greater yield and explain your reasoning.

\[
\begin{align*}
\text{CH}_3 & \quad \text{HNO}_3/\text{H}_2\text{SO}_4 \quad \text{CH}_3 \\
\text{H}_2\text{SO}_4 & \quad \text{O}_2\text{N} \quad \text{CH}_3 \\
\text{HNO}_3 & \quad \text{CH}_3 \\
\text{NO}_2 & \quad \text{CH}_3
\end{align*}
\]

Explanation:

\[
\begin{align*}
\text{O}_2\text{C} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Explanation:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{Br} \\
\text{H}_3\text{C} & \quad \text{CH}_2 \\
\text{H}_3\text{C} & \quad \text{CH}_2 \\
\text{H}_3\text{C} & \quad \text{Br}
\end{align*}
\]

Explanation:

2. (3 points) Design a three-step synthesis of 3-bromocyclopentene from cyclopentane.

\[
\begin{align*}
\text{pentane} & \quad \rightarrow \quad \text{pentane} \\
\text{pentane} & \quad \rightarrow \quad \text{pentane} \\
\text{pentane} & \quad \rightarrow \quad \text{pentane}
\end{align*}
\]
11. (3 points) Provide the major product of the following reaction sequence. If cis/trans is possible, draw only the major isomer. If enantiomers are possible, do not specify configuration.

a. 

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{KMnO}_4
\end{array}
\]

b. 

\[
\begin{array}{c}
\text{CH}_3 \\
\text{HBr}
\end{array}
\]

c. 

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Br}_2/ \text{FeBr}_2
\end{array}
\]

d. 

\[
\begin{array}{c}
\text{CH}_3 \\
1. \text{BH}_3 \\
2. \text{H}_2\text{O}_2/ \text{NaOH}
\end{array}
\]

e. 

\[
\begin{array}{c}
\text{CH}_3 \\
\text{furan}
\end{array}
\]

f. 

\[
\begin{array}{c}
\text{CF}_3 \\
\text{H}_2\text{SO}_4 \text{fuming}
\end{array}
\]
12. (3 points) Provide the major product of the following reaction sequence. If cis/trans is possible, draw only the major isomer. If enantiomers are possible, do not specify configuration.

a.
\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{AlCl}_3 & \quad \text{CH}_3\text{COCl}
\end{align*}
\]

b.
\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{CuLi}^+ & \quad \text{Br} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

1) Br\textsubscript{2}, heat
2) 2 equiv. NaCN DMF

c.

1. Li
2. \text{CH}_3\text{COCH}_2\text{CH}_3
3. H\textsubscript{3}O\textsuperscript{+}

d.

\[
\begin{align*}
\text{Br} & \quad \text{H}_3\text{C}
\end{align*}
\]

3. (6 points Choose one) Construct a multistep synthetic route for the following compounds from benzene. Draw all reactants and products at each step. Indicate all required reagents and conditions at each step.

- p-aminobenzoic acid
- 3-bromo-4-methylacetophenone
13. (8 points) Consider the chain of the reactions given below and draw the structures of the major product for each step. If you think that a particular reaction will not occur, redraw the structure without any changes. Show the formal charges, where applicable. As a start, the benzene ring is drawn for you in each product.

\[
\text{HNO}_3/\text{H}_2\text{SO}_4
\]

\[
\text{Cl}_2/\text{FeCl}_2
\]

\[
1. \text{Mg} \rightarrow 2. \text{ClCOCH}_3
\]

\[
\text{H}_2\text{SO}_4 \quad \Delta \quad \text{Br}_2
\]

\[
\text{NaNH}_2 \quad \text{acid work up}
\]