1. (36 points) Predict the product(s) formed in reasonably significant quantity (> 10%) for each of the following reactions. If no reaction is expected, briefly explain why. Where an EAS reaction takes place, you may assume that only one substitution takes place on a single aromatic molecule. However, in some cases, more than one isomeric product is possible.

A)

\[
\begin{align*}
\text{NH}_2 & \quad \rightarrow \quad \text{NH}_2 \\
\text{Cl}_2 & \quad \text{FeCl}_3
\end{align*}
\]

\[
\begin{align*}
\text{very minor} \quad (0 \% \text{ to exclude})
\end{align*}
\]

B)

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

\[
\begin{align*}
\text{N} & \quad \text{N}
\end{align*}
\]

\[
\begin{align*}
\text{(major)}
\end{align*}
\]

\[
\begin{align*}
\text{(minor)}
\end{align*}
\]

C)

\[
\begin{align*}
\text{NO}_2 & \quad \rightarrow \quad \text{NR}
\end{align*}
\]

\[
\begin{align*}
\text{\$-NO}_2 \text{ is too deactivating for F-C}
\end{align*}
\]

D)

\[
\begin{align*}
\text{HBr} & \quad \text{60\textdegree C}
\end{align*}
\]

\[
\begin{align*}
\text{Indicate the major product only.}
\end{align*}
\]

E)

\[
\begin{align*}
\text{HBr} & \quad \text{-78\textdegree C}
\end{align*}
\]

\[
\begin{align*}
\text{Indicate the major product only.}
\end{align*}
\]
F) \[ \text{NR - Bulky groups prevent proper conformation of the Diene.} \]

G) \[
\begin{align*}
\text{Cyclic ene} & \quad + \quad \text{Acrolein} & \quad \text{AlCl}_3 & \quad 1) \text{KMnO}_4, \text{OH}^-, \Delta \\
& & & 2) \text{H}_2\text{O}^+ & \quad \rightarrow \\
\end{align*}
\]

H) \[
\text{Cyclic ene} \quad \text{NaNH}_2 \quad \rightarrow \quad \text{Cyclic ene} \quad + \quad \text{NH}_3
\]

I) \[
\begin{align*}
\text{Cyclic ene} & \quad \text{SO}_3 & \quad \text{H}_2\text{SO}_4 & \quad \rightarrow \\
& & & \text{Cyclic ene} \quad + \quad \text{Cyclic ene} \quad \text{SO}_3\text{H}_4
\end{align*}
\]
2. (12 points) Consider the reaction below.

A) Predict the major product.

B) Write a complete arrow-pushing mechanism for the formation of that compound, including the formation of the electrophile and all important resonance structures for any intermediates.

C) In this reaction, AlCl₃ is a Lewis \( \text{ACID} \). Explain what that means – be brief & specific.

\[ \text{Mechanism:} \]

\[ \text{It has an unfilled } p\text{-orbital, making it an excellent lone pair acceptor!} \]
3. (8 points) Consider the reaction below.
   A) Predict the major product.
   B) Explain why the ring substituent directs to the position(s) that it does, and why it does NOT direct to other positions. Include an appropriate intermediate structure or structures with your explanation.

\[
\begin{align*}
\text{HNO}_3 & \quad \text{H}_2\text{SO}_4 \\
\text{PhCO}^+ & \quad \text{PhCO}^+ \\
\end{align*}
\]

\(\text{NO}_2\)

It is a meta-director b/c of its e-withdrawing properties. The carbonyl carbon adjacent to the ring puts a significant partial + charge adjacent to the ring. **META addition avoids putting the + of the EAS intermediate on the carbon adjacent to the carbonyl** (shows C's bearing partial + charges) in EAS intermediate.

Other/Para addition does put the + charge of the EAS intermediate adjacent to the carbonyl and is therefore highly unfavorable.

4. (6 points) Which of the following species are aromatic? **Circle those that are aromatic.** No explanations are needed.

\[
\begin{align*}
\text{[]} & \quad \text{[\text{[]}] for aromaticity} \\
\text{[]} & \quad \text{[\text{[]}] for aromaticity} \\
\text{[]} & \quad \text{[\text{[]}] for aromaticity} \\
\text{[]} & \quad \text{[\text{[]}] for aromaticity} \\
\text{[]} & \quad \text{[\text{[]}] for aromaticity} \\
\text{[]} & \quad \text{[\text{[]}] for aromaticity} \\
\end{align*}
\]
5. (8 points) Consider the molecule below. You may ignore stereochemistry.
   A. Suggest starting materials of seven carbons or less for the formation of the following product.
   B. Show the arrow-pushing mechanism for the forward reaction.

6. (6 points) Relative to reference compound C, compound A has an unusually low pKₐ, while compound B has an unusually high pKₐ. Explain both observations.

A is more acidic than C, b/c when it loses its proton, it forms an aromatic compound: Planar π system with 4n+2 (=6) electrons

B is less acidic than C, b/c when it loses its proton it has 8 e⁻'s in planar π system, and is anti-aromatic
7. (6 points) Which of the following compounds (A or B) will have the shorter \( \lambda_{\text{max}} \)? Explain briefly. Include a discussion of molecular orbitals.

\[ \text{B} \] will have the shorter \( \lambda_{\text{max}} \), b/c it has only 5 \( \text{C=C}'s \) conjugated together, whereas A has 10 \( \text{C=C}'s \) conjugated. The smaller \# of conjugated bonds \( \rightarrow \) larger \( \Delta E \) for the HOMO \( \rightarrow \) LUMO transition. Larger \( \Delta E \) \( \rightarrow \) shorter \( \lambda \).

8. (6 points)

A) Draw all of the resonance structures for the allyl radical formed from the dissociation of a hydrogen atom (H+) from the following molecule.

B) Show an Aufbau diagram of the 3 molecular orbitals formed from the atomic p-orbitals. Indicate the relative energies of the orbitals, provide their appropriate orbital designations, and fill them with electrons in the proper manner.

BONUS (2 points): Sketch the shapes of the 3 MO's.
9. (12 points) Suggest a method for the formation of the following compound starting with benzene, alkyl chlorides and acyl chlorides as your only possible sources of carbon. You may use any other reagents or solvents you choose.