FOURTH EXAMINATION

All answers should be written on the exam in the spaces provided. Clearly indicate your answers in the spaces provided; if I have to guess as to what or where your answer is, it is wrong. Where applicable, outline the logic or mystical principle you used to arrive at your answer, as partial credit may be awarded for correct approaches.

You may assume that standard work-up conditions (i.e. those required to obtain a stable, neutral product, like aqueous acid as example) follow each reaction on the exam. Clearly indicate stereochemistry where appropriate. Be careful not to show stereochemistry where none exists.

This exam is long (as always) for the time allotted. You are strongly advised to read it through completely before you begin.

(1). 10 pts.................._____
(2). 24 pts.................._____
(3). 21 pts.................._____
(4). 20 pts.................._____
(5). 16 pts.................._____
(6). 12 pts.................._____

TOTAL (103 pts)............._____

Percentage.................._____
1. [10 pts] Name the following molecules according to IUPAC rules:
   a. meta-chloroisobutyl benzene or 1-chloro-3-isobutylbenzene

    ![meta-chloroisobutyl benzene](image)

   b. Name as an aniline compound:

    ![4-chloro-3-nitroaniline](image)

2. [24 pts] Fill in the necessary reagents for each of the following steps (A-H):

   A: (CH₃CH₂)₂CuLi
   B: (CH₃CH₂)₂Cl, AlCl₃
   C: HNO₃, H₂SO₄
   D: H₂, Pd/C or
      1. Fe or SnCl₂, HCl, 2. NaOH, H₂O
   E: NaNO₂, HCl, H₂O, 0°C or
      HNO₂, H₂SO₄, H₂O, 0°C
   F: HBF₄, heat
   G: CuCN
   H: H₃O⁺
3. [21 pts] Provide the appropriate reagents and conditions, or products for the following transformations, in a single step.

a. 

\[
\begin{align*}
\text{NO}_2\text{O}_2\text{N} & \quad \text{Br} & \quad \text{heat} & \quad \text{NaNH}_2 & \quad \text{NO}_2\text{O}_2\text{N} & \quad \text{NH}_2 \\
\end{align*}
\]

b. 

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

c. 

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

d. 

\[
\begin{align*}
\text{KMnO}_4, \text{H}_2\text{O} & \quad \text{heat} & \quad \text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\
\end{align*}
\]

e. 

\[
\begin{align*}
\text{Br} & \quad \text{Cl} & \quad \text{AlCl}_3 \\
\end{align*}
\]

f. 

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{OCH}_3 & \quad \text{Na, NH}_3 & \quad \text{HO}_3\text{S} & \quad \text{OCH}_3 \\
\end{align*}
\]

g. 

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{NO}_2 & \quad 1. \text{SnCl}_2 \text{ or Fe, HCl} & \quad 2. \text{NaOH, H}_2\text{O} & \quad \text{NH}_2 \\
\end{align*}
\]
4. [20 pts] Propose a reasonable synthetic route to each of the following compounds, starting from benzene. Partial credit will be given for approaches without reagents. Remember: **Selectivity** is the name of the game—points will be deducted for reactions that result in ortho/para mixtures.

**a.**

\[ \text{Br} \quad \text{NH}_2 \]

1. HNO₃, H₂SO₄
2. H₂, Pd/C
3. acetyl chloride, pyridine
4. Br₂, Fe
5. NaOH, H₂O

Need to place a large Ortho-Para director on the ring to cause the para formation. The amine group can be protected using the acetyl chloride to become a larger ortho-para director than the amine group itself.

**b.**

\[ \text{Cl} \quad \text{H}_2\text{N} \quad \text{OH} \]

1. SO₃, H₂SO₄
2. HNO₃, H₂SO₄
3. Cl₂, Fe
4. NaOH, H₂O
5. H₂, Pd/C

When building a 1,3,5 system, you cannot place an ortho-para director on the ring until two meta directors are in place. If you convert one of the groups to the Ortho-Para director you want or put the chlorine in place too early, the ortho-para director takes control and you won’t get 1,3,5-selectivity.
5. [16 pts] The following questions apply to the theoretical and historical aspects of benzene:

a. Explain how the monobromination experiment of benzene assisted in the assignment of the structure of benzene, to which the molecular formula of \( \text{C}_6\text{H}_6 \) had been assigned. What key information did this experiment provide?

\[
\text{C}_6\text{H}_6 + \text{Br}_2, \text{Fe} \rightarrow \text{C}_6\text{H}_5\text{Br} \text{ (only one product)}
\]

If you only get one product, that means that all of the hydrogen atoms are exactly the same (total symmetry).

b. Explain how the second bromination experiment of bromobenzene assisted in the assignment of the structure of benzene. What key information was gained from this experiment?

\[
\text{C}_6\text{H}_5\text{Br} + \text{Br}_2, \text{Fe} \rightarrow \text{C}_6\text{H}_4\text{Br}_2 \text{ (three products)}
\]

Only three products were obtained, not four as predicted by Kekulé’. Both “ortho” structures were actually the same. (Lead to concept of resonance.)

c. Explain why \( 4n+2 \) is the perfect number of pi electrons for an aromatic system.

Perfect number of pi electrons to completely fill all of the bonding molecular orbitals. Too many and you have to place electrons in the antibonding high energy orbitals and too few and you have unpaired electrons in the bonding molecular orbitals (radicals).

d. Explain why every atom in an aromatic system like benzene must be \( \text{sp}^2 \) hybridized.

In order to have conjugation stability (complete delocalization), every atom in the ring system must have a perpendicular \( p \) orbital for the electron density to move through.
6. [12 pts] Short Answer: Answer 3 of the following 5 questions:

a. Circle the compound below that will have a higher wavelength (\( \lambda_{\text{max}} \)) for ultraviolet absorption.

![Compound A](image1.png)

![Compound B](image2.png)

The first one is more conjugated – higher wavelength.

b. Propose a logical explanation as to why the first molecule shown below has a larger dipole moment than the second molecule.

![Molecule A](image3.png)

![Molecule B](image4.png)

The first one can be aromatic but only if it polarizes the carbonyl:

![Aromatic Molecule](image5.png)

c. When HCl is added to 1,3-butadiene at room temperature or higher, the major product is 1-chloro-2-butene. Explain why this forms in preference to 3-chloro-1-butene.

At high temperatures, more energy is available to allow the allylic carbocation intermediate to form its resonance structure – the higher energy primary allylic carbocation – but this has the more stable alkene in its structure so overall it’s the more stable final product species.

d. Predict which of the two following acids is more acidic. Provide an explanation for the differences in acidity utilizing inductive and/or resonance effects in your answer (whatever is most applicable).

![Acid A](image6.png)

![Acid B](image7.png)

The first compound is more acidic - the anion will be more stable on a ring that has an electron-withdrawing group than on a ring that has an electron-donating group that would destabilize any extra electron density.
e. Explain why an acyl group, like that found in acetophenone (shown below), is a meta director. Use resonance forms in your discussion.

Notice that the most electron-rich positions on the ring occur on the positions that are meta to the group (the ortho and para positions have a full positive charge). As a result, the meta positions are the most electron-rich and reactive with electrophiles.