Before you begin this exam: First: You are allowed to have a simple model set at your seat. Please put away all other materials. Second: Place your student identification on your desk. A proctor will come around to check everyone’s ID. If you do not have ID, tell the proctor and Third: Read through the entire exam. Your goal, as always, is to score as many points as possible. Do not waste time on problems that you can’t do if there are others that look easy. Fourth: It is critically important that your answers be written in a clear, unambiguous manner. Answers in which your intentions are unclear will not receive credit. Fifth: READ THE INSTRUCTIONS FOR EACH PROBLEM. You have 75 minutes to complete this exam. There will be no extensions, so budget your time carefully.

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1. (10 points) The structure of thiamine is shown below. It contains two heterocycles: a thiazine ring (containing S and N) and a pyrimidine ring (containing two N atoms).
   a) Draw in the lone pairs (if any) of electrons on the N and S atoms in both rings.
   b) For each ring, state whether it is aromatic, anti-aromatic, or neither.

   ![Thiamine structure]

   Both rings are aromatic.

2. (10 points) Classify each of the following molecules as either aromatic or antiaromatic. Write your answer on the line beneath the structure.

   ![Molecules]

   Antiaromatic  Antiaromatic  Aromatic

3. (10 points) One of the problems with the Friedel-Crafts alkylation is that multiple additions occur. In other words, dialkylated material is produced along with the desired monoalkylated product. This problem does NOT occur with the Friedel-Crafts acylation. Explain why multiple additions can occur in the alkylation but do not occur in the acylation. Do not exceed the space provided.

   After the first alkylation reaction, the product is more reactive than the starting material and a second alkylation reaction can happen rapidly. However, after the first acylation reaction, the product is less reactive than the starting material, so all of the starting material reacts before the product reacts for a second time.
4. (25 points) Provide the organic product of each of the following reactions. If you believe that two products will be formed in significant quantities (like ortho/para isomers), show both products. If you believe that no reaction will occur, write “no reaction.”

a) \[
\begin{align*}
\text{SO}_3, \text{H}_2\text{SO}_4 & \quad \rightarrow \\
\text{S} & \text{O}_3\text{H} & \text{S} & \text{O}_3\text{H}
\end{align*}
\]

b) \[
\begin{align*}
\text{Li, NH}_3 & \quad \rightarrow \\
\text{N} & \text{N}_3
\end{align*}
\]

c) \[
\begin{align*}
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br}
\end{align*}
\]

1. \[
\begin{align*}
\text{NaNO}_2, \text{HCl} & \quad \rightarrow \\
\text{CN} & \quad \text{CN}
\end{align*}
\]

2. \[
\begin{align*}
\text{CuCN} & \quad \rightarrow \\
\text{CN} & \quad \text{CN}
\end{align*}
\]

d) \[
\begin{align*}
1 \text{ eq.} & \quad \rightarrow \\
\text{AlCl}_3 & \quad \rightarrow \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

e) \[
\begin{align*}
\text{SO}_3\text{H} & \quad \rightarrow \\
\text{NO}_2 & \quad \text{SO}_3\text{H}
\end{align*}
\]
5. (10 points) Chloromethylation is a highly useful reaction that produces a benzyl chloride (a useful species). Provide a mechanism for this reaction. Pay careful attention to your use of mechanism arrows. NOTE: As with most examples of EAS, the first step is the generation of a powerful electrophile, in this case by protonation of CH₂O.

This first part of this mechanism is a classical EAS reaction, the second step is classical S₉₁ (although S₉₂ is acceptable too).
6. (5 points) Circle the compound that is the most likely compound to produce the $^1$H NMR spectrum shown below.
7. (5 points) Large annulenes, like the [18]annulene below, are formally aromatic but do not exhibit the NMR hallmark of aromaticity (ring current) at high temperature. At low temperatures, the outer protons (H_a's) are quite far downfield (9.28 ppm) and the inner protons (H_b's) are shifted upfield (-2.99 ppm), but this difference disappears at elevated temperatures. Provide a viable explanation for why this happens. Do not exceed the space provided.

At high temperatures this compound twists to relieve the crowding of the H_b hydrogens. That breaks conjugation and disrupts aromaticity.

8. (10 points) Propose a structure for an alcohol that fits the following data: M^+ = 88, fragments at 73, 70, and 59.

Mass 59: Fits C_3H_7O. Compound likely includes a propyl and oxygen at a likely fragmentation point.
Mass 70: Fits C_5H_{10}. Loss of 18 from parent (loss of water) leads to pentene.
Mass 73: Loss of 15 (methyl) at a likely fragmentation point in parent.
9. (5 points) The $^1$H NMR spectrum for a compound with the molecular formula $C_8H_9Br$ is given below. Which of the structures below is most likely to have produced this spectrum? (circle one).

![NMR Spectrum Image]

10. (10 points) Show how the compound below can be made from benzene. Note: the product is a cyclohexane. Be sure to show the reagents needed for each step, the product of that step, then the reagents and products needed for the next step. *You do not need to draw mechanisms.*

![Chemical Reaction Diagram Image]

END OF EXAM