Before you begin this exam: First: You are allowed to have a calculator, a stencil, and 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. 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 EACH QUESTION CAREFULLY.

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1. (15 points) Classify each of the following compounds and ions as being either aromatic, antiaromatic, or neither.

![Chemical structures](image1)

AROMATIC  ANTIAROMATIC  AROMATIC

2. (5 points) When HCl is added to enol ethers (the reaction shown below), only one regioisomer is formed. Provide a brief explanation (in the space provided) for the regioselectivity of this reaction.

![Chemical structures](image2)

Look at the resonance forms!

This compound will protonate selectively at this position, not next to oxygen.
3. (10 points) Consider the reaction energy profile diagram below.

![Reaction Energy Profile Diagram]

a) Which of the products (A or B) is the kinetic product? B

b) Which of the products (A or B) is the thermodynamic product? B

4. (10 points) Would you predict that o-xylylene (shown below) would be a VERY GOOD or a VERY BAD Diels-Alder diene? Explain (within the space provided, please).

![o-xylylene]

a) This diene is locked in the s-cis conformation.

b) An aromatic ring is formed in the course of the Diels-Alder reaction. This provides extra driving force for the cycloaddition.
5. (30 points) Provide the expected products from the following reactions. If you believe that two products will be formed (such as ortho and meta isomers, 1,2 and 1,4 addition products, others), show both products. If you believe that no reaction will occur under the conditions given, write “NR.”

a) 
\[
\begin{align*}
\text{NCH}_3 & \quad \xrightarrow{\text{CO}_2\text{CH}_3} \\
\text{CH}_3 & \quad \text{N} \\
\text{CO}_2\text{CH}_3 & \quad \text{CO}_2\text{CH}_3
\end{align*}
\]

Note: Show stereochemistry

b) 
\[
\begin{align*}
\text{O} & \quad \xrightarrow{1 \text{ eq. Br}_2} \\
\text{O} & \quad \text{Br} \\
\text{O} & \quad \text{O} \\
\text{FeBr}_3 & \quad \text{FeBr}_3
\end{align*}
\]

c) 
\[
\begin{align*}
\text{O} & \quad + \quad 2 \text{ eq.} \quad \xrightarrow{1. \text{ Heat}} \quad \xrightarrow{2. \text{ H}_2, \text{Pd/C}} \\
\text{O} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

d) 
\[
\begin{align*}
\text{O} & \quad \xrightarrow{1. \text{ AlCl}_3, \text{CH}_3\text{C}l} \\
\text{O} & \quad \text{SO}_3\text{H}
\end{align*}
\]

e) 
\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{NO}_2 \quad \text{OCH}_3 \\
\text{SO}_3\text{H}_2\text{SO}_4 & \quad \text{H}_3\text{CO} \quad \text{NO}_2 \quad \text{OCH}_3
\end{align*}
\]

f) 
\[
\begin{align*}
\text{Br} & \quad \xrightarrow{1 \text{ eq. HBr}} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]
Problem 5 continued

6. (10 points) Show how the compound below can be synthesized from benzene and any needed reagents. Assume that you can separate ortho and para isomers, if both are formed in any step. Note: More than one step may be (IS) required.
7. (10 points) Treatment of benzene with 1-chloropropane and AlCl₃ leads the formation of both propylbenzene AND isopropylbenzene. Draw mechanisms for the formation of each of these products.
(10 points) Pyrrole reacts readily in the Friedel-Crafts acylation at both the 2- and 3-positions (fastest at the 2-position), while pyridine is quite unreactive to Friedel-Crafts acylation. Draw the intermediates involved in acylation at the 2-position of these heterocycles and explain why one is reactive and the other is not.

\[
\text{Pyrrole} \quad \text{Pyridine}
\]

This intermediate is relatively stable. The nitrogen (8e-) is able to stabilize the positive charge.

The intermediate is unstable. This last resonance form shows that the nitrogen is electron deficient and the lone pairs are unable to assist in stabilizing the cation.

Since the pyrrole-based intermediate is fairly stable, it forms readily (i.e. pyrrole is reactive). Since the pyridine-based intermediate is unstable, it forms only very reluctantly (i.e. pyridine is unreactive).