Note: Your exam should consist of 5 pages including this cover sheet.

From the Wikipedia site:

Antiaromatic molecules are cyclic systems containing alternating single and double bonds, where the pi electron energy of antiaromatic compounds is higher than that of its open-chain counterpart. Therefore antiaromatic compounds are unstable and highly reactive; often antiaromatic compounds distort themselves out of planarity to resolve this instability. Antiaromatic compounds usually fail Hückel's rule of aromaticity.

This article may be too technical for most readers to understand. Please improve this article to make it understandable to non-experts, without removing the technical details. Reason: This paragraph uses many technical terms, acronyms, and shorthand of A & B, making it hard to follow. (September 2010)

I guess the Wikipedians are suggesting that more people should take a few semesters of O-Chem...

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO
1. A C-D bond is harder to break than a C-H bond. Consequently, reactions in which C-D bonds are broken proceed more slowly than reactions in which C-H bonds are broken. What mechanistic information comes from the observation that perdeuterated benzene (C₈D₈) is brominated (Br₂/FeBr₃) at the same rate as normal benzene, C₈H₈? To answer this question, write down a free-energy diagram for the relevant chemical steps and tell me what's going on. 12 pts.

2. Classify each molecule as aromatic, antiaromatic, or nonaromatic. For the aromatic and antiaromatic molecules, give the number of pi electrons in the ring. 12 pts

![Molecules](image)

3. Provide syntheses for the following molecules, using benzene as your starting material. 12 pts

![Syntheses](image)
4. Predict the products. For each reaction, write down the major product(s) to be expected, indicating stereochemistry where appropriate. For the sake of clarity, please draw a circle around your final answer for each reaction. State "NR" if no reaction is to be expected. (4 pts each, 20 points total)

5. (a) Write all resonance structures for the arenium ions that result from electrophilic attack (use E+) on the ortho, meta, and para positions of aniline. Indicate the best contributing resonance structure for each series and use this to justify the known directing effect of the NH₂ group. (b) Employ the usual arguments, using annotated structures, to explain the stability/instability of key intermediates. (10 pts)
6a. The Pictet-Spengler reaction is a useful method for synthesizing biologically relevant molecules. A proton catalyzes the reaction. Draw the structure of the two likely reaction intermediates. 8 pts.

6b. What type of reaction is the Pictet-Spengler reaction? (4 pts)

7. Aside from the benzene ring, there is a Chapter 14 structural element to be found within the Pictet-Spengler substrate shown at the left-hand side of question 6a. What is it? What defines its chemical character? Use structures in your answer. No essays! 8 pts.

8. Carefully explain, using structures & diagrams, why azirines of structure A have never been isolated, whereas the isomeric azirines of structure B are well known. No essays! 8 pts.

9. Mononitration of ethylbenzene yields a substance with the following $^1$H NMR signals: 1.25 ppm (3H, triplet), 2.6 ppm (2H, quartet), 7.53 ppm (1H, triplet), 7.55 ppm (1H, doublet), 7.79 ppm (1H, triplet), 8.03 ppm (1H, doublet). Use the NMR data to assign the product's structure. 8 pts.
Chemistry 110b
FIRST EXAM
February 4, 2011

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