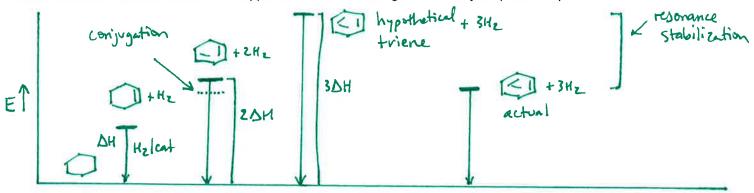
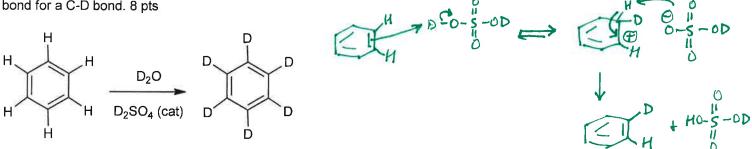
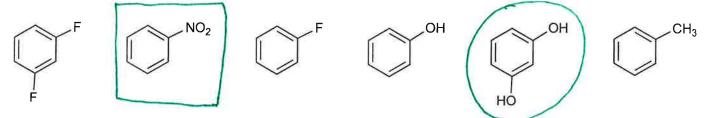
1. Explain, using a potential energy diagram, how hydrogenation data can be used to account for the stability of benzene. Exact numbers need not be used--use approximate relative energies to make your point. 10 pts.



2. Benzene-d<sub>6</sub> is a common NMR solvent. It is prepared commercially by heating benzene, D<sub>2</sub>O (heavy water), and catalytic amounts of deuterated sulfuric acid (D<sub>2</sub>SO<sub>4</sub>). a. Write a mechanism to show how this works for the replacement of one C-H bond for a C-D bond. 8 pts



b. You decide to start a company that makes deuterated aromatic compounds using this commercial method. You want to rush your first product to market as quickly as possible, and so you need a fast chemical reaction for your first production campaign. Which of the following compounds would react the most quickly? [identify with a circle] Which would react the most slowly? [identify with a square]. 8 pts



3. If propene is exposed to a strong base like n-BuLi, one of the methyl hydrogens is removed. On the other hand, if cyclopropene is treated the same way, one of the alkene hydrogens is removed. Use a molecular orbital analysis for each molecule to account for this difference in chemical behavior. 10 pts

South A A cyclopropene lost one of the CH2 protons, then an antiaromatic system is formed in very onlikely. recall the ally anion: - 1/2 resonance 3 Stabilized anion

4. Which of the hydrogen atoms shown below is more acidic? Explain your answer. 6 pts

Solution sulfonic acid R-s-oy produces resonance stabilized anion R-s-o expression point of the stabilized anion R-s-o expression expression of the stabilized of bot still not sufficient stabilization is here basic? Explain your answer 6 nts the prosent  $p|c_{n} < 0$ SO3H Н  $plc_a = 15$ 5. Which of the nitrogen atoms shown below is more basic? Explain your answer. 6 pts in class we learned pyridinism plks is 5.7 Osp3 Ð R-N-H R O SPZ love pair in sp2 (w/marened is character) are held more closely to the nucleus and ... tens basic. 6. The relative basicity of carbonyl oxygen atoms can be measured by studying the strength of their participation in hydrogen

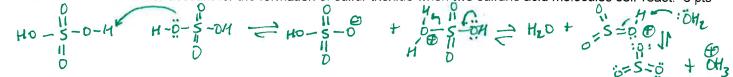
bonding with a reference hydrogen bond donor (like an OH group). Rationalize the observed order of basicities (larger numbers mean greater basicity). 10 pts consider aromatic character

of resonance structures O-reference anti-aromatic (O not very SO) Basicily of oxygen in creases w/ regative charge character of oxygen. H-bond :0:0 aromatic (0 has SO) 31.2 :0.0 117 t-Bu t-Bu

7. Propose a synthesis of the following molecule from benzene and any other reagents. 10 pts

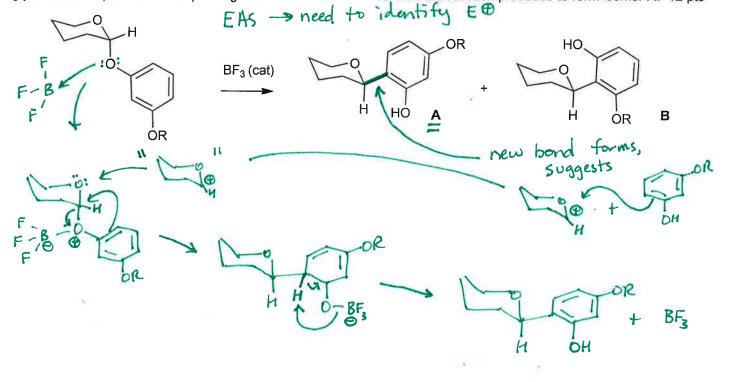
 $CO_2H$ Br NO<sub>2</sub> CO, H

8. Write down a mechanism to account for the formation of sulfur trioxide when two sulfuric acid molecules self-react. 8 pts



4

9. The following intramolecular rearrangement has been used in the synthesis of a class of compounds called C-aryl glycosides. Propose an arrow-pushing mechanism to account for how the reaction proceeds to form isomer A. 12 pts



10. Pyrrole can undergo EAS chemistry (e.g. nitration) to produce monosubstituted pyrroles **C** or **D**. Analyze the mechanism and intermediate structures to predict which isomer predominates. 12 pts

in class we learned that Pyrrole reacts w/ H@ on Carbon, not nitrogen () HNO3 That protonation was adjacent to N H CH3CO2H H C O2N H D	
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2. Classify each molecule as aromatic, antiaromatic, or nonaromatic. For the aromatic and antiaromatic molecules, give the numer of pi electrons in the ring. 12 pts

