Exam 1 Chem 431 Your name_____

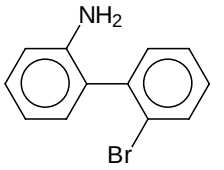
Fall '08 Student ID#_____

1. The first reaction you carried out was the *tert*-butylation of biphenyl. This reaction introduces one *tert*-butyl group to generate 4-tert-butylbiphenyl, followed by the introduction of a second *tert*-butyl group.

a. For the introduction of the first *tert*-butyl group, show a mechanism in as much detail as you can! Your mechanism should explain with resonance forms why the *tert*-butyl group enters predominantly in position 4. (8 pts)

b. *tert*-Butylations are reversible. Thus, 1-bromo-4-tert-butylbenzene can be converted to bromobenzene and a gaseous byproduct by heating with a catalytic amount of aluminum chloride. Propose a balanced reaction equation for this process, use structural formulas. (5 pts)

c. The *tert*-butylated biphenyl you prepared will serve as intermediate in the preparation of compound *a* below. Suggest a reasonable name for compound *a*! (5 pts)

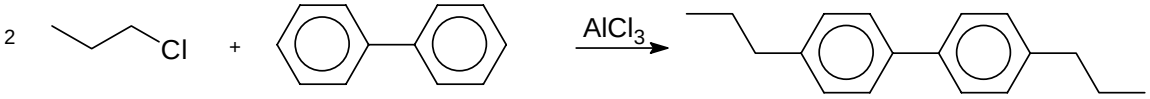


compound a

d. How could you prepare compound *a* from biphenyl? Clearly, you carried out the first step in this synthesis. Propose additional steps to prepare this compound, show reagents and key intermediates. (10 pts)

e. We used nitromethane as a solvent. What other solvents are commonly used for Friedel Crafts alkylations? Name at least one! (5 pts)

f. Chemists have attempted to adapt the synthesis you carried out to the preparation of compound b from biphenyl and 1-chloropropane as shown below, but were unsuccessful. What is the problem with this synthesis? (5 pts)

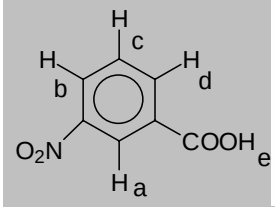


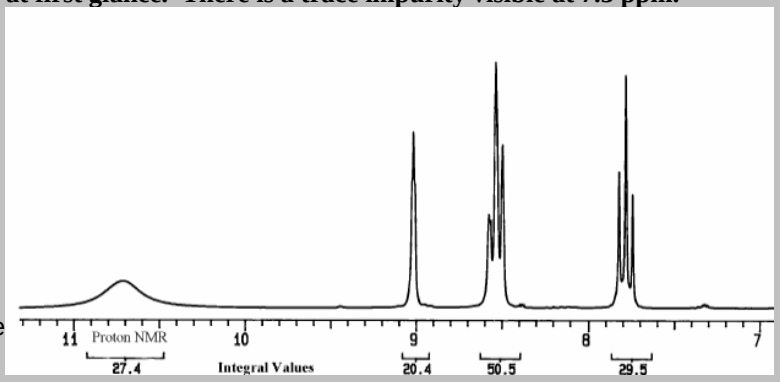
compound b

2. Please consider the attached spectrum of the aromatic region of 2-bromo-4-nitroaniline. Interpret this spectrum in as much detail as you can. Your interpretation should include: a) correlation of each multiplet with a specific proton in the molecule, b) a discussion of the purity of the sample – any indications of impurities? c) An explanation of the observed spin splitting patters. *I have provided a sample discussion below to indicate what I expect you to do.* (8 pts)

Sample discussion of the spectrum of 3-nitrobenzoic acid:

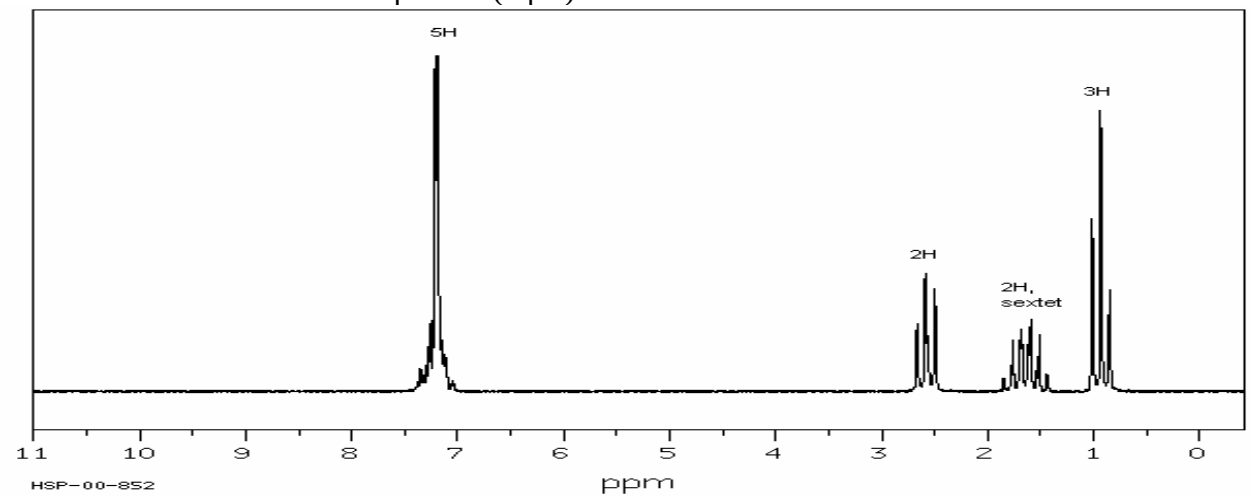
We see two multiplets and two singlets. The very broad singlet clearly corresponds to H_e and is broadened because this proton is exchangeable. The singlet at ~9 ppm belongs to H_a, it is slightly broadened by long range (4-bond) coupling to H_b and quite deshielded due to being flanked by the electron-withdrawing nitro and carboxylic acid groups. H_c is the most shielded and appears as triplet at ~7.8 ppm. H_b and H_d form two overpapping doublets at ~8.5 ppm, giving the misleading appearance of a triplet at first glance. There is a trace impurity visible at 7.3 ppm.



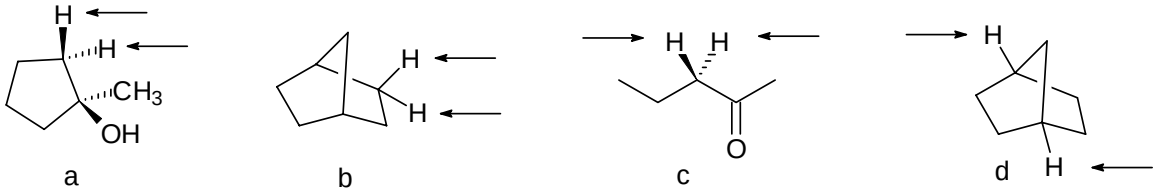


3. In each NMR experiment, you spin the sample you insert. What is the spinning good for? (5 pts)

4. The NMR spectrum belongs to a compound with sum formula C_9H_{12}. Suggest a structural formula for this compound! (8 pts)



5. What are the relationships of the following protons (state homotopic, heterotopic, enatiotopic or diastereotopic) 8 pts

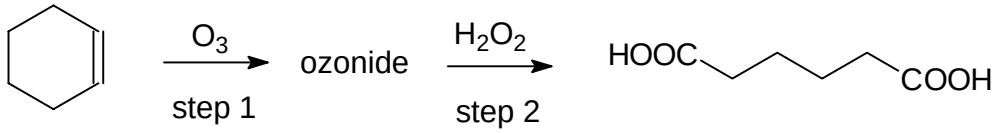


6. We are preparing 3-nitrophenyl phenyl iodonium iodide, by a) treating 1-iodo-3-nitrobenzene in sulfuric acid with potassium persulfate, b) adding benzene, and c) precipitating the product with potassium iodide.

a. Provide a balanced reaction equation for each step! Use structural formulas for organic compounds. (9 pts)

b. What happens in step b, upon addition of benzene? Show a reasonable mechanism for this step! (4 pts)

7. Several of you are converting cyclohexene to hexanedioic acid, by oxidation with ozone and further oxidation of the intermediate ozonide with hydrogen peroxide:

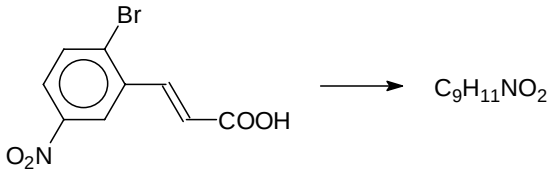


a. What is ozone? Show a <u>complete, valid</u> Lewis dot structure for the ozone molecule! (5 pts)

b. The ozone comes out of a box. What happens inside the box, how is the ozone made? A brief explanation will suffice. (5 pts)

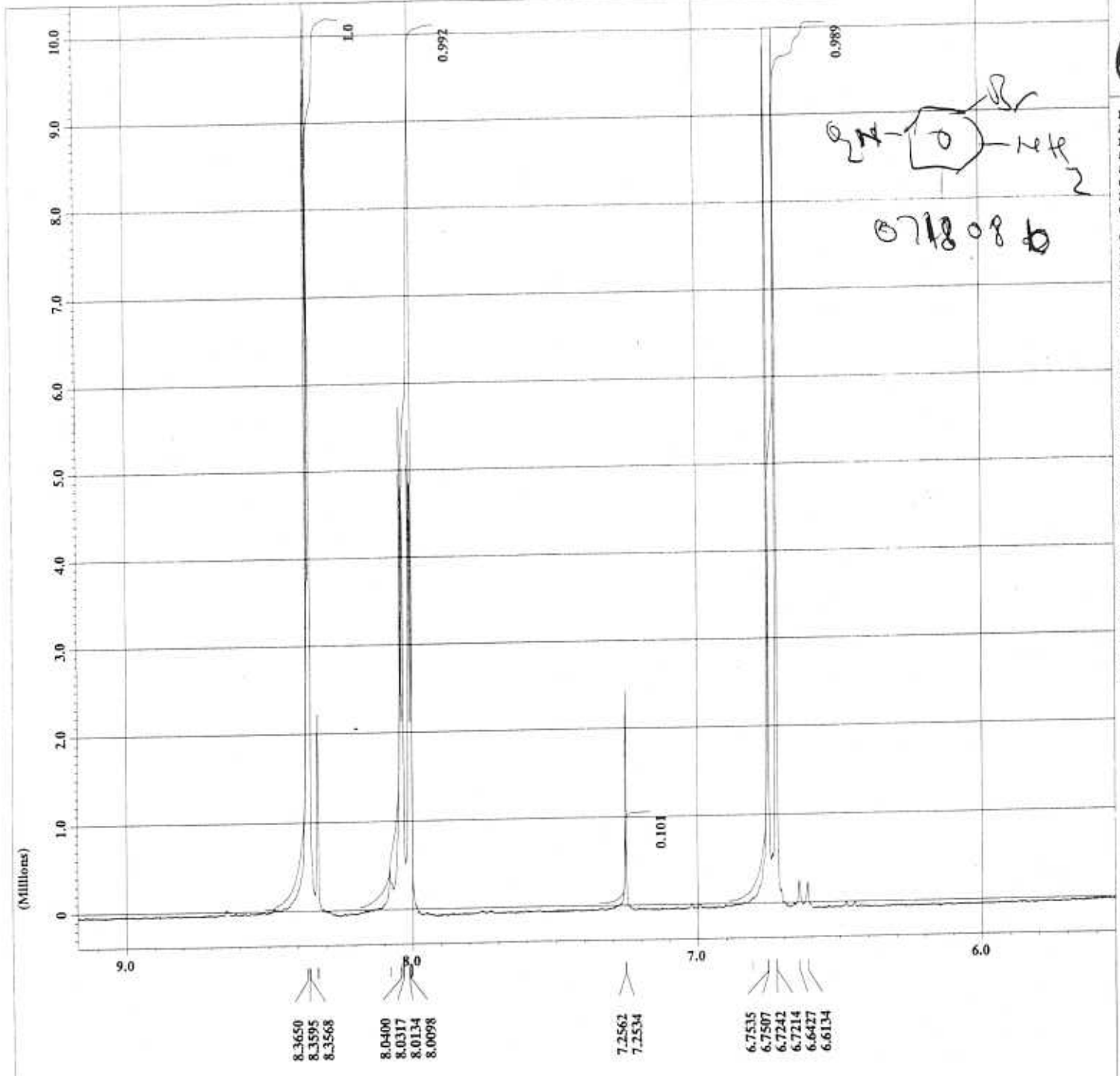
c. Show step 1, the formation of the ozonide, in mechanistic detail! Reminder: we discussed the fact that this reaction is based on two bipolar 2+3 cycloadditions. (8 pts)

8. The hydrogenation of 3-(2-bromo-5-nitrophenyl) propanoic acid with hydrogen over a palladium catalyst generated $C_9H_{11}NO_2$, as shown below:



a. Propose a structural formula for the product! (5 pts)

b. Clearly, the carbon-bromine bond was broken during this hydrogenation. Which catalyst could you use leave the bromine in place? (2 pts)



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