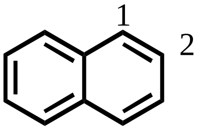
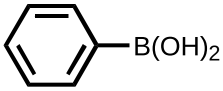
Chemistry 304B, Spring 1999 Problem Set 4

1. Draw resonance structures for the intermediate carbocations in the bromination of naphthalene, and account for the fact that naphthalene undergoes electrophilic bromination at C-1 rather than C-2



2. Account for the fact that phenyl boronic acid is nitrated to give mainly meta substitution. Draw the products and the mechanism, and account for the meta-directing influence of the $B(OH)_2$ group.



Phenyl boronic acid

3. Rank the compounds in each group in terms of their reactivity toward electrophilic substitution.

a. PhCl, o-dichlorobenzene, benzene
b. p-bromonitrobenzene, nitorbenzene, phenol
c. fluorobenzene, benzaldehyde, o-xylene

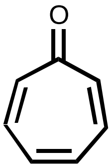
4. Assume you could achieve monomethylation with chloromethane and $AlCl_3$, and predict the major product with the following substrates:

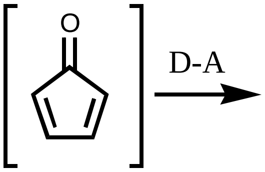
a. bromobenzene
b. p-chloroaniline
c. 2,4-dichlorophenol
d. benzoic acid

5. Would you expect the Friedel-Crafts reaction of benzene with R- 2-chlorobutane to yield predominantly a single stereoisomer or a racemic product? Write the mechanism and the product(s) and explain your analysis.

6. Cycloheptatrienone is a quite stable, "normal" ketone while cyclopentadienone is exceedlingly reactive, in, for example, a self-Diels-Alder reaction.

Draw the Diels-alder product, and rationalize the difference in reactivity.





7. Draw all the "good" resonance structures for phenanthrene and predict which is the shortest carbon-carbon bond length in the molecule.