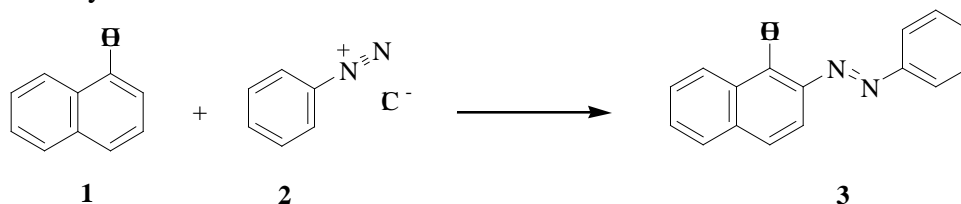


Problem Set #6

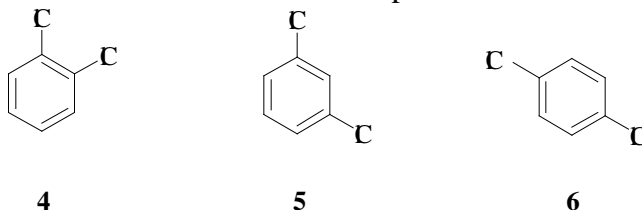
Chemistry 3231

October 9, 2001

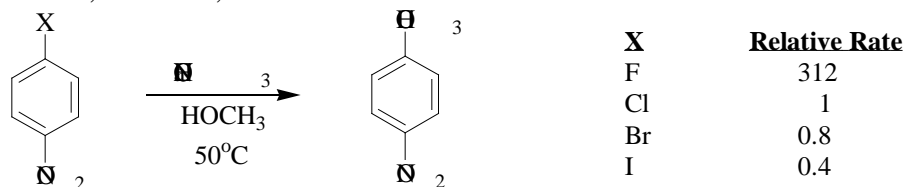
1. 1-Naphthol (**1**) reacts with benzenediazonium chloride (**2**) to produce 2-(phenylazo)-1-naphthol (**3**). The product is very strongly red and is a member of a class of compounds known as azo dyes. Write a reasonable mechanism for the formation of **3**.



2. Isomeric dichlorobenzenes (**4-6**) react with potassium amide (KNH_2) in liquid ammonia to give chloroanilines as products (i.e., one of the $-\text{Cl}$ groups is replaced by $-\text{NH}_2$). For each dichlorobenzene isomer write the possible chloroaniline products formed via the elimination-addition nucleophilic aromatic substitution (NAS) process. Be sure to carefully consider all possibilities in both the elimination and addition steps.



3. Recall that the order of halide leaving group ability is $\text{I} > \text{Br} > \text{Cl} \gg \text{F}$ (i.e., I^- is the best halide leaving group; F^- is the worst). In addition-elimination reactions of p-nitrohalobenzenes, however, the fluorobenzene reacts the fastest:



Explain this trend. (HINT: Carefully consider the what is going on in the rate determining step of the addition-elimination NAS mechanism.)

4. Two isomeric Meisenheimer complexes form on treatment of 2,4,6-trinitroanisole with sodium methoxide. Propose structures for both.
5. Which cyclic ketone, cyclohexanone (**7**) or cyclobutanone (**8**), would you expect to be more hydrated in the presence of water? Why?

