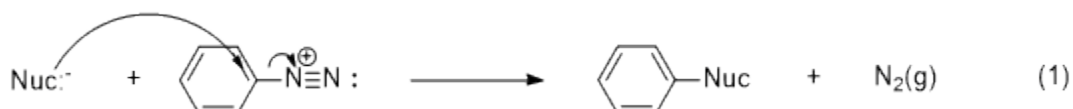
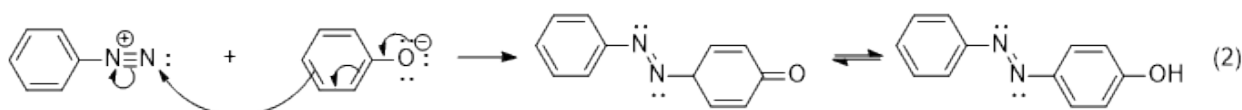


Experiment #4. Reactions of Benzenediazonium Salts: Preparation of 4-Iodonitrobenzene and an Azo Dye.**Relevant Reading:** Smith Chapter 25.13-25.16**Overview**

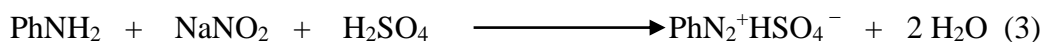
Benzenediazonium salts (ArN_2^+Y^-) are very useful for the synthesis of compounds, such as iodoarenes (ArI) and arenenitriles (ArCN), that are not easily available from electrophilic aromatic substitution reactions. The diazonio group (N_2^+) is a "super" leaving group that makes the attached carbon very electrophilic and susceptible to nucleophilic attack. Thus, benzenediazonium salts can undergo a variety of *nucleophilic aromatic substitution* reactions by nucleophiles such as iodide ion (eq 1, $\text{Nuc}^- = \text{I}^-$). These reactions are irreversible due to the fact that the formed N_2 gas rapidly bubbles out of solution.



The outer nitrogen atom of the diazonium salt is also an electrophilic site and can serve as the electrophilic atom in aromatic substitution reactions on activated benzene rings such as anilines and phenoxides (eq 2). The products of equation 2 are highly colored and referred to as azo dyes.



The diazonium salt is prepared using sodium nitrite and sulfuric acid from the corresponding aromatic amine in a process termed "diazotization" (eq 3).



In this experiment you will carry out the diazotization of *p*-nitroaniline. Half of the resulting *p*-nitrobenzenediazonium salt solution will be reacted with aqueous potassium iodide to form *p*-iodonitrobenzene. The other half will be reacted with 2-naphthoxide to form the well-known azo dye, Para Red.

Procedures

1. Diazotization of *p*-Nitroaniline. Dissolve 1.0 mL $\text{H}_2\text{SO}_4(\text{conc})$ in 10 mL H_2O in a 50-mL Erlenmeyer flask. Swirl the solution while adding 1.0 g *p*-nitroaniline. Chill the mixture on an ice bath. Prepare a solution of 0.5 g NaNO_2 in 4 mL H_2O . After the temperature of the *p*-nitroaniline- H_2SO_4 solution has reached about 5 °C begin a *slow* addition of the NaNO_2 solution. (Use a Pasteur pipet to add the solution one drop at a time.) The rate of addition should be slow enough so that the temperature of the reaction mixture never exceeds 10°C. (Above this

temperature the diazonium salt undergoes nucleophilic substitution by H₂O resulting in phenol formation.) Transfer 7.5 mL of the solution to another flask keeping both flasks on ice until use in the subsequent parts of this experiment.

2. Preparation of *p*-Iodonitrobenzene. Prepare a solution of 1.5 g KI in 30 mL H₂O. Add the KI solution dropwise and with stirring to one of the diazonium solutions from part 1. Collect the precipitate by vacuum filtration and wash it with a 2-3 mL of cold water. Recrystallize the product from 95% ethanol (using activated charcoal to decolorize the hot solution if necessary) and either allow it to air dry for one week or leave under vacuum on the Buchner for at least 10 min. Weigh the dried product, measure the mp and obtain the ¹H NMR spectrum. As always, turn in the product for grading and recycling in a small and fully-labeled zip-loc bag.

3. Preparation of Para Red. Prepare a solution of 0.50 g 2-naphthol in 5.0 mL 2.5 M NaOH. Cool the solution to at least 10 °C and then add it to the other diazonium solution from part 1. Stir the mixture for 5 min and then add 1 M H₂SO₄ to neutralize excess base (check for an acidic pH using litmus paper). Collect the solid by vacuum filtration, washing with cold water, and drying on the Buchner funnel for at least 10 min.

Assigned Questions

- (1) Not all of the positive charge in an arenediazonium salt is located on the nitrogen bonded to the ring (as shown in eq 1). Use resonance theory to explain why.
- (2) What is unusual/unexpected about the NMR spectrum of the iodo compound prepared in this experiment? Explain why the spectrum appears this way.