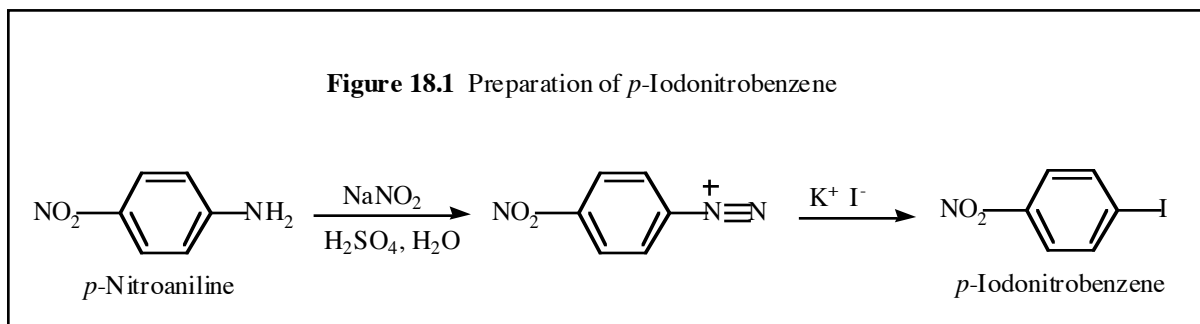


## Experiment 18

### Preparation of *p*-Iodonitrobenzene

In this experiment we will prepare *p*-iodonitrobenzene using a diazotization reaction similar to the one we just used in the methyl orange experiment but in this case we will add iodide as our nucleophile. This will replace the  $\text{N}_2^+$  substituent with evolution of nitrogen gas. We will recrystallize the product from isopropyl alcohol. The reactions are shown in Figure 18.1. For the mechanism of the formation of the diazonium salt, please refer to Figure 17.3, 16.4 or your textbook. A mechanism for this reaction is present in Appendix 18.1.



#### Physical Constants

Compound	Mol. Wt (g/mol)	Density (g/mL)	b.p. (°C)	m.p. (°C)
<i>p</i> -Nitroaniline	138.13	-	260/100 mm/Hg	149-151
<i>p</i> -Iodonitrobenzene	249.01	-	289	175-177
Sulfuric acid	98.09	1.840		
Potassium iodide	166.01		-	-
Sodium nitrite	69.00	2.170		271

#### Procedure:

We first prepare the diazonium salt from *p*-nitroaniline. Mix 10 g ice and 10 mL water in a 400 ml beaker. Slowly add 2.0 mL concentrated sulfuric acid. Cool the solution to 5 °C in an ice bath. Slowly add 1.25 g of *p*-nitroaniline in small portions using a piece of folded weighing paper as a funnel. Add a small portion with your spatula and then stir. Most of the *p*-nitroaniline should dissolve.

Prepare a solution of 0.63 g sodium nitrite dissolved in 5 mL  $\text{H}_2\text{O}$  in a 25 mL Erlenmeyer. When all of the solid has dissolved, cool the solution to 5 °C in an ice bath and then slowly add the sodium nitrite solution to the solution of the *p*-nitroaniline at such a rate so as to **maintain the temperature of the reaction below 10 °C**.

Keep the reaction mixture as cold as possible. Leave it in the ice bath at all times. Remember, you have just formed a diazonium salt and this is unstable if allowed to warm

to room temperature. When you have added all of the sodium nitrite solution, add a spatula tip of urea and stir. (This will react with any excess nitroso ion.)

Prepare a solution of 2.5 g of potassium iodide in 15 mL water in your 400 mL beaker. Slowly pour the diazonium salt solution into the potassium iodide solution with stirring. You will see lots of foaming at this point as the  $N_2$  gas is released. Pour a little of the diazonium salt solution and then stir and wait for the foaming to subside. As you wait, return the diazonium salt solution to the ice bath so as to keep it as cold as possible.

When all the diazonium salt has been added, wait for the foaming to subside and then cool the beaker in your ice bath. Collect the solid product that has formed on the Buchner funnel using suction filtration. Remember to wet the filter paper before filtering.

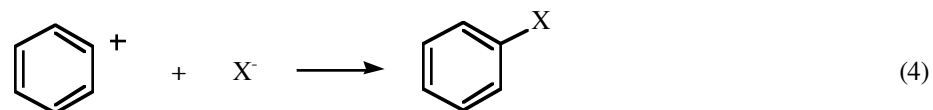
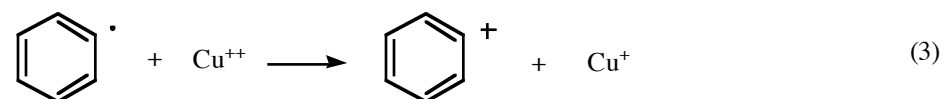
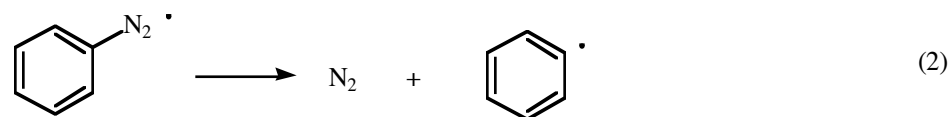
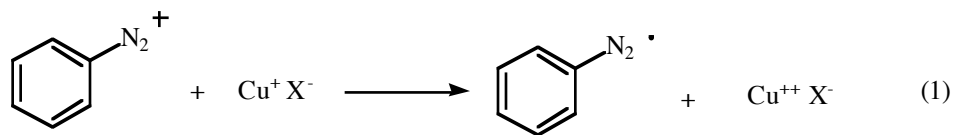
Recrystallize your product from isopropyl alcohol using approximately 20 mL/g of product. You will need around 50 mL in total but do not add all of this at once. Add about 2/3 of the projected amount, heat to boiling using a water bath and then continue adding isopropyl alcohol in small amounts (5-7 mL) until all of the material dissolves.

Collect the recrystallized product by suction filtration on the Buchner funnel (wet the filter paper this time with isopropyl alcohol, not water), weigh your sample and submit it in a vial. Calculate the percent yield, take the melting point range and turn in your Organic Yield Report Sheet.

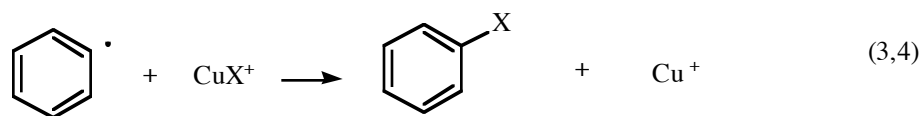
### **Appendix 18.1**

Though most text books state that the mechanism for these reactions is not fully understood, a plausible mechanism is provided by Professor Zavitsas in Figure 18.2. This is a chain reaction, not in radicals, but in copper.

**Figure 18.2** Mechanism of the Sandmeyer Reaction



Actually, steps 3 and 4 are one step, a ligand transfer.



With iodine you don't need the copper to be both an oxidizing and a reducing agent. The redox potentials of the I/ I<sub>2</sub> couple are just right to do both the oxidation and the reduction (see Figure 18.3).

**Figure 18.3** Mechanism of the Sandmeyer Reaction With Iodine

