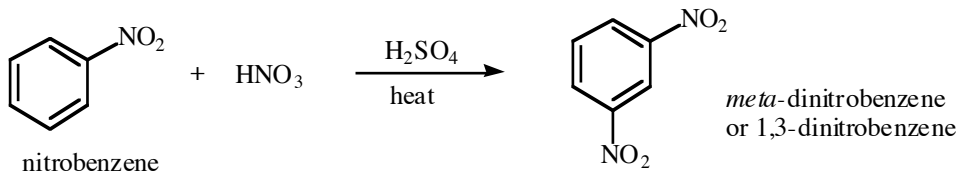
Experiment 10
Preparation of Dinitrobenzene

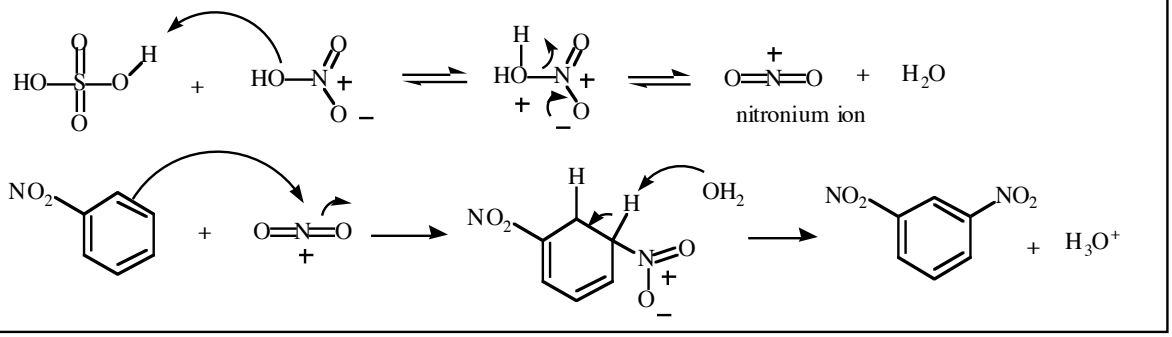
In this experiment you will prepare *meta*-dinitrobenzene from nitrobenzene by means of a nitration reaction. The overall reaction is shown in Figure 10.1.

Figure 10.1 Nitration of Benzene



This reaction is an example of an electrophilic aromatic substitution. The nitro group is a strong electron withdrawing group and directs the incoming substituent

Figure 10.2 Mechanism for Nitration Reaction



Physical Constants

Compound	Mol. Wt (g/mol)	Density (g/mL)	b.p. (°C)	m.p. (°C)
Nitrobenzene	123.11	1.196	210-211	5-6
Sulfuric acid	98.08	1.840	330	
Nitric acid	63.01	1.42	39-40	-97
m-Dinitrobenzene	168.11	1.368	297	88 - 90

Procedure:

Add 3 mL of nitrobenzene to a 125 mL Erlenmeyer flask and then add 8 mL concentrated sulfuric acid. Swirl the contents to ensure mixing.

CAUTION: Do not touch the nitrobenzene with your hands. It can be irritating to the skin. If you get any on your hands, wash them immediately and thoroughly under cold running water.

Prepare an ice bath for cooling. After the nitrobenzene has dissolved, add 5 mL of concentrated nitric acid **ONE mL AT A TIME USING THE MEDICINE DROPPER.** It is important that the reaction not get too hot. After adding the first ml, watch the temperature closely. It should not go ABOVE about 70 °C but it is also important that the temperature does go to at least 60 °C. Add the rest of the 5 mL nitric acid one mL at a time, keeping the

temperature between 60 – 70 °C. Ensure mixing by swirling the flask gently. Keep the ice bath handy in case the temperature gets too hot.

DO NOT ALLOW THE TEMPERATURE TO RISE ABOVE 70 °C. A POTENTIALLY DANGEROUS REACTION COULD OCCUR. IF THE TEMERATURE RISES ABOVE 70 °C SHOUT "LEAVE THE AREA IMMEDIATELY" AND DO SO!!!

Set-up a water bath in a 400 mL beaker. Fill it about 1/2 full of water and set it on your tripod. Heat to boiling using your Bunsen burner.

After the temperature in the Erlenmeyer flask starts dropping, place the flask in the boiling water bath in front of a vent and clamp securely in place so that the reaction mixture is submerged in the bath. Heat at boiling for 15 minutes. Stir the contents with your glass stirring rod.

Again, if you see any brown gas being evolved, please stand back and notify your neighbors and the TA. In some cases there can be a delayed exothermic reaction and there might be splattering of nitric acid out of the Erlenmeyer.

After 15 minutes of heating, remove the Erlenmeyer flask containing your product and pour its contents into a beaker containing 100 mL of ice cold water. Stir the solution as you pour it into the water. The product should form a solid yellow precipitate.

You will collect the solid product by suction filtration, using the same set-up that you used in Experiment 2 for the Adipic acid (see Figure 2.3). Use your Buchner funnel with a piece of the appropriately sized filter paper. Wet the filter paper first with a few mL of water and then connect the sidearm of the filter flask to one of the water aspirators in the lab. Filter the solid. The yellow crystals must now be washed three times with 15 mL portions of water to remove all traces of the nitric and sulfuric acids contaminating the product. Remember that you must disconnect the rubber tubing of the vacuum pump from the filter flask before adding the wash water. If the product forms into big lumps, transfer it to the watch glass, break it up into tiny pieces with the spatula and return it to the Buchner funnel for the washings.

You will purify your product using the technique of **recrystallization**, using ethanol as the solvent.

Recrystallization

Background:

This is a general technique for purifying a solid compound that you will use for the first time in this experiment and then many times in the second semester. The idea behind recrystallization is to dissolve your compound in a minimum of hot solvent and then to allow the solution to cool slowly to room temperature and then in an ice bath. Most compounds will dissolve more readily when the temperature of the solvent is raised and will be less soluble when the temperature is lowered. Ideally the compound will not be soluble in the given volume of cold solvent and will crystallize from the cooled solution and all impurities will remain dissolved in the recrystallization solvent (called the supernatant liquid). The product is then filtered through a Buchner funnel to remove the solvent and to provide pure product while the impurities remain behind in the supernatant liquid.

In this case we will use ethanol. Since ethanol is very flammable we will need to use a water bath heated on the hot plate. Do not use open flames.

The general procedure for a recrystallization is to place your solid material in a large test tube or Erlenmeyer flask and cover it with solvent. The solvent is then heated to its boiling point

in a hot water bath. Stir the mixture vigorously with a spatula. **BE SURE TO ALWAYS LEAVE THE SPATULA IN THE CONTAINER AS YOU HEAT.** The spatula acts like a boiling chip, preventing the hot liquid from boiling violently and spilling out of the container onto your bench top, thereby losing your product.

You want to be careful not to add too much solvent. If you add too much solvent, your product will not crystallize from solution when you cool the solution.

But note that if you use too much recrystallization solvent and you do not get crystals forming when you cool down the mixture, you can always recover from your mistake by boiling off some of the excess solvent in a water bath, reducing the total volume, and then cooling again slowly, first to room temperature and then in the ice bath.

Procedure for Recrystallization of Dinitrobenzene

Place all of your solid dinitrobenzene inside a medium test tube (or small Erlenmeyer flask). Use your spatula to scrape as much of it as possible from the damp filter paper. Cover the solid material with ethanol and then heat the test-tube in your boiling water bath so that the ethanol just begins to boil. Stir the mixture vigorously to aid in the dissolving process. Add more ethanol, a few drops at a time using your medicine dropper and each time you add more solvent be sure to bring the solution back to the boiling point by re-heating in the water bath. Dinitrobenzene is quite soluble in ethanol and you will need only about 2 mL ethanol per gram of product.

Work quickly and do NOT leave the test tube in the bath so long that your solvent begins to boil away. Otherwise you will start to DECREASE the volume of ethanol and your compound will not dissolve.

When all the solid material has dissolved (the solution should now be clear though it will not be colorless) remove it from the water bath and place it in your test tube rack. Allow it to cool slowly to room temperature. Do not stir the solution. The most pure crystals form when the solution is allowed to cool slowly, undisturbed.

When the solution has cooled to room temperature, place the test tube in an ice bath for a few minutes. Filter your product using the Buchner funnel. You can use a few mL of ice-cold ethanol to aid in the transfer of the solid from the test tube. Do not use more than 3-5 ml of the ethanol or you will lose some of your product.

If you do not see a precipitate forming, then this means that you have used too much of the ethanol. You will have to reduce the total volume by placing the test-tube back in the boiling water bath.

After the crystals dry, weigh your compound and calculate the percent yield. Turn in your sample and Yield Report to your teaching assistant. Be sure to get a melting point range and include this on your report sheet.