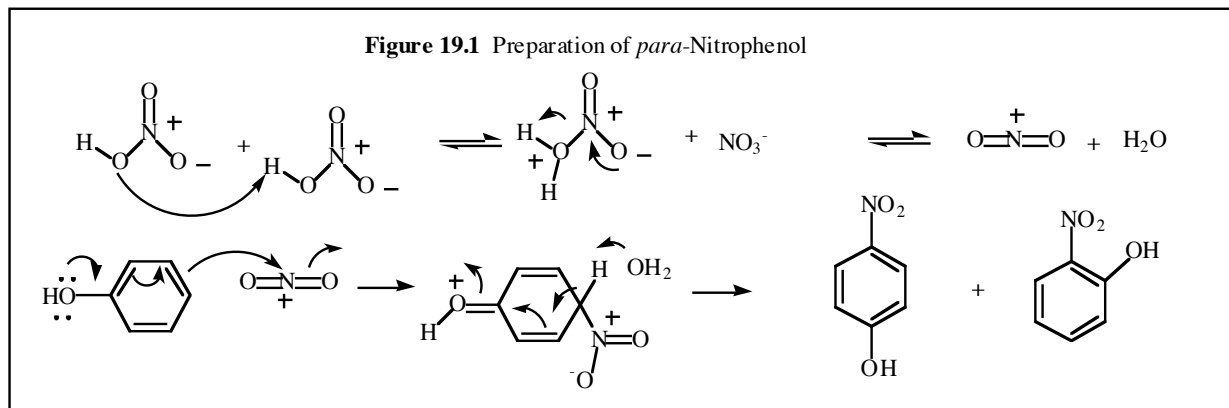


Experiment 19

Preparation of Nitrophenols

In this experiment we are going to prepare *p*-nitrophenol by means of a nitration reaction of phenol. We need to be very careful in this experiment not to get the phenol on our hands since it is very irritating to the skin. The reactions involved are shown in Figure 19.1.



Physical Constants

Compound	Mol. Wt (g/mol)	Density (g/mL)	b.p. (°C)	m.p. (°C)
Phenol	94.11	1.071	182	40-42
Nitric acid	63.01	1.490	-	-
<i>p</i> -Nitrophenol	139.11	1.270	279	113-115
<i>o</i> -Nitrophenol	139.11	1.495	214-215	44-45

Procedure:

Slowly add 10 mL concentrated nitric acid to 35 mL water in a 125 mL Erlenmeyer flask using your medicine dropper. (Note: the 250 mL round bottom flask may also be used, in which case, insert your thermometer into the small neck, using the red neoprene thermometer adapter to hold it securely).

Prepare an ice bath. The stockroom will provide pre-measured portions of phenol (8.0 g) in 2 mL of water. Be careful to not get the phenol on your skin. It is a mild irritant. It is advisable to wear disposable gloves for this experiment. They are provided by the stockroom.

Add the phenol slowly in 1 mL portions (15-20 drops) to the nitric acid solution. Maintain the temperature between 30-35°C. As you add each portion, swirl the flask to ensure thorough mixing. The reaction is exothermic and you will need the ice bath for cooling the reaction mixture. When all the phenol has been added, rinse the test tube with 1 mL of water and add this rinse to the reaction mixture if needed. Allow the reaction mixture to stand for 10 minutes. The reaction mixture becomes very dark.

After 10 minutes, pour the dark, oily mixture into a separatory funnel. In order to facilitate this transfer, it is sometimes useful to warm the flask so that the thick, viscous oil will flow more easily into the separatory funnel. Drain the dark oily layer on the bottom into your 250 mL round bottom flask. (You can also use your 100 mL round bottom flask). Sometimes it is very difficult to see where the bottom layer ends. You can drain off a small portion and then add 10-15 mL water and swirl the separatory funnel. Drain off a small portion of the oily solution and add 10 mL additional water. Usually at this point it is possible to see a clear separation between the two layers.

This is a convenient place to stop if you are out of time. Usually this experiment takes more than one laboratory period to complete.

Add 75 mL of water to the 250 mL flask and mark the total volume with a marking pen on the outside of the flask. (Note: if you are using the 100 mL flask then you should add only about 30 mL water. The general rule is to never fill a reaction or distillation flask more than one-half full. If you are using the 100 mL flask you will need to add an additional 30 mL water after you have distilled the first 30 mL. See below.) Set-up your apparatus for a simple distillation, using 2 ground glass stoppers in the two extra joints of the three-necked round bottom, the three-way adapter with your thermometer adapter (ground glass + rubber adapter) and thermometer, your condensing column with water hoses, your vacuum adaptor and 100 mL round bottom flask as the receiving flask (see Figure 3.3 for reference but note that you are using a 250 mL 2-necked round bottom flask or a 100 mL 3-necked round bottom flask. Since you are distilling only water, it is safe to use a Bunsen burner as a heat source but you should use the wire gauze to help distribute the flame evenly).

Add 30 mL additional water and begin distilling. You will see a yellow liquid coming over along with the water. This is *ortho*-nitrophenol. You must be careful because it can solidify in the condensing column and block the column. **YOU DO NOT WANT TO HEAT A CLOSED SYSTEM!!!** Usually it is necessary to turn off the cold water going to the condensing column at some point so that the solid *ortho*-nitrophenol can melt and slide down into your receiving flask. When this happens, turn the water back on. Otherwise you will start to see steam coming out of your vacuum adaptor.

If the total volume in your distilling flask falls below the 75 mL mark, then turn off the heat, add 20-30 mL more water and continue your distillation until no more yellow oil comes over. The yellow oil will solidify. Collect it by filtration, grind it with a mortar and pestle and let it dry. Obtain the weight and calculate the percent yield as if the theoretical yield were 100% *ortho*. Take the melting point.

To isolate the *para*- isomer, adjust the volume of the residual liquids in the distilling flask to a total of 75 mL. You may need to remove more water by distillation or to add more water. Add 0.5 g of decolorizing charcoal to the residual liquid and reheat to boiling for one minute. Filter into your 400 mL beaker using a coarse fluted filter paper and your stemless funnel. You want to work as quickly as possible so that the solid *para*-nitrophenol does not solidify/crystallize on the filter paper. All you are trying to remove at this point is the charcoal. Many types of colored impurities will adhere to the charcoal and be removed by filtration.

Once you have filtered off the charcoal, cool the 400 mL flask as rapidly as possible in order to obtain crystals. Sometimes this can be tricky. Collect the crystals by suction filtration, dry them, get the weight and melting point and calculate the percent yield of each product.

You can easily remove the oily residue on your glassware using dilute sodium hydroxide solution. Remove any larger pieces of the tar-like residue using your spatula, then add a few mL of dilute NaOH and swirl the flask, using your brush. Flush with clean water. Please leave your glassware CLEAN when you check out of the lab.