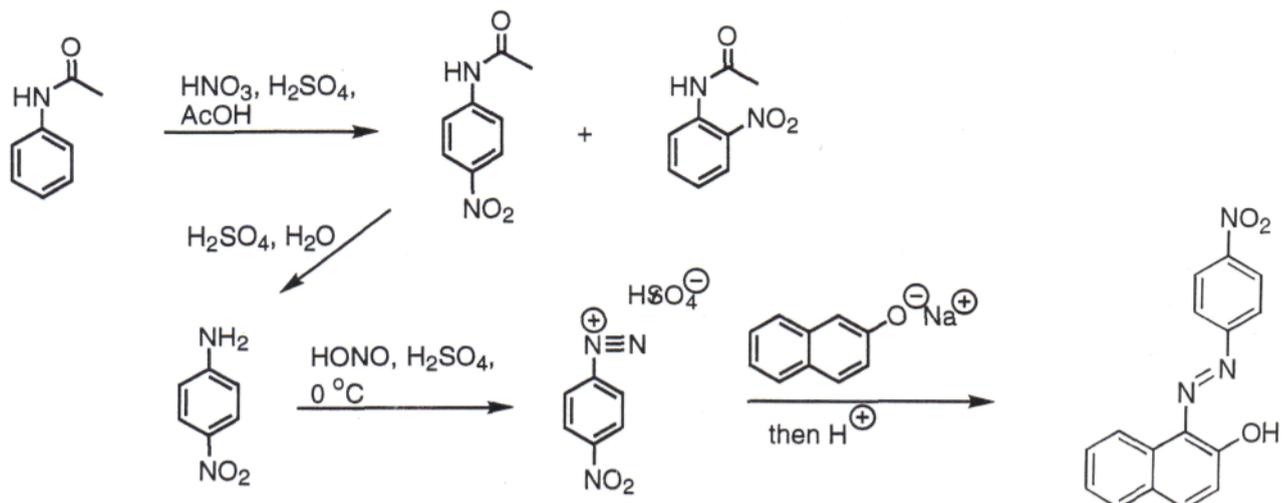


Synthesis of Para Red, part 1

In this lab, you prepare *p*-nitroaniline by the nitration of acetanilide and subsequent hydrolysis of the nitration product. You will then diazotize this compound and use the diazonium salt to synthesize the dye Para Red. You will also dye some fabric by conducting the last step of the synthesis with the fabric in the reaction mixture.



Preparation of *o*- and *p*-nitroacetanilide:

Add 12.0 g of acetanilide to 22 mL of glacial acetic acid in a 125 mL erlenmeyer flask. Carefully pour 22 mL of concentrated sulfuric acid into this mixture while stirring it constantly. The mixture will become warm and the acetanilide will dissolve. Place the flask in an ice bath to cool to $5 - 10\text{ }^\circ\text{C}$.

Meanwhile, prepare a solution of 8 mL of concentrated nitric acid and 5.3 mL of concentrated sulfuric acid. Carefully add this solution dropwise to the acetanilide solution with stirring. Control the rate of addition so that the temperature of the solution does not rise above $20\text{ }^\circ\text{C}$. After all the nitric acid solution has been added, let the reaction mixture stand at room temperature for 20 min (it may be necessary to periodically put it in an ice bath to keep the temperature below $30\text{ }^\circ\text{C}$ during this time).

After the 20 minutes is over, carefully pour the reaction mixture into 100 mL of cold water containing about 50 g of ice. The solid that precipitates is a mixture of *ortho*- and *para*-nitroacetanilide. Allow this mixture to stand for 5 min, stirring occasionally.

Collect the solid by vacuum filtration, and discard the filtrate. Wash the precipitate with cold water until the last portion of the filtrate is only slightly acidic (pH 5 -6). Save and combine your aqueous washings, because they contain the *ortho* product.

To purify the *para* product, recrystallize the solid from ethanol. Record the mp, IR and ^1H NMR spectra.

To isolate the *ortho* product, cool the combined aqueous filtrates in an ice bath and collect the yellow needle-like crystals by vacuum filtration. Record the mp, IR and ^1H NMR spectra.

Synthesis of *p*-nitroaniline:

This procedure is written for 8.8 g of *p*-nitroacetanilide. If you have less than 8.8 g, you will need proportionally adjust the quantities of all reagents in this procedure (and probably subsequent procedures); alternatively, you may repeat the above experiment to try to get a better yield (or at least more material).

Add 8.8 g of the *p*-nitroacetanilide and 22 mL of water to a 100 mL round-bottom flask. Slowly add 22 mL of concentrated sulfuric acid while swirling the flask. Reflux the mixture for 30 min. When the hydrolysis is complete, a 1 mL portion of the reaction mixture will be soluble in 5 mL of water.

Cool the reaction mixture and pour the contents into a mixture of 50 g ice in 75 mL of water. Slowly add an excess of 9 M sodium hydroxide solution until the pH of the mixture reaches 4 -5. During the addition of the sodium hydroxide, the mixture will get hot and should be well-stirred. The resulting precipitate is *p*-nitro aniline. Cool the mixture in an ice bath and collect the crystals by vacuum filtration. Wash the solid 4 times with 75-mL portions of water to remove any acid and inorganic salts.

Determine the melting point, and recrystallize the product from ethanol if necessary. Record the mp, IR and ¹H NMR spectra of the pure product.

Synthesis of Para Red, part 1

Preparation of *o*- and *p*-nitroacetanilide:

Balanced equation (including all reagents):

compound	amount used	m. w.	moles used	physical data (density, mp, etc., as necessary)

Amount of product obtained:

Calculation of percent yield:

Relevant spectral data and assignments:

Preparation of *p*-Nitroaniline

Balanced equation (including all reagents):

compound	amount used	m. w.	moles used	physical data (density, mp, etc., as necessary)

Amount of product obtained:

Calculation of percent yield:

Relevant spectral data and assignments:

Synthesis of Para Red, part 2

Diazotization of *p*-nitroaniline:

Caution: Diazonium salts are explosive if allowed to dry out, and they decompose if allowed to become warm. Keep the diazonium salt solution in an ice-water bath while you are doing these procedures. Do NOT do this procedure on a larger scale than indicated below.

Place a solution of 5 mL of concentrated sulfuric acid in 50 mL of water in a 250 mL flask. Swirl the solution while adding 5.0 g of *p*-nitroaniline. Place the flask in an ice bath to cool to 5 - 10 °C.

While swirling the mixture, slowly pour in a solution of 2.5 g of sodium nitrite in 10 mL of water. Keep the temperature of the reaction under 10 °C in an ice/salt water bath by adjusting the rate of addition of the sodium nitrite solution. Continue to keep the ice-water bath under 10 °C so that the diazonium salt does not decompose before you are ready to use it in the following procedures.

Do **not** attempt to characterize the salt.

Dyeing Cloth Samples with Para Red:

Place 0.5 g of 2-naphthol in a beaker containing 100 mL of hot water. Add 2.5 M NaOH solution dropwise while swirling the mixture until about three-fourths of the 2-naphthol dissolves. (A little more than 1 mL of NaOH should suffice.) It is important not to add too much alkali because it may cause your fabric to disintegrate.

Dilute 5 mL of the cold diazonium salt solution with 15 mL cold water. Thoroughly wet a sample of cotton cloth with the diluted solution for a few minutes using a stirring rod to work it about. Remove the cloth with forceps and drain of some of the excess solution by dragging the cloth along the inside edge of the beaker. Add the cloth to 50 mL of an alkaline 2-naphthol solution. After several minutes, remove the cloth and rinse it repeatedly with water.

Synthesis of Para Red:

Dissolve 2.7 g of 2-naphthol in 50 ml of 2.5M NaOH solution. Cool the solution to 10 °C by adding crushed ice. Carefully pour this solution into the flask containing the remainder of the diazonium salt, while swirling. Continue to swirl the mixture vigorously for a few minutes, then acidify it with 1 M sulfuric acid. Collect the red precipitate by vacuum filtration. Wash the product with water under vacuum filtration and allow it to air-dry. Because Para Red decomposes upon melting, you should not obtain its melting point.

Record IR and ¹H NMR spectra of the pure product.

Synthesis of Para Red, part 2

Preparation of Para Red:

Balanced equation (including all reagents):

compound	amount used	m. w.	moles used	physical data (density, mp, etc., as necessary)

Amount of product obtained:

Calculation of percent yield:

Relevant spectral data and assignments: