The Synthesis of Azo Dyes

INTRODUCTION

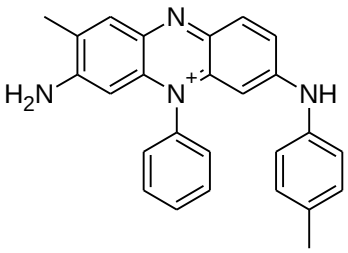
Human's love of color reaches back almost to prehistoric times, yet it is not actually until the modern era that the full range of the rainbow has been accessible to the majority of people in their clothes and other textiles. Ancient or medieval times have often been described as being quite splendid with their "Tyrian Purple" and medieval scarlet, but closer examination shows that some of these colours were quite dull by today's standards.

EARLY HISTORY

The history of dyeing can be divided into two great periods, the "pre-aniline," extending to 1856 and the "post-aniline" period. The former was characterized by a rather limited range of colors that were based on dye-producing animals and plants. The main vegetable dyes available were extracted from madder root (Asia and Europe), producing a brilliant red and leaves of the indigo plant (India), yielding the blue dye still used today in jeans. Among the most important animal based dyes is the famous and expensive "Tyrian Purple" which was obtained from the small shellfish *nurez.* We have the ancients' word that this dye was unbelievably beautiful, but evidence taken from ancient samples prove that it ranges through a rather uninspiring series of reds and purples. After seeing it, we wish that Homer had written about some of today's inexpensive coal-tar purples and reds. **A** far more beautiful natural color was introduced to Europe from Mexico in 1518, the brilliant scarlet dye cochineal, which had been produced from tiny lice which infest certain types of cactus.

MODERN HISTORY

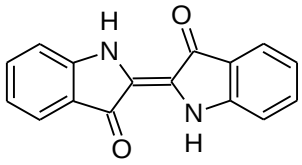
Aniline (C_6H_5-NH_2) became available from coal tar in the 19^{th} century and in 1856, William Henry Perkin at the age of 17 used it in the synthesis of Mauveine (a mixture of 4 compounds, one of which is shown below). The era of synthetic dyes was born.



Structure of Mauveine A

Soon thereafter, the main component of the dye in the madder root, Alizarin, was isolated by Carl Graebe and Carl Liebermann, prepared in the lab and the process commercialized. Starting

in 1865, recognizing the potential of synthetic dyes, Adolph von Baeyer researched the synthesis of indigo and determined its structure and first synthesis in 1870.

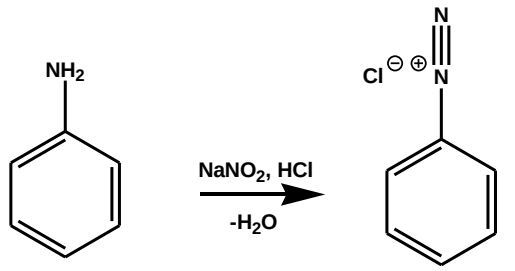


Structure of Indigo

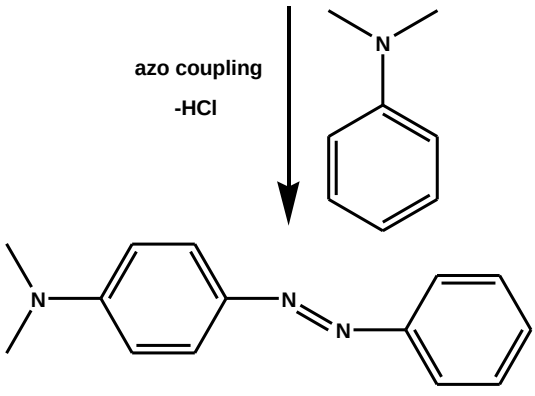
In 1897 the large scale industrial synthesis of indigo started and rapidly reached 10,000 tons a year, completely replacing the agricultural production.

SYNTHESIS

Today's experiments deal with a class of compounds called Azo dyes, compounds that contain two aromatic fragments connected by a N=N double bond. You may have encountered these in chemistry experiments as they are typical pH indicators. Methyl yellow, methyl orange, methyl red, congo red and alizarine yellow are some of the examples. They are straightforward to make and of industrial importance. Azo dyes are prepared in a two step reaction, the first being the synthesis of an aromatic diazonium ion from an aniline derivative. The next step is coupling of the diazonium salt with an aromatic compound (shown below is the preparation of methyl yellow). The colours of azo dyes include different shades of yellow, red, orange, brown, and blue.



diazonium salt



methyl yellow

Each group is assigned a different coupling reaction and all of the dyes synthesized will be compared at the end of the lab session.

Safety

Personal protective equipment including safety goggles, gloves and a lab coat must be worn at all times during the experiment. Long pants should be worn along with close-toed shoes. No food or drink is allowed in the lab. Always work in the fumehood. Be careful when handling the products, they are deeply coloured and will stain your skin and cloth for a long period of time. Do not wipe gloves on lab coats.

Procedures

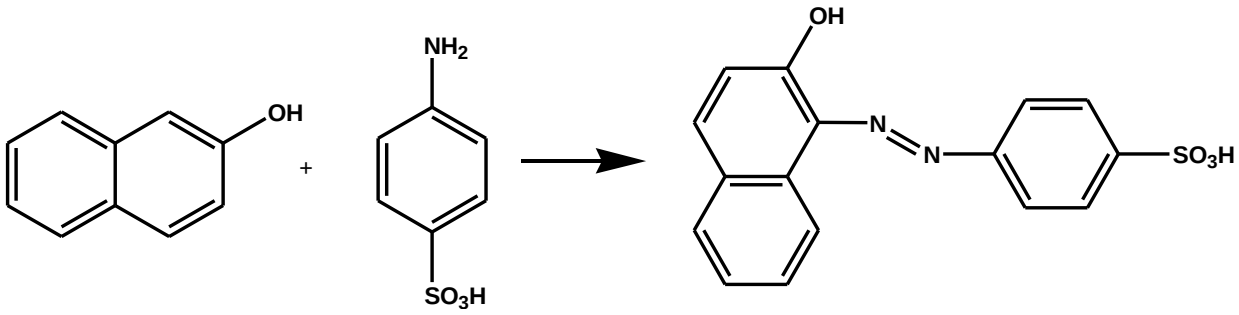
The stoichiometry (a 1:1 mole ratio) must be kept the same and due to changing molecular weights of the starting materials, different amounts of starting materials are used so there are separate procedures for each combination. The literature reference contains 16 different combinations but one of the starting materials is very expensive and we found that the resulting colours are not very different from the others. In the reaction schemes shown below, we have summarized the two step process into one scheme, for fully balanced, stepwise equations see above.

References

Gung, B.W., Taylor, R.T.; **2004**. *J. Chem. Ed.*, *81*, 1630.

Decelles, C.; **1949**, *J. Chem. Ed.*, *26*, 583.

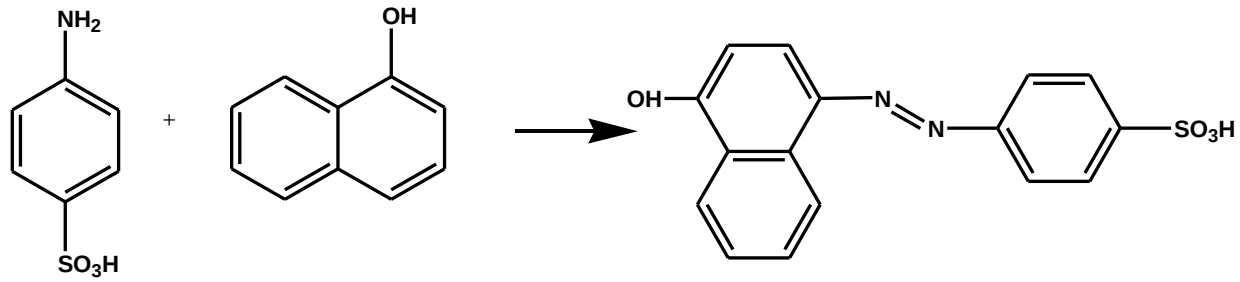
Experiment 1: Coupling between 2-naphthol and 4-aminobenzenesulfonic acid



Procedure

1. In test tube A, add approximately 0.5 mL of conc. HCl and place in an ice water bath.
2. In test tube B, place 0.49 g (2.8 mmol) of sulfanilic acid, 0.13 g of sodium carbonate (Na_2CO_3), and 5 mL of water and place in a hot water bath until a clear solution is obtained.
3. In test tube C, prepare a solution containing 0.2 g of sodium nitrite ($NaNO_2$) and 1 mL of water.
4. Remove test tube B from the hot water bath and pour the contents all at once from test tube C into test tube B.
5. Add the contents from test tube B to test tube A and place in an ice water bath until a significant amount of solid has precipitated.
6. In a 25 mL RBF, add 0.38 g (2.6 mmol) of 2-naphthol, 2 mL of 2.5 M NaOH and a magnetic stir bar and place in an ice-water bath. Turn on the stirrer and ensure the magnetic stir bar is working.
7. Add the contents of test tube A to the RBF while stirring and continue stirring and cooling the reaction for 10 minutes.
8. Remove the RBF from the ice water bath and heat the reaction using a thermowell until boiling commences (check with the instructor to ensure the set-up is correct).
9. Add 1 g of sodium chloride (NaCl) and continue heating until dissolved.
10. Stop stirring the reaction and cool to room temperature, then place in an ice water bath for 15 minutes.
11. Filter the solid using vacuum filtration with a Buchner funnel and wash with a saturated NaCl solution.
12. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

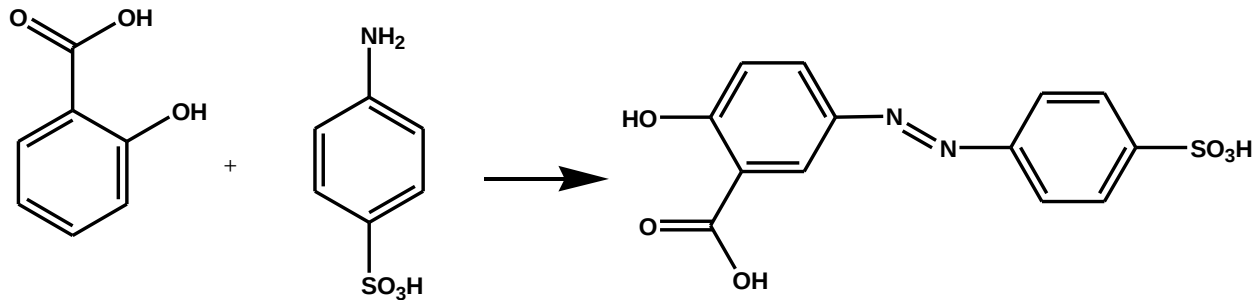
Experiment 2: Coupling between 1-naphthol and 4-aminobenzenesulfonic acid



Procedure

1. In test tube A, add approximately 0.5 mL of conc. HCl and place in an ice water bath.
2. In test tube B, place 0.49 g (2.8 mmol) of sulfanilic acid, 0.13 g of sodium carbonate (Na_2CO_3), and 5 mL of water and place in a hot water bath until a clear solution is obtained.
3. In test tube C, prepare a solution containing 0.2 g of sodium nitrite ($NaNO_2$) and 1 mL of water.
4. Remove test tube B from the hot water bath and pour the contents all at once from test tube C into test tube B.
5. Add the contents from test tube B to test tube A and place in an ice water bath until a significant amount of solid has precipitated.
6. In a 25 mL RBF, add 0.38 g (2.6 mmol) of 1-naphthol, 2 mL of 2.5 M NaOH and a magnetic stir bar and place in an ice-water bath. Turn on the stirrer and ensure the magnetic stir bar is working.
7. Add the contents of test tube A to the RBF while stirring and continue stirring and cooling the reaction for 10 minutes.
8. Remove the RBF from the ice water bath and heat the reaction using a thermowell until boiling commences (check with the instructor to ensure the set-up is correct).
9. Add 1 g of sodium chloride (NaCl) and continue heating until dissolved.
10. Stop stirring the reaction and cool to room temperature, then place in an ice water bath for 15 minutes.
11. Filter the solid using vacuum filtration with a Buchner funnel and wash with a saturated NaCl solution.
12. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

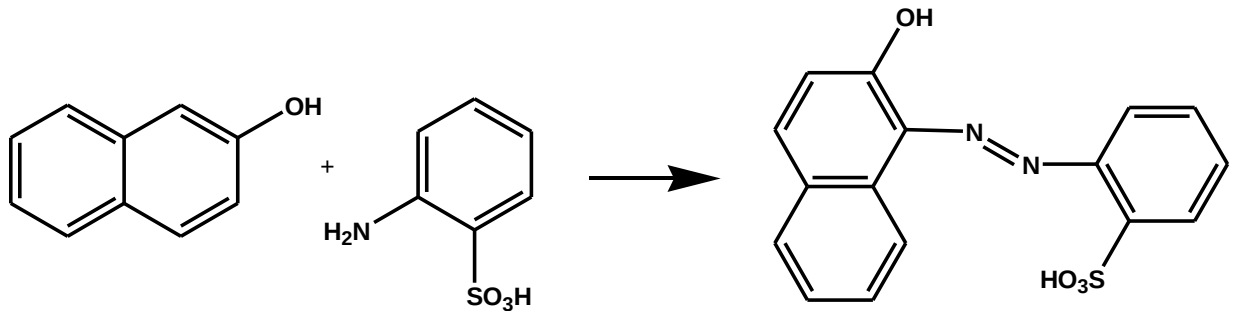
Experiment 3: Coupling between salicylic acid and 4-aminobenzenesulfonic acid



Procedure

1. In test tube A, add approximately 0.5 mL of conc. HCl and place in an ice water bath.
2. In test tube B, place 0.49 g (2.8 mmol) of sulfanilic acid, 0.13 g of sodium carbonate (Na_2CO_3), and 5 mL of water and place in a hot water bath until a clear solution is obtained.
3. In test tube C, prepare a solution containing 0.2 g of sodium nitrite ($NaNO_2$) and 1 mL of water.
4. Remove test tube B from the hot water bath and pour the contents all at once from test tube C into test tube B.
5. Add the contents from test tube B to test tube A and place in an ice water bath until a significant amount of solid has precipitated.
6. In a 25 mL RBF, add 0.36 g (2.6 mmol) of salicylic acid, 2 mL of 2.5 M NaOH and a magnetic stir bar and place in an ice-water bath. Turn on the stirrer and ensure the magnetic stir bar is working.
7. Add the contents of test tube A to the RBF while stirring and continue stirring and cooling the reaction for 10 minutes.
8. Remove the RBF from the ice water bath and heat the reaction using a thermowell until boiling commences (check with the instructor to ensure the set-up is correct).
9. Add 1 g of sodium chloride (NaCl) and continue heating until dissolved.
10. Stop stirring the reaction and cool to room temperature, then place in an ice water bath for 15 minutes.
11. Filter the solid using vacuum filtration with a Buchner funnel and wash with a saturated NaCl solution.
12. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

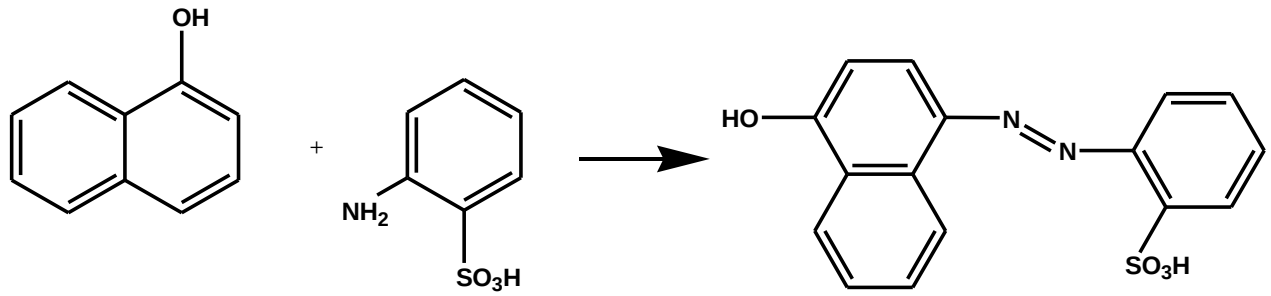
Experiment 4: Coupling between 2-naphthol and 2-aminobenzenesulfonic acid



Procedure

1. In test tube A, add approximately 0.5 mL of conc. HCl and place in an ice water bath.
2. In test tube B, place 0.49 g (2.8 mmol) of aniline-2-sulfonic acid, 0.13 g of sodium carbonate (Na_2CO_3), and 5 mL of water and place in a hot water bath until a clear solution is obtained.
3. In test tube C, prepare a solution containing 0.2 g of sodium nitrite ($NaNO_2$) and 1 mL of water.
4. Remove test tube B from the hot water bath and pour the contents all at once from test tube C into test tube B.
5. Add the contents from test tube B to test tube A and place in an ice water bath until a significant amount of solid has precipitated.
6. In a 25 mL RBF, add 0.38 g (2.6 mmol) of 2-naphthol, 2 mL of 2.5 M NaOH and a magnetic stir bar and place in an ice-water bath. Turn on the stirrer and ensure the magnetic stir bar is working.
7. Add the contents of test tube A to the RBF while stirring and continue stirring and cooling the reaction for 10 minutes.
8. Remove the RBF from the ice water bath and heat the reaction using a thermowell until boiling commences (check with the instructor to ensure the set-up is correct).
9. Add 1 g of sodium chloride (NaCl) and continue heating until dissolved.
10. Stop stirring the reaction and cool to room temperature, then place in an ice water bath for 15 minutes.
11. Filter the solid using vacuum filtration with a Buchner funnel and wash with a saturated NaCl solution.
12. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

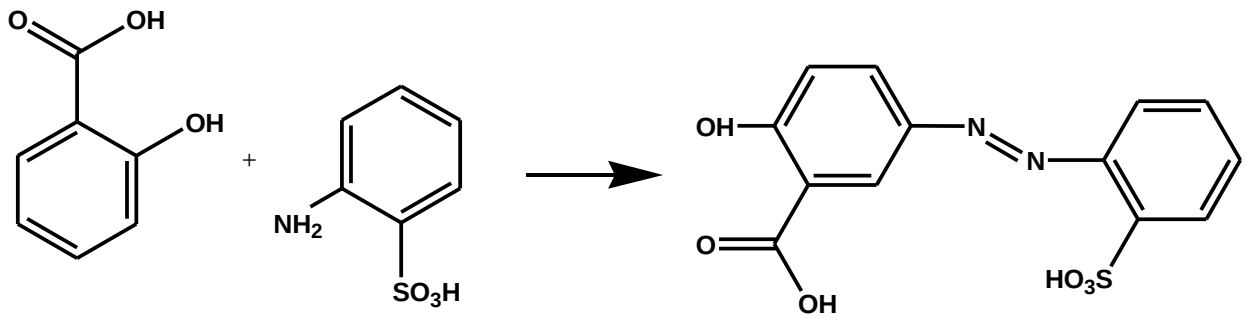
Experiment 5: Coupling 1-naphthol between 2-aminobenzenesulfonic acid



Procedure

1. In test tube A, add approximately 0.5 mL of conc. HCl and place in an ice water bath.
2. In test tube B, place 0.49 g (2.8 mmol) of aniline-2-sulfonic acid, 0.13 g of sodium carbonate (Na_2CO_3), and 5 mL of water and place in a hot water bath until a clear solution is obtained.
3. In test tube C, prepare a solution containing 0.2 g of sodium nitrite ($NaNO_2$) and 1 mL of water.
4. Remove test tube B from the hot water bath and pour the contents all at once from test tube C into test tube B.
5. Add the contents from test tube B to test tube A and place in an ice water bath until a significant amount of solid has precipitated.
6. In a 25 mL RBF, add 0.38 g (2.6 mmol) of 1-naphthol, 2 mL of 2.5 M NaOH and a magnetic stir bar and place in an ice-water bath. Turn on the stirrer and ensure the magnetic stir bar is working.
7. Add the contents of test tube A to the RBF while stirring and continue stirring and cooling the reaction for 10 minutes.
8. Remove the RBF from the ice water bath and heat the reaction using a thermowell until boiling commences (check with the instructor to ensure the set-up is correct).
9. Add 1 g of sodium chloride (NaCl) and continue heating until dissolved.
10. Stop stirring the reaction and cool to room temperature, then place in an ice water bath for 15 minutes.
11. Filter the solid using vacuum filtration with a Buchner funnel and wash with a saturated NaCl solution.
12. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

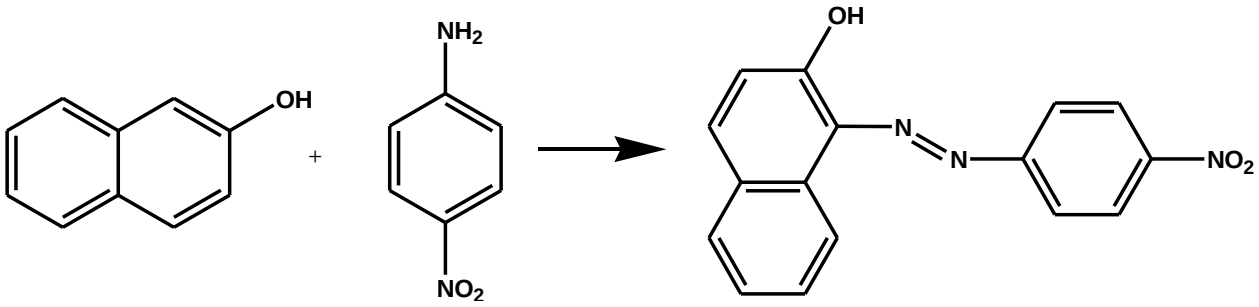
Experiment 6: Coupling between salicylic acid and 2-aminobenzenesulfonic acid



Procedure

1. In test tube A, add approximately 0.5 mL of conc. HCl and place in an ice water bath.
2. In test tube B, place 0.49 g (2.8 mmol) of aniline-2-sulfonic acid, 0.13 g of sodium carbonate (Na_2CO_3), and 5 mL of water and place in a hot water bath until a clear solution is obtained.
3. In test tube C, prepare a solution containing 0.2 g of sodium nitrite ($NaNO_2$) and 1 mL of water.
4. Remove test tube B from the hot water bath and pour the contents all at once from test tube C into test tube B.
5. Add the contents from test tube B to test tube A and place in an ice water bath until a significant amount of solid has precipitated.
6. In a 25 mL RBF, add 0.38 g (2.7 mmol) of salicylic acid, 2 mL of 2.5 M NaOH and a magnetic stir bar and place in an ice-water bath. Turn on the stirrer and ensure the magnetic stir bar is working.
7. Add the contents of test tube A to the RBF while stirring and continue stirring and cooling the reaction for 10 minutes.
8. Remove the RBF from the ice water bath and heat the reaction using a thermowell until boiling commences (check with the instructor to ensure the set-up is correct).
9. Add 1 g of sodium chloride (NaCl) and continue heating until dissolved.
10. Stop stirring the reaction and cool to room temperature, then place in an ice water bath for 15 minutes.
11. Filter the solid using vacuum filtration with a Buchner funnel and wash with a saturated NaCl solution.
12. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

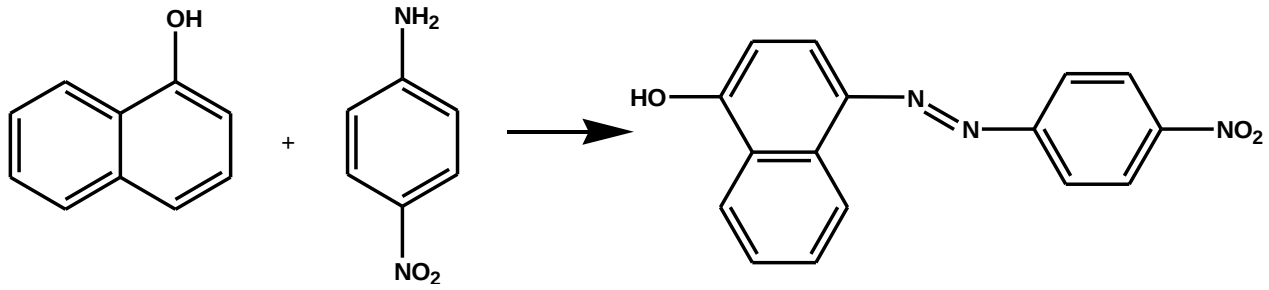
Experiment 7: Coupling between 2-naphthol and 4-nitroaniline



Procedure

1. In a test tube, add 1.5 mL of water and 1.5 mL of conc. HCl and place the test tube in an ice water bath.
2. In a 25 mL RBF, add 0.7 g of nitroaniline (5 mmol), 0.38 g (5.5 mmol) of sodium nitrite ($NaNO_2$), 1.5 mL of water and a magnetic stirbar. Stir the contents rapidly using a stirrer/hotplate.
3. Remove the test tube from the ice water bath and place the RBF in the bath. Add the contents of the test tube to the RBF and stir gently for 10 minutes.
4. Filter the solid into a test tube using a glass funnel and a small cotton plug.
5. In another 25 mL RBF with a magnetic stirbar, dissolve 0.74 g of 2-naphthol (5.1 mmol) in 10 mL of 2.5 M aq. NaOH and place in an ice-water bath.
6. Add the contents of the test tube slowly while stirring and continue stirring for 10 minutes while in the ice-water bath.
7. Slowly add 1.5 mL of conc. HCl.
8. Add 1 g of NaCl and heat the RBF using a thermowell until dissolved (check with the instructor to ensure the set-up is correct).
9. Cool the reaction to room temperature then place in an ice-water bath for 15 minutes.
10. Filter the solid using vacuum filtration with a Buchner funnel and wash the solid with approximately 5 mL of water.
11. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

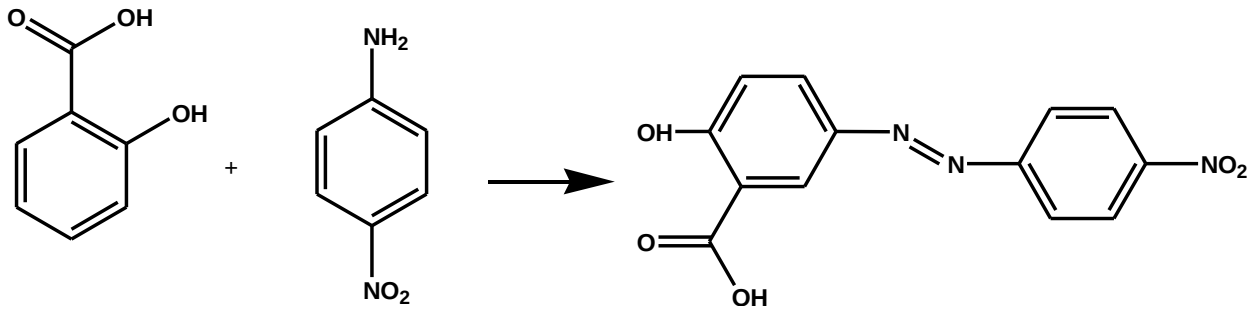
Experiment 8: Coupling between 1-naphthol and 4-nitroaniline



Procedure

1. In a test tube, add 1.5 mL of water and 1.5 mL of conc. HCl and place the test tube in an ice water bath.
2. In a 25 mL RBF, add 0.7 g of nitroaniline (5 mmol), 0.38 g (5.5 mmol) of sodium nitrite ($NaNO_2$), 1.5 mL of water and a magnetic stirbar. Stir the contents rapidly using a stirrer/hotplate.
3. Remove the test tube from the ice water bath and place the RBF in the bath. Add the contents of the test tube to the RBF and stir gently for 10 minutes.
4. Filter the solid into a test tube using a glass funnel and a small cotton plug.
5. In another 25 mL RBF with a magnetic stirbar, dissolve 0.74 g of 1-naphthol (5.1 mmol) in 10 mL of 2.5 M aq. NaOH and place in an ice-water bath.
6. Add the contents of the test tube slowly while stirring and continue stirring for 10 minutes while in the ice-water bath.
7. Slowly add 1.5 mL of conc. HCl.
8. Add 1 g of NaCl and heat the RBF using a thermowell until dissolved (check with the instructor to ensure the set-up is correct).
9. Cool the reaction to room temperature then place in an ice-water bath for 15 minutes.
10. Filter the solid using vacuum filtration with a Buchner funnel and wash the solid with approximately 5 mL of water.
11. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.

Experiment 9: Coupling between salicylic acid and 4-nitroaniline



Procedure

1. In a test tube, add 1.5 mL of water and 1.5 mL of conc. HCl and place the test tube in an ice water bath.
2. In a 25 mL RBF, add 0.7 g of nitroaniline (5 mmol), 0.38 g (5.5 mmol) of sodium nitrite ($NaNO_2$), 1.5 mL of water and a magnetic stirbar. Stir the contents rapidly using a stirrer/hotplate.
3. Remove the test tube from the ice water bath and place the RBF in the bath. Add the contents of the test tube to the RBF and stir gently for 10 minutes.
4. Filter the solid into a test tube using a glass funnel and a small cotton plug.
5. In another 25 mL RBF with a magnetic stirbar, dissolve 0.74 g of salicylic acid (5.4 mmol) in 10 mL of 2.5 M aq. NaOH and place in an ice-water bath.
6. Add the contents of the test tube slowly while stirring and continue stirring for 10 minutes while in the ice-water bath.
7. Slowly add 1.5 mL of conc. HCl.
8. Add 1 g of NaCl and heat the RBF using a thermowell until dissolved (check with the instructor to ensure the set-up is correct).
9. Cool the reaction to room temperature then place in an ice-water bath for 15 minutes.
10. Filter the solid using vacuum filtration with a Buchner funnel and wash the solid with approximately 5 mL of water.
11. If no solid is precipitated, only keep the filtrate. If solid is precipitated, let the solid air dry and keep both the filtrate and the solid.