



Practical 5.15 Preparation of an azo dye



Purpose

To describe and carry out the reaction, where appropriate, of aromatic amines with nitrous acid to form benzenediazonium ions followed by a coupling reaction with phenol to form a dye [5.4.1d]

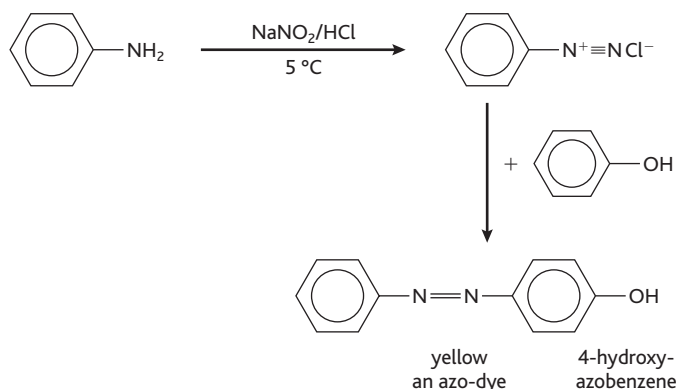


Safety

Wear eye protection. Phenylamine is toxic and volatile. Phenol is corrosive and toxic – wear gloves when handling phenol. Sodium nitrate(III) is oxidising and toxic. 1 M sodium hydroxide is corrosive. 2-naphthol is harmful.

Background

Azo dyes are brightly coloured synthetic dyes. They are produced in a reaction called 'coupling'. The first stage is the preparation of the unstable benzenediazonium ion using phenylamine and nitrous acid. This is followed by the addition of phenol. The reaction scheme is:



Phenylamine is toxic and volatile. A better alternative is its salt phenylammonium chloride, which, although toxic, is much less volatile and therefore avoids the use of a fume cupboard. If phenylamine is used, then it should be stored and used in a fume cupboard.

Each group of students will need:

Eye protection

Gloves (nitrile)

Weighing boats

Boiling tubes and bungs

Dropping pipettes

Thermometer, 0–110 °C

Phenylammonium chloride TOXIC

or Phenylamine TOXIC

Concentrated hydrochloric acid CORROSIVE

Sodium nitrate(III) OXIDISING, TOXIC

1 M sodium hydroxide CORROSIVE

Phenol CORROSIVE, TOXIC

2-naphthol, if required HARMFUL

Deionised water

Ice

Access to:

Balance

Fume cupboard if phenylamine is used



Practical 5.15 (cont.) Preparation of an azo dye

Method

- Put 3 cm³ of phenylamine and 10 cm³ of distilled water in a boiling tube, and add 8 cm³ of concentrated hydrochloric acid.
- Fit the bung to the tube and carefully shake to dissolve the amine (care must be taken as the reaction is exothermic).
- Cool the boiling tube immediately in an ice bath.
- Keep checking the temperature until the solution has cooled down to about 5 °C.
- In the meantime, dissolve 3 g of sodium nitrite in 8 cm³ of water in another boiling tube and add this to the ice bath. Keep checking the temperature until it reaches 5 °C.
- When both boiling tubes have reached 5 °C, carefully add the sodium nitrite solution dropwise to the phenylamine solution, so that the temperature does not rise above 10 °C. You have now made the benzenediazonium chloride solution in the first step of the coupling reaction.
- Into another boiling tube, put 2–3 crystals of phenol with 2 cm³ of 1 M sodium hydroxide.
- Cool this solution on ice and then add the benzenediazonium chloride solution drop by drop.

Questions

- In the preparation of the diazonium ion, why is it necessary to keep the temperature below 10 °C?

- Describe what happens in step 8.

- Write the balanced formula equation for the formation of benzenediazonium chloride from phenylamine and nitrous acid.

- 2-naphthol can be used in place of phenol in this coupling reaction. Draw the structure of the azo dye that would be formed.

