

24. Making an azo dye

Student Sheet

In this exercise, you will prepare a synthetic dyestuff known as an azo dye.

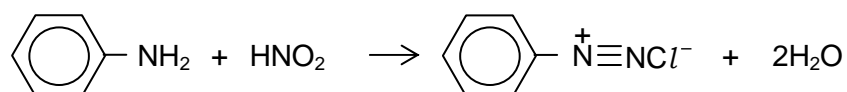
Intended lesson outcomes

By the end of this exercise you should be able to:

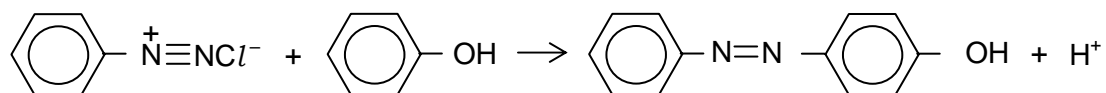
- perform a reaction under low temperature conditions
- appreciate the need to work with care and precision
- recall the chemistry of diazotisation and coupling

Background information

When an aromatic amine (an aryl amine) is treated with nitrous acid, a reaction occurs in which a *diazonium salt* is formed. If the temperature is too high, above 5 °C, then this compound reacts with water and is lost. For this reason, this experiment is performed using a cooling ice/water mixture. The equation below shows the reaction between phenylamine and nitrous acid to form benzene diazonium chloride; this process is known as **diazotisation**.

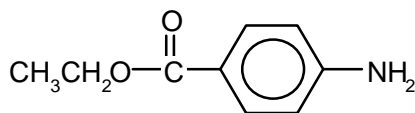


Diazonium salts act as electrophiles in some of their reactions. Thus, they are able to react with aromatic rings, for example benzene, using an electrophilic substitution mechanism. This reaction is known as a **coupling reaction** and the product is known as an **azo dye**, which is a stable molecule. The equation below shows the coupling reaction between benzene diazonium chloride and hydroxybenzene (phenol).

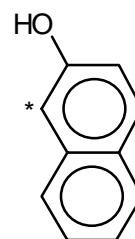


The azo dye formed in this reaction is orange in colour.

You are to prepare an azo dye using slightly more complicated reactants than those shown above. The aryl amine you will use is ethyl 4-aminobenzoate which, for simplicity, will be called substance **A**. This will be diazotised and the resulting diazonium salt will be coupled with naphthalen-2-ol (β -naphthol), which will be called substance **B**.



ethyl 4-aminobenzoate (substance **A**)









naphthalen-2-ol (substance **B**)

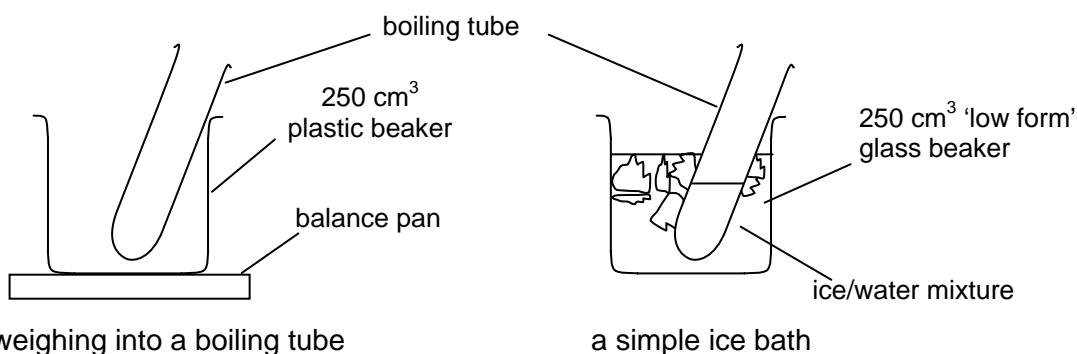
Questions

Draw the structures of the diazonium chloride formed from substance **A** and the azo dye produced when this diazonium chloride couples at position 1 with substance **B**; position 1 is marked on the above diagram with an asterisk (*).

Safety

Materials safety data sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident.

	You must wear eye protection throughout this experiment
	Naphthalen-2-ol (2-naphthol) is harmful
 	Sodium nitrite is oxidising and toxic
	Hydrochloric acid and sodium hydroxide are corrosive
	Naphthalen-2-ol and sodium nitrite are harmful to the environment. Your teacher will tell you how to dispose of them safely.

Procedure

- 1 Weigh 0.25 g of substance **A** into a boiling tube
- 2 Using a measuring cylinder add 10 cm³ of dilute hydrochloric acid to the tube
- 3 Stir to dissolve the solid and place the tube in the ice/water bath (see above) to cool.
- 4 Into a second boiling tube weigh (see above) 0.25 g of sodium nitrite (**Toxic**).
- 5 Using a second measuring cylinder add 5 cm³ of water to the second tube.
- 6 Stir to dissolve and place the tube in the ice bath to cool.
- 7 Place a 100 cm³ glass beaker on the balance and weigh into it 0.50 g of substance **B**.
- 8 Using a measuring cylinder add 5 cm³ of dilute sodium hydroxide solution (**Corrosive**) to the beaker, and place the beaker in the cooling mixture. Stir to dissolve the solid.
- 9 Add the cold solution of sodium nitrite slowly, using a teat pipette, to the acidified solution containing substance **A** prepared above (point 3). While you are doing this, leave both solutions in the cooling mixture to make sure that the temperature does not rise above 5 °C. The product of this reaction is the diazonium chloride.
- 10 Using a teat pipette, add drop-by-drop, and with stirring, the cold solution containing the diazonium chloride to the solution of substance **B**. Again, keeping both solutions in the cooling mixture. The azo dye is formed as a coloured precipitate.

Appendix 2

- 11 Pour the mixture into a 250 cm³ beaker containing cold water.
- 12 Filter the precipitate and wash it with cold water.
- 13 Transfer the precipitate to a watch glass to dry.

Note: Be careful, dyestuffs are meant to colour things – especially clothes and unwary hands!

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Teachers' Notes

This exercise shows how an azo dye may be prepared. The techniques used are relatively straightforward, but great care must be exercised with regard to temperature control and to the safe handling of materials.

Intended learning outcomes

Please see the Student Sheet

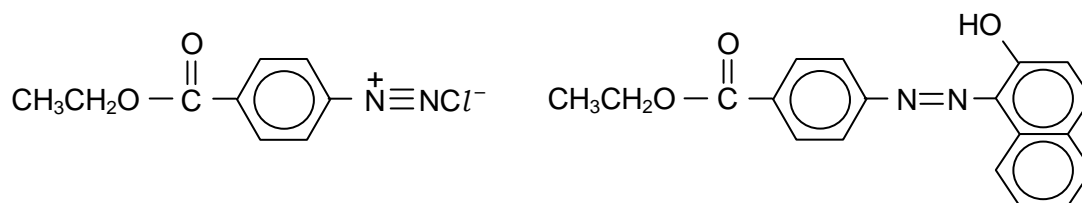
This exercise is likely to be used simply to provide an attractive practical experience and coverage of the chemistry of diazotisation and coupling. It could be extended, however, to extend and consolidate students' understanding. For example:

- The electrophilic substitution mechanism
- Students could be asked to suggest a mechanism for the reaction. More able students may well spot that the mechanism involves an electrophilic attack by the 'outer' nitrogen, with the associated donation of one of the bonding pairs from the triple bond onto the 'outer' nitrogen. The intermediate thus formed undergoing deprotonation in the normal way.
- The variation of colour in molecules with extended delocalised electron systems
- If a range of azo dyes is prepared, then the effect of changing the 'Chromophore' by attaching different arene rings to the azo bridge, or by using different substituents, 'Auxochromes', on these rings can be investigated. The indicator, 'Methyl orange' is an azo dye formed from the sodium salt of 4-aminobenzenesulphonic acid and *N,N*-dimethylphenylamine.
- The position of substitution in a substituted arene

The range of colour available from azo dyes is quite wide. The aryl amine to be diazotised, and the aryl hydroxy compound to which the product is to be coupled, can be varied to suit the availability of starting materials, and the colours required. The basic approach will be the same if different reagents are used but the quantities required will have to be calculated.

The exercise tends to be popular with students and should take around 30–45 minutes to complete. It could be extended to cover the purification of the dyestuff by recrystallisation, and the use of the dyestuff to colour fabric. To do this, the quantities used would need to be scaled up. Students would need to be warned, however, that those who are clumsy in their work are likely to be both colourful and easy to spot!

Answers to questions



Technical Information

Requirements per student/group

- access to ethyl 4-aminobenzoate (substance **A**) – plus a spatula
- access to naphthalen-2-ol, (substance **B**) – plus a spatula
- access to solid sodium nitrite, NaNO_2 – plus a spatula
- access to a balance (reading to at least 0.10 g)
- access to dilute hydrochloric acid (about 1.0 mol dm^{-3})

Appendix 2

- access to dilute sodium hydroxide (about 1.0 mol dm^{-3})
- one 250 cm^3 plastic beaker
- two 10 cm^3 measuring cylinders
- two glass stirrers
- two boiling tubes
- 100 cm^3 glass beaker
- one ice bath (250 cm^3 or larger, low form glass beaker containing ice and water)
- two dropping pipettes
- two thermometers (range $-10 \text{ }^\circ\text{C}$ to $110 \text{ }^\circ\text{C}$)
- filter funnel and filter paper or access to a vacuum filtration system
- watch glass

Safety

The main points are included on the Students' Sheet. However, it should be stressed that it is the responsibility of the teacher to ensure that a full risk analysis has been carried out; this is particularly important if alternative reagents are used. MSDS sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident. Materials that are harmful to the environment should be disposed of according to local regulations.