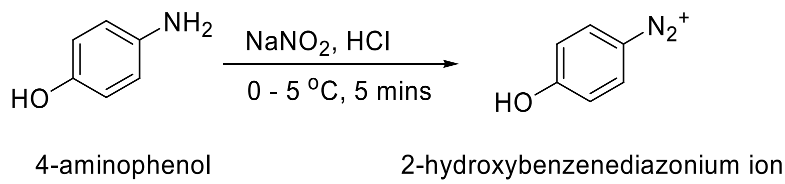
Experiment 8

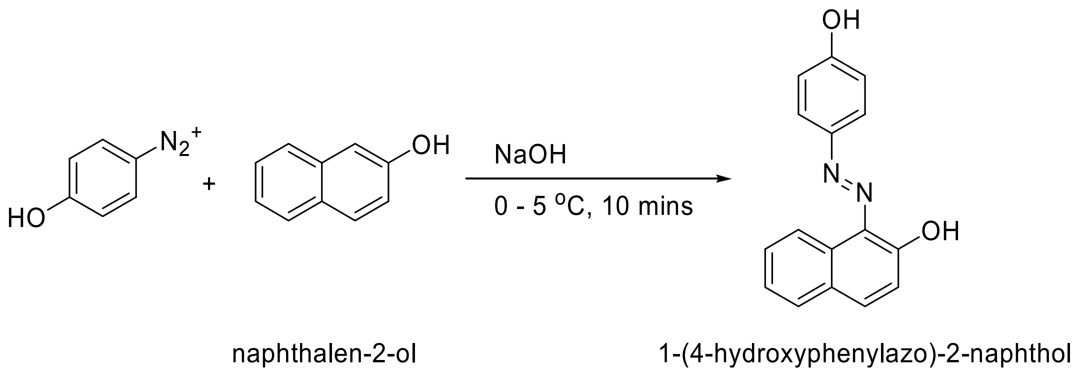
Synthesis of an Azo Dye - the Coupling Reaction of Benzenediazonium Ion with Naphthalen-2-ol

Student Handout

Purpose

To prepare the azo dye 1-(4-hydroxyphenylazo)-2-naphthol by the diazonium coupling reaction of naphthalen-2-ol with the benzenediazonium ion obtained from 4-aminophenol:





Background

Dyes play an indispensable role in human history since ancient time. Dyeing processes are often considered as an important characteristic of a particular civilisation or culture. Dyes are used in almost every commercial product such as food, clothing, pigments and paints, etc.

There are many different classes of dyes in which azo dyes are certainly one of the most important classes. About half of the dyes used in industry are azo dyes. Azo dyes have the basic structure, Ar–N=N–Ar’, where Ar and Ar’ are two aromatic groups.

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The unit containing the nitrogen-nitrogen double bond is called an azo group. The nature of the aromatic substituents on both sides of the azo group controls the colours of the azo compounds as well as the water-solubility of the dyes and how well they bind to a particular fabric.

Preparation of the target azo dye involves the conversion of 4-aminophenol to the diazonium ion intermediate 4-hydroxybenzenediazonium ion followed by the reaction with naphthalen-2-ol.

Notes

This is a typical experiment in organic synthesis. You will encounter many observable changes throughout the experiment. It is very important to record all the observations accurately and in detail. Furthermore, when one makes an observation, it should be written down immediately.

In the experiment you will handle quite a number of different reagents and perform many experimental steps. Make sure you understand the experimental steps and are able to carry out the steps accurately. It is a good practice to read through the procedures carefully and prepare a pictorial flow-chart for the experimental procedures before the experiment. Consult your teacher before the experiment if you have any doubt regarding the experiment.

The reagents that you will handle in the experiment have certain hazards. Read the Safety section carefully.

There are several important steps in the experiment which have to be carried out carefully. The benzenediazonium salt solution is unstable and prone to deteriorate (decompose) upon standing at room temperature. The solution should always be kept at below 10 °C and should be used as soon as it is generated. The alkaline naphthalen-2-ol solution should be prepared prior to the preparation of the benzenediazonium salt solution.

Naphthalen-2-ol dissolves poorly in acidic aqueous solutions. To prevent naphthalen-2-ol from precipitating out prematurely, the addition of the acidic benzenediazonium solution to the naphthalen-2-ol solution should be slow. The mixture forms a thick paste during addition. Stir the mixture efficiently to facilitate the reaction.

The product 1-(4-hydroxyphenylazo)-naphthalen-2-ol is a dye with an intense colour. Handle the compound with care and avoid contact with skin. Gloves are highly recommended.

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The product can be recrystallised from water as fine powder and dried in air for 1-2 days before weighing to determine the yield.

Safety


EYE PROTECTION MUST BE WORN

The experiment should be performed in a well-ventilated laboratory or fumehood. Handle all chemicals with great care. Avoid direct contact of chemicals with skin. Dispose of chemical waste, broken glassware and excess materials according to your teacher's instruction.

Sodium hydroxide solution and concentrated hydrochloric acid are highly corrosive. Avoid contact with skin and put on appropriate protective gloves whenever available. Concentrated hydrochloric acid gives the choking gaseous hydrogen chloride, which is corrosive to the respiratory organs. It should be handled in the fumehood.

The dissolution of sodium hydroxide in water is exothermic and should be performed with care. When diluting concentrated acids, it is important to add the acids to water and never do it in the reverse manner. Heat is evolved in mixing concentrated acids and water. The heat generated during the mixing process may not be able to dissipate efficiently and may cause the solution to boil and spill out.

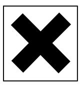
Both naphthalen-2-ol and 4-aminophenol are harmful organic solids. Handle them in a good ventilated area to minimise exposure. Naphthalen-2-ol is a mild irritant and usually in a fine powdery form. Be careful not to breathe in the fine powder.

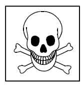
The product 1-(4-hydroxyphenylazo)-2-naphthol is an azo dye. All azo dyes are mildly toxic. Handle the product with care.

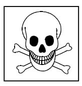
Safety information on the chemicals used in the experiment can be found in the Material Safety Data Sheet (MSDS). Consult your teacher for details.

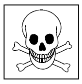
Materials and Apparatus Available

NaOH 
CORROSIVE

Naphthalen-2-ol 
HARMFUL/ IRRITANT

4-Aminophenol  
HARMFUL/ IRRITANT TOXIC

Sodium nitrate(III)  
TOXIC OXIDISING

Concentrated hydrochloric acid   Ice-water bath

CORROSIVE TOXIC

150-cm^3 Conical flask
100-cm^3 Conical flasks (2 pcs.)
50-cm^3 Beakers (2 pcs.)
Büchner funnel
Glass rods
Melting-point apparatus (optional)
Filter paper
Filtering flask/suction flask
Spatula
Droppers
Weighing balance
Watch-glass

Experimental Procedure

Photos of the experiment are available at http://www.chem.cuhk.edu.hk/ssc.htm.

1. Prepare 30 cm^3 of ~10% aqueous sodium hydroxide solution by dissolving 3 g of sodium hydroxide in 27 cm^3 of water in an 150-cm^3 conical flask.
2. Weigh 1.44 g of naphthalen-2-ol (0.01 mol) and dissolve it into the sodium hydroxide solution. Stir the mixture until complete dissolution. Cool the solution with an ice-water bath.
3. The benzenediazonium salt solution can be prepared as below:
   (a) Dissolve 0.70 g of $NaNO_2$ (0.01 mol) in 5 cm^3 of water.
   (b) Put 1.20 g of 4-aminophenol (0.011 mol) into 45 cm^3 of water in a 100-cm^3 conical flask. Add slowly 12 cm^3 of concentrated hydrochloric acid and stir the mixture until the 4-aminophenol is dissolved completely.
   (c) Cool the 4-aminophenol solution in an ice-bath. Some 4-aminophenol may precipitate out upon cooling. While keeping the solution at 0 °C add the sodium nitrate(III) solution slowly with a dropper. The mixture should be well-stirred during addition. When the addition is completed, stir the mixture for another 2 - 3 minutes. The slightly turbid pale grey solution is the benzenediazonium salt solution.
4. To the alkaline naphthalen-2-ol solution add the benzenediazonium salt solution slowly. A large amount of brick red precipitate forms during addition. The addition takes about 5 minutes. The reaction mixture should be stirred efficiently and cooled in an ice-water bath during the addition.
5. When the addition is completed, stir the mixture at 0 °C for 5 - 10 minutes. This is to ensure the reaction goes to completion.
6. Filter the mixture by suction filtration. Wash the solid product on the Büchner funnel with a small amount of cold water. Dry the product on the Büchner funnel with the suction turning on for a few minutes.
7. Transfer the product to a watch-glass. Allow the product to dry for 1 - 2 days. Weigh the product and determine the percentage yield for the reaction.

8. Determine the melting-point of the product. Compare the melting-point with the literature value of 197 - 198 °C. (Optional)

Spectroscopic Analysis

The mass spectrum of the compound 1-(4-hydroxyphenylazo)-2-naphthol is given at the end of this student handout. Identify and assign the characteristic signals present in the spectrum by filling in the 'Spectroscopic Analysis' section in the laboratory report sheet.

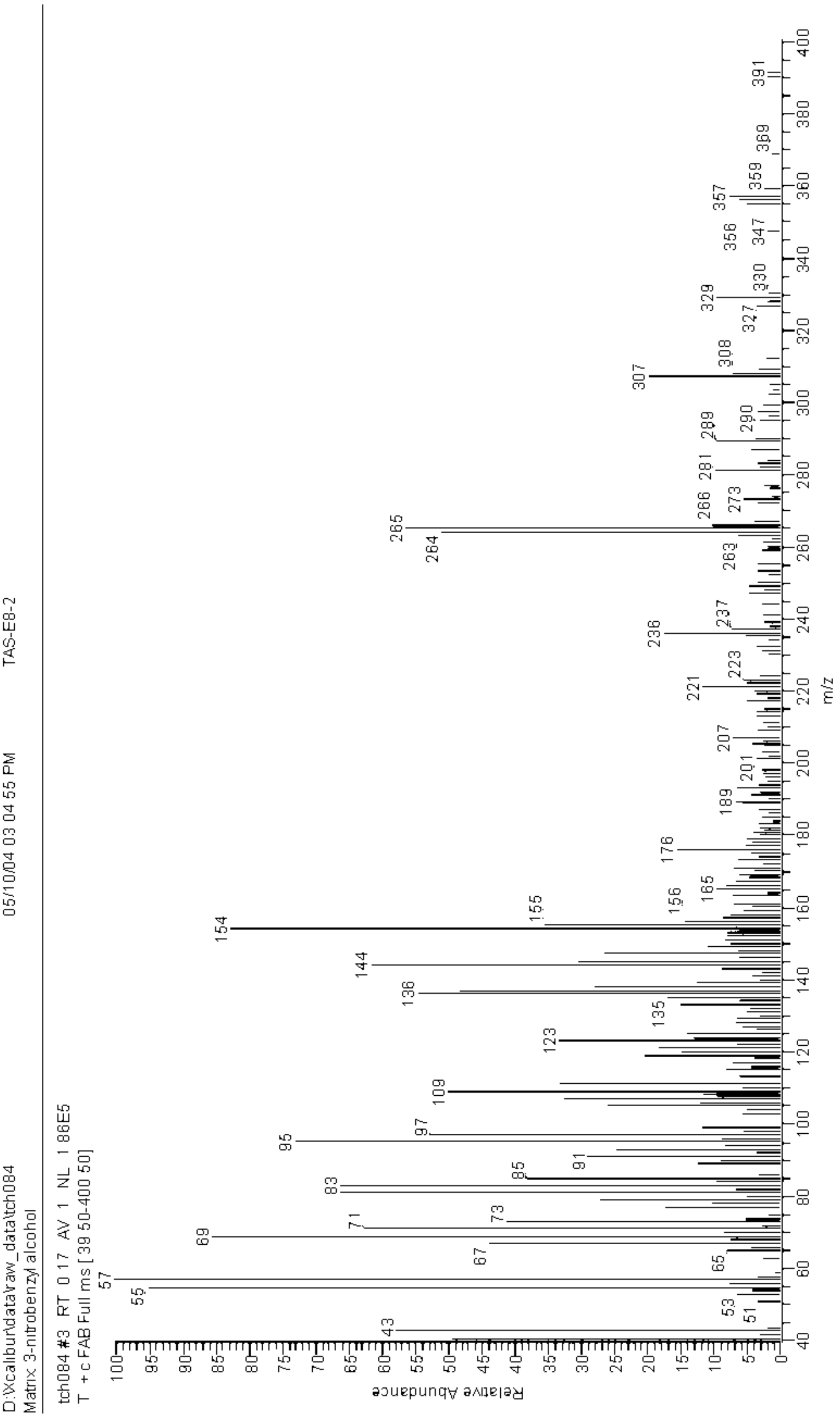
Questions for Further Thought

1. Calculate the percentage yield of azo dye obtained in this experiment.
   (Hint: In this experiment, both naphthalen-2-ol and sodium nitrate(III) are the limiting reagents. Therefore the percentage yield calculation should be based on the amounts of these two reagents used.)
2. A brick red precipitate forms in the reaction of naphthalen-2-ol with the benzenediazonium salt solution. What is the brick red precipitate? Write down the chemical equation for the reaction.
3. When 4-aminophenol reacts with sodium nitrate(III) in the presence of hydrochloric acid, gas bubbles evolve from the solution. What is the gas?
4. Can we obtain an azo compound if the aromatic amine, 4-aminophenol, is replaced by an aliphatic amine such as butan-1-amine? Why?
5. Naphthalen-2-ol dissolves well in sodium hydroxide solution but not in pure water and dilute acids. Why?
6. Why is it advisable to prepare the alkaline naphthalen-2-ol solution before preparing the benzenediazonium salt solution?
7. Explain why the preparation of the benzenediazonium salt must be carried out below 10 °C.

References

1. D. L. Pavia, G. M. Lampman, G. S. Kriz and R. G. Engel, *Introduction to Organic Laboratory Techniques - Small-Scale Approach*, 1st Ed.; Harcourt Brace, Florida, 1998, pp. 313 - 322.
2. J. B. Conant, R. E. Lutz and B. B. Corson, *Organic Syntheses, Collective Volume I*, John Wiley & Sons, New York, 1941, p. 49.

The mass spectrum of 1-(4-hydroxyphenylazo)-2-naphthol



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Synthesis of an Azo Dye - the Coupling Reaction of Benzenediazonium Ion with Naphthalen-2-ol

Laboratory Report

Name: ______________________________ **Date:** ____________________

Title: ____

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Objective: ____

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Materials Used:

	Molecular Weight	Density	Mass/Volume	No. of mole
Sodium nitrate(III)	68.995			
Naphthalen-2-ol	144.17			
Hydrochloric acid (conc.)	36.46			
4-Aminophenol	109.13			
Sodium hydroxide	39.997			

Chemical Reactions:

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Observations:

(a) Preparation of the naphthalen-2-ol solution

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(b) Preparation of the 4-hydroxybenzenediazonium salt solution

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(c) Reaction of 4-hydroxybenzenediazonium salt solution with naphthalen-2-ol

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Results:

Physical Appearance of the product: ____________________

Melting temperature range (°C): ____________________

Mass of 1-(4-hydroxyphenylazo)-2-naphthol obtained: ____________________

No. of mole of 1-(4-hydroxyphenylazo)-2-naphthol obtained: ____________________

No. of mole of naphthalen-2-ol used (the limiting reagent): **0.01 mole**

Percentage yield of the reaction: ____________________

Spectroscopic Analysis:

Mass spectrum

Molecular formula of 1-(4-hydroxyphenylazo)-2-naphthol: ______________________

Molecular weight of 1-(4-hydroxyphenylazo)-2-naphthol: ________________________

Molecular ion peak in the mass spectrum (m/z): _________________________________

Conclusions:

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