Purpose

To synthesize the azo dye, methyl orange, and characterize its usefulness as a dye and pH indicator.

Learning Objectives

To synthesize the synthetic dye

To test the coloring qualities of the dye

To test the dye as a pH indicator

Theory and Background

People have been using dyes since the beginning of time for different purposes, such as drawing pictures, dying hair, applying face colors, and dying fabrics. Natural dyes include madder (a brilliant red dye derived from a root), indigo, and several variations of brown, yellow, and green. But plant dyes do not offer the great variety and brilliance offered by the synthetic dyes (Figure 13B.1). Today we have available an infinite spectrum of colors to dye any type of fabric.

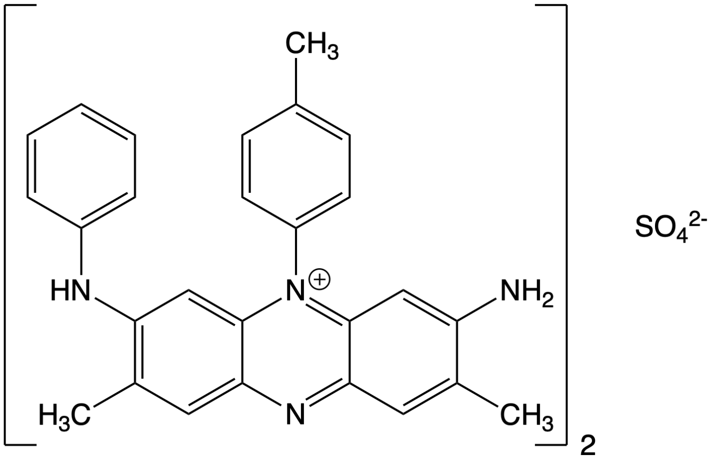
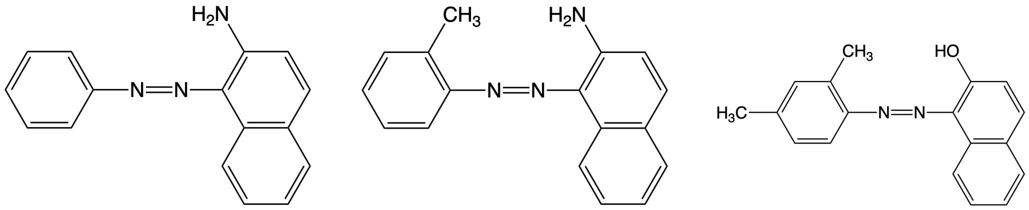


Figure 13B.1: Molecular structure of the dye, mauve.

Many of the early synthetic dyes were derived from aniline ($PhNH_2$) or related aromatic amines. In the mid-1850s an English chemist, W.H. Perkin, was trying to synthesize quinine by oxidizing allyltoluidine with potassium dichromate. He tried this because the molecular formula of quinine is exactly twice the molecular formula of allyltoluidine. This turned out to be an erroneous idea and no quinine was obtained. However, he did see areddish-brown precipitate that turned out to be a good dye for fabrics. When he used aniline, he obtained a black precipitate, which upon extraction with ethanol yielded a beautiful purple color. The purple solution also turned out to be very efficient at dying fabric and became known as mauve. It has a rather complicated structure (Figure 13B.1), and also shows that Perkin's aniline was contaminated with toluidines (amine-substituted toluenes). As a side comment, the black precipitate Perkin obtained was "Aniline Black." Aniline Black is the polymer of aniline, a conducting organic polymer that has been thoroughly investigated during the last twenty years. It has been shown that polyaniline can be processed into conducting fibers and films with numerous technological applications.



FD&C Yellow 3 FD&C Yellow 6 FD&C Red 32

FD&C Orange 1 FD&C Orange 4

FD&C Methyl Orange FD&C Butter Yellow

Figure 13B.2: Structures of various azo dyes.

About ten years after the first synthesis of mauve, the azo dyes were discovered by Griess. These azo dyes revolutionized the dye industry and they are still the most common dyes, from food dyes, fabric dyes, and printing inks to pigments in paint. They all have the same basic structure, namely Ar–N=N–Ar, in which Ar represents any aromatic group. The –N=N– functionality is called an azo group. The extended conjugated system is a strong chromophore, giving these compounds their brilliant colors. The specific color depends on the nature of the aromatic group and the substituents. Many of these colors are FD&C colors (food, drug, and cosmetics, Figure 13B.2) and are safe, while others are carcinogenic. All the azo dyes are synthesized using the same basic reaction, namely an azo coupling between a diazonium ion and an aromatic substrate.

Required Reading

- Azo coupling in Bruice textbook
- Electrophilic Aromatic Substitution in the Bruice textbook.

Table of Reagents

- Prepare a Table of Reagents for this lab.

Reaction Mechanism

Azo coupling occurs between a diazonium salt and an activated aromatic substrate. The mechanism is an electrophilic aromatic substitution in which the positively charged diazonium ion is the electrophile. Therefore the same rules as for any electrophilic aromatic substitution apply: electron-donating groups such as amines, ethers, and alkyl groups activate the aromatic substrate and are ortho-para directors, while groups such as carboxylic esters and nitro groups are deactivators and meta directors.

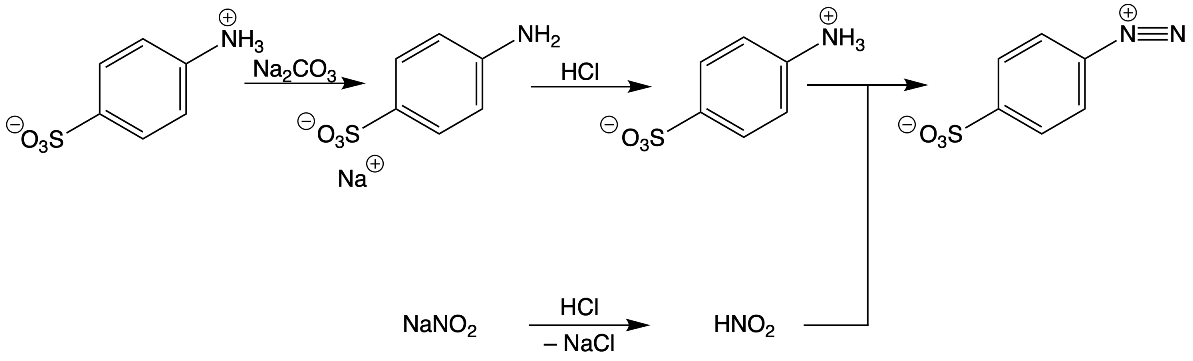


Figure 13B.3: Preparation of the diazonium ion intermediate

The first step in an azo coupling is the formation of the diazonium ion intermediate (Figure 13B.3, top), which is formed by reaction of an aromatic amine with nitrous acid. This process is called diazotation. Nitrous acid is formed in situ by reaction of sodium nitrite and hydrochloric acid. For the reaction in this experiment, the diazonium ion of sulfanilic acid has to be formed. However, sulfanilic acid is not soluble in acidic solution, and the medium in this reaction has to be acidic to form the nitrous acid. This problem is circumvented by dissolving the sulfanilic acid first in alkaline solution by addition of sodium carbonate. At the beginning of the reaction, when HCl is added, two things will happen: nitrous acid will be formed in situ and the sulfanilic acid will precipitate out as a very finely divided precipitate, which is highly reactive. The diazonium salt of the sulfanilic acid will be formed, which is also insoluble in the reaction medium, but again very finely divided. The diazonium ion will react immediately with the highly reactive N,N–dimethylaniline to form methyl orange (**??**).

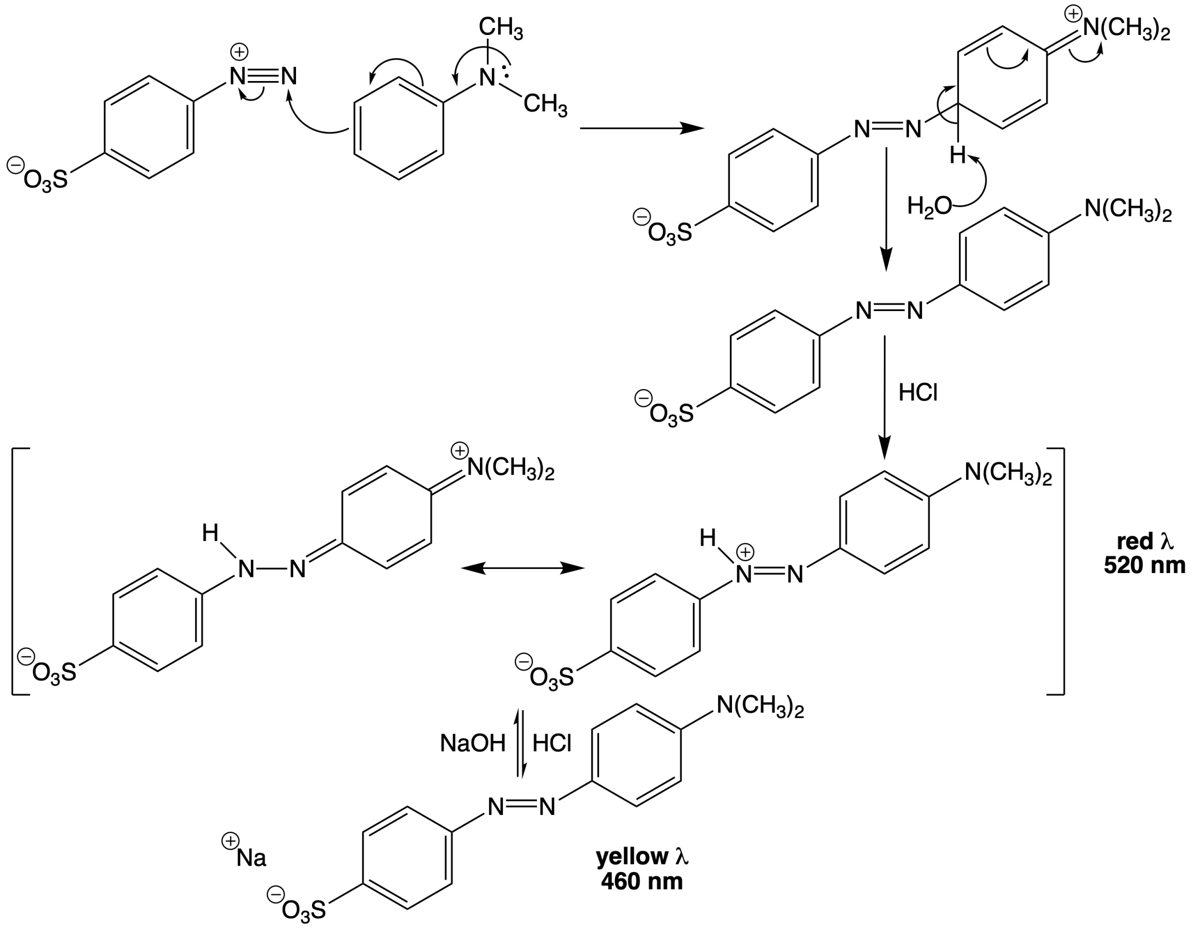


Figure 13B.4: Mechanism of azo dye synthesis.

Methyl orange is an acid–base indicator: At pH > 4.4, methyl orange exists mostly as the yellow negative sulfonate ion, while at pH < 3.2 the dipolar red ion (helianthin) predominates. In higher concentration in basic solution, methyl orange does appear as orange.

It is rather easy to bleach azo dyes. Reducing agents such as sodium hydrosulfite (sodium dithionite), $Na_2S_2O_4$,or stannous chloride in HCl, are often used. They reduce the azo bond to the two amine functionalities.

$$\mathrm{Ar{-}N{=}N{-}Ar'} \xrightarrow{\mathrm{Na_2S_2O_4}} \mathrm{Ar{-}NH_2} \quad + \quad \mathrm{H_2N{-}Ar'}$$

Figure 13B.5: Reduction of azo dyes to amines by sodium hydrosulfite.

Procedure

Safety Precautions

N,N–dimethylaniline is quite toxic. Any contact with the skin should be avoided. Avoid breathing the fumes.

As a general rule all aromatic amines should be considered as carcinogenic. Wear gloves.

Normal precautions apply to the use of concentrated acids.

Synthesis

Diazonium Salt Formation

1. In a small Erlenmeyer flask, dissolve 0.06 g of sodium carbonate in about 5 mL of water.
2. Add 0.2 g of sulfanilic acid monohydrate and heat to reflux until it is homogeneous.
3. Cool to room temperature and add 0.08 g of sodium nitrite and stir until homogeneous.
4. Cool in an ice-water bath for 5–10 minutes until the temperature is below 10 °C.
5. Add 0.25 mL concentrated hydrogen chloride to the solution. The diazonium salt should precipitate as a finely divided white precipitate. Keep this solution cold.

Azo Coupling

1. In a vial or flask, mix 0.14 mL of N,N–dimethylaniline with 0.10 mL of glacial acetic acid.
2. Add this solution dropwise to the diazonium salt suspension. Stir vigorously with a spatula. Keep cold. A red precipitate will start to form. Cool the reaction mixture for another ten minutes in the ice bath.
3. Slowly add 1.5 mL of a 10% NaOH aqueous solution. Check the pH of the reaction mixture with pH paper to ensure that the solution is basic. If not, add more NaOH.

Workup

1. Boil for 10–15 minutes. Most methyl orange will dissolve. Add 0.5 g of NaCland allow the mixture to cool first to room temperature and then in the ice bath.

> Addition of NaCl is a common practice in organic synthesis known as “salting out.” The solubility of the organic compound in aqueous medium is reduced by the addition of salt, thereby facilitating the separation of organic and aqueous parts. The same principle is often used to aid in the separation of organic and aqueous layers in liquid–liquid extractions.

2. Filter and rinse the reaction flask twice with saturated aqueous NaCl solution and wash the filter cake with these rinse solutions.

3. Transfer the product into about 15 mL of boiling water in a beaker and continue heating for a few minutes while stirring with a glass rod. Most of the dye will dissolve, but not all, but all the contaminating salts will dissolve.

4. Cool in the ice bath and filter using a Büchner funnel. Dry the product on the Büchner funnel by maintaining the vacuum for 5–10 minutes.

5. Determine the yield of your product.

Testing the Properties of Methyl Orange

Dyeing Test

Obtain a strip of Multifiber Fabric from your TA. The identity of the different fabrics will be posted in the lab, and they range from nylon and polyester to cotton and silk.

> Clip one end of the fabric strip so that you can still identify the different fabrics once they are dyed.

The dye mixture consists of 50 mg of methyl orange in 30 mL of water containing 1 mL of 15% aqueous sodium sulfate solution and 1 drop of concentrated sulfuric acid.

1. Heat to just below boiling and immerse the fabric strip in the dye bath for 10 minutes.

2. Rinse the fabric well with lots of water.

3. Note the different dye colors on the different fabrics.

Methyl Orange as an Indicator

In a test tube, dissolve a few methyl orange crystals in a small amount of water. Watch the color switch from orange to red as you alternately add acid (dilute HCl) and base (dilute NaOH).

Discussion

- Discuss the azo dye synthesis procedure.
- Comment on the versatility of the azo dyes.
- Discuss the interactions of the dye with the different fabrics.
- Discuss the reason for the color change of these dyes at varying pH.

Name: ______________________________

Section: __________ Date: ______________

Report Sheet:

Synthesis of a Dye, Methyl Orange

Synthesis

Mass of sulfanilic acid (g) ____________

Volume of N,N-dimethylaniline (mL) ____________

Mass of product (g) ____________

Percent yield ____________

Testing the Properties of Methyl Orange

Dyeing Test

Observations of dye colors:

nylon fabric ________________________

polyester fabric ________________________

cotton fabric ________________________

silk fabric ________________________

Methyl Orange as an Indicator

Observations upon adding acid: ____

Observations upon adding base: ____