Synthesis of the Dye, Sudan I
from K. L. Williamson, Macroscale and Microscale Organic Experiments, 2nd Ed. 1994, Houghton Mifflin, Boston Revised 10/18/07

Introduction:

Many synthetic dyes, often called diazo dyes, are based on diazonium chemistry that has been used for over 100 years in synthetic chemistry. This experiment is an example of the synthesis of one such dye, 1-phenylazo-2-naphthol or more simply Sudan I, 4. The reaction involves two steps, the first being the preparation of a solution of the diazonium salt, benzenediazonium chloride, 2, from aniline, 1:

\[
\begin{align*}
\text{NH}_2 & \quad \text{NaNO}_2 \\
\text{HCl, H}_2\text{O} & \quad 0-5°C \\
\rightarrow & \\
\text{N}_2^+ \text{Cl}^- & \\
\text{b.p.} = 184°C
\end{align*}
\]

In the second step, the solution of 2 is added to 2-naphthol, 3, to produce the diazo dye, 4. The dye can be analyzed by visible light spectrophotometry or IR.

\[
\begin{align*}
\text{N}_2^+ \text{Cl}^- & \quad \text{NaOH, H}_2\text{O} \\
0-5°C & \\
\rightarrow & \\
\text{N} & \quad \text{OH} \\
\text{m.p.} = 131-132°C
\end{align*}
\]

Prelaboratory Exercise:

Draw the Lewis structures for nitrite ion (NO\(_2^−\)), nitrous acid (HNO\(_2\)), and a generalized aryl diazonium ion (Ar-N\(_2^+\)).

Cautions:

Aniline, 1, is an anticipated carcinogen. Wear gloves when handling and handle only in a hood. Sodium nitrite and 2-naphthol are toxic. Handle with care! Be careful not to allow the benzenediazonium chloride solution to warm up or it will decompose, leading to undesirable side-products. The 30% KOH solution used for the UV/Vis analysis is very caustic. Handle with care.

Synthesis:

STEP 1: Preparation of Sodium 2-naphtholate solution - In a reaction tube, prepare a solution of 78 mg of 2-naphthol, 3, (m.p. 123°C) in 0.5 mL of 3M NaOH. Set aside in an ice bath to cool until ready for use in step 3.

STEP 2: Preparation of benzene diazonium chloride, 2:

In a hood, carry out an instant microscale distillation of 0.5 to 1.0 mL of aniline (b.p. = 184°C). Refer to the “Synthetics” chapter of the Lab Guide for a description of this type of distillation. Use a boiling chip. Discard the
first two or three cloudy pipet fractions from the instant microscale distillation as these contain mainly water. Then transfer the next 5 to 10 pipetfuls of condensed vapor into a clean reaction tube. The material to be used should be clear and only slightly yellow, not cloudy. [Discard any undistilled aniline into the Nonhalogenated Organics Waste container.]

In a reaction tube, weigh 50 mg of the freshly distilled aniline and add 0.25 mL of concentrated (12M) HCl, and 0.5 mL distilled water. Warm and agitate this solution to dissolve the aniline hydrochloride and then cool it in an ice bath to 0°C; it is important to keep the reaction cooled to 0°C since, above 5°C, diazonium salts can form aryl radicals.

Prepare a solution of 40 mg of sodium nitrite, NaNO₂, in 0.5 mL water in another reaction tube. Add this sodium nitrite solution drop-wise to the acidic aniline solution while maintaining the reaction at ice bath temperature. Agitate the tube by vigorously "flicking" the reaction tube with your finger. Five min. after the addition of the sodium nitrite solution is complete, test the reaction solution for excess nitrous acid, HONO, by touching a small drop of it on the tip the spatula to a piece of KI/starch (starch iodide) paper. If the test is positive (immediate purple color), add urea, a few crystals at a time with cooling and agitation. Test with KI/starch paper again and continue adding urea a few crystals at a time until the KI/starch test is negative.

STEP 3: Preparation of 4 by reaction of 2 with sodium 2-naphtholate:
Add a small piece of ice to the ice cold solution of sodium 2-naphtholate you prepared at the start of this synthesis (step 1). Dropwise, add the benzene diazonium chloride solution from STEP 2 while keeping both solutions at 0-5°C. Agitate the reaction tube by stirring with the bent microspatula to insure complete mixing. The reaction initially forms a blood red solid, but this changes to a reddish orange precipitate as the pH becomes acidic with the addition of the hydrochloric acid/sodium nitrite solution. After complete addition, the reaction mixture is left at ice bath temperature for 15 min. with occasional agitation.

**Isolation and Purification:**
Filter the bright red solid Sudan I on a Hirsch funnel, washing it from the reaction tube twice with one or two mL of cold distilled water. Air-dry this crude product until the next lab. Once dry, weigh the crude dye product, and set aside a small amount for a mp determination of this crude product. Recrystallize the crude product from ethanol. **Do NOT** heat the dye too much because you will turn your nice red dye into a black-brown mess. Filter, dry, and weigh the product. Typical yields are about 40 to 50% or 30 to 40 mg. Determine the melting points of the crude and pure products.

**Visible Light Absorption Analysis (if assigned):**
Prepare a dilute solution for visible light absorption analysis by dissolving about 1 mg of the pure red product in 2 mL of 30% KOH in methanol (30% methanolic KOH will be found on the hooded shelf) in a 125-mL Erlemeyer flask and adding 100 mL of methanol. Use the UV/Vis spectrophotometer in the organic lab instrument room to obtain the visible spectrum between 350 nm and 750 nm. See Lab Guide and operating instructions near the instrument in 206 Whitmore. You should see λ_max between 450 and 490 nm. After running the visible spectrum of this basic solution, add a drop of conc. Hydrochloric acid to the sample cuvette, mix, check that the solution is acidic with pH paper, and run another visible wavelength absorption spectrum. You should see a bathochromic shift in the λ_max as the pH is changed.

- You may need to dilute your solution with methanol. Dilution should be carried out if any peak absorbances are above 1.5 (AU). Keep diluting the solution with methanol until all peaks are at or below 1.5 AU.

**Analysis**
You will be instructed to analyze your final product by IR or UV-Vis. Analyze your sample according to your Assignment sheet; prepare an IR sample as per the instructions on Sample Preparation in Lab Guide (inside back cover). UV/Vis preparation instructions are given above.
Cleaning Up:
Discard undistilled and unused aniline into the Non-Halogenated Organics Waste container. The filtrates from the crude product isolation and recrystallization can also be placed in this container. Solutions from the spectrophotometric analysis can be flushed down the drain.

Final Report:
Attach the annotated IR or UV/Vis spectrum to your report. For IR, annotate the significant stretches that are diagnostic of the product. For UV/Vis, label the absorption maxima ($\lambda_{\text{max}}$), measured in nm, clearly marked on them. Answer the following questions:

1. Why does the reaction between the diazonium ion and 2-naphthol occur primarily on the 1 and not the 3 position as shown in the balanced equation? (Hint: Draw the initially-formed carbonium ion for attack at each position placing the + charge on the C atom at 2 and look at conjugation in the distribution of the remaining C-C double bonds.)

2. The $\lambda_{\text{max}}$ for the product is between 450 and 490 nm. Does this $\lambda_{\text{max}}$ value/range make sense when you consider the observed color of the dye? Explain.