Synthesis of Red 13 Diazo Dye

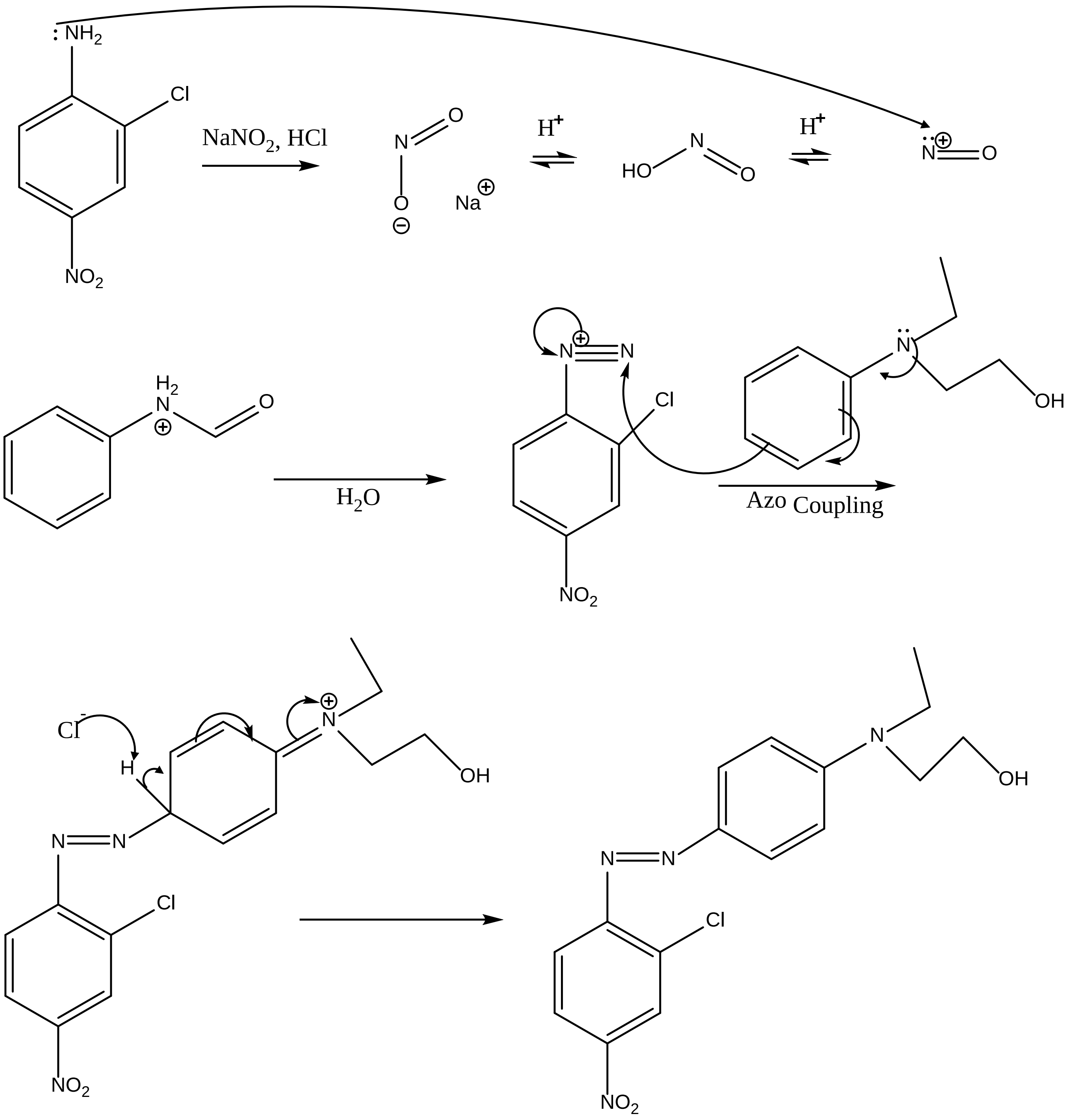
Introduction:

Diazo dyes are widely used in industries such as foods, pharmaceuticals, cosmetics, textiles, and leather for coloring purposes or used as a food additive to make products more appetizing, informative, and appealing. With there being over 10,000 different dyes and pigments, the human eye is capable of distinguishing between different color shades, that helps us easily identify numerous amounts of products created by these industries.[1] Synthetic dyes are classified into different groups, one group being azo dyes that are identified by the presence of azo groups (-N=N-). Due to the nature and the positions of the substituents on the aromatic rings and amino nitrogen atom there are toxic properties related to azo dyes.[1] Unless approved by the FDA, studies have shown that dyes possibly contain toxins, irritants, sensitizers, or carcinogens that cause cancer, hypersensitivity, or behavioral changes. Some studies have also shown some dyes showing mutagenic responses to salmonella and mammalian assay systems.[1]

Diazonium salts are versatile intermediates in organic chemistry and are important for the synthesis of azo dyes. The utility of a diazotization reaction is they are easily formed from corresponding amines and can undergo a variety of reaction such as coupling with activated aryl compounds to form the azo dyes.[2]

The reaction of a diazo dye begins with a Sandmeyer reaction shown in Scheme 1, where the aminobenzene, 2-chloro-4-nitroaniline, reacts with sodium nitrite to form a diazonium salt cation intermediate. Once the diazonium salt intermediate is formed, it undergoes an azo coupling reaction via an electrophilic aromatic substitution reaction, where the diazonium salt acts as an electrophile because it is electron-deficient and the aryl compound act as the nucleophile.[3] The coupling component, 2-(N-ethylanilino) ethanol, reacts with the diazonium salt to form the diazo dye, in this case red 13.

The purpose of this experiment was to synthesize diazo dye red 13 using the principle of combinatorial chemistry and to purify it via recrystallization. The dye formed was then analyzed by melting point, 400 MHz ^{1}HNMR, and UV-Vis spectrophotometry to confirm that the product was formed.



Scheme 1: Mechanism for the synthesis of diazo dye Red 13

Experimental:

Diazo Dye Red 13 (0.269 g, 0.77 mmol). 2-chloro-4-nitroaniline (0.855 g, 0.005 mol), 12M hydrochloric acid (1.60 mL), and distilled water (1.6 mL) were added together and stirred until dissolved. Once dissolved place in an ice bath. Prepared a solution of sodium nitrite (0.381 g, 0.005 mol) and distilled water (1.5 mL). Added this solution to the acidic aniline solution and cooled on an ice bath. Add 2-(N-ethylanilino) ethanol (0.842 g, 0.005 mol) and glacial acetic acid (0.70 mL) together. Slowly add solution to the diazotized sodium nitrite solution. Stirred and cooled on an ice bath for 10 minutes. Filtered solution via vacuum filtration and washed with cold distilled water. Allowed to dry. Purified crude product via recrystallization with 80% ethanol (60 mL of 95% ethanol/12 mL of distilled water). Upon recrystallization isolate product via vacuum filtration and let dry. ^{1}HNMR (400 MHz, DMSO): δ ppm 1.1529-1.1878 (t, 3H), 3.2-3.5 (s, 1H), 3.5470-3.5937 (t, 2H), 3.6167-3.6460 (q, 2H), 6.8964-6.9197 (d, 1H), 7.7691-7.7915 (d, 1H), 7.8313-7.8543 (d, 1H), 8.2259-8.2545 (d, 1H), 8.4 (s, 1H). UV-Vis: λ_{max} 500.6 nm.

Results and Discussion:

In this experiment, the diazo dye red 13 was formed from the coupling of an aminobenzene group, 2-chloro-4-nitroaniline, and an activated aryl amine compound, 2-(N-ethylanilino) ethanol. The formation of the diazonium salt is carried out first through a Sandmeyer synthesis where the aromatic amine reacts with sodium nitrite forming the diazonium salt. Once the diazonium salt is formed, the coupling reaction occurs via an electrophilic aromatic substitution reaction yielding the diazo dye red 13.

From the results, the percent recovery of the product was about 44%. The melting point of the red 13 formed was between 128-130°C, which is in the range of the literature value of 122-129°C and from the UV-Vis spectrophotometry analysis it shows that the λ_{max} absorption is around 500.6 nm, which is similar to the reported wavelength for red 13 dye of 503 nm. To further confirm whether or not the product formed was red 13, a 400 MHz ^{1}HNMR was performed to analyze the structure of the product.

From the 400 MHz ^{1}HNMR, there are nine peaks of interest. The first peak of interest (H_a) is a triplet between 1.1529-1.1878 ppm integrated to three that indicates the presence of a methyl group. The second peak of interest (H_j) is a singlet between 3.2-3.5 ppm integrated to one that indicates the presence of a hydroxyl group. The third peak of interest (H_i,H_h) is a doublet between 3.570-3.5937 ppm that is a triplet that are overlapping due to splitting patterns integrated to four that indicates the presence of a hydroxyethyl group. The fourth peak of interest (H_b) is a quadruplet between 3.6167-3.6460 ppm integrated to two that indicates the presence of an ethyl group. The fifth peak of interest (H_c) is a doublet between 6.8964-6.9197 ppm integrated to two that indicates the presence of two aromatic hydrogens. The sixth peak of interest (H_f) is a doublet between 7.7691-7.7915 ppm integrated to one that indicates that presence of an aromatic hydrogen. The seventh peak of interest (H_d) is a doublet between 7.8313-7.8543 ppm integrated to 2 that indicates two aromatic hydrogens. The seventh peak (H_d) is shifted further downfield than the fifth peak (H_c) because of the neighboring azo group. The eighth peak of interest (H_e) is a doublet integrated to one that indicates the presence of an aromatic hydrogen. The eighth peak (H_e) is shifted further downfield than the sixth peak (H_f) because it is closer to the azo group. And lastly the last peak of interest (H_g) is a singlet at 8.4 ppm that indicates the presence of an aromatic hydrogen and is the furthest shifted downfield because of the chlorine atom and the nitrogen dioxide. From peaks five to nine ($H_{c,d,e,f,g}$), there are a total of 7 aromatic hydrogens, which is the number of aromatic hydrogens that the structure contains. Therefore, based on the analysis of the 400 MHz ^{1}HNMR it can be confirmed that product form was the diazo dye red 13 (Figure 1, Structure of Diazo Dye Red 13).

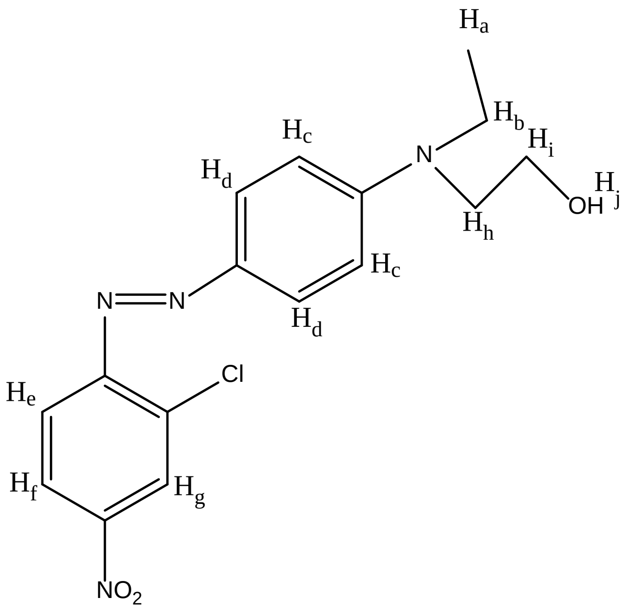


Figure 1: Structure of Diazo Dye Red 13

In conclusion, the product diazo dye red 13 was formed successfully through the electrophilic aromatic substitution reaction according to the 400 MHz ^{1}HNMR that also shows relatively good purity, however the yield was relatively low. Possible sources of error that could explain the low percent recovery could have stemmed from the 2-chloro-4-nitroaniline not fully dissolving in the hydrochloric acid and distilled water resulting in loss of product, during the recrystallization the crude product could have melted during the heating process, etc. Future improvements that can be made is possibly changing the nitrite salt from sodium nitrite to nitrous acid to see if it yields a better formation of diazonium salt and in turn yielding a better product. Bench skills can also always be improved as well.

References:

1. Ferraz, E. R. A., G. A. Umbuzeiro, G. De-Almeida, A. Caloto-Oliveira, F. M. D. Chequer, M. V. B. Zanoni, D. J. Dorta, and D. P. Oliveira. "Differential Toxicity of Disperse Red 1 and Disperse Red 13 in the Ames Test, HepG2 Cytotoxicity Assay, and Daphnia Acute Toxicity Test." *Environmental Toxicology* **2011**, 26.5, 489-97.

2. Parmeggiani, Fabio. "Fear of the Dark: Diazo Printing by Photochemical Decomposition of Aryldiazonium Tetrafluoroborates." *Journal of Chemical Education* **2014**, *91.5*, 692-695

3. Gung, Benjamin W. and Taylor, Richard T. "Parallel Combinatorial Synthesis of Azo Dyes: A Combinatorial Experiment Suitable for Undergraduate Laboratories." *Journal of Chemical Education* **2011**, *81.11*, 1630.

Supplemental Information:

Figure 1: Structure of Diazo Dye Red 13

Figure 2: UV-Vis Spectrum Analysis

Figure 3: 400 MHz ^{1}HNMR

Figure 4: 60 MHz ^{1}HNMR