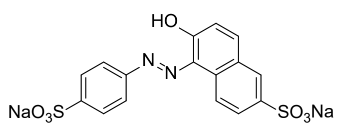
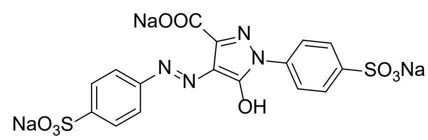
Azo Dye: Synthesis of Yellow 6 (Sunset Yellow)

Introduction

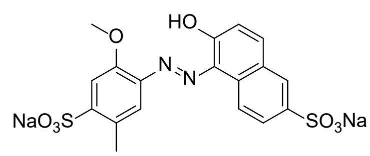
Azo dye are synthetic compounds characterized by one (mono azo) or several intramolecular N=N double bonds. Azo dyes can be found in a wide range of foods, including Cheetos, Sunkist soda drinks, cheese products, and candies. To synthesize azo dyes, aromatic diazonium salt is to be coupled with electron-rich aromatic species. The coupling reaction can be carried out in a basic, neutral or weakly acidic medium.



Yellow 6 - Sunset Yellow
Chemical Formula: $C_{16}H_{10}N_2Na_2O_7S_2$
Molecular Weight: 452.36

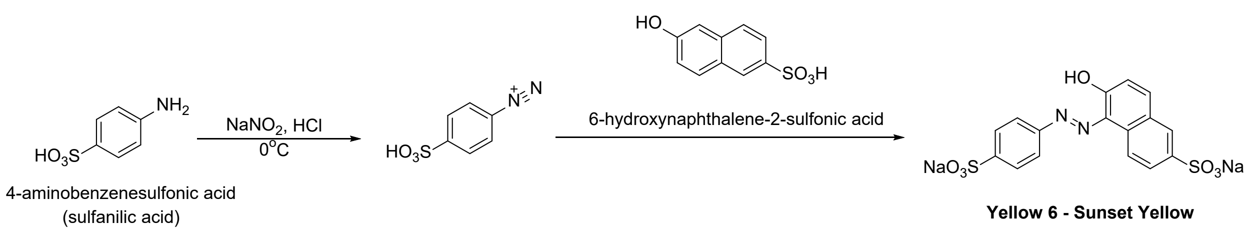


Yellow 5 - Tartrazine
Chemical Formula: $C_{16}H_9N_4Na_3O_9S_2$
Molecular Weight: 534.36



Red 40 - Allura AC
Chemical Formula: $C_{18}H_{14}N_2Na_2O_8S_2$
Molecular Weight: 496.42

In this experiment, a commercial food grade dye called Yellow 6, also known as Sunset yellow, will be synthesized. In this two-step synthesis, 4-aminobenzenesulfonic acid is converted to 4-sulfobenzenediazonium at first. The resulting diazonium salt couples with 6-hydroxynaphthalene-2-sulfonic acid in the second step to yield yellow 6, a bright orange-yellow azo dye.



Procedure

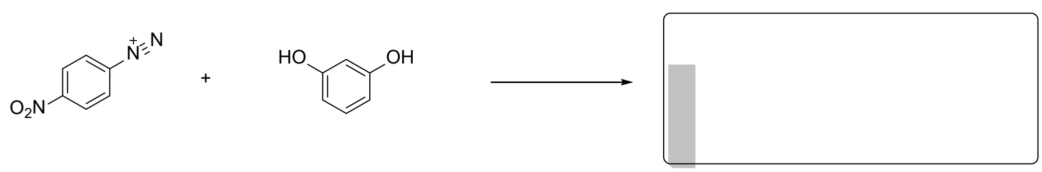
1. Mix 175 mg of sulfanilic acid and 100 mg of sodium carbonate in 5 mL of water in a 50 mL Erlenmeyer flask. Suspension can be heated gently to dissolve all the reagents. Let the solution cool to room temperature.

2. Add 100 mg of sodium nitrite and 1 mL of water to a test tube. Add this $NaNO_2$ solution to the solution in step 1, cool the mixture in an ice-water bath.
3. Slowly add 0.5 mL of concentrated hydrochloric acid to 3 g of ice in a small beaker. (**Caution: Concentrated HCl should be handled in fuming hood by the instructors**.)
4. Slowly add the solution in the Erlenmeyer flask dropwise into the small beaker. Swirl the beaker constantly so the internal temperature doesn't rise above 5°C.
5. After addition is completed, leave the beaker in ice-water bath for another 5 min. Swirl the beaker occasionally.
6. While waiting, dissolve 225 mg of 6-hydroxynaphthalene-2-sulfonic acid in 10 mL of 2.5 M sodium hydroxide solution in a 50 mL Erlenmeyer flask. Add a large stirring bar and cool the solution in ice-water bath for 5 minutes.
7. Slowly add the diazonium salt solution dropwise by a pipette into the NaOH solution with magnetic stirring. (**Caution: Do not turn on the heating**)
8. Leave the resulting mixture in ice-water bath with stirring for another 10 min. Add 1 g of NaCl to the mixture. Flask can be heated gently on a hotplate until all solid dissolves. Cool the mixture to room temperature, then in ice-water bath until precipitate forms. Collect the product by vacuum filtration.
9. Recrystallize the crude product with 1:1 EtOH/water mixture.

Questions

1. Suggest the structures of the product:

A



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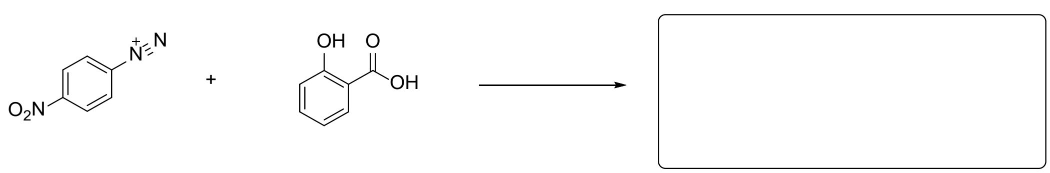

2. During the coupling reaction of diazonium and 6-hydroxynaphthalene-2-sulfonic acid, why does the coupling (electrophilic substitution) only occur in one position? (Hint: Draw the resonance structures of the reaction intermediates)

3. Suggest mechanism for the reaction of 4-aminobenzensulfonic acid with sodium nitrite to form 4-sulfobenzenediazonium.

Reference

1. Tami, K., Popova, A. and Proni, G., Engaging students in real-world chemistry through synthesis and confirmation of azo dyes via thin layer chromatography to determine the dyes present in everyday foods and beverages. *Journal of Chemical Education*, 2017. *94*(4), pp.471-475.
2. Gung, B.W. and Taylor, R.T., Parallel combinatorial synthesis of azo dyes: a combinatorial experiment suitable for undergraduate laboratories. *Journal of chemical education*, 2004. *81*(11), p.1630.
3. http://www.chm.bris.ac.uk/webprojects2002/price/azo.htm