Exp.09: preparation of Methyl Orange

Objectives:

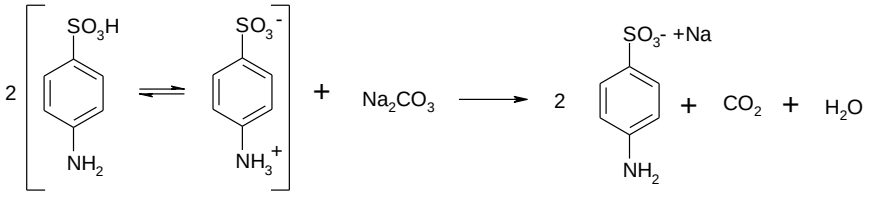
- Preparation of Methyl Orange

Introduction:

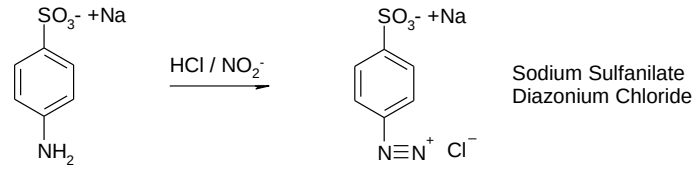
A chromophore is a simple, unsaturated, e^- withdrawing group attached to an aromatic ring system. The extended conjugation due to the chromophore decreases □ E (and increases □$_{max}$) of the □ →□ * transition, so that the □$_{max}$ is in the visible range. Examples include nitro (-NO_2), azo (-N=N-), carbonyl (C=O), and nitrile (-CN).

Preparation:

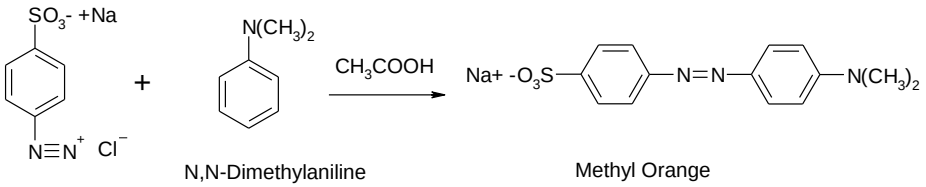
- The first step is called "diazotization." Sodium sulfanilate reacts with sodium nitrite in hydrochloric acid (i.e., nitrosocation) to form an unstable "diazonium salt."
- The second step is the "diazonium coupling reaction." The diazonium ion is used in situ, and reacts with N,N-dimethylaniline to form the acidic azo dye.
- The crude dye will then be isolated, and used to create dyed nylon fabric.



Sulfanilic Acid (zwitterion) Sodium Sulfanilate



Sodium Sulfanilate
Diazonium Chloride



N,N-Dimethylaniline Methyl Orange

Reaction Scheme

Procedure

Pretreatment before Diazotization

1. Dissolve 1.2 g anhydrous Na_2CO_3 with 50 ml DI H_2O in a 125-ml Erlenmeyer flask using a stir bar.
2. Add 3.6 g anhydrous sulfanilic acid, and heat solution with a hot water bath until dissolved. (It may still appear cloudy.)
3. Gravity filter if solids are present, then rinse paper with 3-5 ml of hot water.Discard filtered solids, and cool filtrate to room temperature.

Diazotization Reaction

4. Add 1.5 g $NaNO_2$ to filtrate, and stir until dissolved.
5. Add 5 ml conc. HCl to a 400-ml beaker containing 25 ml of (50% / 50%) ice water while stirring. Caution: Conc. acids are corrosive!
6. Pour sulfanilate solution into 400-ml beaker with HCl solution, and place beaker in an ice bath. The diazonium salt will form as a white solid.

Coupling Reaction

7. Obtain 2.7 g of N,N-dimethylaniline (d = 0.96 g/ml) in a 10-ml graduated cylinder, and pour directly into the 400-ml beaker. Wash cylinder with 2.0-ml conc. acetic acid, and add contents to 400-ml beaker. Stir for 15-20 min at 20-25^{o}C to ensure complete reaction. Caution: N,N-dimethylaniline is toxic and is readily absorbed through the skin! Handle only with gloves! It is also volatile, and needs to remain completely *in the hood* until transfer is complete!
8. Slowly add 30 ml of 10% NaOH. Check pH of aqueous phase. Add additional NaOH solution, if necessary, until basic.

Isolation of Crude Dye

9. Heat to boiling with hot plate for 10-15 minutes. When most of dye is dissolved, add 10 g NaCl (salting out), then cool crude reaction mixture in an ice bath.
10. Vacuum filter, and wash dye twice with 10 ml cold, saturated NaCl solution. Discard filtrate in sink (~110 ml aq salt waste).
11. Remove 0.5 g of dye, and dry remainder in oven overnight to obtain yield.

Data To Collect

- Rather than only pasting reactions and mechanisms into the report, describe the mechanisms qualitatively in a paragraph or two.
- Determine theoretical yield % by finding moles of the product and of the two reagents.
- Also, attach a portion of the dyed fabric to your report.

Laboratory Report

Name: ---------- Date: ----------

Experiment Subject: ----------

- Reaction:

Calculations:

Compound	Mol. Formula	Mol. Wight	Moles	Wight, mg	Density	Volume	Limiting reagent

Purification:

Recrystallization solvent: ----------

Purity check by melting range: ----------

TLC: ----------

Physical Data (Product):

State: ---------- Melting Point: ----------

Color: ---------- Solubility: ----------

Yield:

Characterization:
