Exp.09: preparation of Methyl Orange

Objectives:
- Preparation of Methyl Orange

Introduction:
A chromophore is a simple, unsaturated, \( \text{e}^- \) withdrawing group attached to an aromatic ring system. The extended conjugation due to the chromophore decreases \( \Delta E \) (and increases \( \Delta \text{max} \)) of the \( \Delta \rightarrow \Delta^* \) transition, so that the \( \Delta \text{max} \) 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.
Reaction Scheme

Procedure

Pretreatment before Diazotization
1. Dissolve 1.2 g anhydrous Na$_2$CO$_3$ with 50 ml DI H$_2$O 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°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.
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:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Formula</th>
<th>Mol. Wight</th>
<th>Moles</th>
<th>Wight, mg</th>
<th>Density</th>
<th>Volume</th>
<th>Limiting reagent</th>
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Purification:

Recrystallization solvent: _______________________________________________________

Purity check by melting range: _________________________________________________

TLC: ________________________________

Physical Data (Product):

State: _______________________ Melting Point: _________________________

Color: ________________________ Solubility: _________________________

Yield:

______________________________________________________________________________

______________________________________________________________________________
Characterization: