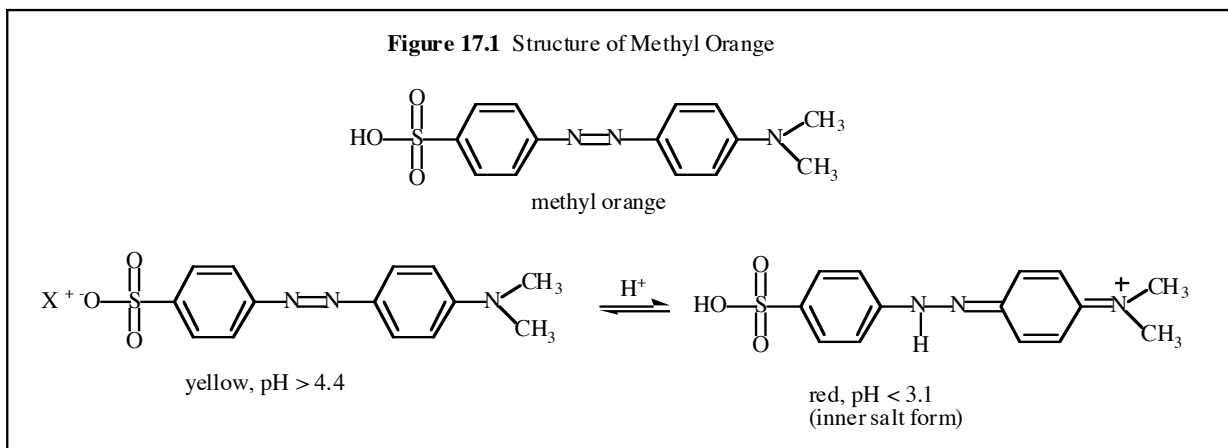


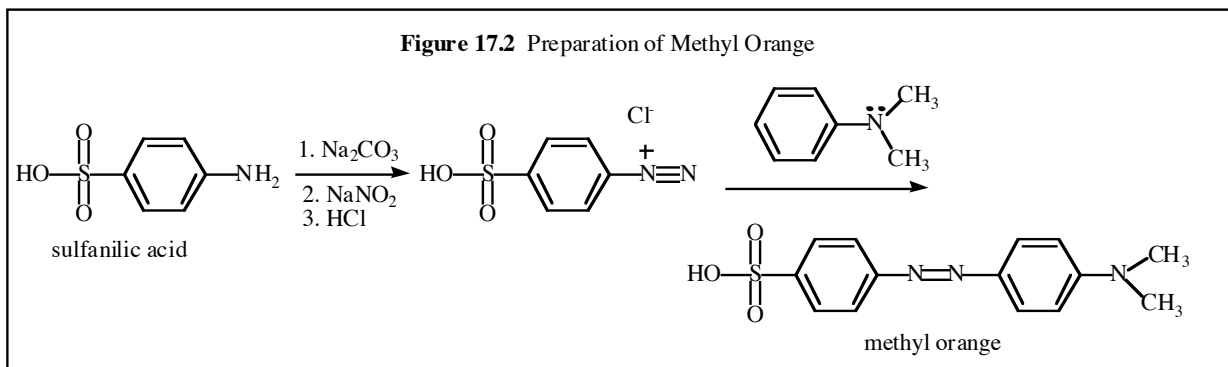
## Experiment 17

### Preparation of Methyl Orange

In this experiment you will prepare methyl orange, an azo dye that forms beautiful orange crystals and is used as an acid-base indicator (Figure 17.1). The anion form is yellow and the acid form is red.

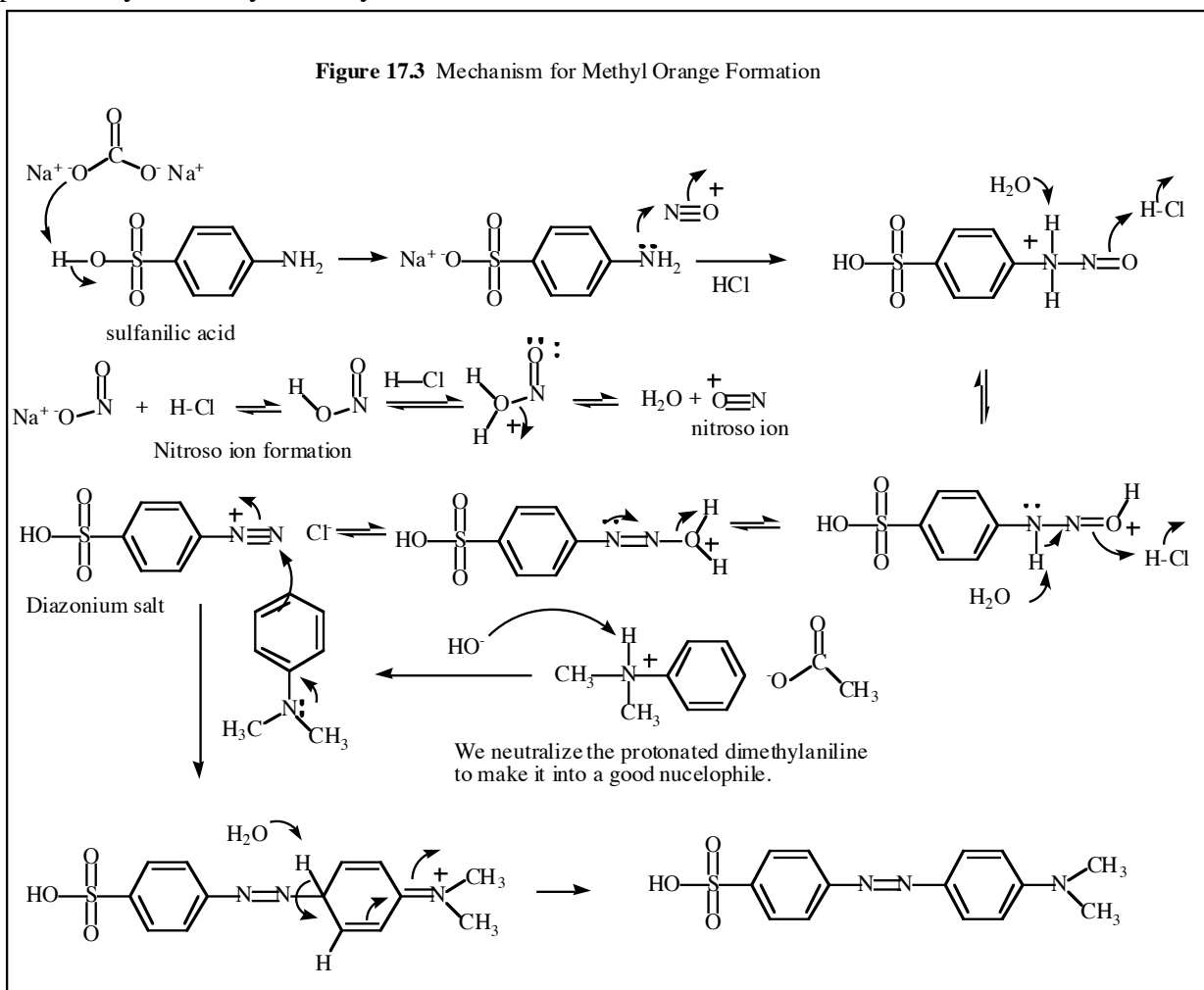


You will synthesize methyl orange from sulfanilic acid and N,N-dimethylaniline using a diazonium coupling reaction just like the one you saw in the previous experiment in the nitrous acid test for primary aromatic amines. The overall reaction is shown in Figure 17.2 and the mechanism is shown in figure 17.3. All of this chemistry is in your text in the chapter on amines. You need to understand it.



The first step is simply an acid base reaction. In order to dissolve the sulfanilic acid in the aqueous solution we add sodium carbonate. Then we form the diazonium salt by the same mechanism that was presented in Figure 16.4 of the previous experiment. When we add the HCl, the nitroso ion is formed from sodium nitrite and this reacts with the amine to form a nitrosoammonium adduct that loses water under the acidic conditions after proton transfer. This gives the diazonium salt. Aromatic diazonium salts are stable at low temperature. The terminal nitrogen of the diazonium salt is very electron deficient. It can be attacked by good nucleophiles. We dissolve the dimethylaniline in

acetic acid. This forms the dimethylaniline acetate salt. Neutralize this *in situ* and the dimethylaniline becomes a good nucleophile due to the activating effect of the dimethylamine substituent. Attack is in the *para* position due to hindrance at the *ortho* position by the bulky dimethylamine substituent.



### Physical Constants

| Compound                       | Mol. Wt (g/mol) | Density (g/mL) | b.p. (°C) | m.p. (°C) |
|--------------------------------|-----------------|----------------|-----------|-----------|
| Sulfanilic acid                | 173.19          | solid          | -         |           |
| N,N-Dimethylaniline            | 121.18          | 0.956          | 193-194   | 1.5-2.5   |
| Sodium carbonate (anhydrous)   | 105.99          | solid          | -         | 851       |
| Sodium carbonate (monohydrate) | 124.01          | 2.250          | -         | -         |
| Sodium nitrite                 | 69.00           | 2.168          | -         | 271       |
| Acetic acid                    | 60.05           | 1.049          | 116-117   | 15-16     |
| Methyl orange                  | 306             |                |           |           |

## Procedure:

In order to avoid any excess of a reagent that could decompose or cause decomposition and produce tar to contaminate our dye, you need to weigh the quantities of solid reagent very carefully to the accuracy of 0.05 g or better.

In this experiment you will have to calculate for yourself some of the amounts of needed reagents. After you have calculated them, confirm your results with the instructor before proceeding.

Dissolve 0.010 mole of sulfanilic acid (anhydride) in about 50 ml of a solution of sodium carbonate containing 0.010 to 0.0125 moles of sodium carbonate in a 125 ml Erlenmeyer flask. The solution is prepared by the stockroom and its strength is indicated on the bottle, but you must calculate the exact amount needed. Warm the mixture slightly to speed up dissolution. Test one drop of the solution to make sure it is alkaline. If not, add a small amount (1-2 mL) sodium carbonate solution and check the pH again. Then add 0.010 moles sodium nitrite and cool to 25 °C (room temperature).

Put 40 g of ice in a 400 mL beaker and add enough hydrochloric acid of a 6M or a 12 M solution in order to provide a total of 0.030 mol HCl in your beaker.

Add the sulfanilate solution prepared above in a fine stream while stirring continuously. Keep this solution cold in the ice bath at all times. It now contains your diazonium salt, which will decompose if it becomes warm. It is only partially soluble in the aqueous solution and will precipitate as a bluish-greenish solid.

Prepare a solution of N,N-dimethylaniline (0.010 mol) in 0.010 mol of acetic acid in a 25 ml Erlenmeyer flask.

Now add the dimethylaniline acetate solution slowly with constant stirring to the suspension of the diazonium salt. A dull, reddish-purple mass should appear.

Now, **VERY SLOWLY** add about 30 mL of 1.0 M sodium hydroxide solution with constant stirring. Add the NaOH a few mL at a time. The addition should take 10 - 15 minutes. The actual coupling reaction does not occur until you add the NaOH. The reaction takes place best at about pH 7. Keep adding the NaOH until the solution becomes basic (blue to litmus.)

If the sodium hydroxide is added too quickly, then free dimethylaniline will separate out as an oily phase. This then leaves an equivalent amount of the diazonium salt unreacted. This excess salt decomposes to brown tar on warming to room temperature and contaminates the otherwise beautiful crystalline orange dye.

At the end of the coupling reaction a yellow-orange or golden color should be observed. The product will now be recrystallized from the reaction mixture. Heat the reaction mixture to boiling using your tripod and Bunsen burner. Everything should dissolve and the solution should be clear (though it will be highly colored). If all the material does not dissolve when the solution is heated to boiling, add more water as needed. Then, allow it to cool slowly to room temperature to crystallize and then place the flask in an ice bath to get it as cold as possible. Remember: do not stir or shake the solution when it is cooling. Allow the crystals to form in an undisturbed flask. They will be much purer and larger if they form slowly in a motionless flask.

Filter the crystals by suction filtration, rinse them with 10 – 15 ml cold water and allow them to dry. Calculate the percent yield and turn in your crystals in a vial along with your Organic Yield Report Sheet.

Do not attempt to take the melting point of your methyl orange as it decomposes on heating. In order to observe the beautiful color change that occurs with our orange indicator dye, dissolve a small amount of the methyl orange in 2-3 mL of 95% ethanol and add 5% HCl a few drops at a time until you see the color change. Describe your results in your notebook.

