**Experiment name :** Methyl orange

**Classification:** Diazonium salts and their coupling reactions

**Reaction scheme:**



**Experimental procedure and purification technique:**

In a 50 ml beaker place sulphanilic acid dihydrate (1.05 g; 5 mmol), anhydrous sodium carbonate (0.27 g; 2.5 mmol) and water (10 ml), and warm until a clear solution is obtained. Cool the solution under the tap to about 15 °C, and add a solution of sodium nitrite (0.37 g; 5.4 mmol) of sodium nitrite in water (1 ml). Pour the resulting solution slowly and with stirring into a 100 ml beaker containing concentrated hydrochloric acid (1 ml) and crushed ice (6 g)[[1]](#footnote-1). Test for the presence of free nitrous acid with potassium iodide-starch paper after 15 minutes. Fine crystals of the diazobenzene sulphonate will soon separate; do not filter these off as they will dissolve during the next stage of the preparation. Dissolve dimethylaniline (0.61 g; 0.6 ml; 5 mmol) in glacial acetic acid (0.3 ml), and add it with vigorous stirring to the suspension of diazotised sulphanilic acid. Allow the mixture to stand for 10 minutes; the red or acid form of methyl orange will gradually separate. Then add slowly and with stirring sodium hydroxide solution (3.5 ml, 20%): the mixture will assume a uniform orange colour due to the separation of the sodium salt of methyl orange in fine particles. Direct filtration of the latter is slow, hence, while stirring the mixture with a thermometer, heat it almost to the boiling point. Most of the methyl orange will dissolve. Add sodium chloride (~1g) (to assist the subsequent separation of the methyl orange) and warm at 80-90 °C until the salt has dissolved. Allow the mixture to cool undisturbed for 15 minutes and then cool in ice-water; this gives a fairly easily filterable product. Filter off the methyl orange at the pump, but apply only gentle suction so as to avoid clogging the pores of the filter paper; rinse the beaker with a little saturated salt solution and drain well. Recrystallise from hot water (about 15 ml are required); filter the hot solution, if necessary, through a hot water funnel or through a preheated Buchner funnel. Reddish-orange crystals of methyl orange separate as the solution cools. Filter these at the pump, drain well, wash with a little ethanol, and finally with a small volume of ether. Predicted yield: 1.3 g (72%). Methyl orange, being a salt, has no well-defined m.p.

Reference source (1): “Vogel’s Textbook of Practical Organic Chemistry (5th edition)”: 951.

Reference source (2): “Denel Organik Kimya (6th edition)”: 890.

1. An alternative procedure is to cool the solution containing the sodium sulphanilate and sodium nitrite in a batlı of crushed ice to about 5 °C and then add concentrated hydrochloric acid (2 ml) diluted with an equal volume of water slowly and with stirring; the temperature must not be allowed to rise above 10 °C and an excess of nitrous acid should be present (the solution is tested after standing for 5 minutes). The subsequent stages in the preparation - addition of dimethylaniline solution, ete. - are as above. [↑](#footnote-ref-1)