SMALL SCALE PREPARATION OF METHYL RED INDICATOR*

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In the preparation of methyl red indicator, both the diazotization of anthranilic acid and the coupling with dimethylaniline are usually carried out in an aqueous medium, e.g. as in the procedure described by Clarke and Kirner (1932). Even on a smaller scale than they describe, the operations are time consuming and the purification tedious. In more than one laboratory, between five and ten grams are sufficient for many months' work ; the method described below is suitable for such small quantities, requires only a brief working time, and gives satisfactory yields. The essential difference of the method is that both diazotization (with butyl nitrite) and coupling are carried out in glacial acetic acid from which the crude indicator is precipitated free from inorganic salts.

Experimental

Anthranilic acid (6·85 g. ; 0·05 mole) is dissolved in glacial acetic acid (50 ml.) with warming if necessary. The solution is cooled in an ice-bath with stirring until the acetic acid begins to crystallize. *n*-Butyl nitrite (5·7 ml. ; 0·05 mole) (*Note 1*) is then added with stirring at such a rate that the temperature does not rise. When the addition is complete, the solution is allowed to stand for 15 minutes. Dimethylaniline (10·3 ml. ; 0·075 mole) is then added rapidly, the reaction mixture is stirred well and allowed to stand in ice and water for at least 3 hours, but preferably overnight. The precipitated methyl red is filtered, washed with 10 ml. of glacial acetic acid, and dried in a vacuum desiccator over solid sodium hydroxide. The crude yield is 7–8 g. (50–60%).

The crude material is best purified by Clarke and Kirner's method (loc. cit.) of extraction with boiling toluene using 10 ml. per gram of dry solid (*Note 2*). When the toluene extract is colourless, the flask is transferred to a boiling water-bath and allowed to cool slowly. After filtration and drying in a steam oven, the purified material appears as shining permanganate coloured plates, m.p. 178–179 °C. (uncorr.), and is suitable for most purposes ; if desired the purification by toluene extraction may be repeated. The efficiency of recovery in the purification stage is 80–90%.

Note 1.—*n*-Butyl nitrite is best prepared by the method of Noyes (1943).

Note 2.—The extraction is conveniently carried out in a " Quickfit " hot extraction apparatus (Catalogue No. EX 1/22). This holds a 25 by 80 mm. Soxhlet thimble which is suitable for a preparation on this scale.

References

CLARKE, H. T., and KIRNER, W. R. (1932).—" Organic Syntheses." Collective Vol. 1, p. 366. (Wiley : New York.)

NOYES, W. A. (1943).—" Organic Syntheses." Collective Vol. 2, p. 108. (Wiley : New York.)

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