

RE-EXAMINATION OF THE AZO COMPOUND FORMED IN THE  
REACTION BETWEEN *N*-SULPHINYLANILINE AND  
*p*-TOLYLHYDROXYLAMINE\*

By G. E. LEWIS† and M. A. G. OSMAN†

It has been claimed by Michaelis and Petou<sup>1</sup> that the azo-compound formed in the reaction between *N*-sulphinylaniline (thionylaniline) and *p*-tolylhydroxylamine is 2,4'-azotoluene. It has now been shown that this is incorrect and that the product is *trans*-4-methylazobenzene.

Careful repetition of the reaction as described by Michaelis and Petou yielded only one azo-compound, m.p. 70–71·5° (lit.<sup>1</sup> 68–72°). The melting point was depressed to the range of 31–39° on admixture with either *cis*- or *trans*-2,4'-azotoluene, both of which have been prepared by unambiguous methods. The product, m.p. 70–71·5°, was identified as *trans*-4-methylazobenzene by comparison with an authentic sample.<sup>2</sup>

*Experimental*

*Identification of the Product from the Reaction of N-Sulphinylaniline with p-Tolylhydroxylamine.*—The reaction was carried out exactly as previously described.<sup>1</sup> The product after chromatography in light petroleum solution on alumina and final crystallization from ethanol yielded orange plates, m.p. 70–71·5° (Found: N, 14·1%. Calc. for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>: N, 14·3%). No depression of melting point was observed following admixture with an authentic sample of *trans*-4-methylazobenzene available from previous work,<sup>2</sup> and the infrared absorption spectra of the two samples in carbon tetrachloride solution were found to be identical.

*trans- and cis-2,4'-Azotoluene.*—A solution of *p*-toluidine (2·65 g) in glacial acetic acid (3 ml) was added to a solution of *o*-nitrosotoluene (3 g) in the same solvent (12 ml) and the mixture allowed to stand overnight. Dilution with a large excess of water then caused precipitation of an orange-brown product which was extracted with light petroleum. The extract was washed free of acetic acid, dried (anhydrous sodium sulphate), and finally passed through a column of alumina. The solid material obtained after evaporation of the solvent was recrystallized from methanol. *trans*-2,4'-Azotoluene was thus obtained as red-orange leaflets, m.p. 51–52° (Found: C, 79·7; H, 6·8; N, 13·3%. Calc. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 80·0; H, 6·7; N, 13·3%). A portion of the pure *trans*-compound was photochemically isomerized by the procedure used by Hartley<sup>3</sup> for the preparation of *cis*-azobenzene. After recrystallization from light petroleum at –15° *cis*-2,4'-azotoluene was obtained as red-orange platelets, m.p. 61–62° (Found: C, 80·2; H, 6·6; N, 13·2%. Calc. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 80·0; H, 6·7; N, 13·3%).

Acknowledgment is made to the U.N.E.S.C.O. Technical Assistance Programme for the award of a Fellowship to one of us (M.A.G.O.) and to the Australian Micro-analytical Service, Melbourne, for the microanalyses.

\* Manuscript received January 20, 1964.

† Department of Organic Chemistry, University of Adelaide.

<sup>1</sup> Michaelis, A., and Petou, K., *Ber. deutsch. chem. Ges.*, 1898, **31**, 984.

<sup>2</sup> Badger, G. M., Drewer, R. J., and Lewis, G. E., *Aust. J. Chem.*, 1963, **16**, 1042.

<sup>3</sup> Hartley, G. S., *J. Chem. Soc.*, 1938, 633.