A New Synthesis of 1-Methylphenazine (1)

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In connection with studies on the biosynthesis of phenazines 1-methylphenazine was required. This paper describes a new convenient synthesis of this compound.

Search of the literature has shown that the title compound has been synthesized utilizing tedious methods resulting in relatively low yields. Condensation of 2,3-diaminotoluene with *o*-benzoquinone is impractical because of the low yield and the difficulties in the preparation of *o*-benzoquinone (2). The same objections are raised against the condensation of 3-methyl-1,2-benzoquinone with phenylenediamine (3). In the condensation of *o*-phenylenediamine with 1-methylcyclohexane-2,3-dione, followed by aromatization, in an over-all yield of 40% (4), the dione is not readily accessible. Application of the Wohl-Aue reaction to *o*-toluidine and nitrobenzene results in a 6-8% yield (5). Synthesis via ring closure of 2-nitro-2′-methyldiphenylamine is lengthy and suffers from a low yield (4%) (2,6).

We have found that 1-methylphenazine can be conveniently prepared in 76% yield according to Morley's method (7) by condensation of 2,3-diaminotoluene with pyrocatechol, followed by oxidation. In view of the discrepancy between the two available ultraviolet spectral data of 1-methylphenazine (6,8), particular care was taken in the determination of the spectrum of our sample.

EXPERIMENTAL (9)

2,3-Diaminotoluene.

2,3-Diaminotoluene was prepared from o-toluidine according to reference (10), followed by catalytic reduction over Raney nickel in an over-all yield of 55%, m.p. 60-60.5° (lit. (11) 61-62°).

1-Methylphenazine.

A mixture of 2,3-diaminotoluene (1.35 g., 11.1 mmoles) and 1.25 g. (11.4 mmoles) pyracatechol (Eastman, practical grade) was finely ground together and heated in a sealed tube under nitrogen at 230° for 24 hours. The product was dissolved in ether, extracted twice with 1 *N* sodium hydroxide and once with water. Removal of ether from the dried solution yielded 2.26 g. of a violet semicrystalline material. It was transferred to a 20 mm-wide tube and placed horizontally in an oven. A slow stream of oxygen was passed through the tube and the temperature was raised to 230°. Yellow crystals of slightly impure 1-methylphenazine deposited in the cold region of the tube during 2-4 hours. The product was chromatographed on alumina (Woelm, grade I) and eluted with benzene and benzene/ether. The yield was 1.62 g. (0.84 mmoles, 76%), m.p. 107-109° (lit. (6) 108°), λ max (ethanol), 253 mμ (log ε 5.01), 364 mμ (log ε 4.10) [lit. (8) 255 (5.13), 362.5 (4.48); lit (6) 251.5 (5.2), 363 (4.2)].

Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.17; H, 5.21; N, 14.15.

REFERENCES

(1) This work was supported by grant GB-6749 from the National Science Foundation.

(2) H. McCombie, H. A. Scarborough, W. A. Waters, *J. Chem. Soc.*, 353 (1928).

(3) C. Mermod, *Helv. Chim. Acta*, 18, 362 (1935).

(4) G. R. Clemo, H. McIlwain, *J. Chem. Soc.*, 1991 (1934).

(5) Y. S. Rozum, *J. Gen. Chem. U.S.S.R.*, 25, 583 (1955); *Chem. Abstr.*, 50, 3462 (1956).

(6) W. Waters, D. Watson, *J. Chem. Soc.*, 2085 (1959).

(7) J. S. Morley, *J. Chem. Soc.*, 4008 (1952).

(8) L. Birkhofer, *Chem. Ber.*, 85, 1023 (1952).

(9) Melting points were obtained with a calibrated Kofler melting point apparatus. The ultraviolet spectrum was measured on a Beckman Model DU spectrophotometer, calibrated according to "Handbook of Analytical Chemistry", L. Meites, Ed., McGraw Hill, New York, N. Y., 1963, Sec. 6, p. 10.

(10) *Org. Synth., Coll. Vol.* IV, 42 (1963).

(11) E. Lellman, *Ann. Chem.*, 228, 243 (1885).

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