Research Laboratories, Canadian Technical Tape Ltd.

Convenient Quantitative Preparation of Phthalazine

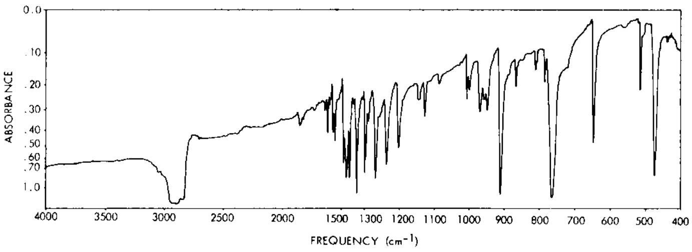
Arthur Hirsch and Demetrius Orphanos

Phthalazine has been obtained by heating hydrazinophthalazine monohydrochloride with copper sulfate (1), by the catalytic reduction of 1-chlorophthalazine with 5% palladium on charcoal (2), by heating an aqueous suspension of tetrachloro- or tetrabromo-*o*-xylene with hydrazine, (3), by the reduction of 1-chlorophthalazine with hydriodic acid and red phosphorous (4), and by heating at 80° an aqueous solution of *o*-phthalaldehyde with hydrazine sulfate in the presence of sodium hydroxide (5).

Repetition of the methods described by Gabriel, *et al.* (3,4) gave unsatisfactory results. The procedure reported by Smith and Otremba (5) claims relatively satisfactory yields (56%). The isolation of pure phthalazine from the dark-green reaction mixture could not be readily achieved. The final product, judging by the reported melting point and color, remains impure. However, this latter method was found accessible to a modification by which the desired compound was obtained more conveniently in an almost pure state and quantitative yield.

EXPERIMENTAL

A solution of 13.4 g. *o*-phthalaldehyde (0.1 mole) (6) in 100 ml. of ethanol was added dropwise with constant stirring, under a blanket of nitrogen, to an ice cooled solution of 15 g. hydrazine hydrate (0.3 mole) in 100 ml. ethanol. The rate of addition (approximately 1 hour) was adjusted to maintain the reaction mixture at 0° C throughout. The light yellowish reaction mixture was kept with constant stirring at 0° for an additional hour. The solution was thereafter permitted to reach room temperature and kept at room temperature for 2 hours. The ethanol, together with excess hydrazine and small amounts of water were removed under reduced pressure. There remained a yellowish oil, which on cooling was solidified to a pale yellow solid. This product was placed overnight in a vacuum desiccator, containing concentrated sulfuric acid, in order to remove the last traces of hydrazine. The product thus obtained melted at 86-88° and weighed 12.8 g. (98.5%).



The crude phthalazine was dissolved in diethyl ether, treated with 0.5 g. charcoal, and filtered. The colorless solution upon evaporation, yielded white hard prisms, melting at 90-91°. The loss from this purification step was negligible and a yield of 12.5 g. (96%) of pure phthalazine was obtained. Aside from the correct melting point, (Rep. m.p. 90-91°) the identity of the compound was further supported by its infrared spectrum (7), which was identical to that given by the substance prepared by means of three different known methods (3,4,5).

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REFERENCES

(1) W. Armarego, *J. Appl. Chem.*, 11, 70 (1961).

(2) E. Stephenson, *Chem. and Ind.*, 174 (1957).

(3) S. Gabriel and G. Pinkus, *Ber.*, 26, 2210 (1893); S. Gabriel and F. Muller, *ibid.*, 28, 1831 (1895).

(4) V. Paul, *ibid.*, 32, 2014 (1899); S. Gabriel, *ibid.*, 36, 3373 (1903).

(5) R. Smith and E. Otremba, *J. Org. Chem.*, 27, 879 (1962).

(6) "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 807.

(7) Infrared spectra were recorded on a Perkin-Elmer Model 337 Spectrophotometer from nujol mulls.

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Montreal 9, Canada