

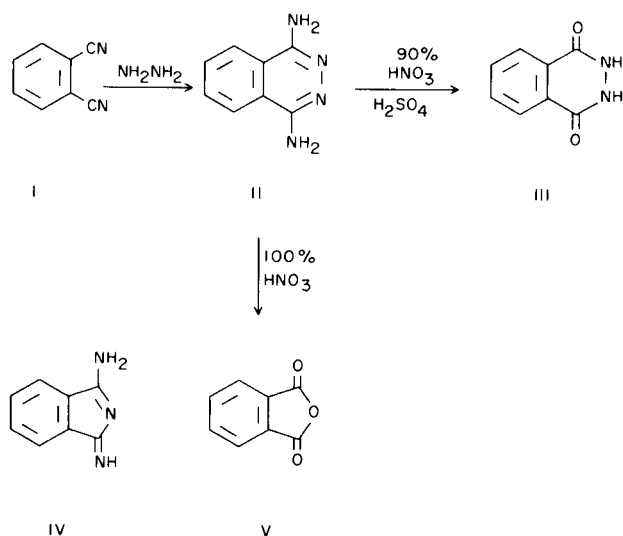
A One-step Synthesis of 1,4-Diaminophthalazine from Phthalonitrile

Lorraine DiStefano (1) and Raymond N. Castle (2)

Department of Chemistry, University of New Mexico

1,4-Diaminophthalazine (II) has been prepared by Wolf and Vollman (3) from 1-amino-3-iminoisoindolenine nitrate (IV), hydrazine sulfate and aqueous sodium hydroxide. Compound IV is relatively inaccessible. Satoda, Kusada and Mori (4) prepared II from 1,4-phthalazinedione (III) in five steps as follows: III \rightarrow 1,4-dichlorophthalazine \rightarrow 1-amino-4-chlorophthalazine \rightarrow 1-amino-4-methoxyphthalazine \rightarrow 1,4-diphenoxypthalazine \rightarrow II.

We have prepared 1,4-diaminophthalazine (II) in 40% yield by heating phthalonitrile (I) with 95% hydrazine in methanol. We were interested in a simple route to 1,4-diaminophthalazine in order to study nitramine formation and subsequent rearrangement of the nitro group into the adjoining benzene ring. When II was allowed to react with a concentrated nitric acid-concentrated sulfuric acid mixture (1:3) at 0-5° only 1,4-phthalazinedione (III) was the product in quantitative yield. Attempts to form a nitramine from II and 100% nitric acid (0-5°) gave phthalic anhydride (V) in 35% yield. No evidence of nitramine formation was observed.



EXPERIMENTAL (5)

1,4-Diaminophthalazine (II).

To a solution containing 2.57 g. (0.02 mole) of phthalonitrile (Fisher No. 7402-P) in 100 ml. of methanol was added dropwise 6 ml. of 95% hydrazine while stirring. The solution was allowed to stir overnight at room temperature and then heated under reflux for 2 hours. After evaporation of about half of the methanol, a light yellow precipitate was removed by filtration and recrystallized from water (Norite). Further evaporation of the original mother liquor afforded more yellow precipitate which was recrystallized from water (Norite) to give a total yield of 1.25 g. (40%) of white needles of 1,4-diaminophthalazine (II), m.p. 254° [lit. m.p. 256° (3)]; U.V. λ max (95% ethanol), 209 (ϵ , 32,050); 329 m μ (ϵ , 52,850); infrared cm⁻¹, 3300(s), 1635(s), 1550(w), 1490(m), 1440(m), 1425(m), 1360(w), 1285(w), 1270(w), 1167(m), 1045(w), 1020(m), 910(s), 790(w), 775(m), 685(m), 605(w), 495(w), (potassium bromide).

Anal. Calcd. for C₈H₈N₄: C, 60.01; H, 4.99; N, 34.99. Found: C, 59.64; H, 5.10; N, 34.65.

Reaction of 1,4-Diaminophthalazine (II) with Concentrated Nitric Acid-Concentrated Sulfuric Acid Mixture.

To 2 ml. of cold concentrated sulfuric acid at 0° was added 0.3 g. (0.0009 mole) of 1,4-diaminophthalazine (II). The mixture was allowed to come to room temperature to effect solution. The solution was then cooled to 0° and 1 ml. of concentrated nitric acid-concentrated sulfuric acid mixture (1:1) was added dropwise with stirring. The solution was stirred for 20 minutes and then ice was added. A yellow precipitate (0.4 g.) was removed by filtration, washed with water and recrystallized from ethanol to give pale yellow crystals, m.p. 336° [lit. m.p. 332-334° (6)]. The product was shown to be 1,4-phthalazinedione (III) by a comparison of the infrared spectrum of the above sample with the spectrum of an authentic sample prepared from phthalic acid by the method of Fieser (7).

The Reaction of 1,4-Diaminophthalazine (II) with 100% Nitric Acid.

To solid powdered 1,4-diaminophthalazine (0.4 g., 0.0025 mole) cooled to 0°, was added 1 ml. of 100% nitric acid with stirring. The red-orange solution was allowed to stir at 0° for 20 minutes. After 20 minutes, evolution of a red-brown gas (nitrogen dioxide?) began. Ice was added immediately to the reaction mixture. A light tan precipitate (0.2 g.) was removed by filtration and dried at about 80°. The precipitate was dissolved in benzene, decolorized (Norite) and 0.12 g. of long white needles of phthalic anhydride, m.p. 128-129° [lit. m.p. 132° (8)] was obtained.

Acknowledgment.

This investigation was supported by Contract No. 13-0565 and Contract No. 58-1634 from Sandia Corporation, Albuquerque, New Mexico. The authors are indebted to Dr. M. Taylor Abegg and Mr. William J. Meikle for their interest, advice and helpful suggestions during the course of this work. Thanks are due to Miss Diane Dottavio for the preparation of starting material and to Mrs. Shigeko Nakagome for the analytical data reported.

This work was performed under auspices of the United States Atomic Energy Commission. Reproduction in whole or in part is permitted for any purpose of the United States Government.

REFERENCES

- (1) Present address: Research Laboratories, Parke, Davis and Company, Ann Arbor, Michigan 48106.
- (2) Inquiries concerning this paper should be addressed to

Professor Raymond N. Castle.

(3) W. Wolf and H. Vollmann, German Patent, 941,845, April 19, 1956; *Chem. Zentr.*, 128, 1047 (1957).

(4) I. Satoda, F. Kusada and K. Mori, *Yakugaku Zasshi*, 82, 233 (1962).

(5) Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared and ultraviolet spectra were recorded on a Perkin-Elmer 337 Infracord and on a Bausch and Lomb Spectronic 505, respectively.

(6) F. M. Rowe and A. T. Peters, *J. Chem. Soc.*, 1331 (1933).

(7) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1955, p. 199.

(8) M. Frankel and S. Patai, "Table for Identification of Organic Compounds," Chemical Rubber Company, Cleveland, Ohio, 1964, p. 156.

Received December 18, 1967

Albuquerque, N. M. 87106