[Contribution from the School of Chemistry of the University of Minnesota and the School of Chemical Technology of the North Dakota Agricultural College]

STRUCTURE OF THE BANDROWSKI BASE. II. N,N′-BIS-(2,5-DIAMINOPHENYL)-*p*-QUINONEDIIMINE

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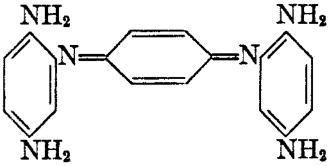
Evidence which indicates that formula II probably represents the correct structure for the Bandrowski base was presented in an earlier communication (1). Since then, additional confirmatory information has been obtained.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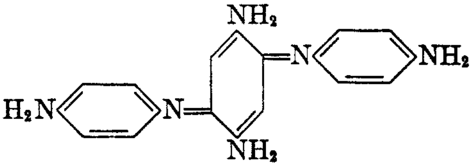
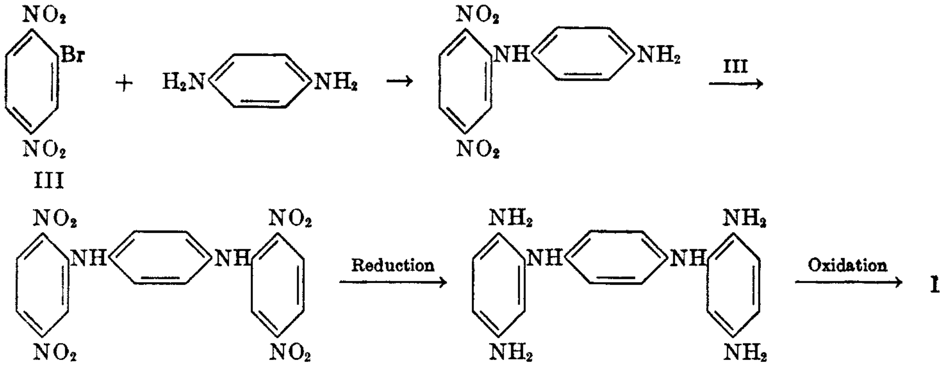

II

These structures were originally suggested by Bandrowski and Green, respectively. Structure I, representing this base as N,N′-bis-(2,5-diaminophenyl)-*p*-quinonediimine, becomes improbable since the following series of reactions led to a product which was not identical with the Bandrowski base.



2-Bromo-1,4-dinitrobenzene (III), m.p. 64–65°, was prepared from *p*-nitroaniline. Since Korner and Contardi (2) reported m.p. 70° for this compound, an alternative route starting with *m*-bromoaniline was followed for the preparation of a small amount of compound III. Identical products were obtained from each of these two starting materials. The following diagram shows the steps which were involved:

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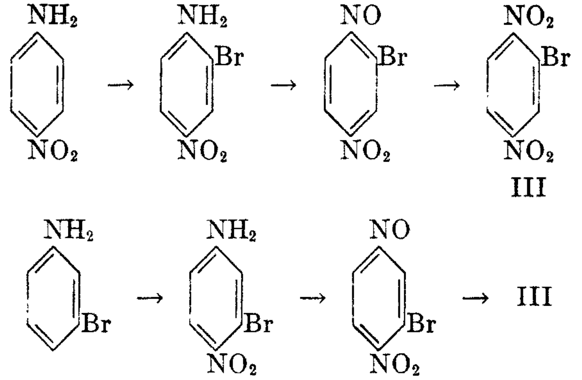

N,N′-Bis-(2,5-dinitrophenyl)-*p*-phenylenediamine was reduced with tin and hydrochloric acid to give the colorless tin double salt. The colorless hydrochloride, which was obtained after removal of the tin with hydrogen sulfide, yielded the free base after treatment with aqueous potassium hydroxide. The free base underwent rapid oxidation to form a bluish-purple substance (I), which differs from the Bandrowski base in the following respects. Although color changes take place on liberation of the reduced Bandrowski base from its salt, the rate of color development is slower and a red instead of a purple color is produced. The N,N′-bis-(2,5-diaminophenyl)-*p*-quinonediimine (I) which was obtained melted at 225–227°. All attempts to purify this base, which was insoluble in the common organic solvents, were fruitless. The melting point of the Bandrowski base (241–242°) was depressed by the addition of I; a mixture of the two melted at 210–220°. Accordingly, N,N′-bis-(2,5-diaminophenyl)-*p*-quinonediimine (I) is an unlikely structure for the Bandrowski base.

EXPERIMENTAL

Bromo-p-dinitrobenzene (III). (a) *From p-nitroaniline.* *p*-Nitroaniline (m.p. 147°) was monobrominated according to the directions of Korner and Contardi (2) giving *o*-bromo-*p*-nitroaniline. After crystallization from water with the aid of Norit, the product melted at 104–105°. (Lit. 104.5°). The major portion of the product was dissolved in ethyl alcohol and filtered while hot into an excess of water so as to obtain it in a finely divided condition for oxidation to the nitroso compound. In the early attempts at converting *o*-bromo-*p*-nitroaniline to *o*-bromo-*p*-nitronitrosobenzene the directions of Bigiavi, Albanese, and Poggi (3) were used, but the yields were very low. Their procedure was modified as follows. *o*-Bromo-*p*-nitroaniline (1.0 g.), ammonium persulfate (3.2 g.), and a mixture of water (100 ml.) with sulfuric acid (2.3 ml.; *sp. gr.* 1.84) were placed in a 250-ml. distillation flask. A rapid stream of steam was then passed through the reaction mixture and the steam-distillate yielded the nitroso compound, (42%, m.p. 119–120°). After recrystallization from methyl alcohol, the substance melted at 122–123°. (Lit. 123°).

The *o*-bromo-*p*-nitronitrosobenzene was oxidized to the dinitro compound according to the procedure of Bamberger and Hübner (4). *o*-Bromo-*p*-nitronitrosobenzene (3.2 g.) and nitric acid (40 ml.; *sp. gr.* 1.26) were heated on a boiling water-bath for five minutes after all the nitroso compound had dissolved. The reaction mixture was poured into excess water and cooled. Filtration yielded a slightly yellow product (3.2 g., 85%). After three crystallizations from dilute alcohol the product melted at 64–65° and steam-distillation followed by crystallization from 95% alcohol caused no change in melting point. Korner and Contardi report m.p. 70°.

Anal. Calc'd for $C_6H_3BrN_2O_4$: C, 29.15; H, 1.21.
Found: C, 28.89; H, 1.13.

(b) *From m-bromoaniline. m*-Bromoaniline was acetylated according to the procedure of Scheufelen (5). The acetyl derivative was nitrated, separated from isomeric products, and hydrolyzed according to the method of Claus and Scheulen (6). Several attempts were made to convert the resulting *m*-bromo-*p*-nitroaniline to the nitroso compound according to the method of Bigiavi, Albanese, and Poggi (3), but only very small amounts of an impure product were obtained. By following the modified procedure as developed for the oxidation of *o*-bromo-*p*-nitroaniline, six 1-g. portions of *m*-bromo-*p*-nitroaniline gave 1.2 g. (18.8%) of crude *m*-bromo-*p*-nitronitrosobenzene. After one crystallization from methyl alcohol, a colorless product was obtained. The purified product melted at 98–99° giving a bluish-green liquid. There was no change in the melting point after two more crystallizations from methyl alcohol.

Anal. Calc'd for $C_6H_3BrN_2O_3$: C, 31.17; H, 1.30.
Found: C, 31.04; H, 1.21.

The *m*-bromo-*p*-nitronitrosobenzene was oxidized to bromo-*p*-dinitrobenzene according to the method of Bamberger and Hübner (4). The nitroso compound (1.5 g.) was heated with nitric acid (24 ml., *sp. gr.* 1.26) on a water-bath. The temperature of the water-bath was raised gradually to 85° when all of the substance was in solution. Water was added to the cooled solution to insure complete precipitation of the reaction product. After three crystallizations, the colorless material melted at 64–65°. A mixture of this bromo-*p*-dinitrobenzene with that prepared from *o*-bromo-*p*-nitronitrosobenzene also melted at 64–65°.

Anal. Calc'd for $C_6H_3BrN_2O_4$: N, 11.33. Found: N, 11.41.

2,5-Dinitro-4'-aminodiphenylamine. A mixture of bromo-*p*-dinitrobenzene (1.0 g.) and *p*-phenylenediamine (2.0 g.) in 95% alcohol (50 ml.) was heated under reflux on a steam-bath for three hours. After the addition of water (75 ml.) the mixture was allowed to stand overnight. A dark blue crystalline precipitate was obtained. Crystallization gave a material (0.7 g.) melting at 194–196°. The substance after recrystallization from chloroform and petroleum ether (b.p. 35–55°) and finally from 95% alcohol melted at 198–199°. There was no change in m.p. on further recrystallizations alternately from chloroform and petroleum ether and from 95% alcohol.

Anal. Calc'd for $C_{12}H_{10}N_4O_4$: C, 52.55; H, 3.65; N, 20.44; M.W., 274.
Found: C, 52.69; H, 3.87; N, 20.87; M.W., 263.

N,N'-Bis-(2,5-dinitrophenyl)-p-phenylenediamine. A mixture of 2,5-dinitro-4'-aminodiphenylamine (0.5 g.) and bromo-*p*-dinitrobenzene (0.8 g.), intimately mixed by grinding, was heated in a Wood's metal bath for two hours at 155–160°. During the early stages of the heating a gas was given off. Litmus paper indicated the presence of hydrobromic acid. At the end of the first hour of heating the mass gradually solidified. The reaction mixture was then extracted three times by refluxing with 175-ml. portions of 95% alcohol. The residue after one crystallization from nitrobenzene melted at 288–288.5°. It was a brownish-red crystalline substance.

Anal. Calc'd for $C_{18}H_{12}N_6O_8$: C, 49.1; H, 2.73; N, 19.09; M.W., 440.
Found: C, 49.16; H, 3.12; N, 18.96; M.W., 435.

Reduction to the tetraamino compound. One gram of N,N'-bis-(2,5-dinitrophenyl)-*p*-phenylenediamine together with hydrochloric acid (30 ml., 12 *N*) was placed in a three-neck, round-bottom flask, equipped with a condenser and stirrer. Then 10–12 g. of mossy tin was added and the mixture heated. The brownish-red color of the tetranitro compound was gradually replaced by the grayish-white of a tin double salt. The temperature was then raised to a gentle reflux and at the end of 45 minutes most of the salt was in solution. The slightly yellow solution was decanted from the excess tin. The unused tin was washed with a few ml. of 12 *N* hydrochloric acid and the washings were added to the main reaction product. After cooling in an ice-bath the colorless tin double salt was removed and dried in a vacuum desiccator over potassium hydroxide. The tin was removed by precipitation with hydrogen sulfide. After concentrating the solution to incipient crystallization, the solution was cooled in an ice-salt mixture to completely precipitate the colorless hydrochloride. During filtration the hydrochloride gradually developed a slight greenish-blue color. As soon as the solvent was removed by filtration, the material was placed in a vacuum desiccator over potassium hydroxide. The precipitation with hydrogen sulfide and crystallization of the hydrochloride of the leuco base was repeated in order to completely remove the last traces of tin. After drying in a vacuum desiccator over potassium hydroxide the salt was dissolved in a small amount of water. A dilute potassium hydroxide solution was added dropwise, the color deepened, and the reduced base precipitated in colorless crystals which rapidly oxidized to a bluish-purple insoluble product. After drying over potassium hydroxide in a vacuum desiccator the substance melted at 225–227°. Further purification was unsuccessful. A mixture with the Bandrowski base, of m.p. 241–242°, melted at 210–222°.

Anal. Calc'd for $C_{18}H_{18}N_6$: C, 67.92; H, 5.66; N, 26.41.

Found: C, 67.43; H, 6.65; N, 25.40.

SUMMARY

The synthesis of N,N′-bis-(2,5-diaminophenyl)-*p*-quinonediimine is reported, and evidence is presented which indicates that it is not identical with the Bandrowski base.

The preparation and properties of several previously unreported intermediates which were used in the foregoing synthesis are described.

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