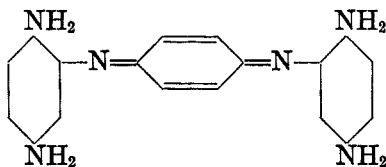


THE STRUCTURE AND MECHANISM OF FORMATION OF THE BANDROWSKI BASE*

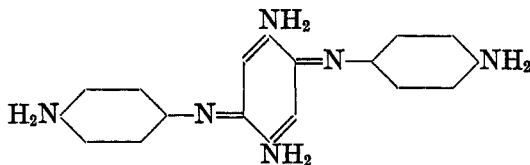
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The oxidation of *p*-phenylenediamine under certain conditions leads to the formation of the compound, $C_{13}H_{18}N_6$, which is known as the Bandrowski base.¹ Two different structures have been proposed for this base; one by Bandrowski (structure I) and the other by Green (structure II).²



I



II

Ritter and Schmitz³ in a brief, critical summary of the previous work on the structure of this base, showed that oxidation yields quinone. Since not more than one mole of quinone was isolated for each mole of the Bandrowski base, they favored structure I. However, in the present work, evidence is introduced which points to structure II as the correct one.

The hydrolysis of the Bandrowski base with 10 per cent. hydrochloric acid gives *p*-phenylenediamine hydrochloride.⁴ Furthermore, on the basis

* Abstracted from the Ph.D. thesis of C. J. Sunde, submitted to the Graduate Faculty of the University of Minnesota, August 1937.

¹ BANDROWSKI, *Ber.*, **27**, 480 (1894); see also MATTHEW KIESS, M. S. Thesis, University of Minnesota, 1928.

² GREEN, *J. Chem. Soc.*, **1913**, 933.

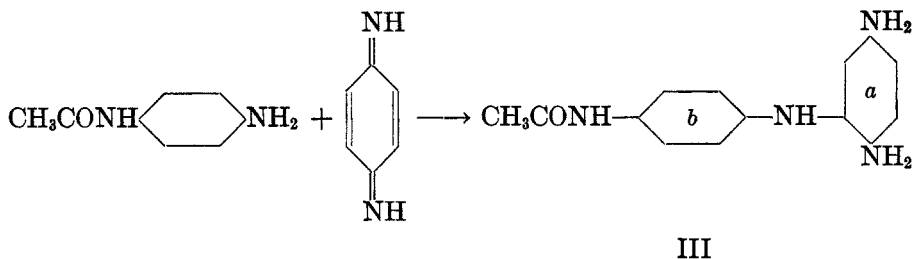
³ RITTER AND SCHMITZ, *J. Am. Chem. Soc.*, **51**, 1587 (1929).

⁴ COX, *Analyst*, **59**, 3 (1934); **60**, 360 (1935).

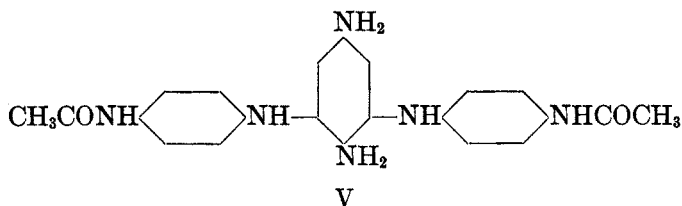
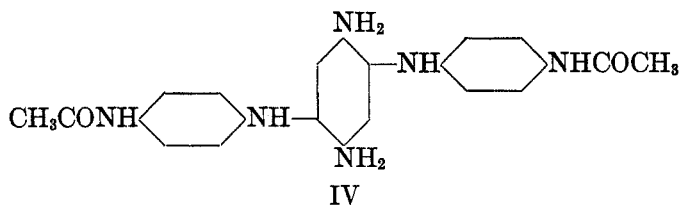
of 1 mole of Bandrowski base giving 2 moles of *p*-phenylenediamine, an 87 per cent. yield of *p*-phenylenediamine hydrochloride was obtained.

Also, a diacetate of the Bandrowski base has been obtained by adding quinonediimine, prepared either according to the method of Willstätter⁵ in ether solution, or according to the method of Erdmann⁶, to a solution of *p*-aminoacetanilide in aqueous methyl alcohol containing a small amount of hydrochloric acid. On acetylation, this diacetate gives the tetraacetate of the Bandrowski base.

The diacetate is very likely formed in steps, the first step being the addition of *p*-aminoacetanilide to quinonediimine as follows:

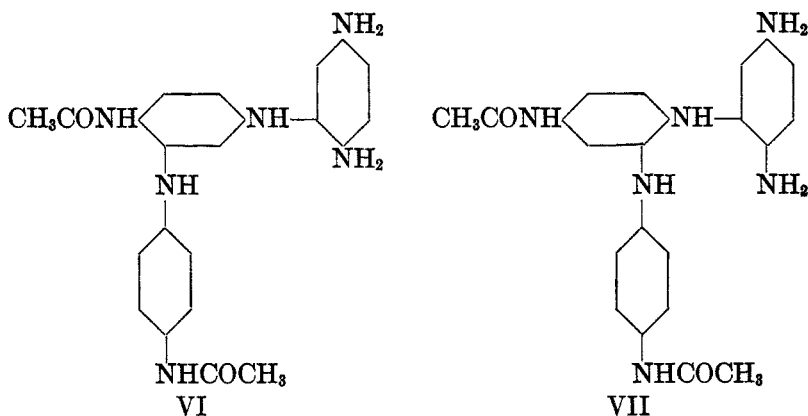


The intermediate III in the presence of quinonediimine may: (1) add to quinonediimine, or (2) be oxidized to the quinoid form. If the former takes place several products are possible, but since none of these can be diacetates, this possibility must be excluded. In the second instance four products are possible, IV and V by oxidation of ring *a* followed by the addition of *p*-aminoacetanilide, and VI and VII if ring *b* is involved in the

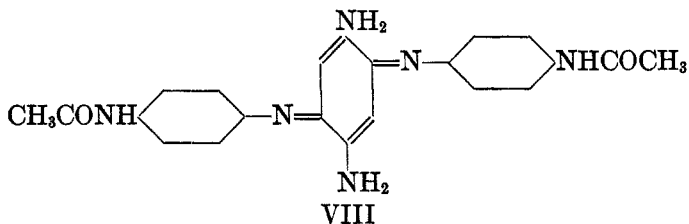


⁵ WILLSTÄTTER AND PFANNENSTIEL, *Ber.*, **37**, 4605 (1904).

⁶ ERDMANN, *ibid.*, **37**, 2906 (1904).



oxidation. Of these V, VI, and VII are easily excluded on the ground that if the leuco base of the Bandrowski base has any of these structures oxidation to the quinoid form followed by hydrolysis would not give two molecules of *p*-phenylenediamine. On the other hand, if the leuco base has the structure corresponding to IV, two moles of *p*-phenylenediamine would be expected on hydrolysis of the quinoid form (VIII).



Bandrowski did not formulate any mechanism for the formation of the base. Erdmann assumed that quinonediimine was the primary oxidation product of *p*-phenylenediamine and that 3 moles of the diimine polymerized to yield the Bandrowski base. It has been shown⁷, however, that the polymer of quinonediimine differs from the base. The mechanism for the formation of the diacetate of the Bandrowski base, proposed in the present paper requires a ratio of three moles of quinonediimine to two moles of *p*-aminoacetanilide. It is of interest to point out that an increase in the amount of *p*-aminoacetanilide over the above ratio did not increase the yield of diacetate whereas a decrease led to a lower yield. Since the diacetate is readily converted to the tetraacetate of the Bandrowski base, it is reasonable to suppose that the mechanism adopted for the formation of the diacetate will also be the mechanism of formation of the base itself.

⁷ WILLSTÄTTER AND MAYER, *ibid.*, **37**, 1494 (1904); see also reference 4.

EXPERIMENTAL

Hydrolysis of the Bandrowski base.—One gram of the base (m.p. 242–243°), prepared by the oxidation of *p*-phenylenediamine with potassium ferricyanide, was refluxed for two hours with 20 ml. of 10% hydrochloric acid. After removal of a black residue by filtration, the solution was evaporated until crystals appeared. The solution was then cooled to room temperature and several ml. of concentrated hydrochloric acid were added. One gram of crude product was obtained after cooling in an ice-salt bath. Purification by crystallization from dilute hydrochloric acid yielded a colorless product (0.90–0.95 g.). The hydrochloride upon treatment with sodium hydroxide was converted to the free base, which was identified as *p*-phenylenediamine (m.p. and mixture m.p. 139–140°).

Synthesis of the diacetate of the Bandrowski base.—(a) A filtered solution of quinonediiimine in ether prepared from one gram of *p*-phenylenediamine according to the method of Willstätter⁵ was added dropwise with mechanical stirring to a solution of *p*-aminoacetanilide (2.8 g.; m.p. 162–163°) in 20 ml. of water and 40 ml. of methyl alcohol containing 0.4 ml. of 12*N* hydrochloric acid, keeping the temperature at 0°. After standing for one hour at room temperature, the reaction mixture was made alkaline by the addition of water (100 ml.) containing 4 to 5 ml. of 15*N* ammonium hydroxide. The ether was then removed by evaporation, and after filtration the solid product was digested for a short time with about 100 ml. of boiling methyl alcohol. The average yield of crude product (ochre yellow, m.p. 296–298°) was 0.52 g.

This substance is difficultly soluble in methyl alcohol, but after extracting in a Soxhlet apparatus for a considerable period, the product isolated from the alcohol melts at 310–311°.

Anal. Calc'd for $C_{22}H_{22}N_6O_2$: C, 65.67; H, 5.47; mol. wt., 402.

Found: C, 64.89; H, 5.81; mol. wt. (Rast camphor method), 381.

The same diacetate with an identical yield was obtained using 0.95 g. of *p*-aminoacetanilide (*i.e.*, one-third of the amount used in the experiment described). The use of 0.48 g. of *p*-aminoacetanilide decreased the yield of the diacetate to 0.20 g.

(b) The diacetate of the base was also prepared using an aqueous solution of quinonediiimine and *p*-aminoacetanilide. The quinonediiimine was prepared according to the method of Erdmann.

Tetraacetate of the Bandrowski base.—The diacetate was acetylated with excess acetic anhydride at the temperature of the steam bath. It was crystallized once from dilute acetic acid and twice from nitrobenzene; m.p. 293–294°. The tetraacetate prepared in this way is identical with that obtained by the acetylation of the Bandrowski base.

SUMMARY

Evidence has been presented in support of Green's structure for the Bandrowski base, and a mechanism for the formation of this base has been discussed.