Summary

A study has been made of the drop in yield of Grignard reagents when the halide is added very rapidly to magnesium in ether and some generalizations have been drawn from these results.

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THE CONSTITUTION OF BANDROWSKI'S BASE

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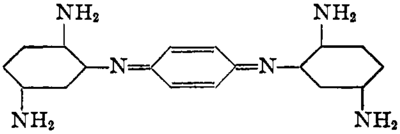
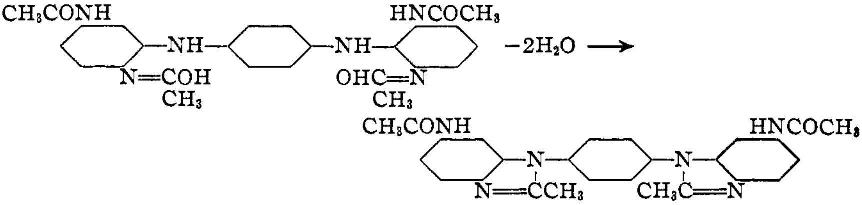
RECEIVED JANUARY 22, 1929 PUBLISHED MAY 6, 1929

Introduction

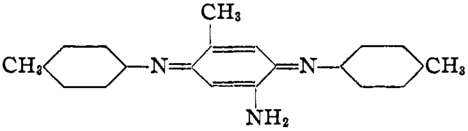
Bandrowski[1] obtained, on ferricyanide oxidation of *p*-phenylenediamine in aqueous ammoniacal solution, a product to which he assigned the structure shown. This constitution is based on elementary analysis, molecular weight determination, production of *p*-phenylenediamine on zinc-dust distillation, the formation of a tetra-acetyl derivative, and ring-closure with the formation of a dipyrazole on reduction of the tetra-acetyl derivative, as follows





In view of the fact that *p*-toluidine has been shown by Barsilowski[2] and Green[3] to yield on oxidation a base of the formula (A), it appears quite

A



possible that *p*-phenylenediamine might behave similarly, to yield the following isomer (B) of the Bandrowski base. Its properties, as observed

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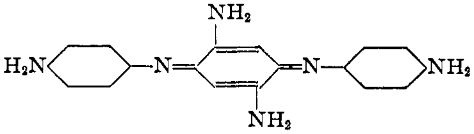
[1] Bandrowski, *Monatsh.*, **10**, 123 (1889); *Ber.*, **27**, 480 (1894).

[2] Barsilowski, *ibid.*, **6**, 1209 (1873); *ibid.*, **8**, 695 (1875).

[3] Green, *ibid.*, **26**, 2772 (1893).

B



by Bandrowski and by others,[4] up to the present fail to establish either structure as the correct one. Comparison of the two will show their ability to respond to all of the known reactions of the substance. Our attention was also arrested by the fact that the oxidation of *p*-phenylenediamine does not proceed further under the conditions of the experiment. The second structure, in which para-diamine groupings capable of assuming the quinoid structure are absent, is in closer harmony with this behavior than the first, in which the two non-quinoid nuclei might be expected to oxidize readily. The present work was undertaken to throw some light on this point.

We have now succeeded in obtaining evidence which confirms the structure already assigned to the substance. This was accomplished by the method of Willstätter and Dorogi,[5] in which quinone-imides were oxidized with yields of 85–95% to benzoquinone with lead peroxide and sulfuric acid. The benzoquinone obtained was determined by the method of J. Rzymkowski[6] by titration against sodium thiosulfate solution, using Wurster's indicator (*p*-amidodimethylaniline). It is apparent, by comparison of the two alternative formulas, that one mole of the substance of the first formula can yield but one-third of a mole of quinone on oxidation, while one mole of a substance of the second formula should yield two-thirds of a mole of quinone. The results of several experiments confirm the former structure, which is therefore the correct one.

Experimental Part

Preparation of Bandrowski's Base.—This substance was prepared both by the use of potassium ferricyanide and of hydrogen peroxide as oxidizing agents; the latter was found to yield a pure product directly. In a typical experiment, 10 g. of *p*-phenylenediamine (recrystallized once from benzene) was dissolved in 750 cc. of water to which 3 cc. of concentrated ammonia solution had been added, and the solution was treated with 125 cc. (2.5 moles) of 3% hydrogen peroxide solution. After standing for twenty-four hours at room temperature, 2 g. of pure oxidation product was filtered off. Further portions were filtered off after similar time intervals. After seventy-two hours three portions thus separated totaled 3.6 g. The first portion, consisting of well-defined bronze leaflets, was of high purity. The material separating subsequently consisted of finer particles which seemed to be somewhat contaminated with foreign matter. In the experiments to be described, only that portion first separating was used, after drying to constant weight at 100°; m. p. 238° (corr.).

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[4] A. Heidushka and E. Goldstein, *Arch. Pharm.*, **254**, 584–625 (1916); R. Willstätter and Mayer, *Ber.*, **37**, 1505 (1904); E. Erdmann, *ibid.*, **37**, 2908 (1904).

[5] Willstätter and Dorogi, *ibid.*, **42**, 2166 (1909).

[6] Rzymkowski, *Z. Elektrochem.*, **31**, 371–382 (1925).

Oxidation of the Base to Benzoquinone.—Five g. of lead peroxide and 5 g. of concd. sulfuric acid were ground together in a mortar until a uniform thin paste was obtained. This was added slowly, with cooling, to 25 cc. of 25% sulfuric acid, contained in a 100 cc. Erlenmeyer flask. To this mixture a weighed amount (about 0.3 g.) of the base was added, the mixture shaken until the base had completely dissolved, stoppered loosely and allowed to stand for twenty-four hours. At the end of this time, the resulting solution was of a clear yellow color. The benzoquinone was extracted from the aqueous acid solution by repeated shaking with small amounts of ether (10 cc. at a time), in the reaction vessel. The ethereal washings were separated by decantation and combined. This operation was repeated until a fresh portion of the ether extracted nothing further from the reaction mixture, six to eight such extractions being sufficient. The final extract is recognized by the fact that it is colorless and leaves no residue on evaporation. That the combined ethereal extracts contained pure benzoquinone was determined in one experiment by evaporation of a portion and determination of the melting point of the solid thus obtained, without recrystallization. It was found to melt at 115°, while pure benzoquinone has the recorded melting point of 115.7°.

Analysis of the Ethereal Extracts.—An approximately equal volume of water and 3 cc. of glacial acetic acid were added to the ethereal solution of benzoquinone and the mixture was titrated against standard sodium thiosulfate solution. The ether–water mixture was well shaken after each addition of thiosulfate. The color of the quinone may be used as indicator, or *p*-amidodimethylaniline may be used externally. The latter method was found to give a sharper end-point and more concordant results and was used throughout. Benzoquinone and sodium thiosulfate react in dilute acetic acid solution as follows[6]

$$2C_6H_4O_2 + 4H^+ + 2S_2O_3^{=} = C_6H_2(OH)_2(S_2O_3H)_2 + C_6H_4(OH)_2$$

Standardization of the Sodium Thiosulfate Solution.—The thiosulfate solution used was standardized against twice resublimed benzoquinone, using *p*-amidodimethylaniline as indicator: (1) 0.2032 g. of quinone in 50 cc. of water and 3 cc. of acetic acid used 20.27 cc.; (2) 0.3342 g. of quinone in 50 cc. of water and 3 cc. of acetic acid used 33.40 cc.; therefore 1 cc. of thiosulfate = 0.0100 g. of quinone.

TABLE I

ANALYTICAL RESULTS

Sample, g.	Thiosulfate, cc.	Quinone, g.	Calcd. for 1/3 mole	Calcd. for 2/3 mole	% of 1/3 mole	% of 2/3 mole
0.3116	9.57	0.0957	0.1058	0.2116	90.4	45.2
.3045	9.00	.0900	.1034	.2068	87.0	43.5
.2901	9.00	.0900	.0985	.1970	91.4	45.7

Summary

1. The yield of benzoquinone obtained by oxidation of Bandrowski's base by lead peroxide and sulfuric acid has been determined.
2. The results of such determinations confirm the constitution previously assigned to the compound.

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