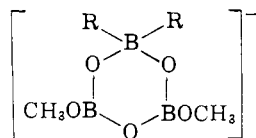


time fivefold. A 5% yield of mesitylboronic acid was obtained from this reaction after 24 hours.

The results give some insight into the path of the reaction. Of especial significance is the tendency for the boron atom to acquire two aryl groups rather than three in the presence of a large excess of Grignard reagent. This apparently reflects the high stability of the boroxine ring, and when coupled with the well-known fact that in processes of this type the introduction of one hydrocarbon onto the boron atom facilitates attack by a second molecule of the Grignard reagent,<sup>4</sup> suggests an intermediate of the type



Several observations support this suggestion. The first is the fact that a 16% yield of borinic acid was obtained at a 3:1 mole ratio of Grignard reagent to boroxine. This ratio provides sufficient Grignard reagent so that one aryl group is available for each boron atom. Similarly, a 13% yield of borinic acid was obtained when the Grignard re-

agent in a 2:1 mole excess was added to the boroxine—conditions which should strongly favor boronic acid formation. In both of these cases, appreciable disubstitution on boron atoms occurred, but no trisubstitution was detected. This constitutes significant evidence for the anion-type intermediate.

A third observation of possible significance is the fact that yields of borinic acids never exceeded 63%. This may be fortuitous, or it may mean that only two of the three boron atoms of the boroxine can be used in borinic acid formation. This could be related to the solubility of the intermediate. It is conceivable that once two boron atoms of the boroxine acquire a pair of aryl groups, the intermediate may precipitate from solution. A white precipitate having approximately the composition of the intermediate is formed during the reaction.

Finally, it is likely that the boroxine ring is stable until the reaction mixture is hydrolyzed with acid. Otherwise, considerable quantities of triarylboranes would be expected among the products. Only traces of these compounds have been obtained from reactions at 35°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

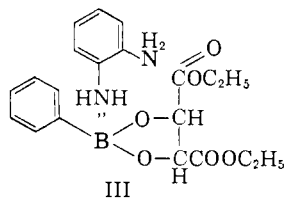
## Organoboron Compounds. VIII. Dihydrobenzoboradiazoles<sup>1</sup>

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RECEIVED MAY 5, 1958

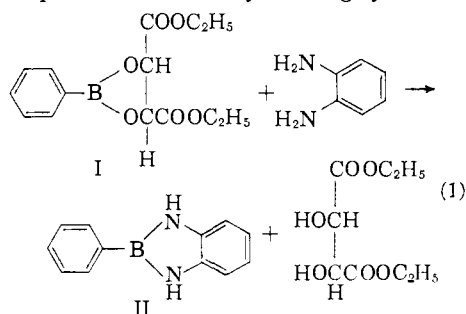
Phenylenediamine reacts with boronic acids and esters to form substituted dihydrobenzoboradiazoles, representatives of a new class of heterocyclic compounds. These substances serve as good derivatives for the characterization of the boronic acids. Boradiazole formation from phenylenediamine and the ethyl tartrate ester of benzeneboronic acid is rapid in benzene solution at room temperature.

In the course of investigating the manner in which complex formation involving boron can affect organic reactions, we examined the reaction of *o*-phenylenediamine with the ethyl tartrate ester of benzeneboronic acid (I). Molecular models indicated that in the amine complex (III), should it form, the second amino group of phenylenediamine would be close to the carboxyl group. It was of interest to see whether amide formation would be accelerated as a consequence.



*o*-Phenylenediamine and Compound I did react readily in refluxing toluene solution. The product, m.p. 215–216°, was not, however, the expected amide. On the basis of the analysis, molecular weight, infrared spectrum and hydrolysis

data it was assigned structure II, 2-phenyl-1,3-dihydro-2,1,3-benzoboradiazole. As such, it is the first example of this heterocyclic ring system.



Compound II hydrolyzes very rapidly in dilute acids solutions to give benzeneboronic acid and phenylenediamine. In neutral solution hydrolysis is much slower. With hydrogen chloride in toluene it forms a dihydrochloride. There was no evidence for B–N cleavage by hydrogen chloride to give phenyldichloroborane, even for a reaction carried out for eight hours in refluxing toluene. By contrast, hydrogen chloride converted methylaminodimethylborane to dimethylchloroborane and methylamine hydrochloride (a two-hour reaction

(1) For paper VII see R. L. Letsinger and J. R. Nazy, *J. Org. Chem.*, **23**, 914 (1958). This work was supported by the National Science Foundation.

at 20°),<sup>2</sup> and boric trianilide to triphenyltrichloroborane, triphenyltrichloroborane nitride and aniline hydrochloride.<sup>3</sup>

It then was found that boronic acids themselves react with *o*-phenylenediamine in refluxing toluene to give dihydrobenzoboradiazoles. Data for a series of compounds thus prepared are summarized in Table I. It may be noted that the reaction is applicable to the aliphatic (f) as well as the aromatic boronic acids.

TABLE I

R group	M.p., °C.	Yield, %	Nitrogen, %	
			Calcd.	Found
a C <sub>6</sub> H <sub>5</sub> -	215-216	89	14.51	14.8
b <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	258-258.5	83	12.56	12.62
c <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	232-233	91	10.31	10.56
d <i>p</i> -CH <sub>2</sub> =C <sub>6</sub> H <sub>4</sub> -	237-238	91	12.02	12.16
e α-C <sub>10</sub> H <sub>7</sub> -	149-150	93	11.53	11.79
f <i>n</i> -C <sub>4</sub> H <sub>9</sub> -	86-86.5	75	15.99	16.15

The infrared spectra for these substances, taken in potassium bromide plates, showed two particularly characteristic bands; one at 7.0 μ (strong, absent in the boronic acids and in phenylenediamine) and the other at 2.9 μ (strong and sharp, due to N-H; borazole also shows this band). There were also aromatic bands at 6.7 (weak) and 7.9 μ (strong). Absorption in the region of 7.4 μ, which seems to be characteristic of trivalent boron compounds,<sup>4</sup> was strong but somewhat less pronounced than in the boronic acids. Santucci and Gilman<sup>5</sup> have suggested for boronic acids that bands at 8.35-8.5 μ and 9.1-9.2 μ are due to B-O and B-C bonds, respectively. The dihydrobenzoboradiazoles also absorbed at 8.5 μ, though weaker than the boronic acids. Surprisingly, absorption at 9.2 μ was very weak in these nitrogen compounds generally, and absent in the derivative of butaneboronic acid. A band which appears at 9.7-9.8 μ in the aromatic boronic acids also appears in the phenylenediamine derivatives, displaced to slightly longer wave lengths (9.8-9.9 μ).

Boronic acids usually undergo partial dehydration during isolation or melting point determinations to give mixtures of the acids and anhydrides which melt over a broad temperature range. The consequent difficulties in the characterization of these substances recently have been emphasized by several workers<sup>5,6</sup>. Since the dihydrobenzoboradiazoles are prepared easily and melt sharply, they serve as good derivatives for characterization of the boronic acids. In this respect they are more

(2) E. Wiberg and K. Hertwig, *Z. anorg. u. allgem. Chem.*, **255**, 141 (1947).

(3) R. G. Jones and C. R. Kinney, *THIS JOURNAL*, **61**, 1378 (1938).

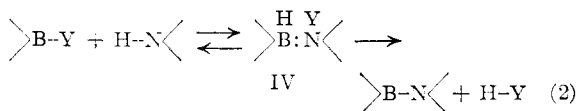
(4) A variety of trivalent boron compounds, including the borate esters, boron trichloride, alkyl and aryl borinic and boronic acids and esters, and triarylborines, absorb strongly in this region. In cases where the boron is complexed with an amine, as in the ethanolamine esters of boronic acids, the diethanolamine esters of the boronic acids, and ammonia complexes of triarylborines, this strong absorption disappears or is replaced by weak, sharper bands.

(5) L. Santucci and H. Gilman, *THIS JOURNAL*, **80**, 193 (1958).

(6) H. R. Snyder, A. J. Reedy and W. J. Lennarz, *ibid.*, **80**, 835 (1958).

generally satisfactory than the diethanolamine esters,<sup>7</sup> which are difficult to recrystallize.

An interesting feature of the phenylenediamine reaction is that a >B-N< compound is formed by cleavage of a B-O bond. Numerous examples of reaction 2 are known in which Y is halogen.<sup>8</sup> With Y = OH or OR, the reaction will proceed as



far as complex IV<sup>8</sup>; however, there seems to be little general tendency for it to go further. Thus Jones and Kinney<sup>3</sup> found no evidence of reaction between ethyl borate and aniline, even at the boiling point. Chaudhuri<sup>9</sup> claimed to have made C<sub>6</sub>H<sub>5</sub>NBO by heating aniline and boric acid in the presence of zinc chloride; however later work revealed that his product was only a double salt of aniline and zinc chloride.<sup>10</sup> An example of reaction 2, Y = OR, was provided by Goubeau and Ekhoﬀ,<sup>11</sup> who obtained a low yield of H<sub>2</sub>NB(OCH<sub>3</sub>)<sub>2</sub> from a pyrolysis of B(OCH<sub>3</sub>)<sub>3</sub>:NH<sub>3</sub>.

In order to learn more about the formation of B-N bonds, we examined the reaction of benzeneboronic acid with aniline and ethylenediamine in boiling toluene solutions. From the aniline experiment was isolated benzeneboronic anhydride, and from the ethylenediamine reaction, a 1:1 complex of ethylenediamine and benzeneboronic anhydride.<sup>12</sup> No >B-N< compound was formed in either case. Therefore, the facility with which phenylenediamine reacts with benzeneboronic acid cannot be attributed merely to the fact that phenylenediamine is an aromatic amine or that it is a diamine capable of forming a five-membered ring product. It seems reasonable to assume that the unusual reactivity of phenylenediamine is related to its particular geometry and the stability of the ring system which is formed.<sup>13</sup>

Further investigation of reaction 1 revealed that it proceeded rapidly in benzene solution even at room temperature! A 57% yield of the dihydroboradiazole was isolated from an experiment in which the temperature never rose above 27°. Under these conditions the boronic acids did not react. The optical rotation data which are summarized in Table II were accumulated to gain evidence on the position of equilibrium in reaction 1 prior to crystallization of the product.

(7) R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2492 (1955).

(8) A summary of reactions of this type is given by M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(9) T. C. Chaudhuri, *J. Chem. Soc.*, **117**, 1081 (1921).

(10) C. R. Kinney and D. F. Pontz, *THIS JOURNAL*, **57**, 1128 (1935). Attempts by T. Savereide, unpublished work, to prepare boron-nitrogen compounds according to Chaudhuri's procedure were likewise unsuccessful.

(11) J. Goubeau and E. Ekhoﬀ, *Z. anorg. Chem.*, **266**, 145 (1952).

(12) Aliphatic amines are sufficiently basic to form relatively stable complexes with aromatic boronic acids and anhydrides, whereas aniline does not give this reaction: D. L. Yabroﬀ and G. E. K. Branch, *THIS JOURNAL*, **55**, 1663 (1933).

(13) A reaction of 1,8-diaminonaphthalene (kindly supplied by Mr. W. J. Vullo) and benzeneboronic acid in toluene yielded 73% (calculated as a dihydroboradiazole) of a crude, red product, m.p. 74-76°, which had an infrared band at 2.9 μ. Attempts at recrystallization, however, led to very extensive decomposition.

TABLE II<sup>a</sup>

Expt.	Solute(s)	$\alpha^{27D}$
1	Ethyl tartrate	+1.33°
2	Ethyl tartrate + <i>o</i> -phenylenediamine	+1.34
3	Ethyl tartrate + II	+1.34
4	I	+0.95
5	I + <i>o</i> -phenylenediamine	+1.32
6	I + aniline	+0.96

<sup>a</sup> All readings were made in a 4-dm. tube at 27°. Benzene solutions (50.0-cc. volume) were prepared with 0.0100 mole of each solute, except for aniline, where 0.0200 mole was used. The weights of the solutes were: ethyl tartrate, 2.0619 g.; *o*-phenylenediamine, 1.0814 g.; II, 1.9405 g.; I, 2.9108 g.; aniline, 1.8624 g.

The rotation of ethyl tartrate was not changed (within the experimental error) by addition of an equimolar amount of phenylenediamine or the boradiazole II. On the other hand, the rotation of the solution containing the ethyl tartrate ester of benzenboronic acid (I) was increased by phenylenediamine, the final value being essentially that for ethyl tartrate itself. These data support the view that the equilibrium in equation 1 (benzene solution) lies well to the right. An alternative explanation for the difference in rotation for experiments 4 and 5 would be that complex III had formed to an appreciable extent. Experiment 5, however, renders this explanation unlikely. Since aniline and *o*-phenylenediamine do not differ greatly in basicity, one would expect aniline to complex with I if phenylenediamine does; aniline had no significant effect on the rotation of I.

### Experimental Part

**General Method for Preparation of Dihydrobenzoboradiazoles.**—Equimolar amounts of the boronic acid and phenylenediamine were dissolved in toluene and heated to reflux temperature. The water azeotrope was removed with a takeoff adapter. After all the water had been removed, excess toluene was distilled at reduced pressure. The product, which crystallized on cooling, was filtered, washed with pentane, and recrystallized from carbon tetrachloride or benzene. Melting points, yields, and nitrogen analyses are reported in Table I. A complete analysis was made of 2-phenyl-1,3-dihydro-2,1,3-benzoboradiazole (II), which sublimes near the melting temperature without decomposition.

*Anal.*<sup>14</sup> Calcd. for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>B: C, 74.27; H, 5.72; N, 14.51; B, 5.57; mol. wt., 194. Found: C, 73.77; H, 5.80; N, 14.82; B, 5.52; mol. wt., 192 (Rast method).

**Hydrolysis of II.**—Two grams of II was shaken with a solution of 20 cc. of water, 5 cc. of ethanol and 3 cc. of hydrochloric acid for a few minutes until all the solid had dissolved. Extraction with ether yielded 1.11 g. (88%) of benzenboronic acid, m.p. 216–220°. The aqueous layer was then made basic and re-extracted with ether to give 1.00 g. (90%) of phenylenediamine, m.p. 99–102°.

In contrast to the rapid hydrolysis in dilute acid solution, the dihydroboradiazole ring system was moderately stable in neutral solutions. For example, a 3-g. sample of II was added to 70 cc. of 85% ethanol and the mixture heated to boiling on a hot-plate. After all the solid had dissolved, 50 cc. of water was added and the mixture set aside. Compound II crystallized out on cooling; the recovery was 35%.

Compound II could not be isolated, however, from solutions of similar concentration made up from benzenboronic acid and phenylenediamine, indicating that, once hydrolyzed, II would not re-form in aqueous solutions.

**Reaction of II with Hydrogen Chloride.**—Anhydrous hydrogen chloride was passed through a solution of II (19.4 g., 0.10 mole) in refluxing toluene (500 cc.) for an 8-hour period.

A large amount of solid precipitated on cooling the solution, and a further amount was obtained by concentrating the toluene filtrate; total weight 24.16 g. (91% calculated as the dihydrochloride of II), m.p. 180–193°. A potentiometric titration with sodium hydroxide showed two breaks; the first corresponding to 0.965 mole of hydrochloric acid per mole of II, and the second to a total of 1.93 moles of hydrochloric acid per mole of II. No phenyldichloroborane could be detected as a product of the hydrogen chloride reaction. As further evidence that the dihydrobenzoboradiazole ring had not been ruptured, a sample of the dihydrochloride (1.46 g.) was shaken with ether and 10% aqueous sodium carbonate solution. The ether layer was then separated and dried over magnesium sulfate. Evaporation of ether at reduced pressure (the temperature was never allowed to go above room temperature) yielded 0.93 g. (66%) of II, m.p. 212–215°; after recrystallization, m.p. 215–216°. The infrared spectrum of the product, m.p. 212–215°, before heating or recrystallization, was that of the boradiazole, II.

**Reaction of Benzenboronic Acid with Aniline.**—The reaction was carried out as in the previous cases (phenylenediamine reactions) with 50 cc. of toluene, 3.40 g. (0.028 mole) of benzenboronic acid and 5.20 g. (0.056 mole) of aniline. Concentration of the toluene gave 1.91 g. (66%) of benzenboronic acid anhydride, identified by infrared spectra and melting point.

**Reaction of Benzenboronic Acid with Ethylenediamine.**—Benzenboronic acid (3.05 g., 0.025 mole) and ethylenediamine (1.95 g., 0.025 mole) were heated as usual in toluene, the solution concentrated, then the product precipitated by addition of pentane. A crystalline material separated; m.p. on a Fisher-Johns block, 151–155°; m.p. in a sealed capillary tube, 154–155°, with preliminary softening at 152°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>28</sub>O<sub>3</sub>N<sub>2</sub>B<sub>3</sub>: N, 7.57. Found: N, 7.85.

Attempts at recrystallization from carbon tetrachloride led to decomposition of the material with a spreading of the melting range; after the first recrystallization the melting point was 152–162°, neut. equiv., 210 (titration with HCl); after the second, m.p. 149–162°, neut. equiv., 218. The neutralization equivalent calculated for a 1:1 complex of ethylenediamine and benzenboronic anhydride is 186 (that calcd. for a tetrahydrobenzoboradiazole structure, 68). The infrared spectrum of the complex had a weak band at 3.1  $\mu$ , typical of >B:NH<sub>2</sub>R complexes such as triarylboraneammonia and the ethanolamine esters of diarylboronic acids.

The behavior described above indicates that the complex of ethylenediamine and the boronic anhydride dissociates when heated. This property was confirmed by heating a sample of the complex (0.45 g.) at 140° (2 mm.) in a drying pistol for six hours. There remained 0.35 g. (90%) of benzenboronic anhydride, identified by its melting point (216–220°) and infrared spectrum.

**Reaction of I with *o*-Phenylenediamine.**—The boronate ester I was prepared by heating benzenboronic acid and (+)-ethyl tartrate in toluene with azeotropic distillation of water; 90% yield, m.p. 48–49°, reported<sup>15</sup> m.p. 46–48°.

A sample of I (2.91 g., 0.01 mole) in 20 cc. of benzene was mixed with a solution of 1.08 g. (0.01 mole) of *o*-phenylenediamine in 30 cc. of benzene at room temperature (27°). Benzene was then removed by the vacuum of a water-pump, without raising the temperature, until the volume had been reduced to one-half of the original. The crystals which formed were removed by filtration and washed with cold carbon tetrachloride to remove any ethyl tartrate which contaminated the product. The process of concentration, filtration, and washing was repeated five times. The total crude yield was 1.31 g. (67.5%); recrystallization from carbon tetrachloride afforded 1.14 g. (57%) of purified material, m.p. 215–216°. The infrared spectrum was identical with that for II prepared in refluxing toluene from I and from benzenboronic acid. The lower yield compared to that for the reaction with benzenboronic acid may be attributed at least in part to the difficulty of separating the boradiazole from ethyl tartrate.

EVANSTON, ILL.

(14) The C, H and N analyses were made by Miss H. Beck.

(15) H. G. Kuivila, A. H. Keough and E. J. Soboczenski, *J. Org. Chem.*, **19**, 780 (1954).