pound from the paper chromatogram with ethyl alcohol and examining the ultraviolet absorption spectrum of this solution. This spectrum was identical to one obtained from an alcoholic solution of an authentic sample of the *para* isomer.

Boron–Nitrogen Compounds. VIII.[1,2] 2-Dimethylamino-1,3,2-benzodiazaboroline

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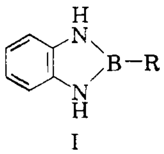
Schupp and Brown[3] first investigated the reaction of boron compounds with *o*-phenylenediamine. On interaction of dichlorophenylborane, for instance, compound I with R = C_6H_5 was obtained. Considerable interest has since developed

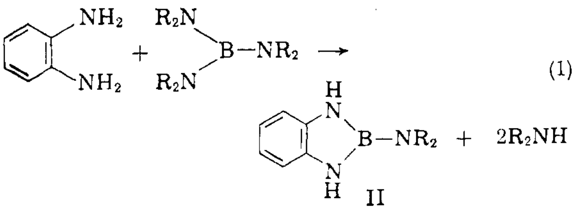


I

in compounds of this aromatic, boron-containing heterocyclic system[4] and several preparative approaches have been investigated.[5-9] However, no 2-amino-1,3,2-benzodiazaborolines (I. R = NR_2') have been reported. In connection with our previous work on the diazaboroline system[10] and on B-aminoborazines[11,12] the preparation of such compounds seemed of interest.

Results and Discussion

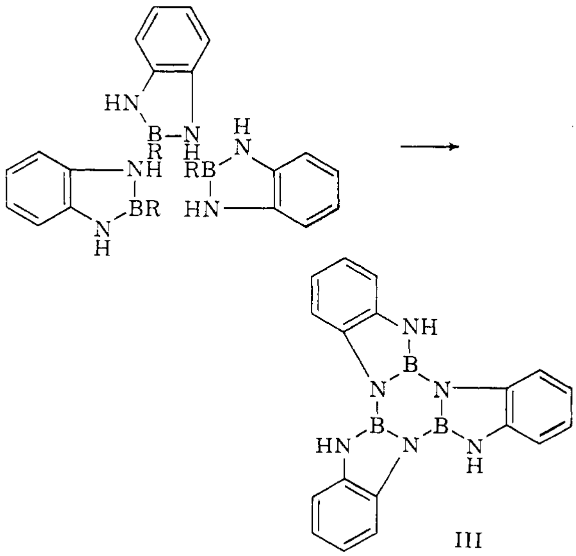
Recently the preparation of the 1,3,2-benzodiazaboroline (I) with R = Cl has been reported.[13] Attempts to aminolize the boron–chlorine linkage under mild conditions did not yield the desired 2-amino-1,3,2-benzodiazaboroline (II). Therefore a transamination reaction as illustrated in equation 1 was used to synthesize this compound. On refluxing *o*-phenylenediamine and tris(dimethylamino)borane, in ether, compound II was obtained in good yield and could be isolated from the crude reaction mixture by vacuum sublimation.


(1)

The infrared spectrum of 2-dimethylamino-1,3,2-benzodiazaboroline shows a distinct N—H stretching frequency near 3390 cm.$^{-1}$. Two extremely strong absorptions were recorded at 1468 cm.$^{-1}$. and 1378 cm.$^{-1}$ and consequently assigned as B—N absorptions. This seems to be in general agreement with our previous observation[10] that boron–nitrogen compounds with one central boron atom linked to two different nitrogen atoms affords two different B—N absorptions.

When a higher boiling solvent, for instance xylene, was employed in the preparation described above, compound II was not obtained but III could be isolated in nearly quantitative yield.

It has been shown previously,[14,15] that the final product from the interaction of boron trichloride and *o*-phenylenediamine likewise is the borazine derivative (III). Similarly, III was obtained on refluxing tris(ethoxy)borane with *o*-phenylenediamine in xylene.[9]



III

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[1] Part VII, K. Niedenzu, *Inorg. Chem.*, **1**, 943 (1962).

[2] Supported by the U. S. Army Research Office (Durham).

[3] L. J. Schupp and C. A. Brown, Abstracts of Papers, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., 1955, p. 48-R.

[4] Several nomenclatures have been introduced into the literature to refer to compounds of type I. The benzodiazaboroline designation is one recommended by the Committee on the Nomenclature of Boron Compounds of the American Chemical Society.

[5] M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

[6] R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5411 (1958).

[7] E. Nyilas and A. H. Soloway, *ibid.*, **81**, 2681 (1959).

[8] M. F. Hawthorne, *ibid.*, **81**, 5836 (1959).

[9] R. J. Brotherton and H. Steinberg, *J. Org. Chem.*, **26**, 4632 (1961).

[10] K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

[11] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 3561 (1959).

[12] K. Niedenzu, D. H. Harrelson, and J. W. Dawson, *Chem. Ber.*, **94**, 671 (1961).

[13] L. F. Hohnstedt and A. M. Pellicciotto, Final Report, Office of Naval Research Contract Nonr 2793(00), 1961.

[14] C. A. Brown, Final Report, Office of Naval Research Contract Nonr 1439(02), 1956.

[15] B. Rudner and J. J. Harris, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p. 61-P.

Such observations suggest the intermediate formation of I with R = Cl, NR_2', or OR′ in all of these reactions which can easily undergo condensation to III. (See col. 2, p. 4701.)

This is substantiated by the following experimental data: (1) refluxing of the diazaboroline (II) in xylene for about thirty minutes provided III in quantitative yield; (2) treatment of I where R = Cl in boiling benzene with triethylamine yields III; (3) although transamination has been found an extremely useful tool for the facile preparation of boron–nitrogen bonded materials,[16] the transamination of the NR_2-group of II could not be effected under relatively mild conditions. At higher temperatures, condensation of three molecules of II occurs yielding again the borazine derivative (III).

On the basis of this evidence it seems understandable that diazaborolines of type II with R other than alkyl or aryl groups are not common. The intermolecular condensation reaction to yield the borazine derivative (III) appears to predominate over normal substitution reactions at the boron atom, thus indicating a preference for this particular ring system.

The transamination reaction illustrated in equation 1 appears to be generally applicable. This is demonstrated by the facile preparation of 2-phenyl-1,3,2-benzodiazaboroline (II. $R = C_6H_5$) on the interaction of bis(dimethylamino)phenylborane with *o*-phenylenediamine.

Experimental[17]

2-Dimethylamino-1,3,2-benzodiazaboroline (II).—A mixture of 30 g. (0.21 mole) of tris(dimethylamino)borane and 21.6 g. (0.2 mole) of *o*-phenylenediamine was covered with 250 cc. of dry ether and gently heated at reflux for 15 hr. Volatile components were evaporated under reduced pressure and the remaining solid material was sublimed in vacuum at 120–130° using an oil bath. II was obtained as a white crystalline material in 83% yield (26.5 g.), softening at 158–162° and apparently decomposing near 220°. The residue of the sublimation contained a small amount of III.

Anal. Calcd. for $BN_3C_8H_{12}$: B, 6.7; N, 26.2; C, 59.7; H, 7.6. Found: B, 6.7; N, 26.0; C, 59.1; H, 8.0.

2-Phenyl-1,3,2-benzodiazaboroline (I. $R = C_6H_5$).—In an analogous procedure, a slight excess of bis(dimethylamino)phenylborane reacted with *o*-phenylenediamine to yield 2-phenyl-1,3,2-benzodiazaboroline in 88% yield. The material did not depress the melting point of an authentic sample prepared by a previously described method[7]; their infrared spectra were identical.

5H,12H,19H-Tris(1,3,2-benzodiazaborolo)borazine (III).—(a) Four grams (0.025 mole) of II was covered with 30 cc. of xylene and refluxed for 30 min. After cooling to room temperature, the crude solid product was filtered off and recrystallized from acetone to yield 3.7 g. (94%) of III, softening near 350° and apparently decomposing near 380°. (b) 2-Chloro-1,3,2-benzodiazaboroline (7.6 g., 0.05 mole) was covered with 100 cc. of dry benzene and 10.1 g. (0.1 mole) of triethylamine added. The mixture was refluxed for 10 hr. Recrystallization of the solid residue yielded 4.4 g. (82%) of III, identical with a sample obtained from (a) and a purified sample obtained on thermal decomposition of the 2-chloro-1,3,2-benzodiazaboroline.

Anal. Calcd. for $B_3N_6C_{18}H_{15}$: B, 9.3; N, 24.2; C, 62.2; H, 4.3. Found: B, 9.3; N, 23.9; C, 61.9; H, 4.1.

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[16] See and *cf.* ref. 10 and literature cited therein.

[17] Analysis by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points were taken in sealed capillary tubes on a Mel-Temp block. Infrared spectra were recorded as mulls and potassium bromide pellets on a Perkin–Elmer Model 21 spectrophotometer using sodium chloride optics.

Alkaloid Studies. XXXIX.[1] The Occurrence of Dihydrocorynantheol and Aricine in *Aspidosperma marcgravianum* Woodson

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In the course of our systematic study of the alkaloids of the genus *Aspidosperma*, we have encountered principally alkaloids of the N-acyldihydroindole type.[2-5] In common with the findings of other authors[6] we have also found tetracyclic indoles such as N-methyltetrahydroellipticine[7] and ulein.[8] More recently two alkaloids with the sarpagine skeleton, polyneuridine and normacusine-B, have been isolated from *A. polyneuron* M. Arg.,[9] a species which also synthesizes the biogenetically distinct quebrachamine and aspidospermine. Species of this genus are also able to produce alkaloids of the yohimbine type,[10] and we have found β-yohimbine in an, as yet, unidentified[11] *Aspidosperma species.*

We now wish to report the isolation of two other alkaloid types related to yohimbine from the bark

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[1] Paper XXXVIII, C. Djerassi, H. W. Brewer, C. L. Clarke, and L. J. Durham, *J. Am. Chem. Soc.*, **84**, 3210 (1962).

[2] C. Djerassi, A. A. P. G. Archer, T. George, B. Gilbert, and L. D. Antonaccio, *Tetrahedron*, **16**, 212 (1961).

[3] B. Gilbert, J. M. Ferreira, R. J. Owellen, C. E. Swanholm, H. Budzikiewicz, L. J. Durham, and C. Djerassi, *Tetrahedron Letters*, 59 (1962).

[4] C. Djerassi, T. George, N. Finch, H. F. Lodish, H. Budzikiewicz, and B. Gilbert, *J. Am. Chem. Soc.*, **84**, 1499 (1962).

[5] C. Djerassi, L. D. Antonaccio, H. Budzikiewicz, J. M. Wilson, and B. Gilbert, *Tetrahedron Letters*, in press.

[6] For leading references see (a) J. Schmutz, *Pharm. Acta Helv.*, **36**, 103 (1961); (*b*) M. A. Ondetti and V. Deulofeu, *Tetrahedron*, **15**, 160 (1961).

[7] Isolated from *A. parvifolium* A. DC.. by Dr. T. George in our laboratory.

[8] B. Gilbert, L. D. Antonaccio, A.A.P.G. Archer, and C. Djerassi, *Experientia*, **16**, 61 (1960).

[9] L. D. Antonaccio, N. A. Pereira, B. Gilbert, H. Vorbrueggen, H. Budzikiewicz, J. M. Wilson, L. J. Durham, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 2161 (1962).

[10] (a) E. Fourneau and H. Page, *Bull. sci. pharmacol.*, **21**, 7 (1941); (b) K. Biemann, M. Friedmann-Spiteller, and G. Spiteller, *Tetrahedron Letters*, 485 (1961).

[11] Originally identified (see ref. 9) incorrectly as *A. eburneum* F. Allem; a specimen of this as yet unidentified species exists in the Rio de Janeiro Botanical Garden under the number R.B. 11.4085.