addition the solution was heated briefly at 80° and then evaporated under reduced pressure. The residual brown gum was dissolved in 50 ml. of cold benzene. Addition of 75 ml. of petroleum ether (b.p. 40–60°) precipitated 7.7 g. of a white solid. The solid was dissolved in 40 ml. of water and the solution was made slightly alkaline with 10% sodium hydroxide solution. Di-*n*-butylamine, 2.8 g., separated and was removed. The remaining aqueous solution was extracted with three 5-ml. portions of chloroform, and the extract was dried with anhydrous sodium sulfate and evaporated to dryness. The residual white solid was recrystallized from a benzene–petroleum ether (b.p. 40–60°) mixture to obtain 0.7 g. (16%) of the isopropyl phosphinate, m.p. 79–80°.

Anal. Calcd. for $C_9H_{15}N_2O_2P$: C, 50.48; H, 7.05; P, 14.46; N, 13.08. Found: C, 50.16; H, 7.03; P, 14.66; N, 13.30.

In an experiment where di-*n*-butylamine was replaced with triethylamine, similar results were obtained.

Hydrolysis of isopropyl bis(2-cyanoethyl)phosphinate. A solution of 5.0 g. (0.023 mole) of the phosphinate in 20 ml. of concd. hydrochloric acid was refluxed for 2 hr. The solution was evaporated to dryness under reduced pressure, and the residual solid was dissolved in 40 ml. of 10% sodium hydroxide solution. The solution was heated to reflux, and nitrogen was bubbled through it until the liberation of ammonia was complete. The solution was acidified with dilute hydrochloric acid and evaporated to dryness under reduced pressure. The residual solid was extracted with 50 ml. of hot glacial acetic acid. Addition of 50 ml. of acetone to the cooled extract precipitated 2.7 g. (56%) of bis(2-carboxyethyl)phosphinic acid, m.p. 153–158°. Recrystallization from a mixture of acetone and acetic acid gave an analytical sample, m.p. 159–160°. A mixed melting point with an authentic sample prepared by hydrogen peroxide oxidation of bis(2-carboxyethyl)phosphine oxide[16] was not depressed.

Anal. Calcd. for $C_6H_{11}O_6P$: C, 34.29; H, 5.28; P, 14.74. Found: C, 34.56; H, 5.25; P, 14.84.

Bis(2-carboxyethyl)phosphine oxide. A solution of 40.0 g. (0.25 mole) of bis(2-cyanoethyl)phosphine oxide in 200 ml. of concd. hydrochloric acid was refluxed for 2.5 hr. and then evaporated to dryness on the steam bath. The crystalline residue was dried at 60° in a vacuum oven for 24 hr. and extracted with 200 ml. of boiling glacial acetic acid. The extract was cooled, filtered, and evaporated to dryness under vacuum. The white crystalline residue was washed with acetonitrile and dried in a vacuum desiccator over potassium hydroxide to obtain 46 g. (84%) of the acid, m.p. 124–125°. A portion was recrystallized from isopropyl alcohol to furnish an analytical sample, m.p. 131.5–133°.

Anal. Calcd. for $C_6H_{11}O_5P$: C, 37.12; H, 5.71; P, 15.96. Found: C, 37.25; H, 5.76; P, 16.25.

Acknowledgment. The authors wish to thank Dr. V. P. Wystrach for his continuing interest and encouragement. The authors are also indebted to Mrs. E. C. Grim and Dr. J. A. Kuck for microanalyses, and to Mr. N. Colthup for assistance in interpreting infrared spectra.

STAMFORD, CONN.

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[16] W. C. Firth, unpublished work.

[CONTRIBUTION FROM U. S. BORAX RESEARCH CORP.]

Direct Preparation of Some Cyclic Boron-Nitrogen Compounds from Alkoxyboranes[1]

R. J. BROTHERTON AND H. STEINBERG

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Borazine derivatives have been prepared by reactions of trialkoxyboranes with *o*-phenylenediamine or *o*-aminophenol. Comparable reactions of a trialkoxyborane with an aromatic monofunctional or *para* difunctional amine resulted in much slower alcohol evolution. Tris(anilino)borane was isolated from the reaction of isopropyl borate with aniline.

INTRODUCTION

There have been few reported attempts to displace allkoxy groups in esters of boric or boronic acids with amines. Previous work in this laboratory and earlier reports[2,3] in the literature suggest that this type of amine displacement is extremely difficult, and that the equilibrium shown in Equation 1 must lie far to the left in the direction of the trialkoxyborane.

$$B(OR)_3 + 3RNH_2 \rightleftharpoons B(NHR)_3 + 3ROH \tag{1}$$

It should be pointed out, however, that in some cases orthoborates form intermediate complexes with amines.[4] More recently, several syntheses of cyclic materials containing boron-nitrogen bonds from boron-oxygen derivatives have been reported.[5–8] During the course of the present investigation, several new syntheses of cyclic boron-nitrogen compounds from boric and boronic acid esters have been developed including the first re-

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[1] This work was presented in part by A. L. McCloskey, H. Goldsmith, R. J. Brotherton, H. Steinberg, and G. W. Willcockson at the 135th Meeting of the American Chemical Society, Boston, Mass., April 1959.

[2] W. Gerrard, M. F. Lappert, and C. A. Pearce, *J. Chem. Soc.*, 381 (1957).

[3] R. G. Jones and C. R. Kinney, *J. Am. Chem. Soc.*, **61**, 1378 (1938).

[4] See M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956) for a summary of reactions in which orthoborate-amine complexes are formed.

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

[6] E. Nyilas and A. H. Soloway, *J. Am. Chem. Soc.*, **81**, 2681 81959).

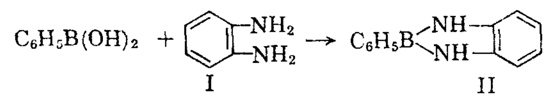
[7] J. M. Sugihara and C. M. Bowman, *J. Am. Chem. Soc.*, **80**, 2443 (1958).

[8] S. S. Chissack, M. J. S. Dewar, and P. M. Maitlis, *J. Am. Chem. Soc.*, **81**, 6329 (1959).

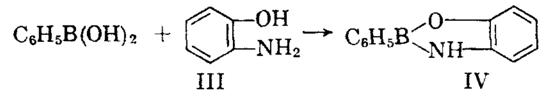
ported direct preparation of borazines from orthoborates.

RESULTS AND DISCUSSION

Previously reported syntheses of boron-nitrogen compounds from boron-oxygen derivatives have involved the reactions of benzeneboronic acids with *o*-phenylenediamine[5,6] or *o*-aminophenol[7] (Equations 2 and 3) and the reaction of the ethyl tartrate ester of benzeneboronic acid with *o*-phenylenediamine.[5] Boron-nitrogen bond formation from *o*-amine derivatives is unique in these cases, since comparable reactions of benzeneboronic acid with aniline gave only triphenylboroxine[5] and reaction with ethylenediamine only a 1:1 adduct of the boroxine.[5] The general scope of the *o*-phenylenediamine reaction has now been extended to include Reactions 4 and 5 in which good yields of 2-phenyl-1,3,2-benzodiazaboroline (II) have been obtained from triphenylboroxine (V) and diisopropoxyphenylborane (VI), respectively. The related compound, 2-phenyl-1,3,2-benzoöxaazaboroline (IV) which was prepared originally from *o*-aminophenol and benzeneboronic acid[7] has now been obtained in good yields from diisopropoxyphenylborane (Equation 6).


I II

+ $2H_2O$ (2)


III IV

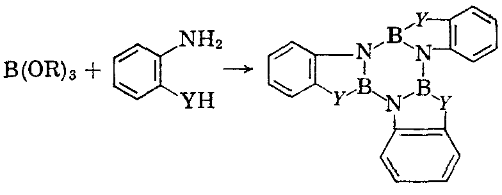
+ $2H_2O$ (3)

$$(C_6H_5BO)_3 + 3I \longrightarrow 3II + 3H_2O \qquad (4)$$

$$\underset{VI}{C_6H_5B[OCH(CH_3)_2]_2} + I \longrightarrow II + 2(CH_3)_2CHOH \qquad (5)$$

$$VI + III \longrightarrow II + 2(CH_3)_2CHOH \qquad (6)$$

When *o*-phenylenediamine was refluxed in xylene with triethoxy- or triisopropoxyborane, 5*H*,12*H*,19*H*-tris[1,3,2-benzodiazaborolo]borazine (VII)[9] was obtained. This material was characterized by a molecular weight determination, elemental analyses, and spectral data. This compound is probably the same as that prepared originally by Brown[10] from boron trichloride and *o*-phenylenediamine and more recently by Rudner and Harris[11] who also isolated it from the reaction of boron trichloride and *o*-phenylenediamine. However, the direct preparation of a borazine from an orthoborate has not been described previously. A similar reaction of triisopropoxyborane with *o*-aminophenol led to the related compound, tris(1,3,2-benzooxaazaborolo)-borazine (VIII) which has also been prepared recently from boron trichloride and either *o*-aminophenol or *o*-anisidine.[10] The borazines (VII and VIII) were isolated as white solids which decomposed at 380–390° and 210–280°, respectively, in sealed capillaries. The *o*-phenylenediamine derivative (VII) appeared to be very stable in a neutral homogeneous water-acetone solution but hydrolyzed rapidly in acidic or basic solutions.


VII, *Y* = NH
VIII, *Y* = O

In order to reexamine the reactions of other aromatic amines with alkoxyboranes, the reactions of aniline and *p*-phenylenediamine with triisopropoxyborane were investigated. Alcohol evolution was very slow with the *p*-diamine, but significant amounts of isopropyl alcohol were displaced by aniline, and the expected product tris(anilino)borane was obtained.

$$3C_6H_5NH_2 + B[OCH(CH_3)_2]_3 \longrightarrow B(NHC_6H_5)_3 + 3(CH_3)_2CHOH$$

The isolation of the aminoborane contradicts the early work of Jones and Kinney[3] but has been confirmed recently by an independent investigation[12] in which aminoborane derivatives of aromatic amines were obtained in good yields by refluxing various alkoxyboranes with monofunctional aromatic amines at the boiling points of the amines.

It appears, however, that the spatial relationship of the amino groups in *o*-phenylenediamine is very important and the resulting five-membered ring is formed much more easily than boron-nitrogen derivatives of monofunctional amines or *p*-diamines.

EXPERIMENTAL[13]

Preparation of 2-phenyl-1,3,2-benzodiazaboroline. a. From diisopropoxyphenylborane. A solution of 4.25 g. (21.6 mmoles) of diisopropoxyphenylborane and 2.33 g. (21.6 mmoles) of *o*-phenylenediamine in 20 ml. of xylene was

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[9] This nomenclature was originally suggested in *The Nomenclature of Boron, Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds*, Division of Organic Chemistry, American Chemical Society, January 1958.

[10] C. A. Brown, Final Report, Office of Naval Research Contract No. Nonr 1439 (02) Project No. NR 052-355, September 1956.

[11] B. Rudner and J. J. Harris, 138th Meeting, American Chemical Society, New York, September 1960, Abstracts of Papers, p. 61-P.

[12] B. M. Mikhailov and P. M. Aronovich, *Zhur. Obshchei Khim.*, 29, 3124 (1959).

[13] Elemental carbon, hydrogen, and nitrogen analyses were done by Dr. Adelbert Elek, Los Angeles, Calif. Boron analyses were performed by previously described sodium carbonate or sodium peroxide fusion methods: D. L. Hunter, L. L. Petterson, and H. Steinberg, *Anal. Chim. Acta*, 21, 523 (1959). All experiments were conducted in a moisture free atmosphere of air or nitrogen.

heated at reflux temperature for 1 hr. The resulting isopropyl alcohol (2.59 g., 96%) was removed by distillation through a packed column. The residual reaction mixture was cooled to room temperature and the resulting solid separated by filtration and dried to give 3.45 g. (82.5%) of 2-phenyl-1,3,2-benzodiazaboroline. This compound and that described in the following paragraph did not depress the melting point of a sample of 2-phenyl-1,3,2-benzodiazaboroline prepared by a previously described method[5,6] and their infrared spectra were identical.

b. *From triphenylboroxine.* A solution of 5.0 g. (16.2 mmoles) of triphenylboroxine and 5.0 g. (46.3 mmoles) of *o*-phenylenediamine in 70 ml. of benzene was heated at reflux temperature for 2–3 hr. The resulting water (0.9 g., *ca.* 100% yield) was collected in a Dean-Stark water trap and the residual solution cooled to room temperature. The solid product was collected on a filter and dried to give 7.98 g. (81% yield) of 2-phenyl-1,3,2-benzodiazaboroline as fine colorless crystals.

2-Phenyl-1,3,2-benzooxaazaboroline. A solution of 26.8 g. (0.130 mole) of diisopropoxyphenylborane and 14.15 g. (0.130 mole) of *o*-aminophenol in 53 ml. of xylene was heated at reflux for 155 min. The resulting isopropyl alcohol (15.75 g., 100% yield) was removed by continuous distillation and the residual solution cooled to 0°. Successive filtrations and concentrations of the xylene solution gave 24.42 g. (94% yield) of crude product, m.p. 97.5–101°; recrystallization from toluene gave pure 2-phenyl-1,3,2-benzooxaazaboroline, m.p. 101–102° (lit. m.p., 99–101°[7]).

Anal. Calcd. for $C_{12}H_{10}NOB$: B, 5.55; mol. wt. 195. Found: B, 5.37; mol. wt., 200 (cryoscopic in benzene).

Reaction of triisopropoxyborane with o-phenylenediamine. A mixture of 40.09 g. (0.213 mole) of triisopropoxyborane and 23.05 g. (0.213 mole) of *o*-phenylenediamine was heated for 18 hr. in refluxing xylene. The reaction mixture temperature rose from 136° to 150° as isopropyl alcohol (35.05 g., 86%) was removed by slow fractional distillation through a packed column. After cooling to room temperature, the residual crude solid product was separated by filtration and recrystallized from acetone to give 19.96 g. (80.5%) of 5*H*,12*H*,19*H*-tris[1,3,2-benzodiazaborolo]-borazine, m.p., sealed capillary tube, 380–390° dec., after previous softening at 350–355°.

Anal. Calcd. for $C_{18}H_{15}N_6B_3$: C, 62.2; H, 4.32; N, 24.2; B, 9.33; mol. wt., 347. Found: C, 61.8; H, 3.96; N, 23.0; B, 9.33; mol. wt., 321 (cryoscopic in dioxane).

The borazine is insoluble in hexane, benzene, and ether but can be recrystallized from dioxane or cyclohexane as well as acetone. It is soluble in hot dimethylformamide, bis-2-ethoxyethyl ether and methanol (with reaction).

The reaction of one molar equivalent of *o*-phenylenediamine with 1.4 equivalents of triethoxyborane (the excess was necessary since the resulting ethanol-triethoxyborane azeotrope was removed continuously) gave the same borazine derivative.

Reaction of triisopropoxyborane with o-aminophenol. A mixture of 31.85 g. (0.169 mole) of triisopropoxyborane and 18.45 g. (0.169 mole) of *o*-aminophenol was heated for 16.5 hr. at 130–150° in 50 ml. of refluxing xylene. Isopropyl alcohol (94.8% yield) was removed by continuous fractional distillation. After cooling to room temperature, the reaction mixture was filtered to give 19.2 g. of crude product. Washing with dry diethyl ether yielded a residue of 15.7 g. (79%) of tris[1,3,2-benzooxaazaborolo]borazine, m.p. 210–280° dec. in a sealed capillary tube.

Anal. Calcd. for $C_{18}H_{15}N_3O_3B_3$: C, 61.5; H, 3.41; B, 9.25; mol. wt., 351. Found: C, 60.1; H, 3.52; B, 9.44; mol wt., 338 (cryoscopic in dioxane).

The borazine was soluble in ethyl acetate and ethylene glycol dimethyl ether, partially soluble in acetone, dioxane, and tetrahydrofuran and insoluble in most other organic solvents.

Attempted reaction of triisopropoxyborane with p-phenylenediamine. A refluxing equimolar mixture of triisopropoxyborane and *p*-phenylenediamine in xylene resulted in only trace amounts of isopropyl alcohol in 0.7 hr. When bis-2-ethoxyethyl ether was used as the solvent, 21.3% of the isopropyl alcohol was recovered in 7.3 hr.

Reaction of triisopropoxyborane with aniline. A solution of 32.38 g. (0.172 mole) of triisopropoxyborane and 47.99 g. (0.516 mole) of aniline was heated for 5.5 hr. in 50 ml. of refluxing xylene. Isopropyl alcohol (7.17 g., 23.2% yield) was removed by continuous distillation, and the final residue was cooled to room temperature. The resulting crude solid was collected on a filter and recrystallized from xylene to give 2.74 g. (5.6% yield) of tris(anilino)borane, m.p. 168–170° (lit. m.p., 166–169°[3]). The boron content of this product was 3.83% compared to 3.77% for tris(anilino)-borane and its infrared spectrum was identical with that of an authentic sample.

ANAHEIM, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, UNION CARBIDE PLASTICS COMPANY, A DIVISION OF UNION CARBIDE CORP.]

Nature of the Interaction of Aqueous Sulfide Ion with Organotin Oxides and Related Substances

WALTER T. REICHLE

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The mechanism of the interaction of aqueous sulfide ion with polydiphenyl-, -dimethyl-, -di-*n*-butyl-and -di-*n*-octyltin oxides has been investigated. This reaction is believed to proceed *via* a water-soluble hexacoordinate metal ion, which on acidification yields the known diaryl- or dialkyltin sulfide trimers quantitatively. The corresponding selenides and tellurides, similarly prepared, are unstable and decompose. Diphenylgermanium oxide trimer, polydiphenyllead oxide and bis(triphenyltin) oxide also undergo this reaction with sulfide ion followed by acidification, to yield the corresponding sulfides.

INTRODUCTION

The Group Va alkyl- and aryl metal oxides or hydroxides react with aqueous hydrogen sulfide or ammonium sulfide to yield the metal sulfides.[1] For example, phenylantimony oxide reacts with hydrogen sulfide in aqueous ammonia followed by acidification to yield the corresponding sulfide.

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(1) E. Krause and A. von Grosse, *Die Chemie der metallorganischen Verbindungen*, p. 483, 548, 613, 599, 605; Verlag Borntraeger, Berlin, 1937.