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Boron–Nitrogen Compounds. XII.[1,2] Reaction of Some Silicon–Nitrogen Compounds with Boron Derivatives

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Reactions of aminosilanes with some boron compounds have been investigated. N-Silylated mono-, bis-, and trisaminoboranes were prepared by transamination. A study of the interaction of bis(trimethylsilyl)amine with (dimethylamino)-chlorophenylborane yielded a new type of bisborylamine.

In the search for convenient starting materials for the synthesis of B–N–Si heterocycles and other novel boron- and nitrogen-containing ring and linear systems, reactions of aminosilanes with some boron compounds have been studied.

Since transamination had been found a valuable tool in preparative boron–nitrogen chemistry,[3] the interaction of some B–N compounds with Si–N derivatives was investigated. Under the mild conditions of the normal transamination reaction (*i.e.*, refluxing the components in organic solvents at temperatures below 100°) mono-, bis-, and trisaminoboranes reacted smoothly with triorganosilylamine, R_3SiNH_2, to yield N-silylated aminoboranes.

$$R_2'BNR_2'' + H_2NSiR_3 \longrightarrow R_2'BNHSiR_3 + HNR_2'' \quad (1)$$

Further, bisaminoboranes and trisaminoboranes can also be partially transaminated.

$$C_6H_5B[N(CH_3)_2]_2 + H_2NSiR_3 \longrightarrow C_6H_5B[N(CH_3)_2](NHSiR_3) + HN(CH_3)_2 \quad (2)$$

However, bis(dimethylamino)phenylborane did not react with either bis(methylamino)diphenylsilane or bis(trimethylsilyl)amine under these mild conditions. In the former case reaction was observed when the components were refluxed without solvent. Apparently amine exchange occurred, followed by condensation of the boron component with elimination of methylamine. The only boron-containing product isolated analyzed for (I) with $x = 3$.

$$CH_3HN[BC_6H_5NCH_3]_xH$$

I

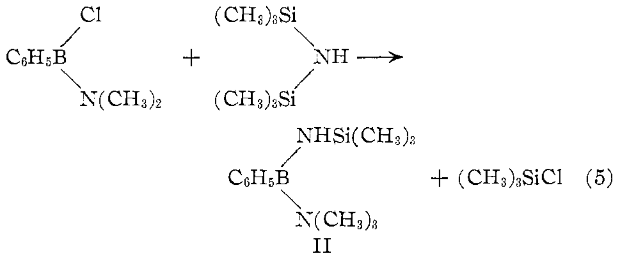
Recently the reaction of bis(trimethylsilyl)amine with trichloroborane was reported.[4] No adducts of the amine borane type were found; rather, cleavage of the Si–N bond occurred, resulting in the formation of (trimethylsilylamino)dichloroborane.

$$[(CH_3)_3Si]_2NH + BCl_3 \longrightarrow (CH_3)_3SiNHBCl_2 + (CH_3)_3SiCl \quad (3)$$

Nöth[5] did not isolate the aminoborane but observed elimination of an additional molecule of $(CH_3)_3SiCl$ and the formation of B-trichloroborazine.

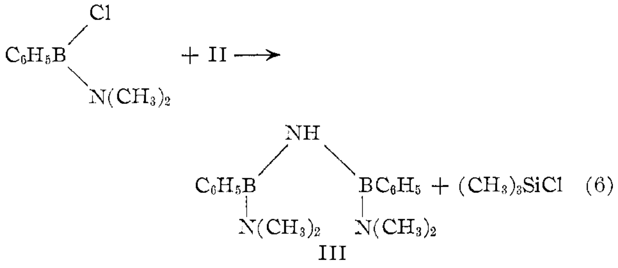
$$3BCl_3 + 3[(CH_3)_3Si]_2NH \longrightarrow (BClNH)_3 + 3(CH_3)_3SiCl \quad (4)$$

We found that a stepwise reaction mechanism is indeed indicated. When (dimethylamino)chlorophenylborane was treated with bis(trimethylsilyl)amine, it was possible to isolate the (dimethylamino)(trimethylsilylamino)-phenylborane (II). With additional (dimethylamino)-chlorophenylborane a bisborylamine (III) was obtained.



$$C_6H_5B(Cl)N(CH_3)_2 + [(CH_3)_3Si]_2NH \longrightarrow C_6H_5B(NHSi(CH_3)_3)N(CH_3)_3 + (CH_3)_3SiCl \quad (5)$$

II



$$C_6H_5B(Cl)N(CH_3)_2 + II \longrightarrow [C_6H_5B(N(CH_3)_2)]NH[BC_6H_5(N(CH_3)_2)] + (CH_3)_3SiCl \quad (6)$$

III

Since compounds of type II can now be prepared by two independent methods in good yield their utilization for further studies as illustrated in eq. 6 is indicated. Subsequent cyclization of the products presents interesting possibilities.

Experimental[6]

(Triethylsilylamino)di-*n*-amylborane, $[(C_2H_5)_3SiNH]B(C_5H_{11})_2$. —A solution of 12.0 g. (0.054 mole) of (diethylamino)di-*n*-amylborane[7] and 7.1 g. (0.054 mole) of triethylsilylamine in 50 cc. of benzene was refluxed for 3 hr. After evaporation of the solvent, the residue was distilled under vacuum to yield 9.4 g. (67%) of the

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[1] Part XI: H. Beyer, J. W. Dawson, H. Jenne, and K. Niedenzu, *J. Chem. Soc.*, in hand of editors.

[2] Supported by the U. S. Army Research Office (Durham). Presented in part at the Symposium "Current Trends in Organometallic Chemistry," Cincinnati, Ohio, June, 1963.

[3] See K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962), and references cited therein.

[4] M. Becke-Goehring and H. Krill, *Chem. Ber.*, **94**, 1059 (1961).

[5] H. Nöth, *Z. Naturforsch.*, **16b**, 618 (1961).

[6] Infrared spectra of the materials were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer using sodium chloride optics. Melting points were taken in sealed tubes on a Mel-Temp block. Analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[7] K. Niedenzu, H. Beyer, J. W. Dawson, and H. Jenne, *Chem. Ber.* **96**, 2653 (1963).

desired compound, b.p. 114–117° (3 mm.). *Anal.* Calcd. for $BNSiC_{16}H_{38}$: C, 67.8; H, 13.4; B, 3.8; N, 4.95; Si, 9.9. Found: C, 66.9; H, 13.9; B, 4.1; N, 5.8; Si, 9.9.

Bis(triphenylsilylamino)phenylborane, $[(C_6H_5)_2SiNH]_2BC_6H_5$.—A solution of 8.8 g. (0.05 mole) of bis(dimethylamino)phenylborane and 27.5 g. (0.1 mole) of triphenylsilylamine in 200 cc. of benzene was refluxed for 6 hr. On cooling the reaction mixture to room temperature, white crystals precipitated. Partial evaporation of the solvent yielded a second fraction. Both fractions were combined, washed with *n*-hexane, and dried under vacuum; yield 26.5 g. (84%), m.p. 181–184°. *Anal.* Calcd. for $BN_2Si_2C_{42}H_{37}$: C, 79.3; H, 5.9; B, 1.7; N, 4.4; Si, 8.8. Found: C, 79.3; H, 5.9; B, 1.8; N, 4.4; Si, 8.8.

Bis(triethylsilylamino)phenylborane, $[(C_2H_5)_3SiNH]_2BC_6H_5$.—This compound was prepared in a 59% yield using the same technique and molar ratios as described above. After evaporation of the solvent, the residue was distilled under vacuum and the fraction of b.p. 146–154° (3 mm.) was collected. *Anal.* Calcd. for $BN_2Si_2C_{18}H_{37}$: C, 62.1; H, 10.7; B, 3.1; N, 8.0; Si, 16.1. Found: C, 61.8; H, 10.7; B, 3.3; N, 8.3; Si, 16.3.

(Dimethylamino)(triethylsilylamino)phenylborane, $[(CH_3)_2N][(C_2H_5)_3SiNH]BC_6H_5$.—The material was prepared by an analogous procedure utilizing a 1:1 molar ratio in 79% yield. After evaporation of the solvent, the residue was distilled under vacuum, b.p. 119–122° (3 mm.). *Anal.* Calcd. for $BN_2SiC_{14}H_{27}$: C, 64.1; H, 10.3; B, 4.1; N, 10.6; Si, 10.6. Found: C, 64.0; H, 10.4; B, 4.2; N, 10.8; Si, 10.9.

Tris(triethylsilylamino)borane, $B[NHSi(C_2H_5)_3]_3$.—A mixture of 3.6 g. (0.025 mole) of tris(dimethylamino)borane and 9.8 g. (0.075 mole) of triethylsilylamine was refluxed for 1 hr. and subsequently rectified under vacuum. The fraction of b.p. 96–130° (3 mm.) was collected and redistilled to yield 7 g. (70%) of tris(triethylsilylamino)borane, b.p. 118–122° (3 mm.). *Anal.* Calcd. for $BN_3Si_3C_{18}H_{48}$: C, 53.8; H, 11.9; B, 2.6; N, 10.4; Si, 20.9. Found: C, 54.0; H, 12.0; B, 2.9; N, 10.6; Si, 21.2.

Bis(dimethylamino)triethylsilylaminoborane, $[(CH_3)_2N]_2[(C_2H_5)_3SiNH]B$.—A solution of 7.15 g. (0.05 mole) of tris(dimethylamino)borane and 6.55 g. (0.05 mole) of triethylsilylamine in 100 cc. of benzene was refluxed for 3 hr. and the solvent was stripped off. Distillation of the residue under vacuum yielded 9.7 g. (84%) of a fraction, b.p. 83–91° (3 mm.), which was analyzed without further purification. *Anal.* Calcd. for $BN_3SiC_{10}H_{28}$: C, 52.4; H, 12.2; B, 4.7; N, 18.3; Si, 12.2. Found: C, 50.4; H, 12.2; B, 5.1; N, 18.2; Si, 12.6.

Attempted Reaction of Bis(dimethylamino)phenylborane with Bis(trimethylsilyl)amine.—A solution of 4.4 g. (0.025 mole) of bis(dimethylamino)phenylborane and 8.05 g. (0.05 mole) of bis(trimethylsilyl) amine in 50 cc. of benzene was refluxed for 8 hr. No reaction occurred and the starting materials were recovered unchanged.

Reaction of Bis(dimethylamino)phenylborane with Bis(methylamino)diphenylsilane.—When the two compounds were refluxed in benzene solution no reaction was observed but the starting materials were recovered unchanged. On refluxing the components in a molar ratio of 1:2 without solvent slow evolution of methylamine was observed. After refluxing for 8 hr., a crystalline precipitate was filtered off, washed with ether, and dried; m.p. 252–256°. The analysis corresponds to structure I with $x = 3$. *Anal.* Calcd.: C, 69.0; H, 7.4; B, 8.5; N, 14.7. Found: C, 69.0; H, 7.1; B, 8.9; N, 14.6. The material did not contain silicon.

(Dimethylamino)(trimethylsilylamino)phenylborane, $[(CH_3)_2N][(CH_3)_3SiNH]BC_6H_5$.—To 16.7 g. (0.1 mole) of (dimethylamino)chlorophenylborane [obtained through disproportionation of dichlorophenylborane and bis(dimethylamino)phenylborane by refluxing equimolar amounts for 1 hr. and subsequent rectification under vacuum] 16.1 g. (0.1 mole) of bis(trimethylsilyl)amine was added while cooling the reaction mixture with ice. The mixture was stirred for 2 hr. at room temperature and trimethylchlorosilane was removed under vacuum. The residue was distilled under vacuum to yield 15.6 g. (21%) of the desired material, b.p. 82–83° (3 mm.). *Anal.* Calcd. for $BN_2SiC_{11}H_{21}$: C, 60.0; H, 9.5; B, 4.9; N, 12.7; Si, 12.7. Found: C, 60.1; H, 9.7; B, 4.7; N, 12.9; Si, 12.7.

Bis(dimethylaminophenylboryl)amine, $[(CH_3)_2NBC_6H_5]_2NH$.—A quantity (14.7 g., 0.088 mole) of (dimethylamino)chlorophenylborane was added with stirring to a solution of 7.08 g. (0.044 mole) of bis(trimethylsilyl)amine in 25 cc. of toluene while cooling the reaction mixture with an ice bath. After being warmed to room temperature, the mixture was refluxed for 8 hr. and a small precipitate of B-triphenylborazine was filtered off. Trimethylchlorosilane and solvent were removed under reduced pressure, and the residue was distilled under vacuum to yield 14 g. (57%) of a fraction of b.p. 158–160° (3 mm.) which was analyzed without further purification. *Anal.* Calcd. for $B_2N_2C_{16}H_{23}$: C, 68.9; H, 8.2; B, 7.7; N, 15.0. Found: C, 68.4; H, 8.3; B, 7.6; N, 14.4.

B-Triphenylborazine from Dichlorophenylborane and Bis(trimethylsilyl)amine.—A solution of 7.9 g. (0.05 mole) of dichlorophenylborane and 8.05 g. (0.05 mole) of bis(trimethylsilyl)amine in 50 cc. of benzene was refluxed for 30 min. B-Triphenylborazine was isolated in practically quantitative yield.

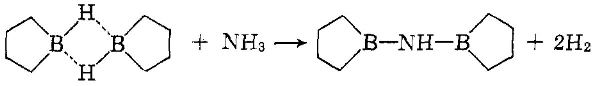
Discussion

Transamination as illustrated in eq. 1 provides a facile method of preparing N-silylated aminoboranes. However, under mild conditions only aminosilanes having an NH_2 group can be utilized in this manner, and thus far we have been unable to cause both N-attached hydrogens to react. For instance, a bisborylsilylamine, $\gtrdot SiN(B{=})_2$, could not be obtained when bis(dimethylamino)phenylborane was treated with triethylsilylamine in a 2:1 molar ratio. Only (triethylsilylamino)(dimethylamino)phenylborane was produced; the excess of bis(dimethylamino)phenylborane was recovered.

N-Silylated aminoboranes are very similar to the corresponding N-alkylated derivatives. In general they are sensitive to moisture and are readily hydrolyzed. Molecular weight determinations by the cryoscopic method in benzene solution indicated the existence of the monomeric species only.

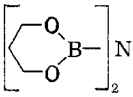
The infrared spectra of the N-silylated aminoboranes contained numerous absorptions and unequivocal assignment is difficult. Since B–N absorptions are usually the strongest bands in the spectra of boron–nitrogen compounds, it might be possible to assign the very strong peaks near 1380 cm.$^{-1}$ to a B–N stretch. Those N-silylated aminoboranes with more than one N linkage to a central boron atom (for instance, II) exhibited two extremely strong absorptions which might be related to a B–N stretch. They were centered at 1300–1330 and 1400–1425 cm.$^{-1}$, respectively. NH-Containing silylaminoboranes evidenced the NH absorption near 3400 cm.$^{-1}$. The corresponding band of bis(trimethylsilyl)amine is found in the same region.

Most interesting, however, appears to be the facile synthesis of the bisborylamine (III). Compounds of this type are virtually unknown. Nöth[5] has briefly mentioned the formation of $(R_2B)_2NH$ (R = butyl or propyl) on reaction of a diorganochloroboranes with bis(trimethylsilyl)amine, but no experimental data were presented. Some analogous compounds in which the boron is incorporated in an aliphatic ring have been obtained by Koester and Iwasaki[8] through the reaction of bisborolanes with ammonia or primary amines


(7)

and Lappert[9] reported the preparation of $[(RHN)_2B]_2NH$ (R = *t*-butyl) by the interaction of bis(*t*-butylamino)chloroborane with *t*-butylamine. Finally, the formation of a material as illustrated (IV) has been mentioned.[10]

III now illustrates the existence of a new type of bisborylamine which is the intermediate between those compounds reported by Nöth and those reported by Lappert. Their potential for utilization in the synthesis of B- and N-containing heterocycles and linear B–N compounds is obvious and will be investigated.


IV

In the infrared spectrum of III, the NH absorption was recorded as a weak band near 3390 cm.$^{-1}$. Two extremely strong absorptions near 1300 and 1400 cm.$^{-1}$, respectively, might be assigned to B–N stretching.

III disproportionates easily to trisaminoborane and B-trisaminoborazine. Analogous observations have been made in our laboratory with bisborylamines of the type $(R_2B)_2NH$, which readily yield triorganoboranes and B-triorganoborazines.

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A Study of the Chemistry of the Polyvanadates Using Salt Cryoscopy

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Glauber's salt cryoscopy and pH measurements have been made on sodium vanadate solutions in the pH range 2.5 to 7. Vanadium was found to exist in neutral solutions as a tetramer of VO_3^-. At lower pH values, confirmation was found for the equilibria

$$V_{10}O_{28}^{-6} \overset{H^+}{\rightleftharpoons} HV_{10}O_{28}^{-5} \overset{H^+}{\rightleftharpoons} H_2V_{10}O_{28}^{-4} \overset{H^+}{\rightleftharpoons} VO_2^+$$

No evidence was found for a hexavanadate in the pH range studied. The formation of a heteropolyanion between vanadium and phosphorus was indicated. The heteropolyanion forms from $H_2V_{10}O_{28}^{-4}$, but not from the other anionic polyvanadates.

Introduction

Despite the efforts of numerous investigators, the nature of the anionic vanadium(V) species in neutral and acidic solutions remains in doubt. The degree of aggregation, $\bar{n}$, of the metavanadate ion, *i.e.*, the anion present in neutral solutions, is variously reported as being 3 or 4.[1-3] Similarly, degrees of aggregation ranging from 2 to 10 have been reported for the species existing in acidic solutions.[4-9]

Rossotti and Rossotti,[9] whose potentiometric titrations probably represent the most definitive work that has been done on acidic vanadium solutions, found the species and equilibria that best fit their results were as shown below.

$$V_{10}O_{28}^{-6} \rightleftharpoons HV_{10}O_{28}^{-5} \rightleftharpoons H_2V_{10}O_{28}^{-4} \rightleftharpoons VO_2^+$$

Since the Rossottis' work, a number of others[10-16] have re-examined the vanadium system using a variety of methods. In many cases these newer data have supported the Rossottis' findings, but often only by being consistent with them, rather than by being unambiguous verifications. On the other hand, support for a hexavanadate has continued to appear,[17,18] and there has been disagreement as to whether an $\bar{n}$ of 10 or an $\bar{n}$ of 6, and multiples thereof, best fits the Rossottis' data.[19,20]

In addition to isopolyanions, vanadium forms heteropolyanions with phosphorus. Both octavanadate[21] and hexavanadate[22] have been proposed as the basic

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