AD-A240 168

SECURITY CLASSIFICATION OF THIS PAGE

2

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: prepared for publication distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): UK/DC/TR-37	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Department of Chemistry, University of Kentucky	6b. OFFICE SYMBOL (If applicable)
6c. ADDRESS (City, State, and ZIP Code): Lexington, KY 40506-0055	7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
8c. ADDRESS (City, State, and ZIP Code): 800 North Quincy Street, Arlington, VA 22217-5000	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: R & T Code 4135003-1
	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.
7b. ADDRESS (City, State, and ZIP Code): 800 North Quincy Street, Arlington, VA 22217-5000	

SEP 11 1991

S D

11. TITLE (Include Security Classification): STUDIES ON 1-TRIMETHYLSILYL-2,4,6-TRIETHYLBORAZINE AND RELATED SPECIES (unclassified)

12. PERSONAL AUTHOR(S): K. Niedenzu, J. Serwatowska, J. Serwatowski

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
interim technical	FROM _____ TO _____	91/9	9

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	1-trimethylsilylborazines borazines aminoborazines

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The unsymmetrically substituted borazine $(C_6H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has been obtained from the reaction of $C_6H_5BCl_2$ with $HN[Si(CH_3)_3]_2$, and an improved synthesis of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has been developed. The reaction of the latter with an excess of BCl_3 proceeds with the ultimate formation of $Cl_3B_3N_3H_2[Si(CH_3)_3]$, whereas the reaction with one molar equivalent of BBr_3 leads to the formation of $Br(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$, but which is contaminated by substantial amounts of $Br(C_2H_5)_2B_3N_3H_3$ besides a diborazinyl and additional products. $C_6H_5BBr_2$ reacts with $N[Si(CH_3)_3]_3$ to give the aminoborane $[(CH_3)_3Si]_2NBBr(C_6H_5)$, but $C_6H_5BCl_2$ does not undergo a reaction under analogous conditions.

This document has been approved for public release and sale; its distribution is unlimited.

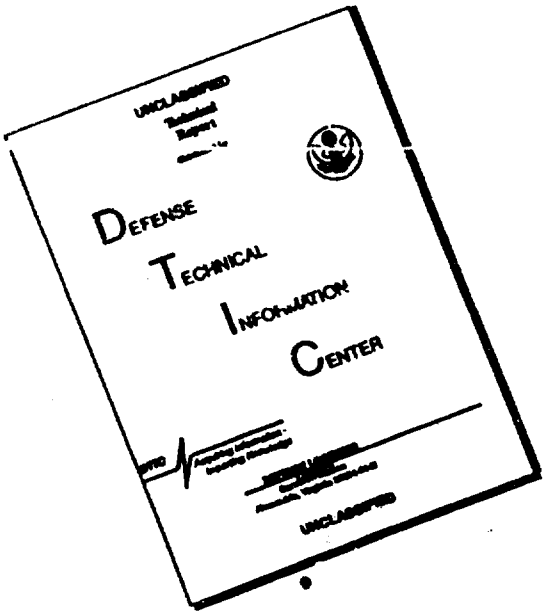
91-10249

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. Kurt Niedenzu	22b. TELEPHONE (Include Area Code): (606) 257-7073 / 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE: UNCLASSIFIED

91 [illegible] 044

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

OFFICE OF NAVAL RESEARCH

Contract No. N00014-83-K-0611

R & T Code 4135003-1
Replaces old
Task No. NR 053-842

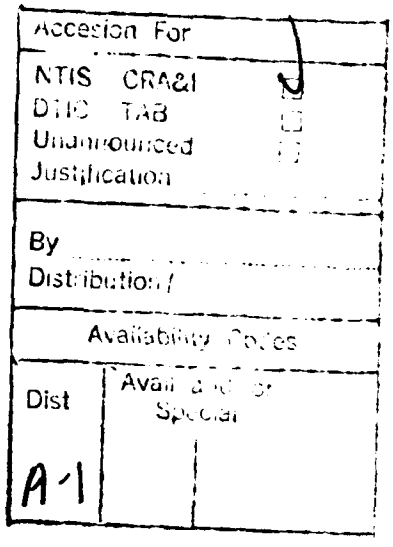
TECHNICAL REPORT NO. UK/DC/TR-37

Studies on 1–Trimethylsilyl–2,4,6–triethylborazine and Related Species

by

K. Niedenzu, J. Serwatowska, and J. Serwatowski

Prepared for publication



University of Kentucky
Department of Chemistry
Lexington, KY 40506

September 1991

Studies on 1-Trimethylsilyl-2,4,6-triethylborazine and Related Species

Kurt Niedenzu,* Joanne Serwatowska, and Janusz Serwatowski

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, USA

The unsymmetrically substituted borazine $(C_6H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has been obtained from the reaction of $C_6H_5BCl_2$ with $HN[Si(CH_3)_3]_2$, and an improved synthesis of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has been developed. The reaction of the latter with an excess of BCl_3 proceeds with the ultimate formation of $Cl_3B_3N_3H_2[Si(CH_3)_3]$, whereas the reaction with one molar equivalent of BBr_3 leads to the formation of $Br(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$, but which is contaminated by substantial amounts of $Br(C_2H_5)_2B_3N_3H_3$ besides a diborazinyl and additional products. $C_6H_5BBr_2$ reacts with $N[Si(CH_3)_3]_3$ to give the aminoborane $[(CH_3)_3Si]_2NBBr(C_6H_5)$, but $C_6H_5BCl_2$ does not undergo a reaction under analogous conditions.

Introduction

The cleavage of a Si–N bond by reaction with a haloborane has been widely utilized as a convenient method for the formation of B–N bonds, i. e., equations 1 and 2 [1].

$$>B–X + HN[Si(CH_3)_3]_2 \longrightarrow >B–NH[Si(CH_3)_3] + (CH_3)_3SiX \quad (1)$$

$$>B–X + 2\ HN[Si(CH_3)_3]_2 \longrightarrow >B–NH–B< + 2\ (CH_3)_3SiX \quad (2)$$

However, in a study of the reaction between BCl_3 and various silylamines it has been found that, besides the "normal" Si–N bond cleavage with the elimination of $(CH_3)_3SiCl$, N–C (as well as Si–H) cleavage may also occur [2]. Indeed, the Si–N bond cleavage on reaction with haloboranes is not as selective as is generally assumed, and another noteworthy example for an unusual cleavage of a silylamine on reaction with a haloborane, i. e., N–H cleavage, was observed recently: In the synthesis of the borazine $(-BC_2H_5–NH–)_3$ by the reaction of $HN[Si(CH_3)_3]_2$ with $C_2H_5BCl_2$ [3], the unsymmetrically substituted species $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ could be isolated as a substantial byproduct [4]. Yields of this latter borazine were found to be irregular and ranged between 10 and 40 %. Variations of the experimental conditions did not establish a clear trend, although relatively large–scale syntheses (1 molar scale and above) and working at about 0°C (rather than at lower temperatures) tended to give somewhat higher yields of the unsymmetrical species [4].

Results and Discussion

The reaction of $C_6H_5BCl_2$ with $HN[Si(CH_3)_3]_2$ following the previously outlined procedure [3] gave the expected borazine $(-BC_6H_5–NH–)_3$ in excellent yield and there was no indication whatever that a N–silyated borazine was formed as a byproduct. The same held true when benzene was used as a diluent, but replacing benzene by toluene as reaction medium and working at slightly higher temperatures (i. e., near 0°C), yielded a mixture of approximately equimolar quantities of the two borazines $(-BC_6H_5–NH–)_3$ and $(C_6H_5)_3B_3N_3H_2[Si(CH_3)_3]$, which are formed by the two competing reactions according to equations 3 and 4, respectively.

$$3\,RBCl_2 + 3\,HN[Si(CH_3)_3]_2 \longrightarrow 6\,(CH_3)_3SiCl + (-BR-NH-)_3 \quad (3)$$

$$3\,RBCl_2 + 3\,HN[Si(CH_3)_3]_2 \longrightarrow 5\,(CH_3)_3SiCl + HCl + R_3B_3N_3H_2[Si(CH_3)_3] \quad (4)$$

Based on this experience, an improved preparation of the corresponding $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ by the interaction of $C_2H_5BCl_2$ with $HN[Si(CH_3)_3]_2$ could be developed. However, it should be noted that with increasing formation of the unsymmetrically substituted borazine, there is an overall decrease in the yield of isolable boron compounds.

The chemistry of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has not yet been explored in detail, although the compound has been utilized for the synthesis of some polyborazinyls via condensation reactions with B–halogenated borazines [5]. These latter reactions generally proceed with the elimination of $(CH_3)_3SiX$ (X = Cl, Br) and formation of a B–N linkage according to equation 5.

$$(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3] + XR_2B_3N_3R'_3 \longrightarrow (CH_3)_3SiX + (C_2H_5)_3B_3N_3H_2[R_2B_3N_3R'_3] \quad (5)$$

The interaction of BX_3 (X = Cl, Br) with 2,4,6–triorganylborazines, (–BR–NR′–), has recently been found to proceed with successive displacement of the B–bonded organic substituents and the exclusive formation of RBX_2 and B–halogenated borazines. The process has been used for the preparation of various B–monohalo– and B,B′–dihaloborazines as is illustrated in equations 6 and 7 (X = Cl, Br) [4,6].

$$(-BR-NR'-)_3 + BX_3 \longrightarrow XR_2B_3N_3R'_3 + RBX_2 \quad (6)$$

$$(-BR-NR'-)_3 + 2\,BX_2 \longrightarrow X_2RB_3N_3R'_3 + 2\,RBX_2 \quad (7)$$

In view of these preceding results, it seemed of interest to study the reaction of a borazine such as $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with a boron trihalide, where alkyl/halogen exchange could potentially compete with a Si–N bond cleavage.

Even when equimolar amounts of reagents were employed, boron trichloride reacted readily with $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ to give a mixture of the borazines $Cl(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$, $Cl_2(C_2H_5)B_3N_3H_2[Si(CH_3)_3]$, and $Cl_3B_3N_3H_2[Si(CH_3)_2]$, as is based on mass spectral data of the reaction

product. The latter compound became the major product after prolonged reaction times in boiling heptane and in the presence of a considerable excess of BCl_3. No cleavage of the N–Si bond was observed under these circumstance. Hence, in this case the alkyl/halogen exchange is clearly the dominant (and probably the sole) process.

The interaction of BBr_3 with $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ proceeded more complicated than in the case of BCl_3. When the reaction was performed at room temperature or below in 1:1 molar ratio, mass spectroscopic and NMR data indicated that $Br(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$ was indeed a major product, but which was always contaminated with the previously [4] characterized $Br(C_2H_5)_2B_3N_3H_3$. In addition, the diborazinyl $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$ [5] could be identified (by mass spectroscopy) as one of the products, and there were also indications for the formation of the diborazinyl $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_2\{Si(CH_3)_3\}]$. Furthermore, the amount of the $Br(C_2H_5)_2B_3N_3H_3$ increased with the reaction time, and the formation of $(CH_3)_3SiBr$ clearly illustrated that alkyl/halogen exchange was not the sole process.

The formation of $Br(C_2H_5)_2B_3N_3H_3$ in this latter reaction can be interpreted by the initial formation of $Br(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$ which, once formed, can condense with the formation of the diborazinyls $Br(C_2H_5)_2B_3N_3H_2[(C_2H_5)_2B_3N_3H_2\{Si(CH_3)_3\}]$ and $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$. Indeed, it has been shown earlier [5], that the formation of diborazinyls on interaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with a B–monohaloborazine is always accompanied by additional condensation processes whereby, besides the desired species, another (N)H–borazine (here: $Br(C_2H_5)_2B_3N_3H_3$) as well as polyborazinyls are formed. Thus it is not surprising that the reaction between $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ and BBr_3 could not be developed as a useful preparative procedure, as was possible in the case of the corresponding reaction of BCl_3.

The reaction of $Cl_3B_3N_3H_2[Si(CH_3)_3]$ with $Br(C_2H_5)_2B_3N_3H_3$ (1:1 molar ratio, 1 hour at 150°C) also proceeded in nonselective fashion. Instead of the expected diborazinyl $Cl_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$, an inseparable mixture of products was obtained, consisting primarily (as is based on mass spectroscopic data) of the borazines $Cl_3B_3N_3H_3$, $Cl_2(C_2H_5)B_3N_3H_3$, and $Cl(C_2H_5)_2B_3N_3H_3$.

These observations tend to support the previous [5] assumption that in such condensation reactions involving borazines and proceeding with the elimination of $(CH_3)_3SiX$, initially present B_3N_3 rings are opened and substantial redistribution reactions occur. Although new borazines result as products, their specific nature cannot readily predicted and the process generally also involves the formation of polyborazines.

The reaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with $C_6H_5BCl_2$ (2:1 molar ratio, 3 hours heating at 160°C) was also investigated. Mass spectroscopic and NMR data indicated the presence of the borazines $(-BC_2H_5-NH-)_3$ and $(C_6H_5)(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$ in the crude product mixture, but again no individual pure compound could be isolated, and there was no evidence for the formation of the expected di(borazin-1-yl)borane $C_6H_5B[H_2N_3B_3(C_2H_5)_3]_2$.

In a related study it was observed that $C_6H_5BCl_2$ did not react with $N[Si(CH_3)_3]_3$ at room temperature or below, whereas under analogous conditions the reaction of $C_6H_5BBr_2$ proceeded readily with the formation of the aminoborane $[(CH_3)_3Si]_2N-BBr(C_6H_5)$. The latter compound is thermally quite stable and can be distilled under reduced pressure without decomposition. This result further documents noteworthy differences in the chemical behavior of B-Br versus B-Cl species.

Experimental Section

Reactions and transfers were carried out in an inert atmosphere. Melting points (uncorrected) were determined in sealed capillaries on a Mel-Temp block. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received.

NMR spectra were recorded on solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 or XL-200 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR). Abbreviations are as follows: s = singlet, d = doublet, t = triplet,

q = quartet, p = quintuplet, m = unresolved multiplet; an asterisk denotes a broad signal. Coupling constants *J* are given in Hz. EI mass spectral data were obtained on a VD ZAB–2F instrument under standard operating condition; data are given in *m/z* = 30 for 5 % or greater relative abundances (in parentheses) only.

1–Trimethylsilyl–2,4,6–triphenylborazine, $(C_6H_5)_3B_3N_3H_2[Si(CH_3)_3]$

To a solution of 27.6 g (174 mmol) of $C_6H_5BCl_2$ in 50 mL of toluene, kept at 0°C, was added dropwise 30.0 g (191 mmol) of $HN(Si(CH_3)_3]_2$ over a period of 30 minutes. The cooling bath was removed and the stirred mixture autogeneously warmed to about 35°C and was subsequently heated for two hours in an oil bath of 120°C. After cooling to room temperature, volatiles (toluene and $(CH_3)_3SiCl$) were removed under reduced pressure, and the solid residue was stirred overnight with 120 mL of hexane. Insolubles were collected, washed with two 40–mL portions of hexane, and dried under vacuum to give 6.4 g of pure $(–BC_6H_5–NH–)_3$ [1]. The clear filtrate was concentrated to about 1/4 of the original volume and, on prolonged standing at room temperature, a crystalline material slowly precipitated, which was collected and dried to give the title compound, m.p. 78–80°C. Essentially complete evaporation of the hexane from the filtrate gave additional product (but which contained traces of $(–BC_6H_5–NH–)_3$) for an overall yield of 11.1 g.

Analysis for $C_{21}H_{26}B_3N_3Si$ (380.98)

Found C 66.43 H 6.88 B 8.62 N 10.99 Si 7.27,

Calcd C 66.21 H 6.88 B 8.51 N 11.03 Si 7.37.

NMR data: δ^1H = 7.66 (6 H, m), 7.46 (9 H, m), 5.67* (2 H, s), –0.21 (9 H, s); $\delta^{11}B$ 37.6 (2 B, s, $h_{1/2}$ = 800 Hz), 33.0 (1 B, s, $h_{1/2}$ = 700 Hz). – The 10–eV mass spectrum exhibited no parent ion, but the base peak was that of [M minus CH_3]$^+$ with *m/z* = 368 (6), 367 (30), 366 (100), 365 (72), 364 (18) (calcd *m/z* = 368 (7), 367 (27), 366 (100), 365 (65), 364 (14)).

1–Trimethylsilyl–2,4,6–triethylborazine, $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$

A 500–mL flask was charged with 81 g (0.73 mol) of $C_2H_5BCl_2$ and cooled to –10°C. While

maintaining a temperature between −10 to 0°C, 130 g (0.80 mol) of $HN[Si(CH_3)_3]_2$ was added dropwise with stirring. The resultant slurry was stirred until it reached ambient temperature and a small amount of insoluble material was filtered off. $(CH_3)_3SiCl$ (113 g) was distilled from the clear filtrate through a 30–cm silver–mantle column under atmospheric pressure. The residue was distilled under reduced pressure to give about 5 g of $(-BC_2H_5-NH-)_3$, b.p. 56–57°C(2 Torr) [3], and 25 g of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$, b.p. 65–68°C(2 Torr) [4]. As is based on NMR and mass spectroscopic data, a higher boiling residue (b.p. 100–105°C(1 Torr), ca. 10 g) contained the diborazinyl $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$ [5] and some other unidentified (high–molecular weight) products, but the latter mixture could not be separated.

1–Trimethylsilyl–2,4,6–trichloroborazine, $Cl_3B_3N_3H_2[Si(CH_3)_3]$

A mixture of 1.42 g (6.0 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ and 60 mL of a 1 M solution of BCl_3 in heptane was heated to reflux for five hours. Volatile materials were removed under reduced pressure and the oily residue was distilled under vacuum to give 1.25 g (81 %) of $Cl_3B_3N_3H_2[Si(CH_3)_3]$, b.p. 53°C(1 Torr), m.p. 21–23°C.

Analysis for $C_3H_{11}B_3Cl_3N_3Si$ (256.02)

Found C 14.40 H 4.49 B 12.41 Cl 41.67 N 16.30 Si 10.82,

Calcd C 14.07 H 4.33 B 12.67 Cl 41.54 N 16.41 Si 10.98.

NMR data: $\delta^1H = 0.44$ (s); $\delta^{11}B = 31.8$ (s, 2B, $h_{1/2} = 160$ Hz), 29.5 (s, 1 B, $h_{1/2} = 140$ Hz); $\delta^{13}C = 3.9$. – Mass spectrum (8 eV): *m/z* = 245 (7), 244 (30), 243 (27), 242 (97), 241 (75), 240 (100), 239 (68), 238 (18); calcd for [M minus 15]$^+$: *m/z* = 245 (5), 244 (30), 243 (27), 242 (90), 241 (68), 240 (100), 239 (62), 238 (15).

Reaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with BBr_3

To a solution of 3.05 g (12.9 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ in 40 mL of hexane was added 14.8 mL of a 0.87 M solution of BBr_3 (12.9 mmol) in hexane at −30°C. A precipitate formed immediately which slowly dissolved when the mixture as warmed to room temperature with stirring (ca.

one hour). Volatile materials were evaporated under reduced pressure to leave 2.6 g of oily residue. The volatile material contained $(CH_3)_3SiBr$ (δ^1H = 0.59), $C_2H_5BBr_2$ ($\delta^{11}B$ = 65.1), and some $Br(C_2H_5)_2B_3N_3H_3$ ($\delta^{11}B$ = 36.5 + 27.7 [4]). The residue was distilled under reduced pressure to yield about 20 % of a forerun, b.p. 40–45°C(1 Torr), which was essentially pure $Br(C_2H_5)_2B_3N_3H_3$; ca. 60 % of a main fraction, b.p. 66–73°C(1 Torr), consisting of a mixture of some $Br(C_2H_5)_2B_3N_3H_3$ and mostly the desired $Br(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$ ($\delta^{11}B$ = 39.1 (2 B) + 27.7 (1B); 13–eV mass spectral data: *m/z* = 290 (23), 289 (19), 287 (34), 286 (19), 285 (14), 275 (11), 274 (98), 273 (85), 272 (100), 271 (51). 270 (17); calcd for M^+ (= $C_7H_{21}B_3BrN_3Si$): *m/z* = 290 (13), 289 (87), 288 (71), 287 (100), 286 (60), 285 (14); calcd for [M minus CH_3]$^+$: *m/z* = 275 (13), 274 (87), 273 (71), 272 (100), 271 (62), 270 (14)); and ca. 20 % of residue. The mass spectrum of the latter exhibited ion clusters as high as *m/z* = 350, with major clusters at *m/z* = 186 (containing Br) and *m/z* = 165 (Br–free). The main fraction could not be further separated and some $Br(C_2H_5)_2B_3N_3H_3$ was always contained in the $Br(C_2H_5)_2B_3N_3H_2[Si(CH_3)_3]$. As is based on mass spectral data, the residue contained the diborazinyl $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$ [5] as well as a trimethylsilylated derivative thereof.

Reaction of $Cl_3B_3N_3H_3[Si(CH_3)_3]$ with $Br(C_2H_5)_2B_3N_3H_3$

Equimolar quantities of $Cl_3B_3N_3H_2[Si(CH_3)_3]$ (1.14 g = 4.45 mmol) and $Br(C_2H_5)_2B_3N_3H_3$ (0.96 g = 4.45 mmol) were heated in an oil bath of 150°C for one hour. Volatile materials were removed at 40°C and under reduced pressure to leave a gummy residue (1.2 g), from which ca. 0.5 g of distilled at 30–36°C(1 Torr), leaving a glassy residue. The distillate was identified (by mass spectral and ^{11}B NMR data) as a mixture of the chloroborazines $Cl_3B_3N_3H_3$, $Cl_2(C_2H_5)_2B_3N_3H_3$, and $Cl(C_2H_5)_2B_3N_3H_3$. The residue showed a broad and unresolved ^{11}B NMR signal with maxima at 29.8 (highest intensity), 31.8, 36.8, and ca. 40.1 ppm. The proton NMR spectrum showed ethyl groups as well as (N)H and (Si)CH_3 signals. The mass spectrum exhibited prominent clusters as high as *m/z* = 657, 530, and 479, but could not be interpreted. No evidence for the desired diborazinyl $Cl_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$ was observed.

The preceding observations suggest that, initially, the desired diborazinyl $Cl_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$ may be formed (as evidenced by the formation of $(CH_3)_3SiBr$), which then decomposes with the formation of the cited chloroborazines and the polymeric residue.

Bis(trimethylsilyl)amino–phenylbromoborane, $[(CH_2)_3Si]_2NBBr(C_6H_5)$

To a solution of 3.17 g (13.6 mmol) of $N(Si(CH_3)_3]_3$ in 20 mL of dichloromethane was added a solution of 1.68 g (6.78 mmol) of $C_6H_5BBr_2$ in 10 mL of dichloromethane. The mixture was stirred for two hours at room temperature and volatile material was evaporated under reduced pressure. The oily residue was distilled under vacuum to give a forerun of unreacted $N[Si(CH_3)_3]_3$ and 1.85 g (83 %) of $[(CH_3)_3Si]_2NBBr(C_6H_5)$, b.p. 70°C(1 Torr).

Analysis for $C_{12}H_{23}BBrNSi_2$ (328.21)

Found C 44.07 H 7.18 B 3.54 Br 24.33 N 4.14 Si 17.06,

Calcd C 43.92 H 7.06 B 3.29 Br 24.34 N 4.27 Si 17.12.

NMR data: δ^1H = 7.70 (2 H, d, J = 6.3), 7.38 (3 H, m), 0.24 (18 H, s); $\delta^{11}B$ = 47.4 (s, $h_{1/2}$ = 330 Ha). – The mass spectrum exhibited a very weak parent ion cluster, a strong peak for [M minus CH_3]$^+$ in the m/z = 313 region, and the base peak was observed at m/z = 248.

This work was supported by the U.S. Office of Naval Research (K. N.).

---

[1] *Gmelin Handbuch der Anorganischen Chemie*; Springer–Verlag: West Berlin, 1975. Vol. 22, Supplement Boron Compounds 4.

[2] R. H. Neilson, Inorg. Chem. **19**, 755–758 (1980).

[3] J. Bielawski, M. K. Das, E. Hanecker, K. Niedenzu, and H. Nöth, Inorg. Chem. **25**, 4623–4628 (1986).

[4] J. Bai, K. Niedenzu, J. Serwatowska, and J. Serwatowski, Inorg. Chem. **30**, 0000–0000 (1991).

[5] J. Bai, K. Niedenzu, J. Serwatowska, and J. Serwatowski, Inorg. Chem., in hand of editor.

[6] J. Bai and K. Niedenzu, Inorg. Chem. **30**, 2955–2956 (1991).

DL/1113/89/1

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	No. Copies
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 high quality
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1

ABSTRACT DISTRIBUTION LIST

Professor O. T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Alan Berry
Chemistry Division, Code 6120
Naval Research Laboratory
4555 Overlook Ave., SW
Washington, DC 20375-5000

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907

Professor Steven L. Buchwald
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Professor N. John Cooper
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Professor Carlo Floriani
Institut de Chimie
Minerale et Analytique
Universite de Lausanne
Place du Chateau 3
CH-1005 LAUSANNE, SWITZERLAND

Professor Mark J. Hampden-Smith
Department of Chemistry
University of New Mexico
Albuquerque, MN 87131

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. Kelvin Higa
Chemistry Division
Research Department
Naval Weapons Center
China Lake, CA 93555

Professor Lisa McElwee-White
Department of Chemistry
The Leland Stanford Junior University
Stanford, CA 94305