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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Symmetrically substituted B-triorganylborazines, (RBNR) ₃ , react with an equimolar quantity of boron trihalide, BX ₃ (X = Cl, Br), to form B-monohaloborazines, XR ₂ B ₂ N ₃ R ₃ , besides RBX ₂ , and with 2 molar equiv of BX ₃ to form the B-dihaloborazines, X ₂ RB ₃ N ₃ R ₃ . The compounds are obtained in good yield and purity, and are easily converted to other unsymmetrically B-substituted borazines. The borazines X(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ (X = SCH ₃ , NH ₂ , C ₄ H ₉ , N[Si(CH ₃) ₂]), X(C ₂ H ₅) ₂ B ₃ N ₃ H ₃ (X = Br, SCH ₃), Cl(C ₂ H ₅) ₂ B ₃ N ₃ (CH ₃) ₃ , X ₂ (C ₂ H ₅) ₂ B ₃ N ₃ H ₃ (X = Br, SCH ₃), Cl(C ₆ H ₅) ₂ B ₃ N ₃ H ₃ , and Cl ₂ (C ₂ H ₅)B ₃ N ₃ (CH ₃) ₃ have been prepared and characterized. The compound (H ₂ N)(C ₂ H ₅) ₂ B ₃ N ₃ H ₃ could not be obtained in pure state; rather, it slowly condenses (even at room temperature) with the formation of the bis(borazin-2-yl)amine HN[(C ₂ H ₅) ₂ B ₃ N ₃ H ₃] ₂ and the tris(borazin-2-yl)amine N[(C ₂ H ₅) ₂ B ₃ N ₃ H ₃] ₃ . The borazine (H ₂ N)(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ condenses at temperatures from 250-270 °C to give HN[(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃] ₂ . Reaction of this bis(borazin-2-yl)amine with LiC ₄ H ₉ yields (C ₄ H ₉)(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ and (NHLi)(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ ; the latter then reacts with Cl(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ to regenerate HN[(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃] ₂ . The unsymmetrically N-substituted borazine (C ₂ H ₅) ₃ B ₃ N ₃ H ₂ [Si(CH ₃) ₃] has been isolated and characterized.			
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Preparation of Unsymmetrically B-Substituted Borazines and
Characterization of Tris(4,6-diethylborazin-2-yl)amine

by

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**Preparation of Unsymmetrically B-Substituted Borazines and
Characterization of Tris(4,6-diethylborazin-2-yl)amine**

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

Received

Symmetrically substituted B-triorganylborazines, $(\text{RBNR}')_3$, react with an equimolar quantity of boron trihalide, BX_3 ($\text{X} = \text{Cl}, \text{Br}$), to form B-monohaloborazines, $\text{XR}_2\text{B}_2\text{N}_3\text{R}'_3$, besides RBX_2 , and with 2 molar equiv of BX_3 to form the B-dihaloborazines, $\text{X}_2\text{RB}_3\text{N}_3\text{R}'_3$. The compounds are obtained in good yield and purity, and are easily converted to other unsymmetrically B-substituted borazines. The borazines $\text{X}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ ($\text{X} = \text{SCH}_3, \text{NH}_2, \text{C}_4\text{H}_9, \text{N}[\text{Si}(\text{CH}_3)_2]$), $\text{X}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ ($\text{X} = \text{Br}, \text{SCH}_3$), $\text{Cl}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$, $\text{X}_2(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ ($\text{X} = \text{Br}, \text{SCH}_3$), $\text{Cl}(\text{C}_6\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$, and $\text{Cl}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3(\text{CH}_3)_3$ have been prepared and characterized. The compound $(\text{H}_2\text{N})(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ could not be obtained in pure state; rather, it slowly condenses (even at room temperature) with the formation of the bis(borazin-2-yl)amine $\text{HN}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_2$ and the tris(borazin-2-yl)amine $\text{N}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_3$. The borazine $(\text{H}_2\text{N})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ condenses at temperatures from 250–270 °C to give $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$. Reaction of this bis(borazin-2-yl)amine with LiC_4H_9 yields $(\text{C}_4\text{H}_9)(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ and $(\text{NHLi})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$; the latter then reacts with $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ to regenerate $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$. The unsymmetrically N-substituted borazine $(\text{C}_2\text{H}_5)_3\text{B}_3\text{N}_3\text{H}_2[\text{Si}(\text{CH}_3)_3]$ has been isolated and characterized.

Introduction

Borazine is the foremost example of an inorganic compound that can be closely compared to an organic species, i.e., benzene. Hence, studies on this six-membered B_3N_3 heterocyclic system have been popular and literally hundreds of borazine derivatives are known. However, most of them are symmetrically substituted species of the type $(RBNR')_3$. Relatively few unsymmetrically substituted derivatives have been described and their chemistry has been investigated only sparingly.¹

Within the context of preparative studies on discrete polycyclic boron-nitrogen systems as potential precursors for macromolecular materials, the synthesis of the tris(borazin-2-yl)amine framework seemed to be an interesting point of origin. Detailed studies on such species require convenient access to unsymmetrically B-substituted borazines of the types $XR_2B_3N_3R'_3$ and $X_2RB_3N_3R'_3$ (and where X is a reactive site) in high purity. The present report describes the preparation and characterization of various such unsymmetrically B-substituted borazines as well as attempts to synthesize the tris(borazin-2-yl)amine skeleton.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for 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 downfield 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); s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. Field desorption (FD) mass spectra were recorded on a Finnigan MAT 250 instrument, and field ionization (FI) mass spectra were obtained on a Varian MAT-CH5 instrument, courtesy of Professor A. Meller, University of Göttingen, Germany. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative

abundances (in parentheses) only. Infrared spectra (frequencies in cm^{-1}) were recorded on a BOMEM Model DA3 spectrometer under standard operating conditions.

Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. All preparations were performed in an anhydrous atmosphere under argon cover; solvents were dried by standard procedures.

$\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$.² NMR data: $\delta(^1\text{H})$ 3.00 (2 H, s), 2.90 (1 H, s), 0.52 (2 H, s); $\delta(^{11}\text{B})$ 37.2 (2 B, s, $h_{1/2} = 175$ Hz), 30.7 (1 B, s, $h_{1/2} = 125$ Hz); $\delta(^{13}\text{C})$ 34.6, 34.5, -0.6^* . Solution in CCl_4 :³ $\delta(^1\text{H})$ 2.99 (2 H, s), 2.89 (1 H, s), 0.51 (2 H, s). EI mass spectrum: m/z 187 (14), 186 (33), 185 (62), 184 (100), 183 (28), 182 (15), 172 (18), 171 (16), 170 (62), 169 (44), 168 (14), 167 (7), 166 (12), 165 (8), 152 (8), 129 (22), 128 (11), 115 (10), 102 (11), 101 (5), 95 (9), 88 (6), 86 (16), 85 (10), 79 (6), 68 (7), 66 (16), 65 (11), 54 (18), 53 (6), 52 (15), 51 (12), 44 (15), 43 (24), 42 (8), 41 (16), 40 (9), 39 (6), 38 (7), 32 (19).

$(\text{CH}_3\text{S})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (2d). A stirred mixture of 15.2 g (49 mmol) of $\text{Pb}(\text{SCH}_3)_2$, 11.6 g (62 mmol) of (crude) $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$, and 150 mL of hexane was heated to reflux for 12 h. The mixture was filtered and the solvent was evaporated from the clear filtrate under reduced pressure to leave an oily residue. Some volatile impurities were sublimed off at 40°C (3 Torr) and the remaining product was distilled under vacuum to give 7.0 g (57%) of the compound, bp $98\text{--}102^\circ\text{C}$ (1 Torr). Anal. Calcd for $\text{C}_6\text{H}_{18}\text{B}_3\text{N}_3\text{S}$ ($M_r = 196.73$): C, 36.63; H, 9.22; B, 16.49; N, 21.36; S, 16.30. Found: C, 36.81; H, 9.28; B, 16.31; N, 21.33; S, 16.28.

NMR data: $\delta(^1\text{H})$ 2.98 (2 H, s), 2.84 (1 H, s), 2.14 (1 H, s), 0.46 (2 H, s); $\delta(^{11}\text{B})$ 35.6 (s, $h_{1/2} = 250$ Hz); $\delta(^{13}\text{C})$ 35.5, 34.2, 11.5, -0.8^* . EI mass spectrum (13 eV): m/z 199 (7), 198 (15), 197 (100), 196 (96), 195 (18), 185 (11), 184 (9), 183 (9), 182 (18), 181 (15), 180 (9), 167 (7), 166 (6), 150 (44), 149 (18), 148 (7), 48 (44).

$(\text{H}_2\text{N})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (2e). Dry ether (15 mL) was mixed with ca. 10 mL of anhydrous liquid NH_3 at -50°C . A solution of 2.93 g (14.9 mmol) of $(\text{CH}_3\text{S})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_2$ in 10 mL of ether was added and the stirred reaction mixture was slowly warmed to room temperature. It was heated to reflux (30 min) and solvent was evaporated to leave a colorless residue. The latter was purified by sublimation under vacuum to give 2.1 g (84%) of product, mp $84\text{--}85^\circ\text{C}$ (lit.:² mp 87°C).

NMR data: $\delta(^1\text{H})$ 2.80 (3 H, s), 2.72 (6 H, s), 2.30* (2 H), 0.42 (6 H, s); $\delta(^{11}\text{B})$ 36.1 (2 B, s, $h_{1/2}$ = 180 Hz), 25.9 (1 B, s, $h_{1/2}$ = 140 Hz); $\delta(^{13}\text{C})$ 34.3, 31.6, -0.4° . EI mass spectrum (8 eV): m/z 167 (16), 166 (100), 165 (76), 165 (25), 163 (5).

HN[(CH₃)₂B₃N₃(CH₃)₃]₂ (1a). Method A: (H₂N)(CH₃)₂B₃N₃(CH₃)₃ (7.0 g, 42 mmol) was slowly heated with stirring. Evolution of NH₃ began at a temperature near 150 °C and the material was ultimately heated to 280 °C for 4 h. It was cooled to room temperature and then recrystallized from hexane to give 4.5 g (68%) of pure, hydrolytically very sensitive product, mp 139–142 °C; bp 358–360 °C, 240 °C (2 Torr). Anal. Calcd for C₁₀H₃₁B₆N₇ (M_r = 314.27): C, 38.22; H, 9.94; B, 20.64; N, 31.20. Found: C, 38.17; H, 9.71; B, 20.89; N, 31.34.

NMR data: $\delta(^1\text{H})$ 2.86 (6 H, s), 2.75 (12 H, s), 2.40 (1 H, s), 0.47 (12 H, s); $\delta(^{11}\text{B})$ 37.0 (2 B, s, $h_{1/2}$ = 340 Hz), 28.3 (1 B, s, $h_{1/2}$ = 270 Hz); $\delta(^{13}\text{C})$ 34.7, 33.4, -0.2° . FD mass spectrum: m/z 317 (8), 316 (84), 315 (100), 314 (62), 313 (14); FI mass spectrum: m/z 316 (12), 315 (78), 314 (100), 313 (61). Major fragments in the EI mass spectrum appeared at m/z 284 and 269. The IR spectrum exhibited a strong N–H stretching band at 3409 cm⁻¹. Lit.:⁴ mp 142–145 °C (material obtained by Method B, below); NMR data: $\delta(^1\text{H})$ 2.87, 2.78, 0.5; $\delta(^{11}\text{B})$ 37.2, 30.0.

Method B: A solution of 1.8 g (11 mmol) of [(CH₃)₃Si]₂NH in 15 mL of ether was added to a solution of 4.0 g (22 mmol) of Cl(CH₃)₂B₃N₃(CH₃)₃ in 40 mL of ether. The mixture was stirred at ambient temperature for 12 h and volatiles were removed under reduced pressure to leave a colorless solid material. The latter was recrystallized from hexane to give 2.8 g (82%) of 1a, mp 140–142 °C, identical (NMR data) to the material obtained by the preceding procedure.

O[(CH₃)₂B₃N₃(CH₃)₃]₂.⁵ NMR data: $\delta(^1\text{H})$ 2.87 (1 H, s), 2.72 (2 H, s), 0.47 (2 H, s); $\delta(^{11}\text{B})$ 37.3 (2 B, s, $h_{1/2}$ = 340 Hz), 23.6 (1 B, s, $h_{1/2}$ = 260 Hz); $\delta(^{13}\text{C})$ 34.3, 31.2, -0.7° ; (solution in C₆D₆):⁴ $\delta(^1\text{H})$ 2.79, 2.77, 0.49; $\delta(^{11}\text{B})$ 37, 24; $\delta(^{13}\text{C})$ 34.45, 31.55, -0.25 . EI mass spectrum (13 eV): m/z 316 (30), 315 (45), 314 (31), 313 (13), 301 (19), 300 (26), 299 (16), 284 (5), 140 (5), 139 (5), 126 (14), 125 (9), 113 (7), 112 (8), 111 (100), 110 (80), 109 (19), 31 (25), 30 (32).

The Reaction of $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$ (1a) with LiC_4H_9 and $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$. A mixture of 1.01 g (3.5 mmol) of $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$ (1a) and 10 mL of ether was cooled to $-78\text{ }^\circ\text{C}$ and 2.2 mL of a 1.6 M solution of $n\text{-C}_4\text{H}_9\text{Li}$ in hexane was added slowly with stirring. The mixture was stirred at $-50\text{ }^\circ\text{C}$ for 4 h to give a clear solution. A solution of 0.65 g (3.5 mmol) of $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ in 10 mL of ether was added and the mixture was stirred for 4 h at $-50\text{ }^\circ\text{C}$ and then for 10 h at ambient temperature. LiCl was filtered off and solvent was evaporated from the clear filtrate to leave a mixture of $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$ (1a) and $(\text{C}_4\text{H}_9)(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (2f).

The latter compound (2f) was purified by distillation to give 0.59 g (82%) of product, bp $75\text{--}78\text{ }^\circ\text{C}$ (1 Torr). NMR data: $\delta(^1\text{H})$ 2.89 (6 H, s), 2.86 (3 H, s), 1.27–1.41 (4 H, m), 1.05 (2 H, m), 0.91 (3 H, t, $J = 7$), 0.47 (6 H, s); $\delta(^{11}\text{B})$ 36.2 (s, $h_{1/2} = 230\text{ Hz}$); $\delta(^{13}\text{C})$ 34.3, 34.0, 26.6, 26.2, 15.3*, 13.7, -0.5^* . EI mass spectrum (13 eV): m/z 208 (10), 207 (68), 206 (58), 205 (15), 192 (5), 178 (5), 166 (16), 165 (91), 164 (100), 163 (30), 162 (5), 150 (41), 149 (26), 148 (7).

$[\{(\text{CH}_3)_3\text{Si}\}_2\text{N}](\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (2g). A mixture of 1.81 g (9.89 mmol) of $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ and 15 mL of ether was cooled to $-40\text{ }^\circ\text{C}$ and a solution of 1.82 g (9.80 mmol) of $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ in 15 mL of ether was added dropwise with stirring. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 2 h and for 12 h at ambient temperature. The precipitate (NaCl) was filtered off and solvent was removed under reduced pressure from the clear filtrate. The liquid residue was distilled under vacuum to give 1.3 g (43%) of product, bp $113\text{ }^\circ\text{C}$ (1 Torr).

NMR data: $\delta(^1\text{H})$ 2.85 (2 H, s), 2.84 (1 H, s), 0.44 (2 H, s), 0.07 (6 H, s); $\delta(^{11}\text{B})$ 37.8 (2 B, s, $h_{1/2} = 310\text{ Hz}$), 30.6 (1 B, s, $h_{1/2} = 300\text{ Hz}$); $\delta(^{13}\text{C})$ 34.5, 34.3, 2.5, -0.2^* . EI mass spectrum (13 eV): m/z 311 (6), 310 (19), 309 (14), 308 (5), 297 (10), 296 (21), 295 (100), 294 (62), 293 (17), 239 (7), 238 (5), 224 (5).

$\text{Cl}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (2h). A solution of 15.6 mmol of BCl_3 in heptane (15.6 mL of a 1 M solution) was added to 3.22 g (15.6 mmol) of cold (ice bath) $(\text{C}_2\text{H}_5\text{BNCH}_3)_3$. The stirred mixture was warmed to ambient temperature, and after 5 h volatile material was removed under reduced pressure. The residue was distilled under vacuum to give 2.9 g (89%) of product, bp $84\text{--}86\text{ }^\circ\text{C}$ (1 Torr). Anal. Calcd for

$C_7H_{19}B_3ClN_3$ ($M_r = 213.14$): C, 39.45; H, 8.98; B, 15.22; Cl, 16.63; N, 19.72. Found: C, 39.40; H, 9.02; B, 15.09; Cl, 16.61; N, 19.76.

NMR data: $\delta(^1H)$ 3.01 (6 H, s), 2.96 (3 H, s), 1.1–0.9 (10 H, m); $\delta(^{11}B)$ 37.3 (2 B, s, $h_{1/2} = 250$ Hz), 31.1 (1 B, s, $h_{1/2} = 170$ Hz); $\delta(^{13}C)$ 33.9, 33.1, 7.5, 6.7*. EI spectrum (9 eV): m/z 215 (35), 214 (35), 213 (100), 212 (74), 211 (21).

$Cl(C_6H_5)_2B_3N_3H_3$ (2a). To a stirred mixture of 3.30 g (10.7 mmol) of $(C_6H_5BNH)_3^1$ and 60 mL of toluene kept at 10 °C, 10.7 mL of a 1 M solution of BCl_3 in heptane was added dropwise. The mixture was slowly warmed to room temperature and then heated to 80 °C until a clear solution was obtained (ca. 1 h). Volatiles were removed under reduced pressure to leave 2.80 g (98%) of crude solid containing traces of unreacted $(C_6H_5BNH)_3$. The material was purified by sublimation under vacuum at a bath temperature of 90 °C (not higher!) to give a pure compound, mp 62–65 °C. Anal. Calcd for $C_{12}H_{13}B_3ClN_3$ ($M_r = 267.00$): C, 53.93; H, 4.91; B, 12.13; Cl, 13.30; N, 15.73. Found: C, 53.27; H, 4.97; B, 12.05; Cl, 13.10; N, 15.58.

NMR data: $\delta(^1H)$ 7.70 (4 H, m), 7.48 (6 H, m), 5.90* (1 H, s), 5.60* (2 H, s); $\delta(^{11}B)$ 33.5 (2 B, s, $h_{1/2} = ca. 375$ Hz), 30.3 (1 B, s, $h_{1/2} = ca. 300$ Hz); $\delta(^{13}C)$ 132.1, 130.7, 128.5. EI mass spectrum (11 eV): m/z 270 (8), 269 (38), 268 (35), 267 (100), 266 (68), 265 (18).

$(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (5) was obtained as a byproduct in the synthesis of $(C_2H_5BNH)_3$ from $C_2H_5BCl_2$ and $HN[Si(CH_3)_3]_2$.⁶ After distilling off $(C_2H_5BNH)_3$ from the crude reaction mixture, variable amounts of higher boiling material remain. From this, 5 was obtained as colorless liquid, bp 52–54 °C (1 Torr). Anal. Calcd for $C_9H_{26}B_3N_3Si$ ($M_r = 236.71$): C, 45.63; H, 11.07; B, 13.69; N, 17.74; Si, 11.87. Found: C, 45.55; H, 11.14; B, 13.71; N, 17.78; Si, 12.08.

NMR data: $\delta(^1H)$ 4.9* (2 H, s), 0.97 (12 H, unsym s with broad unresolved base), 0.84 (3 H, t); 0.27 (9 H, s); $\delta(^{11}B)$ 38.5 (2 B, s), 35.7 (1 B, s); $\delta(^{13}C)$ 12.8*, 9.8, 8.9*, 8.3, 4.6. The 20–eV EI mass spectrum exhibited a small parent ion cluster at m/z 237 and a base peak for $[M \text{ minus } 15]^+$ at m/z 222.

$Br(C_2H_5)_2B_3N_3H_3$ (2b). A stirred solution of 3.80 g (23.3 mmol) of $(C_2H_5BNH)_3^6$ in 20 mL of dichloromethane was cooled to –10 °C and 5.80 g (23.3 mmol) of BBr_3 was added dropwise. The

resultant thick slurry was warmed to room temperature to form a clear solution. It was stirred for 30 min at ambient temperature and volatiles were removed under reduced pressure. A colorless wet solid remained which was purified by sublimation under vacuum to give 4.9 g (97%) of material, mp 34–36 °C. (A small amount of the byproduct $\text{Br}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3\text{H}_3$ could not be removed.) Anal. Calcd for $\text{C}_4\text{H}_{13}\text{B}_3\text{BrN}_3$ ($M_r = 215.40$): C, 22.28; H, 6.08; B, 15.04; Br, 37.09; N, 19.51. Found: C, 21.98; H, 5.94; B, 14.91; Br, 37.31; N, 19.27.

NMR data: $\delta(^1\text{H})$ 5.10* (2 H, s), 4.95* (1 H, s), 1.05–0.80 (10 H, m); $\delta(^{11}\text{B})$ 36.6 (2 B, s, $h_{1/2} = 200$ Hz), 27.6 (1 B, s, $h_{1/2} = 150$ Hz); $\delta(^{13}\text{C})$ 9.0*, 8.2. EI mass spectrum (10 eV): m/z 217 (67), 216 (60), 215 (100), 214 (54), 213 (19). The 70-eV EI mass spectrum exhibited an ion cluster at m/z 186 as the strongest peak group of the spectrum, with the parent ion cluster appearing in about 80% relative intensity thereof.

$(\text{CH}_3\text{S})(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ (2c). A stirred mixture of 1.32 g (6.13 mmol) of $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$, 3.0 g (10 mmol) of $\text{Pb}(\text{SCH}_3)_2$, and 10 mL of hexane was refluxed for 24 h, filtered, and solvent was evaporated off the clear filtrate under reduced pressure. The remaining crude liquid (0.75 g, 67%) was purified by distillation under vacuum, bp 44–45 °C (1 Torr). Anal. Calcd for $\text{C}_5\text{H}_{16}\text{B}_3\text{N}_3\text{S}$ ($M_r = 182.59$): C, 32.86; H, 8.83; B, 17.75; N, 23.00; S, 17.56. Found: C, 32.93; H, 8.91; B, 17.41; N, 22.74; S, 17.31.

NMR data: $\delta(^1\text{H})$ 4.75* (s, 3 H), 2.10 (3 H, s), 0.97 (6 H, unsym t), 0.87 (4 H, unsym q); $\delta(^{11}\text{B})$ 35.9 (2 B, s), 34.2 (1 B, s); $\delta(^{13}\text{C})$ 9.0*, 8.3, 8.2. The EI mass spectrum exhibited a parent ion cluster at m/z 183 as the base peak of the spectrum.

The Reaction of NH_3 with $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ – Formation of $\text{HN}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_2$ (1b) and $\text{N}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_3$ (4). Dry ether (15 mL) was mixed with ca. 30 mL of anhydrous liquid NH_3 at –78 °C. A solution of 3.65 g (17.0 mmol) of $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ in 15 mL of ether was added and the stirred reaction mixture was slowly warmed to room temperature. It was filtered and volatiles were evaporated under reduced pressure to leave 2.5 g of crude product.

When the volatile material was removed rapidly and a ^{11}B NMR spectrum was recorded on the crude product, $(\text{H}_2\text{N})(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ could be identified ($\delta(^{11}\text{B})$ 36.2 (2 B, $h_{1/2} = 230$ Hz), 25.5 (1 B, $h_{1/2}$

= 170 Hz)). However, even at room temperature the compound condensed with the formation of the bis(borazin-2-yl)amine $\text{HN}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_2$ (**1b**) and also of the tris(borazin-2-yl)amine **4**.

A small amount of liquid, bp 115–120 °C (1 Torr), was distilled off the crude product and identified as **1b**. NMR data: $\delta(^{11}\text{B})$ 36.4 (2 B, $h_{1/2}$ = 450 Hz), 26.3 (1 B, $h_{1/2}$ = 440 Hz). EI mass spectrum (12 eV): m/z 288 (14), 287 (79), 286 (100), 285 (55), 284 (28), 283 (7), 260 (10), 259 (31), 258 (33), 257 (21), 256 (10). Calculated for the parent ion: m/z 288 (8), 287 (74), 286 (100), 285 (60), 284 (19), 283 (3).

During the distillation, a second material, **4**, mp 146–148 °C, deposited in the distillation head. (The NMR and mass spectral data of this sublimate were identical with that of the residue.) Anal. Calcd for $\text{C}_{12}\text{H}_{39}\text{B}_9\text{N}_{10}$ (M_r = 420.51): C, 34.24; H, 9.35; B, 23.11; N, 33.30. Found: C, 34.14; H, 9.29; B, 23.19; N, 33.19.

NMR data: $\delta(^1\text{H})$ 4.6* (3 H, s), 0.95 (6 H, unsym t), 0.83 (4 H, unsym q); $\delta(^{11}\text{B})$ 36.8 (2 B, $h_{1/2}$ = ca. 680 Hz), 28.5 (1 B, $h_{1/2}$ = ca. 730 Hz); $\delta(^{13}\text{C})$ 9.3*, 8.5. EI mass spectrum (10 eV): m/z 423 (7), 422 (87), 421 (100), 420 (87), 419 (20), 418 (6), 287 (6), 286 (28), 285 (53), 284 (21), 283 (5). Calculated for the parent ion of **4**: m/z 423 (8), 422 (54), 421 (100), 420 (92), 419 (51), 418 (19), 417 (5).

$\text{Br}_2(\text{C}_2\text{H}_5)_3\text{B}_3\text{N}_3\text{H}_3$ (**3b**) was obtained by adding 76.2 g (0.304 mol) of BBr_3 to a stirred solution of 25.0 g (0.152 mol) of $(\text{C}_2\text{H}_5\text{BNH})_3$ in 100 mL of dichloromethane at –10 °C over a period of 1 h. The mixture was warmed to room temperature and then refluxed for 1 h to give an almost clear solution. It was filtered and volatiles were evaporated under reduced pressure to leave 40.2 g (99%) of crude product. This was sublimed under vacuum (40–50 °C bath temperature) to give a material of mp 27–29 °C. (The material contains traces of $(\text{BrBNH})_3$, which are difficult to remove.) Anal. Calcd for $\text{C}_2\text{H}_8\text{B}_3\text{Br}_2\text{N}_3$ (M_r = 266.26): C, 9.01; H, 3.03; B, 12.17; Br, 60.02; N, 15.77. Found: C, 8.83; H, 2.92; B, 12.01; Br, 60.24; N, 15.45.

NMR data: $\delta(^1\text{H})$ 5.3* (3 H, s), 1.05–0.8 (5 H, m); $\delta(^{11}\text{B})$ 37.3 (1 B, s, $h_{1/2}$ = 190 Hz), 27.9 (2 B, s, $h_{1/2}$ = 140 Hz); $\delta(^{13}\text{C})$ 7.9, 7.7*. This 15-eV EI mass spectrum exhibited a parent ion cluster at m/z 267 in the calculated isotopic distribution.

$(\text{CH}_3\text{S})_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3\text{H}_3$ (**3c**) was prepared in a manner analogous to that of **2c** (above) from 4.6 g (17 mmol) of $\text{Br}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3\text{H}_3$ and 11.0 g (36.5 mmol) of $\text{Pb}(\text{SCH}_3)_2$ (65 mL of hexane, 24 h reflux). After filtration, the clear solution was concentrated to a volume of about 10 mL and cooled and 2.45 g (71%) of **3c** precipitated; mp 58–62 °C. Anal. Calcd for $\text{C}_4\text{H}_{14}\text{B}_3\text{N}_3\text{S}_2$ ($M_r = 200.63$): C, 23.92; H, 7.63; B, 16.15; N, 20.93; S, 31.97. Found: C, 23.41; H, 7.02; B, 16.08; N, 20.64; S, 31.88.

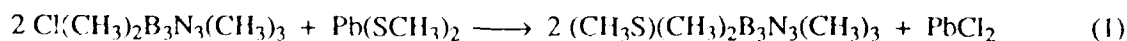
NMR data: $\delta(^1\text{H})$ 4.7* (3 H, s), 2.10 (6 H, s), 1.1–0.8 (5 H, m); $\delta(^{11}\text{B})$ 35.8 (1 B, s, $h_{1/2} = 290$ Hz), 34.1 (2 B, s, $h_{1/2} = 175$ Hz); $\delta(^{13}\text{C})$ 9.1*, 8.24, 8.16. The EI mass spectrum exhibited a parent ion cluster at m/z 201.

$\text{Cl}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3(\text{CH}_3)_3$ (**3d**) was prepared from 41.2 mL of a 1 M solution of BCl_3 in heptane and 4.25 g (20.6 mmol) of $(\text{C}_2\text{H}_5\text{BNCH}_3)_3$ (stirring overnight at ambient temperature, then 6 h at 60 °C). After removal of volatiles under reduced pressure, the residue was distilled under vacuum to give 4.35 g (96%) of **3d**, bp 78–80 °C (1 Torr). Anal. Calcd for $\text{C}_5\text{H}_{14}\text{B}_3\text{N}_3\text{Cl}_2$ ($M_r = 219.53$): C, 27.36; H, 6.43; B, 14.77; Cl, 52.30; N, 19.14. Found: C, 27.32; H, 6.48; B, 14.20; Cl, 31.19; N, 19.07.

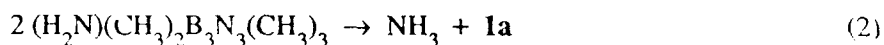
NMR data: $\delta(^1\text{H})$ 3.10 (3 H, s), 3.05 (6 H, s), 1.09 (2 H, q, $J = 7$), 0.98 (3 H, t, $J = 7$); $\delta(^{11}\text{B})$ 37.9 (1 B, s, $h_{1/2} = 250$ Hz), 31.4 (2 B, s, $h_{1/2} = 140$ Hz); $\delta(^{13}\text{C})$ 35.1, 34.2, 7.4, 7.1*. Mass spectrum (10 eV): m/z 223 (19), 222 (12), 221 (78), 220 (62), 219 (100), 218 (72), 217 (22), 216 (8).

Results and Discussion

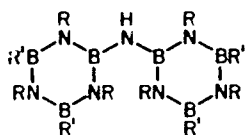
The chemistry of unsymmetrically substituted borazines has not yet been well explored, since access to such species in pure state is fairly difficult.¹ The most readily available unsymmetrically B-substituted borazine of the type $\text{XR}_2\text{B}_3\text{N}_3\text{R}'_3$ is probably the monochloro compound $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$, which can be obtained from $(\text{ClBNCH}_3)_3$ by a Grignard reaction. However, the purification of the product is fairly laborious.² On the other hand, it has now been observed that the crude material as obtained from the cited Grignard reaction can be converted to $(\text{CH}_3\text{S})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (**2d**) by reaction with $\text{Pb}(\text{SCH}_3)_2$ according to eq 1, and the resultant (liquid) monomethylthio compound is then readily purified by distillation.



In many instances the (B)SCH₃ site is just about as reactive as a (B)Cl site. For example, 2-amino-1,3,4,5,6-pentamethylborazine has previously been prepared by the reaction of Cl(CH₃)₂B₃N₃(CH₃)₃ with NH₃.^{2,7} In the present work, the reaction of (CH₃S)(CH₃)₂B₃N₃(CH₃)₃ with anhydrous NH₃ gave a good yield of (H₂N)(CH₃)₂B₃N₃(CH₃)₃ (**2c**), which has now been characterized by NMR data. Thermal condensation of **2c** was found to begin near 150–160 °C, but temperatures as high as 250–270 °C were required for efficient conversion of the compound to yield the bis(borazin-2-yl)amine HN[(CH₃)₂B₃N₃(CH₃)₃]₂ (**1a**) with the elimination of NH₃, eq 2.



The same bis(borazin-2-yl)amine has previously been mentioned as the product of such a thermal condensation but was not characterized.⁸ More recently, it has been obtained by the interaction of Cl(CH₃)₂B₃N₃(CH₃)₃ with HN[Si(CH₃)₃]₂ and the structure of the species has been determined¹ by single crystal X-ray diffraction.⁴



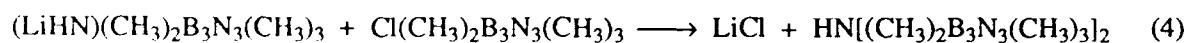
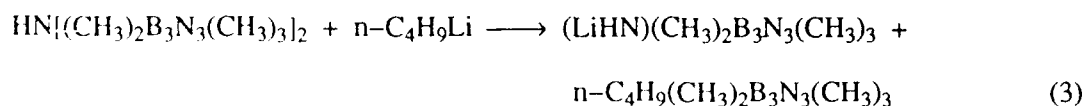
1

a: R = R' = CH₃

b: R = H, R' = C₂H₅

HN[(CH₃)₂B₃N₃(CH₃)₃]₂ (**1a**) is extremely sensitive to moisture and hydrolyzes with the formation of the previously described^{4,5,9} O[(CH₃)₂B₃N₃(CH₃)₃]₂ as the initial product. On the other hand, it is thermally quite stable. For example, on heating of the pure compound to its boiling point under atmospheric pressure, no thermal condensation to yield N[(CH₃)₂B₃N₃(CH₃)₃]₃ was observed but increasing amounts of hexamethylborazine were slowly formed in a rearrangement process.

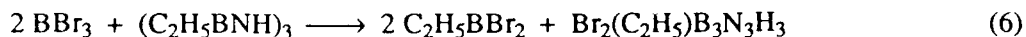
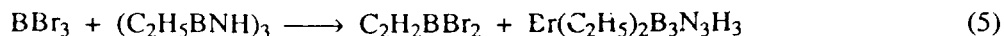
In another approach to generate the tris(borazin-2-yl)amine skeleton, $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$ was reacted with 1 molar equiv each of $n\text{-C}_4\text{H}_9\text{Li}$ and then $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$. It was intended to form, initially, the N-lithiated bis(borazinyl)amine, which was then expected to react with the chloroborazine to form tris(pentamethylborazin-2-yl)amine. However, the reaction proceeded unexpectedly. Apparently, initial cleavage of the bis(borazinyl)amine according to eq 3 occurs under the impact of LiC_4H_9 , and the original bis(borazinyl)amine is subsequently regenerated according to eq 4. (It should be noted that the reaction according to eq 3 has a precedent, i. e., it parallels the interaction of the diborylamine $\text{HN}[\text{B}(\text{CH}_3)_2]_2$ with LiCH_3 to yield $(\text{CH}_3)_2\text{BNHLi}$ and $\text{B}(\text{CH}_3)_3$.¹⁰)



In additional attempts to synthesize $\text{N}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_3$, the interaction of equimolar amounts of $(\text{CH}_3\text{S})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ and $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$ at temperatures as high as 200 °C was studied. However, the starting materials were recovered unchanged. Similarly, no reaction occurred when $\text{Cl}(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ was treated with $\{[(\text{CH}_3)_3\text{Si}]_2\text{N}\}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]$ in 2:1 molar ratio in refluxing hexane.

The preceding results seemed to suggest, that the formation of the tris(borazinyl)amine is impaired by the presence of the N-bonded organic substituents. Thus, attention was directed to the preparation of unsymmetrically B-substituted borazines containing annular NH groups.

A very convenient approach for the synthesis of unsymmetrically B-substituted borazines has emerged recently, when the reaction of $(\text{C}_2\text{H}_5\text{BNCH}_3)_3$ with BBr_3 was studied. It was found that a $\text{Br}/\text{C}_2\text{H}_5$ exchange occurred readily and proceeded with the exclusive transfer of only one Br from BBr_3 to the borazine. Thus, interaction of a 1:1 molar ratio of the reagents gave $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ in excellent yield and high purity, and a 1:2 ratio provided for $\text{Br}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3(\text{CH}_3)_3$.¹¹ In an extension of this work, $(\text{C}_2\text{H}_5\text{BNH})_3$ was reacted with BBr_3 to give $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ (**2b**) and $\text{Br}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3\text{H}_3$ (**3b**), respectively, depending on the stoichiometry of the reagents, as is shown in the following equations.



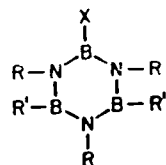
Moreover, the catalyst as previously employed¹¹ was found to be not required. Hence, this method provides for a very convenient and efficient access to unsymmetrically B-substituted borazines, since the $\text{C}_2\text{H}_5\text{BBr}_2$ can be recovered and reconverted to the originating borazine, $(\text{C}_2\text{H}_5\text{BNH})_3$.

It should be noted that the reactions according to eqns 5 or 6 must be performed in the presence of solvent: A substantial amount of solid intermediate is formed, which impairs the stirring of a neat reagent mixture. This formation of intermediates seems to be an effect of the annular NH groups, but the presence of NH rather than NCH_3 groups does not affect the yield of final product, which was excellent in all cases. The effect of the annular NH groups is further seen in the properties of the products. Whereas $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ is thermally stable and can be purified by distillation, $\text{Br}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ is thermally fairly sensitive and not only begins to decompose at its melting point, but slow decomposition is also observed on prolonged storage of the material at ambient temperature. Hence, it is suggested that only freshly purified (sublimed) material is employed in any subsequent reactions.

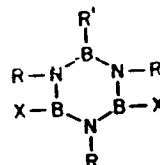
It has also been found that the halogen/alkyl group exchange as described in eqns 5 and 6 is not limited to the use of BBr_3 as halogen source, but reactions analogous to that of B-triorganylborazines with BBr_3 proceed equally well when BCl_3 is employed as reagent. Thus, the species $\text{Cl}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ and $\text{Cl}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3(\text{CH}_3)_3$ could be obtained readily and in good yield. However, under the same experimental conditions, the reaction of $(\text{C}_2\text{H}_5\text{BNH})_3$ with BCl_3 did not proceed as cleanly as in the case of $(\text{C}_2\text{H}_5\text{BNCH}_3)_3$. For example, for the 1:1 molar reaction the major product clearly was the desired $\text{Cl}(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3$ [bp 53–55 °C (1 Torr); $\delta(^1\text{H})$ 4.9* (3 H, s), 1.0–0.8 (10 H, m); $\delta(^{11}\text{B})$ 36.6 (2 B, s, $h_{1/2} = 220$ Hz), 29.9 (1 B, s, $h_{1/2} = 170$ Hz)], but $\text{Cl}_2(\text{C}_2\text{H}_5)\text{B}_3\text{N}_3\text{H}_3$ [bp 38–42 °C (1 Torr), mp 28.5 °C; $\delta(^1\text{H})$ 5.1* (3 H, s), 0.96 (3 H, t), 0.87 (2 H, q); $\delta(^{11}\text{B})$ 37.2 (1 B, s, $h_{1/2} = 240$ Hz), 29.9 (2 B, s, $h_{1/2} = 140$ Hz)] as well as $(\text{ClBNH})_3$ were also formed, and it was extremely difficult to separate the products. Similar results were obtained when the reaction was performed in 1:2 molar ratio.

Hence, in this case this reaction is not as useful for preparative purposes as that employing BBr_3 , and it again illustrates that differences exist between the reactivity of borazines containing annular NH groups as compared to those containing a N-bonded hydrocarbon substituent. On the other hand, $Cl(C_6H_5)_2B_3N_3H_3$ was readily obtained from the reaction of $(C_6H_5BNH)_3$ with BCl_3 , suggesting that the boron substituents may also affect the process.

Several additional unsymmetrically B-substituted borazines of the types $XR_2B_3N_3R'_3$ (2) and $X_2RB_3N_3R'_3$ (3) were subsequently prepared originating from the halogenated species. The following unsymmetrically B-substituted (mono)borazines have been prepared and characterized during the course of the present study.



2



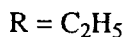
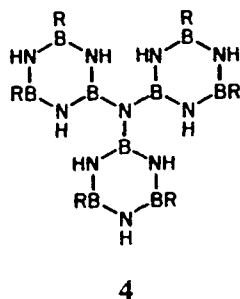
3

- a: $X = Cl, R = H, R' = C_6H_6$
 b: $X = Br, R = H, R' = C_2H_5$
 c: $X = SCH_3, R = H, R' = C_2H_5$
 d: $X = SCH_3, R = R' = CH_3$
 e: $X = NH_2, R = R' = CH_3$
 f: $R = C_4H_9, R = R' = CH_3$
 g: $X = N[Si(CH_3)_3]_2, R = R' = CH_3$
 h: $X = Cl, R = CH_3, R' = S_2H_5$

- a: $X = Cl, R = H, R' = C_2H_5$
 b: $X = Br, R = H, R' = C_2H_5$
 c: $X = SCH_3, R = H, R' = C_2H_5$
 d: $X = Cl, R = CH_3, R' = C_2H_5$

When $Br(C_2H_5)_2B_3N_3H_3$ was reacted with anhydrous NH_3 , the desired $(H_2N)(C_2H_5)_2B_3N_3H_3$ could be identified in the crude reaction product only when the excess of NH_3 and the solvent were removed rapidly [$\delta(^{11}B)$ 36.2 (2 B, $h_{1/2} = 230$ Hz), 25.5 (1 B, $h_{1/2} = 170$ Hz)]. However, even at room temperature

the compound condensed with the formation of the bis(borazin-2-yl)amine $\text{HN}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_2$ (**1b**, $\delta(^{11}\text{B})$ 36.4 (2 B, $h_{1/2} = 450$ Hz), 26.3 (1 B, $h_{1/2} = 440$ Hz)]. After a short period of time, the formation of a third species was observed [$\delta(^{11}\text{B})$ 36.8 (2 B, $h_{1/2} = \text{ca. } 680$ Hz), 28.5 (1 B, $h_{1/2} = \text{ca. } 730$ Hz)], which



was identified as the tris(borazin-2-yl)amine **4**. Ultimately, only a mixture of $\text{HN}[(\text{C}_2\text{H}_5)_2\text{B}_3\text{N}_3\text{H}_3]_2$ (**1b**) and **4** remained, from which small amounts of pure **1b** and **4** could be isolated and characterized.

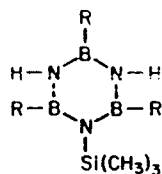
The separation of **1b** and **4** proved quite difficult. The bis(borazin-2-yl)amine is thermally quite stable and has no ready tendency to undergo condensation to form **4** when heated under atmospheric pressure at 200 °C for several h. On the other hand, when **1b** was heated at 200 °C under vacuum for 1 h, most of it converted to **4**, but adhering traces of **1b** were difficult to remove.

Compound **4** is the first known tris(borazin-2-yl)amine and seems to offer great potential for the preparation of two-dimensional network structures of linked borazine rings. Ongoing studies are directed to explore this possibility.

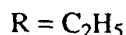
It is of interest to note the distinct broadening of the ^{11}B NMR signals in the above series monoaminoborazine — bis(borazinyl)amine (**1b**) — tris(borazinyl)amine (**4**). It is definitely not due to an overlap of signals from mixtures of compounds of similar ^{11}B chemical shifts, but parallels the observations made in the series $(\text{H}_2\text{N})(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3$ (**2e**) — $\text{HN}[(\text{CH}_3)_2\text{B}_3\text{N}_3(\text{CH}_3)_3]_2$ (**1a**). It is possible that this indicates the overlap of signals, which would suggest that the borazine rings of individual poly(borazine) species are not coplanar. This has indeed been established by an X-ray structure determination of **1a**.⁴

In summary, the current study clearly documents that unsymmetrically B-substituted borazines of types 2 and 3 are conveniently obtained originating from symmetrically substituted B-triorganylborazines. Thus, such compounds are no longer laboratory curiosities but are readily available starting materials for molecular architecture, which opens the door for an extensive exploration of the chemistry of unsymmetrically B-substituted borazines. Most interesting seems to be the application of the species for the formation of poly(borazines), i. e., compounds in which individual borazine rings are linked to form polycyclic systems. The bis(borazin-2-yl)amines 1a and 1b and the tris(borazin-2-yl)amine $N[(C_2H_5)_2B_3N_3H_3]_3$ (4) are examples of such materials, and the synthesis of a variety of poly(borazine) structures is currently under investigation.

Finally, one other observation is worth mentioning. During the course of preparing the starting material $(C_2H_5BNH)_3$ by the reaction of $C_2H_5BCl_2$ with $HN[Si(CH_3)_3]_2$,⁶ considerable variations in the yield were observed, even under apparently identical reaction conditions. Concurrently, the formation of variable amounts of a byproduct was noted, the amount of which increased when the yield of $(C_2H_5BNH)_3$ decreased. This (higher boiling) byproduct has now been identified as the unsymmetrically N-substituted borazine $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (5).



5



Attempts to modify the reaction conditions in order to make 5 the main product did not yet lead to any reasonable conclusions. However, yields of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (5) ranging from 10–40% were usually obtained, especially when the reaction was performed on a relatively large scale. Thus, it presents the possibility to study in N-unsymmetrically substituted borazines in more detail.

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References

- (1) *Gmelin Handbuch der Anorganischen Chemie*; Springer-Verlag: West Berlin, 1978; Vol. 51, Supplement Boron Compounds 17.
- (2) Toeniskoetter, R. H.; Hall, F. R. *Inorg. Chem.* **1963**, *2*, 29-39.
- (3) Adcock, J. L.; Melcher, L. A.; Lagowski, J. J. *Inorg. Chem.* **1973**, *12*, 788-791.
- (4) Narula, C. K.; Lindquist, D. A.; Fan, M.-M.; Borek, T. T.; Duesler, E. N.; Datye, A. K.; Schaeffer, R.; Paine, R. T. *Chem. Mater.* **1990**, *2*, 377-384.
- (5) Toeniskoetter, R. H.; Killip, K. A. *J. Am. Chem. Soc.* **1964**, *86*, 690-694.
- (6) Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1986**, *25*, 4623-4628.
- (7) Meller, A. *Monatsh. Chem.* **1968**, *99*, 1670-1679.
- (8) Clément, R.; Proux, Y. *Bull. Soc. Chim. France* **1969**, 558-563.
- (9) Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* **1962**, *1*, 99-106.
- (10) Fußstetter, H.; Nöth, H. *Chem. Ber.* **1978**, *111*, 3596-3607.
- (11) Bai, J.; Niedenzu, K. *Inorg. Chem.* **1991**, *30*, 0000-0000.

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