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J. Bai and K. Niedenzu

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The reaction of $(C_2H_5BNCH_3)_3$ with one molar equivalent of BBr_3 yields $Br(C_2H_5)_2B_3N_3(CH_3)_3$, which was transformed into the derivatives $(CH_3S)(C_2H_5)_2B_3N_3(CH_3)_3$ by reaction with $Pb(SCH_3)_2$, and to $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ by reaction with anhydrous ammonia. The reaction of $(C_2H_5BNCH_3)_3$ with two molar equivalents of boron tribromide proceeds in similar fashion to yield $Br_2(C_2H_5)B_3N_3(CH_3)_3$, which was converted to $(H_2N)_2(C_2H_5)B_3N_3(CH_3)_3$ and to $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$.

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Convenient Synthesis of Unsymmetrically *B*–Substituted Borazines

by

J. Bai and K. Niedenzu

University of Kentucky
Department of Chemistry
Lexington, KY 40506

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Contribution from the Department of Chemistry,

University of Kentucky, Lexington, Kentucky 40506–0055

Convenient Syntheses of Unsymmetrically *B*–Substituted Borazines

J. Bai and K. Niedenzu*

Received

Literally hundreds of borazines, $(RBNR')_3$, are known, but only relatively few unsymmetrically substituted derivatives of the six–membered B_3N_3 heterocycle have been characterized and their chemistry has hardly been explored.[1] The most readily available unsymmetrically *B*–substituted borazine of the type $XR_2B_3N_3R'_3$ is the monochloro compound $Cl(CH_3)_2B_3N_3(CH_3)_3$, which can be prepared from $(ClBNCH_3)_3$ by a Grignard reaction. However, the purification of the product is fairly laborious, due to the presence of substantial amounts of byproducts.[2] It has now been found that a very convenient access to unsymmetrically *B*–substituted borazines is available by the reaction of a *B*–triorganylborazine with boron tribromide.

Initially, $(C_2H_5BNCH_3)_3$ and BBr_3 were reacted in 3:1 molar ratio, in anticipation that all of the bromine of the BBr_3 would exchange with the ethyl groups of the borazine to give $(C_2H_5)_3B$ and $Br(C_2H_5)_2B_3N_3(CH_3)_3$. However, even when a mixture of the two neat reagents was heated to reflux, the sole products of any significance were $Br(C_2H_5)_2B_3N_3(CH_3)_3$ and $C_2H_5BBr_2$ (besides unreacted $(C_2H_5BNCH_3)_3$). This result indicated that the Br/C_2H_5 exchange stops with the generation of $C_2H_5BBr_2$ rather than to proceed with the formation of $(C_2H_5)_3B$. Consequently, when equimolar amounts of the two reagents were reacted for several hours, and even at room temperature, $Br(C_2H_5)_2B_3N_3(CH_3)_3$ was formed in excellent yield according to eq 1; only $C_2H_5BBr_2$ as well as traces of $Br_2(C_2H_5)B_3N_3(CH_3)_3$ were obtained as byproducts.

$$(C_2H_5BNCH_3)_3 + BBr_3 \longrightarrow Br(C_2H_5)_2B_3N_3(CH_3)_3 + C_2H_5BBr_2 \quad (1)$$

The $Br(C_2H_5)_2B_3N_3(CH_3)_3$ was subsequently converted to $(CH_3S)(C_2H_5)_2B_3N_3(CH_3)_3$ by the reaction with $Pb(SCH_3)_2$, and to $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ by the reaction with anhydrous NH_3, as is shown in the following equations (R = C_2H_5, R′ = CH_3):

$$2\,BrR_2B_3N_3R'_3 + Pb(SCH_3)_2 \longrightarrow 2\,(CH_3S)R_2B_3N_3R'_3 + PbBr_2 \quad (2)$$

$$BrR_2B_3N_3R'_3 + 2\,NH_3 \longrightarrow (H_2N)R_2B_3N_3R'_3 + NH_4Br \quad (3)$$

Similarly, when $(C_2H_5BNCH_3)_3$ was reacted with two molar equivalents of BBr_3, the desired $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was readily obtained. Formation of a precipitate was observed when the reaction was performed at room temperature or below, but the latter disappeared on gentle heating of the reaction mixture. In this case, the only byproduct, besides $C_2H_5BBr_2$, was some $(BrBNCH_3)_3$.

Subsequently, $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was converted to $(H_2N)_2(C_2H_5)B_3N_3(CH_3)_3$ and $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$, as additional representatives of unsymmetrically *B*–substituted borazines.

All of the compounds were obtained in excellent purity, and were characterized by their ^1H, ^{11}B, and ^{13}C NMR data. As yet it is still uncertain if simple Br/C_2H_5 exchange occurs or if a BBr moiety is exchanged with a BC_2H_5 unit. The exclusive formation of $C_2H_5BBr_2$ as byproduct tends to support the latter assumption.

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 $CDCl_3$ 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). Abbreviations are as follows: s = singlet, 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. Electron impact (EI) mass spectral data 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.

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.

2–Bromo–4,6–diethyl–1,3,5–trimethylborazine. A few grains of $NaBH_4$ were added to 60.7 g (0.294 mol) of $(C_2H_5BNCH_3)_3$,[3] and then 73.5 g (0.294 mol) of BBr_3 were added slowly with stirring. An exothermic reaction occurred and a small amount of an initial precipitate dissolved with time. The mixture was stirred at ambient temperature for 3 h, $C_2H_5BBr_2$ was removed under reduced pressure, and the residue was distilled under vacuum to give 64.5 g (85%) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$, bp 90–92 °C (0.5 Torr). Anal. Calcd for $C_7H_{19}B_3BrN_3$ (M_r = 257.59): C, 32.64; H, 7.44; B, 12.59; Br, 12.59; N, 16.31. Found: C, 32.21; H, 7.49; B, 12.51; Br, 30.96; N, 16.26.

NMR data: $\delta(^1H)$ 3.08 (6 H, s), 2.96 (3 H, s), 1.1–0.9 (10 H, m); $\delta(^{11}B)$ 37.2 (2 B, s, $h_{1/2}$ = 250 Hz), 31.6 (1 B, s, $h_{1/2}$ = 160 Hz); $\delta(^{13}C)$ 36.4, 33.2, 7.5, 7.2*. EI mass spectrum (9 eV): *m/z* 260 (16), 259 (80), 258 (76), 257 (100), 256 (56), 255 (16), 207 (16), 206 (12), 178 (8).

2–Amino–4,6–diethyl–1,3,5–trimethylborazine. A solution of 23.7 g (92.0 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$ in 100 mL of ether was added slowly with stirring to a mixture of 100 mL of ether and ca. 20 mL of anhydrous liquid ammonia cooled in a Dry–Ice bath. The mixture was allowed to warm to room temperature and was stirred for 12 h. It was filtered and volatiles were evaporated off the clear filtrate under reduced pressure. The remaining colorless liquid was distilled under vacuum to give 14.8 g (83%) of product, bp 85–86 °C (0.5 Torr). Anal. Calcd for $C_7H_{21}B_3N_4$ (M_r = 193.71): C, 43.40; H, 10.93; B, 16.74; N, 28.92. Found: C, 43.26; H, 10.97; B, 16.66; N, 28.91.

NMR data: $\delta(^1H)$ 2.89 (3 H, s), 2.76 (6 H, s), 2.33* (2 H, s), 0.99–0.95 (10 H, m); $\delta(^{11}B)$ 36.4 (2 B, s, $h_{1/2}$ = 230 Hz), 26.2 (1 B, s, $h_{1/2}$ = 160 Hz); $\delta(^{13}C)$ 33.0, 31.0, 8.0, 6.6*. EI mass spectrum (11 eV): *m/z* 195 (23), 194 (100), 193 (70), 192 (19), 191 (6), 181 (6), 180 (6), 179 (8), 178 (7), 165 (8), 164 (8).

2–Methylthio–4,6–diethyl–1,3,5–trimethylborazine. A stirred mixture of 4.70 g (18.2 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$, 7.7 g (26 mmol) of $Pb(SCH_3)_2$, and 20 mL of hexane was heated to reflux for 24 h. The mixture was cooled to room temperature, filtered, and hexane was evaporated from the clear filtrate. The remaining colorless liquid was distilled under reduced pressure to give 2.2 g (54%) of product, bp 124–127 °C (0.5 Torr). Anal. Calcd for $C_8H_{22}B_3N_3S$ (M_r = 224.78): C, 42.75; H, 9.86; B, 14.43; N, 18.69; S, 14.26. Found: C, 42.73; H, 9.81; B, 14.29; N, 18.56; S, 14.18.

NMR data: $\delta(^1H)$ 3.03 (6 H, s), 2.94 (3 H, s), 2.17 (3 H, s), 1.10–0.90 (10 H, m); $\delta(^{11}B)$ 36.5 (s, $h_{1/2}$ = 260 Hz); $\delta(^{13}C)$ 34.8, 33.0, 11.8, 7.6, 6.9*. EI mass spectrum (15 eV): *m/z* 227 (6), 225 (72), 224 (59), 223 (19), 215 (6), 214 (6), 213 (12), 212 (13), 211 (9), 210 (25) 209 (16), 208 (8), 198 (6), 197 (7), 196 (31), 195 (32), 194 (16), 193 (10), 184(9), 183 (8), 182 (16), 181 (11), 180 (8), 179 (10), 178 (38), 177 (28), 176 (9), 150 (16), 149 (9), 119 (12), 117 (12), 114 (12), 68 (20), 50 (12), 49 (13), 48 (100), 47 (50), 46 (11).

2,4–Dibromo–6–ethyl–1,3,5–trimethylborazine. A few grains of $NaBH_4$ were added to 20.6 g (99.7 mmol) of $(C_2H_5BNCH_3)_3$, and then 50.0 g (199 mmol) of BBr_3 were added slowly with stirring. An exothermic reaction occurred and a small amount of precipitate appeared. The mixture was stirred at ambient temperature for 2 h and subsequently heated to 85 °C (bath temperature) for 16 h to give a clear solution. $C_2H_5BBr_2$ was removed under reduced pressure, and the residue was distilled under vacuum to give 27.5 g (89%) of product, bp 105–108 °C (0.5 Torr), mp 27–28 °C. Anal. Calcd for $C_5H_{14}B_3Br_2N_3$ (M_r = 308.44): C, 19.47; H, 4.58; B, 10.52; Br, 51.81; N, 13.62. Found: C, 19.31; H, 4.52; B, 10.39; Br, 51.79; N, 13.70.

NMR data: $\delta(^1H)$ 3.23 (3 H, s), 3.11 (6 H, s), 1.12 (2 H, unsym q, J = 7), 0.97 (3 H, unsym t, J = 7); $\delta(^{11}B)$ 37.6 (1 B, s, $h_{1/2}$ = 270 Hz), 31.7 (2 B, s, $h_{1/2}$ = 160 Hz); $\delta(^{13}C)$ 40.0, 36.6, 7.2, 7.1*. EI mass spectrum (10 eV): *m/z* 311 (35), 310 (30), 309 (100), 308 (79), 307 (60), 306 (30).

2,4–Di(methylthio)–6–ethyl–1,3,5–trimethylborazine. This compound was prepared in a fashion analogous to that of $(CH_3S)(C_2H_5)_2B_3N_3(CH_3)_3$ from 19 g (63 mmol) of $Pb(SCH_3)_2$ and 9.73 g (31.6 mmol) of $Br_2(C_2H_5)_2B_3N_3(CH_3)_3$ (30 mL of hexane, 24 h reflux). After filtration and solvent

evaporation, the residue was distilled under reduced pressure to give 5.2 g (68%) of product, bp 128–132 °C (0.5 Torr). Anal. Calcd for $C_7H_{20}B_3N_3S_2$ (M_r = 242.82): C, 34.62; H, 8.30; B, 13.36; N, 17.30; S, 26.41. Found: C, 34.55; H, 8.29; B, 13.21; N, 17.26; S, 26.40.

NMR data: $\delta(^1H)$ 3.13 (3 H, s), 3.00 (6 H, s), 2.18 (6 H, s), 1.1–0.9 (5 H, m); $\delta(^{11}B)$ 36.8 (s, $h_{1/2}$ = 200 Hz); $\delta(^{13}C)$ 37.0, 34.6, 11.7, 7.5, 6.8*. The 12–eV mass spectrum exhibited only an ion cluster at *m/z* 243.

2,4–Diamino–6–ethyl–1,3,5–trimethylborazine. This compound was prepared in a fashion analogous to that of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$. Originating from 9.07 g (29.4 mmol) of $Br_2(C_2H_5)B_3N_3(CH_3)_3$, 2.43 g (46%) of product, bp 95–98 °C (0.5 Torr), were obtained. Anal. Calcd for $C_5H_{13}B_3N_5$ (M_r = 180.67): C, 33.24; H, 10.04; B, 17.95; N, 38.76. Found: C, 33.17; H, 9.98; B, 17.21; N, 38.58.

NMR data: $\delta(^1H)$ 2.72 (6 H, s), 2.57 (3 H, s), 2.24* (4 H, s), 0.98–0.92 (5 H, m); $\delta(^{11}B)$ 36.2 (1 B, s, $h_{1/2}$ = 220 Hz), 26.2 (2 B, s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 31.1, 29.2, 8.1, 6.1*. EI mass spectrum (10 eV): *m/z* 182 (11), 181 (100), 180 (65).

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