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Abstract

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L. L. Shchukovskaya, M. G. Voronkov, and O. V. Pavlova

New Routes for the Synthesis of B-Monohalogen-Substituted N-Dialkylborazenes and N-Trialkylborazanes

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Recently (1) a method was described for obtaining the previously rather inaccessible N-alkyl-B-monohaloborazanes by the action of the corresponding hydrogen halide on N-alkylborazanes according to the scheme:

$$R_nH_{3-n}N\cdot BH_3 + HX \rightarrow R_nH_{3-n}N\cdot BH_2X + H_2,$$

$$X = Cl,\ Br,\ J^*$$

Along with hydrogen halides, free halogens (chlorine, bromine, and iodine), as well as boron halides, were used. Reduction of boron halides with lithium or sodium borohydrides leads to complete replacement of all halogens at the boron atom by hydrogen (2), and compounds containing both hydrogen and halogens at the boron atom cannot be obtained. We have developed a new method for the synthesis of B-monohalogen-substituted borazenes and borazanes, based on the reduction of readily available B-trihalogen-N-trialkylborazanes (complexes of boron trihalides with trialkylamines) and N-dialkyl-B-dihalogenoborazenes by compounds containing the Si–H bond. As such compounds we used triethylsilane, which readily reduces halogen derivatives of a series of elements (3,4).

The reaction proceeds smoothly in the presence of catalytic amounts of colloidal nickel according to the scheme:

$$R_3N\cdot BX_3 + (C_2H_5)_3SiH \xrightarrow{Ni} R_3N\cdot BH_2X + (C_2H_5)_3SiX.$$

Small amounts of N-trialkylborazane $R_3N\cdot BH_3$ and $R_3N\cdot HCl$ are formed as by-products. Colloidal nickel is obtained directly in the reaction vessel by reduction of nickel chloride with triethylsilane. The reduction reaction of boron tribromide proceeds very vigorously even on cooling to −80°. We carried out the reduction by adding BBr_3 dropwise to a mixture of triethylsilane and triethylamine. It turned out that the reaction leads to the formation, in equal yield ($\sim 35\%$), of both $(C_2H_5)_3N\cdot BH_3$ and $(C_2H_5)_3N\cdot BH_2Br$. The latter compound was obtained for the first time.

Reduction of the complex $(C_2H_5)_3N \cdot BCl_3$ at room temperature proceeds over many days. When heated to 130°, the reaction proceeds much more rapidly, and, upon distillation of excess triethylsilane and the triethylchlorosilane formed from the filtrate, a crystallizing residue of N-triethyl-B-chloroborazane is rapidly obtained (yield 42%).

In the reduction of N-dialkyl-B-dihalogenoborazenes, previously unknown N-dialkyl-B-halogenoborazenes are formed:

$$R_2N = BX_2 + (C_2H_5)_3SiH \xrightarrow{\text{Ni}} R_2N = BHX + (C_2H_5)_3SiX.$$

In this way, for example, we obtained N-dimethyl-B-bromoborazene in 30% yield.

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* In the case $X = \mathrm{F}$, the reaction proceeds differently:

$$RNH_2 \cdot BH_3 + 3HF \rightarrow RNH_2 \cdot BF_3 + 3H_2,$$

$$R = C(CH_3)_3,$$

with formation of N-alkyl-B-trifluoroborazane.

Experimental Part

Starting reagents: boron tribromide was obtained by the reaction of amorphous boron with bromine at 700–750° (5). Yield 74%, calculated on the starting bromine. BCl_3 was prepared by heating a mixture of $AlCl_3$ and KBF_4 (6). Triethylsilane was synthesized by the action of ethylmagnesium bromide on ethyldichlorosilane. It was purified by distillation over sodium. B.p. 107–108°; n_D^{20} 1.4117.
N-Dimethyl-B-dibromoborazene was prepared by the procedure of (7) and had b.p. 45.5-47° (10 mm); 162-163° (772 mm); n_D^{20} 1.4965; d_4^{20} 1.755. Yield 53.5%. Literature data (8): b.p. 163°, m.p. 21.5°.
N-Triethyl-B-trichloroborazane was obtained according to Lappert (9) and, after recrystallization from 80% alcohol, had m.p. 89–91°. Literature data: m.p. 91–92°.

Reduction of N-dimethyl-B-dibromoborazene, $(CH_3)_2N = BBr_2$**.** In a 0.1-liter three-necked flask equipped with a thermometer, dropping funnel, and reflux condenser connected to a trap cooled to −70°, 45.0 g of triethylsilane was placed, and at room temperature 25.0 g of N-dimethyl-B-dibromoborazene was gradually added dropwise. No warming was observed. The reaction mixture was left for 4 days. Even after this, and after 4 hours' boiling (119–120°), no visible interaction of the components was observed. When a catalytic amount

(~0.15 g) of $NiCl_2$ was introduced into the flask, crystals immediately separated on its bottom and walls. To complete the reaction, the reaction mixture was heated to boiling (121°). After cooling, the precipitated crystals were separated, washed with dry petroleum ether, and sublimed twice in vacuo (68–70° at 10–11 mm). This gave 6 g (30% yield) of white, lustrous, needle-shaped crystals with m.p. 122–125°, possessing a camphor-like odor.

The substance is insoluble in water, readily soluble in hot petroleum ether, from which, after recrystallization, it has m.p. 122–124° (lustrous plates).

Found, %: N 10.42; 10.48; C 18.14; 18.17; H 5.37; 5.43; B 7.96; 8.19; Br 60.07

C_2H_7BBrN. Calculated, %: N 10.31; C 17.68; H 5.19; B 7.96; Br 58.86

On distillation of the filtrate, 35.0 g of the starting triethylsilane was obtained (b.p. 106–110; n_D^{20} 1.4145) and 18.0 g of triethylbromosilane (b.p. 160–165°; n_D^{20} 1.4550). Along with these, a small amount of dimethylamine hydrobromide and 2.0 g of a liquid higher-boiling substance, which was not further investigated, were isolated.

Catalytic reaction of boron tribromide with triethylsilane in the presence of triethylamine. In an apparatus analogous to that described above, connected to a trap cooled with liquid nitrogen, 40 g of freshly distilled dry triethylsilane and ~0.2 g of $NiCl_2$ were placed. The mixture was boiled until the $NiCl_2$ was reduced. After cooling, 12 g of dry triethylamine was added to it, after which the apparatus was swept with dry nitrogen purified of oxygen. Then, with the flask cooled with solid carbon dioxide, 25 g of BBr_3, also cooled with solid carbon dioxide, was added dropwise over the course of 40 min.

On the following day the precipitate that had formed, $(C_2H_5)_3N \cdot HBr$ (1.7 g), was filtered off and purified by sublimation in vacuo, m.p. 250°. The filtrate was distilled in vacuo. This gave 20 g of unchanged $(C_2H_5)_3SiH$ and 30 g of $(C_2H_5)_3SiBr$. The residue in the distillation flask with n_D^{20} 1.4855 was fractionated twice in vacuo (<0.1 mm). In this process two substances were isolated: N-tri-

ethylborazane $(C_2H_5)_3N \cdot BH_3$ (I) (bath temperature 90–95°) n_D^{20} 1.4420; d_4^{20} 0.7885; yield 4 g (35%, calculated on the starting BBr_3).

Found, %: C 62.27; 62.30; H 15.66; 15.85; B 9.36
$C_6H_{18}BN$. Calculated, %: C 62.70; H 15.70; B 9.40

Literature data for $(C_2H_5)_3N \cdot BH_3$ (^{10}): b.p. 42° (10^{-4} mm); m.p. −2°.

N-Triethyl-*B*-bromoborazane $(C_2H_5)_3N \cdot BH_2Br$ (II) (bath temperature 150–155°); crystals, after two recrystallizations from dry petroleum ether, m.p. 65–67°; yield 7.0 g (36%, calculated on the starting BBr_3).

Found, %: C 37.14; 37.28; H 8.80; 8.87; B 5.37; 5.57; Br 41.35; 41.65; N 7.20
$C_6H_{17}BNBr$. Calculated, %: C 37.15; H 8.76; B 5.57; Br 41.28; N 7.22

Reduction of *N*-triethyl-*B*-trichloroborazane. To a suspension of colloidal nickel in 12.0 g of triethylsilane there was added at room temperature, all at once, 7.0 g of unrecrystallized $(C_2H_5)_3N \cdot BCl_3$. The reaction mixture was heated for 6 h at 85°, after which over 5 h the temperature was raised to 130°. Upon cooling, the precipitate $(C_2H_5)_3N \cdot HCl$ (m.p. 253°) was filtered off (0.2 g). The filtrate was fractionated in vacuo. This gave, along with the starting $(C_2H_5)_3SiH$ and the formed $(C_2H_5)_3SiCl$, 2.0 g of crystals of *N*-triethyl-*B*-chloroborazane, which after two recrystallizations from dry petroleum ether had m.p. 42–43°. Yield 42%. Literature data (1): m.p. 43°.

In addition to $(C_2H_5)_3N \cdot BH_2Cl$, 0.5 g of $(C_2H_5)_3N \cdot BH_3$ with n_D^{20} 1.4438, distilling in vacuo at a bath temperature of 110°, was isolated.

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Institute of Silicate Chemistry
Academy of Sciences of the USSR

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