# HETEROATOM DERIVATIVES OF AZIRIDINE

## VI. Reaction of Ethyleneimine with Boron Trichloride and Tribromide*

L. A. Fedotova and M. G. Voronkov

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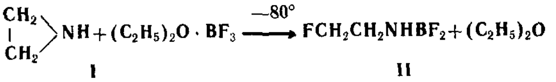
Reaction of ethyleneimine with boron trichloride and tribromide below −20° C, with reactants in ratios 1:1 and 2:1, gives labile N-β-halogenoethyl-substituted halogenoborazenes of the types $XCH_2CH_2NHBX_2$ and $(XCH_2CH_2NH)_2BX$ (X = Cl, Br). These compounds decomposed spontaneously on coming to room temperature, with the evolution of HX and formation of substances whose compositions are, respectively $C_2H_4NBX_2$ and $C_4H_9N_2BX_2$. With a 3:1 ratio of reactants the product is the relatively stable tris(β-halogenoethylamino)borane $(XCH_2CH_2NH)_3B$ (X = Cl, Br), which loses only one molecule of HX when heated under vacuum.

Boron trichloride and tribromide give 1:1 coordination complexes with primary and secondary amines which, however, readily lose a molecule of halogen hydride to give the corresponding borazenes [2–12]:

$$R_2NH + BX_3 \rightarrow R_2NH \cdot BX_3 \xrightarrow{-HX} R_2N \rightleftarrows BX_2 \qquad (1)$$

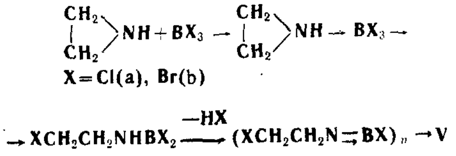
It appeared to us to be of interest to study the behavior of ethyleneimine (I) in this reaction.

We previously showed [13, 14] that I reacts with boron trichloride in ether at −80°, with opening of the aziridine ring, and formation of N-β-fluoroethyl-B-difluoroborazene (II):


I II (2)

It would have been expected that the other boron trihalides would react like I.

Actually, reaction between equimolecular quantities of reagents in carbon tetrachloride at −20° C or methylene chloride at −78° C gives the corresponding crystalline N-β-halogenoethyl-B-dihalogenoborazenes. On warming to room temperature, however, they spontaneously decompose with evolution of hydrogen halide and formation of substances whose compositions correspond to $C_4H_4NBX_2$. The latter are obviously trimeric N, N', N''-(β-halogenoethyl)-B, B', B''-trihalogenoborazoles (IV), or other corresponding polymers V.


III IV (3)

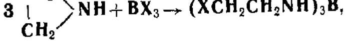
Use of a molar ratio I: $BX_3$ = 2:1 gives bis(β-halogenoethylamino)borhalide (VI), which also readily loses a molecule of hydrogen halide with conversion to polymers or, possibly, to a borazole derivative VII:

X = Cl(a), Br(b)

$$\underset{VI}{(XCH_2CH_2NH)_2BX} \xrightarrow{-HX} \underset{VII}{(C_4H_9BN_2X_2)_n}, \qquad (4)$$

Hydrogen halide is readily split out of III or VI even at room temperature, and is accompanied by evolution of heat.

Use of I: $BX_3$ in the ratio 3:1 gives tris(β-halogenoethylamino)borane (VIII) [15]:


VIII (5)

X = Cl(a), Br(b)

When heated under vacuum VIII can lose only one molecule of hydrogen halide. A solid substance of composition $C_6H_{14}N_3BX_2$ is formed.

VIII are solids which keep relatively well in sealed ampuls. They are gradually hydrolyzed by moist air, and on heating decompose with evolution of hydrogen halide. VIII is insoluble in the usual organic solvents. Water hydrolyzes them to boric acid.

## EXPERIMENTAL

**Starting materials.** Commercial 97–98% ethyleneimine was dried over Na and distilled. Bp 56°–57° C; $n_D^{20}$ 1.4120. Boron trichloride and boron tribromide were prepared by heating potassium tetrafluoroborate with aluminum chloride or bromide [16].

**Analysis.** All the substances analyzed were readily soluble in water. Their boron contents were determined by titrating a weighed amount with 0.05 N NaOH in the presence of mannite (naphtholphthalein indicator), or by refluxing a weighed amount of the substance with methanol or ethanol in the presence of conc $H_2SO_4$, distilling off trimethyl borate and alcohol, diluting the distillate with water, and titrating the boric acid in the usual way. Nitrogen was determined by the micro-dumas method, C and H by the micro-Pregl method, halogen by the Schoniger method. The IR spectra were determined by means of a UR-10 twin-beam spectrometer.

**Reaction of ethyleneimine (I) with $BCl_3$.**

a) Ratio I: $BCl_3$ = 1:1. A solution of 1.1 g (0.025 mole) I in 5 ml dry $CCl_4$ was added, with stirring, to a solution of 3.0 g (0.025 mole) $BCl_3$ in 20 ml $CCl_4$ cooled to −20° C.

The whole was stirred for 1 hr at that temperature, after which the precipitate was filtered off with suction. Even on the filter it evolved heat on warming up to room temperature, and decomposed with evolution of HCl. The viscous product of this reaction solidified some

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*For Part V see [1].

time later. Decomposition temperature was about 120° C. It was soluble in water (with hydrolysis), but insoluble in organic solvents, so that its molecular weight could not be determined. The composition was that of compound IVa or Va. Found: C 19.18; H 5.13; N 11.61; B 8.82; Cl 56.45%, calculated for $C_2H_4BCl_2N$: C 19.39; H 3.23; N 11.31; B 8.73; Cl 57.35%.

b) Ratio I: $BCl_3$ = 2:1. A solution of 3.32 g (0.077 mole) I in 10 ml $CCl_4$ was added to a solution of 4.53 g (0.038 mole) $BCl_3$ in 30 ml $CCl_4$ cooled to −20°. The white precipitate formed was filtered off. On warming up to room temperature it underwent spontaneous heating with evolution of HCl, then solidified. Melted with decomposition at 180−190° C. Found: C 26.24; H 5.89; N 15.48; B 6.44; Cl 46.00%, calculated for $C_4H_9BCl_2N_2$: C 28.78; H 5.41; N 16.79; B 6.49; Cl 42.58%. The composition of the substance approximated to that of VIIa. It was soluble (with hydrolysis) in water, but insoluble in ordinary organic solvents, making it difficult to purify, and impossible to determine its molecular weight.

c) Tris(β-chloroethylamino)borane (VIIIa) (ratio I: $BCl_3$ = 3:1). A solution of 2.21 g (0.52 mole) I in 50 ml $CCl_4$ was slowly added, with constant stirring, to a solution of 2.0 g (0.171 mole) $BCl_3$ in 150 ml $CCl_4$ cooled to −20° C. The precipitate formed was filtered off and washed first with $CCl_4$, then with hexane, and vacuum dried, yield of VIIIa 3.8 g (91%). On heating it softened at 140° C, and decomposed with the evolution of HCl at 190°−200° C. In air VIIIa gradually undergoes hydrolysis to a viscous mass. Water hydrolyzes it with the evolution of heat and formation of boric acid. It is readily solutble in EtOH, and to a limited extent in EtOAc, but it is insoluble in ordinary organic solvents. VIIIa could not be recrystallized. Found: C 28.34; H 6.38; N 16.84; B 4.28; Cl 44.03%, calculated for $C_6H_{15}BCl_3N_3$: C 29.23; H 6.14; N 17.06; B 4.39; Cl 43.20%.

0.5 g VIIIa was heated under vacuum (15 mm) to constant weight. The residue weighted 0.4 g, and had mp 235°−240° C, i.e. 0.1 g HCl came off (theoretical 0.11 g). Found: C 32.34; H 7.38; N 19.02; B 5.15; Cl 32.41%, calculated for $C_6H_{15}BCl_2N_3$: C 34.25; H 6.70; N 20.04; B 5.15; Cl 33.85%.

**Reaction between ethyleneimine (I) and $BBr_3$.** a) Ratio I: $BBr_3$ = 1:1. A solution of 0.4 g (0.093 mole) ethyleneimine in 3 ml $CCl_4$ was added with cooling to a constantly stirred solution of 2.3 g (0.092 mole) $BBr_3$ in 15 ml $CCl_4$ cooled to −15° C. After 1 hr the precipitate was filtered off. On warming up to room temperature it decomposed with heating and evolution of HBr. Yield 1.95 g, or 100% theoretical. It melted about 120° C with evolution of HBr. It composition corresponded to IVb or Vb. Found: C 11.80; H 3.53; N 7.09; B 5.06; Br 72.00%, calculated for $C_2H_4BBr_2N$: C 11.29; H 1.88; N 6.58; H 5.08; Br 75.20%.

b) Ratio I: $BBr_3$ = 2:1. A solution of 2.19 g (0.051 mole) I in 10 ml $CCl_4$ was added, with stirring, to a solution of 6.4 g (0.0255 mole) $BBr_3$ in 50 ml $CCl_4$ cooled to −20° C. After 1 hr the white precipitate was filtered off. At room temperature it decomposed with evolution of HBr. Yield 4.6 g (71.5%). The substance melted at 180°−190° C, with evolution of HBr. It dissolved in water with hydrolysis. Its elementary composition corresponded to that of VIIb. Found: C 17.89; H 4.10; N 9.59; B 4.21; Br 62.70%, calculated for $C_4H_9NBBr_2$: C 18.77; H 3.51; N 10.95; B 4.26; Br 62.54%.

c) Tris(β-bromoethylamino)boron (VIIIb) (ratio I: $BBr_3$ = 3:1). A solution of 2.15 g (0.05 mole) I in 20 ml $CCl_4$ was added, with stirring and cooling to −20° C, to a solution of 4.17 g (0.016 mole) $BBr_3$ in 50 ml $CCl_4$, after which the stirring at −20° C was continued for 2 hr more, and then the precipitate isolated by reverse suction filtration, washed twice with cold $CCl_4$ (50 ml portions), and vacuum dried to constant weight. Yield of VIIIb 6.3 g, or 100% theoretical. It was a white hygroscopic crystalline substance, which on heating to 170° C darkened, and evolved HBr with decomposition at 190°−200° C. It was gradually hydrolyzed in air. It was soluble in EtOH but insoluble in ordinary organic solvents. Found: C 18.21; H 3.88; N 11.25; B 2.88; Br 63.57%, calculated for $C_6H_{15}N_3BBr_3$: C 18.96; H 3.98; N 11.07; B 2.88; Br 63.11%. On heating under vacuum VIIIb lost one molecule of HBr. Found: C 22.69; H 4.96; N 12.72; B 3.44; Br 54.81%, calculated for $C_6H_{14}N_3BBr_2$: C 24.10; H 4.68; N 14.06; B 3.65; Br 53.53%.

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Institute of Organic Synthesis,
AS LatvSSR, Riga