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## Abstract

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## Chemistry

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# Polymethylene-bis-(alkylamino)-boronium Salts and 1-Alkylaminoboracycloalkanes

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One of the interesting properties of boron is its ability to form cationic complexes. Studies in recent years show that boronium salts are formed from organoboron chlorides ($^{1-4}$), boron halides ($^{5,6}$), chloroborane ($^{7}$), alkylmercaptoboranes ($^{3,8,9}$), and diborane ($^{6,10}$). Continuing investigations in this area of boron chemistry, we undertook a study of derivatives of cyclic boron compounds with respect to their tendency to be converted into boronium salts. The objects of study were 1-chloroboracyclopentane, 1-chloroboracycloheptane ($^{11}$), and 1-*n*-butylmercaptoboracyclopentane. It turned out that the chlorides of borocyclic compounds (I), under the action of amines, are converted, like noncyclic organoboron halides, into salts of polymethylene-bis-(alkylamino)-boronium (II) or into substitution products—alkylaminoboracycloalkanes (III), or simultaneously form both types of compounds. The course of the process in one direction or another, and the ratio of the reaction products, are determined chiefly by the nature of the amine and, to a lesser extent, by the nature of the organoboron compound.

$$(\mathrm{C\overset{\smile}{H}_2})_n\mathrm{BCl} + 2\mathrm{NH_2R} \longrightarrow \begin{cases} \left[(\mathrm{C\overset{\smile}{H}_2})_n\mathrm{B(NH_2R)_2}\right]^+ \mathrm{Cl}^- & (II) \\ (\mathrm{C\overset{\smile}{H}_2})_n\mathrm{BNHR} + \mathrm{NH_3RCl} & (III) \end{cases}$$

$$(I)$$

In the interaction of methyl- or ethylamine with 1-chloroboracyclopentane, an unambiguous course of the reaction is observed toward the formation only of the boronium salt—tetramethylene-bis-(alkylamino)-boronium chloride (IV).

$$\text{1-chloroboracyclopentane} + 2\mathrm{NH_2R} \longrightarrow \left[\text{tetramethylene-B}\!\begin{smallmatrix}/\ \mathrm{NH_2R} \\ \backslash\ \mathrm{NH_2R}\end{smallmatrix}\right]^+ \mathrm{Cl}^-$$

$$(IV)$$

$$\mathrm{R} = \mathrm{CH_3},\ \mathrm{C_2H_5}.$$

This direction of the reaction is also predominant in the interaction of methylamine with 1-chloroboracycloheptane; however, in this case, along with hexamethylene-bis-(methylamine)-boronium chloride ($V$, R = $CH_3$), a small amount of the substitution product—1-methylaminoboracycloheptane ($VI$, $R = CH_3$)—is formed:

$$\text{1-chloroboracycloheptane} + 2NH_2R \longrightarrow \left[\text{hexamethylene-B}\begin{matrix} / NH_2R \\ \backslash NH_2R \end{matrix}\right]^+ Cl^- + \text{1-RNH-boracycloheptane.}$$

$(V)$ $(VI)$

With an increase in the alkyl radical in the amine, the yield of the substitution product (III) increases, as is seen in the example of the reaction of 1-chloroboracycloheptane with *n*-butylamine, leading predominantly to the substitution product (60%). The course of the reaction is also affected by the ratio of the starting reagents. Thus, if the reaction of 1-chloroboracycloheptane with *n*-butylamine is carried out not at a ratio of 1:2, but at a ratio of 1:1.5, the main reaction product is hexamethylene-bis-(*n*-butylamino)-boronium ($V$, R = *n*-$C_4H_9$), and only 16% of the substitution product is obtained.

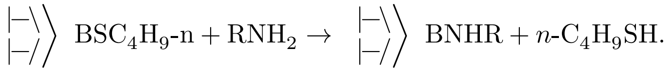
This fact confirms the conclusion that, in the process of substitution of the atom

halide to the alkylamino group, the boronium salt takes part. Such a mechanism is also supported by the ability of chlorohexamethylene-bis-(methylamine)-boronium to be converted, under the action of *n*-butylamine, into 1-*n*-butylaminoboracycloheptane. In this case, evidently, *n*-butylamine displaces a methylamine molecule from the cation and then abstracts a proton from the complex-bound molecule of *n*-butylamine. Under the influence of methylamine or triethylamine the indicated boronium salt undergoes no change. When allylamine acts on 1-chloroboracycloheptane the main reaction product is 1-allylaminoboracycloheptane (VI, R = $C_3H_5$), while with aniline only the substitution product—1-phenylaminoboracycloheptane (VI, R = $C_6H_5$)—is formed.

The size of the organoboron ring also has an effect on the course of the reaction. Thus, in contrast to 1-chloroboracyclopentane, 1-chloroboracycloheptane reacts with ethylamine to form not only the boronium salt but also the substitution product—1-ethylaminoboracycloheptane (30%).

1-Alkylaminoboracycloheptanes are colorless mobile liquids existing in monomeric form.

We have previously shown that the nature of the anion has a substantial effect on the stability of boronium salts ($^9$). Thus, mercaptides of bis-(alkylamine)-boronium are less stable than the corresponding chlorides. It was of interest to determine the influence of the nature of the anion on the stability of boronium salts with a cyclic grouping in the cation. For this purpose we undertook a study of the reaction of 1-*n*-butylmercaptoboracyclopentane with various amines. With all the amines taken for the study (dimethyl-, ethyl-, *n*-butyl, allylamine, aniline), the reaction proceeded with formation only of substitution products:



$$R = CH_3,\ C_2H_5,\ n\text{-}C_4H_9,\ C_3H_5,\ C_6H_5.$$

In contrast to the 1-alkylamino derivatives of boracycloheptane, 1-alkylaminoboracyclopentanes are prone to polymerization. Some of them, namely 1-ethylamino- and 1-phenylaminoboracyclopentane, already on short standing are converted into polymers insoluble in benzene and ether. The polymerization of 1-*n*-butylamino- and 1-allylaminoboracyclopentane proceeds more slowly. In the IR spectra of partially polymerized 1-*n*-butylaminoboracyclopentane, intense absorption bands are observed at 3420 $cm^{-1}$ and less intense ones at 3320 $cm^{-1}$.

## Experimental Part

**Action of amines on 1-chloroboracycloalkanes.** To 1-chloroboracycloalkane (0.05-0.1 mole) mixed with 150-200 ml of isopentane, 2-2.3 equivalents of amine were slowly added. The precipitate that separated was filtered off, washed with isopentane, and dried to constant weight. The solvent was distilled off from the filtrate, and the residue (1-(R-amino)-boracycloalkane) was distilled in vacuo.

**Chloride of tetramethylene-bis-(methylamine)-boronium.** From 10.2 g of 1-chloroboracyclopentane and 7 g of methylamine at −15° there were isolated 16.15 g (98.2%) of boronium salt, free of admixture of amine hydrochloride. M.p. 178–197° (with decomposition).

Found, %: C 43.60; H 10.97; B 6.62; Cl 21.48
$C_6H_{18}BN_2Cl$. Calculated, %: C 43.80; H 11.03; B 6.58; Cl 21.56

**Chloride of tetramethylene-bis-(ethylamine)-boronium.** From 5.3 g of 1-chloroboracyclopentane and 5.2 g of ethylamine at −15° there were obtained 9.63 g (97%) of boronium salt, m.p. 110–130° (with decomposition).

Found, %: C 49.97; H 11.71; B 5.60; Cl 18.40
$C_8H_{22}N_2BCl$. Calculated, %: C 49.90; H 11.52; B 5.62; Cl 18.41

**Hexamethylene-bis-(methylamino)-boronium chloride.** 9.13 g of 1-chloroboracycloheptane (12) and 4.9 g of methylamine were mixed at −70°. 12.2 g of a boronium salt were obtained, somewhat contaminated with the hydrochloride salt of the amine. For purification, the boronium salt was extracted with boiling chloroform. Found, %: C 50.06; H 11.45; B 5.67; Cl 18.90; $C_8H_{22}N_2BCl$. Calculated, %: C 49.90; H 11.52; B 5.62; Cl 18.41.

**Hexamethylene-bis-(ethylamino)-boronium chloride. 1-Ethylaminoboracycloheptane.** From 8.45 g of 1-chloroboracycloheptane and 6.1 g of ethylamine at −15°, 2.7 g of 1-ethylaminoboracycloheptane (30%) was obtained. The precipitate (10.7 g; found: Cl 17.6%), consisting of 70% boronium salt and 30% hydrochloride salt of the amine, was dissolved in chloroform and the amine hydrochloride was precipitated with ether; by partial evaporation of the filtrate the boronium salt was isolated in analytically pure form (11).

**Hexamethylene-bis-(n-butylamine)-boronium chloride. 1-Butylaminoboracycloheptane.** a) From 4.9 g of 1-chloroboracycloheptane and 6.6 g of *n*-butylamine (1 : 2.4) at 20°, 3.9 g of 1-*n*-butylaminoboracycloheptane (62%) was obtained. After extraction of the precipitate with ether, a pure boronium salt was isolated from the ether filtrate (11).

b) From 6.5 g of 1-chloroboracycloheptane and 7.4 g of *n*-butylamine (1 : 1.5) at −70°, 1-*n*-butylaminoboracycloheptane was obtained (15%, calculated on the amine taken), and a crystalline precipitate (10.2 g; found: Cl 16.3%) containing 83% boronium salt.

**1-Allylaminoboracycloheptane.** From 8.5 g of 1-chloroboracycloheptane and 9 g of allylamine at 20°, 6.6 g of precipitate and 7.3 g (74%) of 1-allylaminoboracycloheptane were obtained; as a result of fractional distillation, it was isolated in analytically pure form.

**1-Phenylaminoboracycloheptane.** In the experiment, 6.2 g of 1-chloroboracycloheptane and 8.9 g of aniline were taken; 7.7 g (82%) of 1-phenylaminoboracycloheptane was obtained. Mol. weight

**Table 1**

*N-Substituted 1-aminoboracycloalkanes* $(CH_2)_nBNRR'$

| $n$ | R | R′ | b.p., °C (mm Hg) | $n_D^{20}$ | $d_4^{20}$ | $MR$, found | $MR$, calc. | Found, % C | Found, % H | Found, % B | Calculated, % C | Calculated, % H | Calculated, % B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | H | $C_2H_5$ | 82.5–84.5 (16) | 1.4560 | 0.8460 | 45.30 | 44.52 | 68.94 | 13.35 | 7.73 | 69.10 | 13.05 | 7.78 |
| 6 | H | *n*-$C_4H_9$ | 58–58 (8) | 1.4454 | 0.8383 | 54.54 | 54.70 | 71.49 | 13.26 | 6.56 | 71.87 | 13.27 | 6.48 |

| $n$ | R | R′ | b.p., °C (mm Hg) | $n_D^{20}$ | $d_4^{20}$ | $MR$, found | $MR$, calc. | Found, % C | Found, % H | Found, % B | Calculated, % C | Calculated, % H | Calculated, % B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | H | $CH_2=CH-CH_2$ | 85.5–86 (17) | 1.4700 | 0.8630 | 48.82 | 49.48 | 71.65 | 12.08 | 7.27 | 71.56 | 12.01 | 7.16 |
| 6 | H | $C_6H_5$ | 90.5–91 (2) | 1.5458 | 0.9760 | 60.69 | 60.37 | 77.23 | 9.95 | 5.88 | 77.03 | 9.71 | 5.78 |
| 4 | $CH_3$ | $CH_3$ | 38–39 (24) | 1.4460 | 0.8167 | 36.26 | 36.28 | 65.21 | 12.66 | 9.74 | 64.90 | 12.71 | 9.75 |
| 4 | H | $C_2H_5$ | 37.5–38.5 (15) | 1.4452 | 0.8180 | 36.13 | 36.41 | 64.94 | 12.43 | 9.82 | 64.90 | 12.71 | 9.75 |
| 4 | H | $n$-$C_4H_9$ | 55 (8) | 1.4490 | 0.8227 | 45.31 | 45.10 | 68.22 | 13.67 | 7.94 | 69.09 | 13.05 | 7.79 |
| 4 | H | $CH_2=CH-CH_2$ | 37–38 (8) | 1.4513 | 0.8668 | 38.84 | 37.74 | 68.46 | 11.55 | 8.80 | 68.34 | 11.47 | 8.80 |
| 4 | H | $C_6H_5$ | 78.5–79 (3) | 1.5565 | 0.9840 | 52.20 | 51.97 | 75.24 | 8.79 | 6.93 | 75.52 | 8.87 | 6.89 |

found 187.3, calculated 187.2. In the experiment, 6.15 g (100%) of aniline hydrochloride was isolated.

**Action of *n*-butylamine on bis-(methylamino)-tetramethyleneboronium chloride.** To 6.5 g of the boronium salt, 12 g of *n*-butylamine was added. The salt dissolved on heating. After the excess *n*-butylamine was distilled off from the residue in vacuo, 3.7 g (66%) of *n*-butylaminoboracyclopentane was distilled off, b.p. 66–70° (12 mm). After repeated distillation the substance boiled at 57.5–58° (9.5 mm). Mol. wt. found 142, calculated 139. After several days the substance thickened. Mol. wt. found 390.

**Action of amines on 1-*n*-butylmercaptocyclopentane.** The reaction of 1-*n*-butylmercaptoboracyclopentane (13) with amines was carried out by gradual addition, at 20°, to thioether of amine in a ratio of 1:1.3–1.5 and was accompanied by slight warming. After heating the reaction mixture for 1.5–3 h at 50° and subsequent fractional distillation, 1-alkylaminoboracyclopentanes were obtained in yields of 62–65%. Molecular weights were determined cryoscopically in benzene.

**1-Ethylaminoboracyclopentane.** The reaction was carried out with 3.3 g of ethylamine and 7.8 g of 1-*n*-butylmercaptoboracyclopentane. 3.65 g of 1-ethylaminoboracyclopentane was obtained as a mobile liquid, which soon began to thicken. After one day the mol. wt. found was 337; for the monomeric form calculated 111. After two weeks the substance had turned into a polymer insoluble in benzene and ether, m.p. 60–63°.

**1-*n*-Butylaminoboracyclopentane.** From 8.5 g of *n*-butylamine and 11.85 g of 1-*n*-butylmercaptoboracyclopentane, 6.82 g of 1-*n*-butylaminoboracyclopentane was obtained. Mol. wt. found 143; $C_8H_{18}BN$; calculated 139. After three days the mol. wt. found was 410.

**1-Allylaminoboracyclopentane.** From 7.5 g of allylamine and 13.6 g of 1-*n*-butylmercaptoboracyclopentane, 6.5 g of a substance was obtained, which on standing turns into a viscous liquid. Mol. wt. found 352; calculated for the monomeric form 123.

**1-Phenylaminoboracyclopentane.** From 7.8 g of aniline and 9.9 g of 1-butylmercaptoboracyclopentane, 6.3 g of a substance was obtained in the form of a mobile liquid, which on standing turns into a solid polymer (m.p. 68–75°) insoluble in ether and hydrocarbons.

**1-Dimethylaminoboracyclopentane.** From 6.8 g of dimethylamine and 11.2 g of 1-*n*-butylmercaptoboracyclopentane, 5.6 g (73%) of the substance was obtained as a colorless mobile liquid. Mol. wt. found 109, calculated 111. On standing, the molecular weight of the substance does not change.

The physical properties of the N-substituted 1-aminoboracycloalkanes obtained are given in Table 1.

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*Note: Figure translations are in progress. See original paper for figures.*