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Abstract

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ON THE ACTION OF AMINES AND AMMONIA ON ISOAMYLBORON DICHLORIDE

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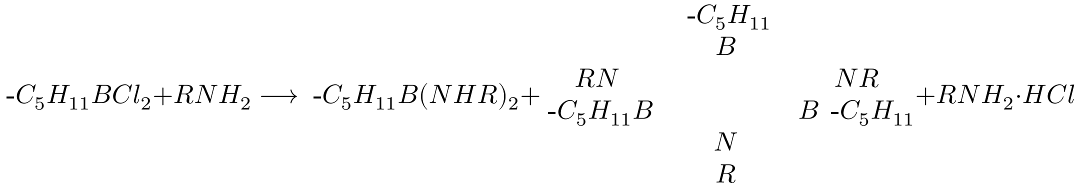
The study of reactions between phenylboron dichloride and amines showed that their course is determined by the nature of the amine. Under the action of ethylamine on phenylboron dichloride, phenyl-bis(ethylamino)boron and B-triphenyl-N-triethylborazole are formed. With aniline, phenylboron dichloride gives only phenyl-bis(phenylamino)boron (^{1}); under the action of ammonia, the dichloride is smoothly converted into B-triphenylborazole (^{2}).

It was of interest to study the behavior of alkylboron dichlorides with respect to amines and ammonia. Isoamylboron dichloride, prepared by the previously described method consisting in the action of phosphorus pentachloride on esters of alkylboronic acids (^{3}), was chosen as the object of investigation.

Under the action of ethylamine, isoamylboron dichloride is converted into isoamyl-bis(ethylamino)boron ((I), $R = C_2H_5$) and B-triisoamyl-N-triethylborazole ((II), $R = C_2H_5$). The reaction with isobutylamine proceeds analogously; as a result, isoamyl-bis(isobutylamino)boron ((I), $R =$ -C_4H_9) and B-triisoamyl-N-isobutylborazole ((II), $R =$ -C_4H_9) are obtained. The course of the reactions is expressed by the following scheme:

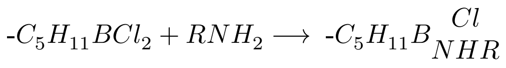


$$\text{-}C_5H_{11}BCl_2 + RNH_2 \longrightarrow \text{-}C_5H_{11}B(NHR)_2 + \underset{\text{-}C_5H_{11}B}{RN}\ \overset{\overset{\text{-}C_5H_{11}}{B}}{\underset{\underset{R}{N}}{\quad}}\ \underset{B\ \text{-}C_5H_{11}}{NR} + RNH_2{\cdot}HCl$$

(I) (II)

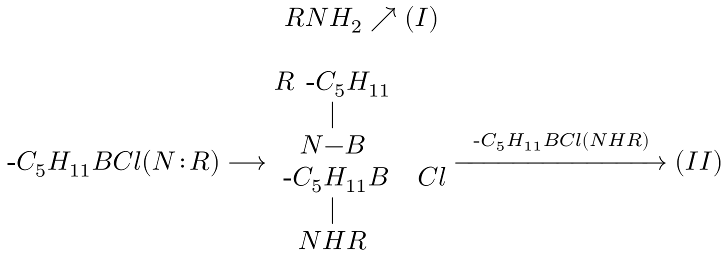
$R = C_2H_5,$ -C_4H_9

At the first stage of the process, evidently, alkyl-alkylaminochloroboron (III) is formed, which then reacts both with the next molecule of amine to form (I) and condenses to borazole (II):



$$\text{-}C_5H_{11}BCl_2 + RNH_2 \longrightarrow \text{-}C_5H_{11}B\begin{matrix}Cl\\NHR\end{matrix}$$

(III)



$$\text{-}C_5H_{11}BCl(N\!:\!R) \longrightarrow \begin{matrix} R\ \text{-}C_5H_{11} \\ | \\ N-B \\ \text{-}C_5H_{11}B \quad Cl \\ | \\ NHR \end{matrix} \xrightarrow{\text{-}C_5H_{11}BCl(NHR)} (II), \qquad RNH_2 \nearrow (I)$$

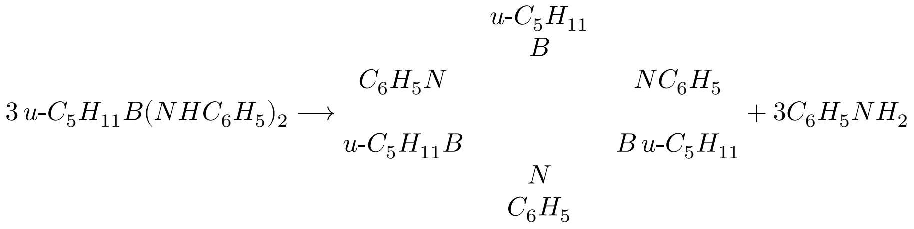
Substituted alkylboron amines had previously been obtained by one of us and T. A. Shchegoleva by the action of amines on esters of alkylchloroboronic acids (4). The synthesized borazole derivatives are the first representatives of unsymmetrical hexaalkylborazoles.

Under the action of aniline, isoamylboron dichloride forms isoamyl-bis(phenylamino)boron (IV).

$$\text{-}C_5H_{11}BCl_2 + 4C_6H_5NH_2 = \text{-}C_5H_{11}B(NHC_6H_5)_2 + 2C_6H_5NH_2 \cdot HCl$$

(IV)

The latter, at 300-360°, is converted in good yield into B-triisoamyl-N-phenylborazole (V), which is a representative of the hitherto unknown B-trialkyl-N-triarylborazoles.



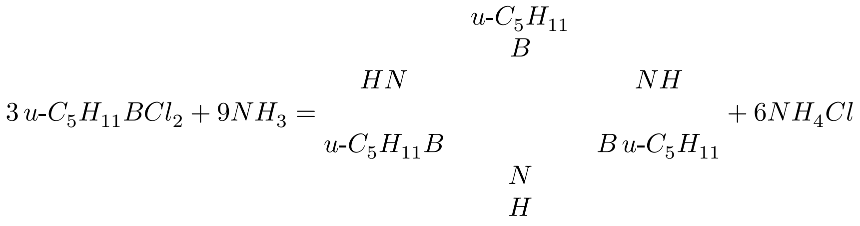
(V)

The reaction between isoamylboron dichloride and diethylamine proceeds with the formation of isoamyl-bis(diethylamino)boron (VI).

$$u\text{-}C_5H_{11}BCl_2 + 4NH(C_2H_5)_2 = u\text{-}C_5H_{11}B\left[N(C_2H_5)_2\right]_2 + 2(C_2H_5)_2NH \cdot HCl$$

$$(VI)$$

When ammonia is passed into an ethereal solution of isoamylboron dichloride, B-triisoamylborazole (VII) is formed.



$$3\,u\text{-}C_5H_{11}BCl_2 + 9NH_3 = \begin{array}{ccccc} & & u\text{-}C_5H_{11} & & \\ & & B & & \\ & HN & & NH & \\ & u\text{-}C_5H_{11}B & & B\,u\text{-}C_5H_{11} & \\ & & N & & \\ & & H & & \end{array} + 6NH_4Cl$$

$$(VII)$$

B-trialkyl compounds of borazole had previously been obtained by heating alkyldiboranes and borotrialkyls with ammonia at 200-330° (5). But and Kraus (6) note that, under the action of sodium in liquid ammonia on *n*-butylboron dichloride, they obtained butylborimine, probably in the form of a polymer.

Experimental Part

All operations were carried out in a nitrogen atmosphere.

1. Esters of isoamylboronic acid

Esters of isoamylboronic acid were obtained by the method of Snyder et al. (7), by the action of isoamylmagnesium chloride on trimethyl borate, followed by esterification of isoamylboronic acid with the corresponding alcohols.

Isobutyl ester of isoamylboronic acid was obtained in 50% yield of the theoretical. B.p. 105-106°/12.2 mm, d_4^{20} 0.8167; n_D^{20} 1.4156.

Found, %:	C 68.43;	68.54;	H 12.69;	12.55;	B 4.67;	4.74
$C_{13}H_9BO_2$. Calculated, %:	C 68.42;	H 12.79;	B 4.74			

Cyclohexyl ester of isoamylboronic acid was obtained in 40% yield of the theoretical. B.p. 146.5-147° (5.5 mm); d_4^{20} 0.9137; n_D^{20} 1.4600.

Found, %: C 73.01; 72.94; H 11.99; 11.86; B 3.64; 3.44
$C_{13}H_{33}BO_2$. Calculated, %: C 72.91; H 11.79; B 3.86

2. Isoamylboron dichloride

To 102.7 g (0.45 mole) of the isobutyl ester of isoamylboronic acid, 187.5 g (0.9 mole) of phosphorus pentachloride was added gradually, with stirring, over the course of 3 hours. The first half of the chloride entered into reaction with self-heating; subsequently the reaction mixture was heated. After the addition of PCl_5 was complete, the reaction mixture was boiled for 1.5 hours and then subjected to fractional distillation on a column.

43 g (61%) of isoamylboron dichloride was obtained, b.p. 124–125.5°; d_4^{20} 0.9940.

Found, %: C 39.45; 39.48; H 7.34; 7.26; B 7.10; 6.92; Cl 45.95
$C_5H_{11}BCl_2$. Calculated, %: C 39.28; H 7.26; B 7.07; Cl 46.39

The substance ignites in air.
In the experiment, 60.9 g of isobutyl chloride and 123.4 g of $POCl_3$ were obtained.

3. Isoamyl-bis(ethylamino)boron

B-Triisoamyl-N-triethylborazole. To 20.1 g (0.13 mole) of isoamylboron dichloride, cooled to −40°, 50 ml of ether was slowly added with stirring. The resulting ethereal solution was added over 45 min to a stirred mixture of 35.2 g (0.77 mole) of ethylamine and 300 ml of ether, cooled to −50°. The reaction mixture was left overnight. The separated ethylamine hydrochloride (19.6 g) was filtered off, the solvent was distilled off, and the residue was fractionated. Obtained:

1) 7.1 g (31.6%) of isoamyl-bis(ethylamino)boron, b.p. 94–94.5°/19 mm, d_4^{20} 0.8040; n_D^{20} 1.4337.

Found, %: C 63.53; 63.76; H 13.57; 13.56; B 6.40; 6.73
$C_9H_{23}N_2$. Calculated, %: C 63.55; H 13.62; B 6.36

2) 7.5 g (47.7%) of B-triisoamyl-N-triethylborazole, crystallizing on standing. B.p. 113-114°/0.06 mm, m.p. 43–45°.

Found, %: C 67.00; 67.03; H 12.83; 12.70; B 8.55; 8.54
$C_{21}H_{48}B_3N_3$. Calculated, %: C 67.24; H 12.90; B 8.66

M found 384, calculated 375.
The substance is readily soluble in ether, benzene, and isopentane; stable in air.

4. Isoamyl-bis(isobutylamino)boron

B-Triisoamyl-N-triisobutylborazole. In an experiment carried out as described above, 19.7 g (0.13 mole) of isoamylboron dichloride and 44 g (0.61 mole) of isobutylamine were taken. The following compounds were obtained:

1) 11.1 g (38.1%) of isoamyl-bis(isobutylamino)boron, b.p. 112–113° (7 mm); d_4^{20} 0.8028; n_D^{20} 1.4381.

Found, %: C 69.30; 69.14; H 13.67; 13.74; B 4.74; 4.78
$C_{13}H_{31}BN_2$. Calculated, %: C 69.02; H 13.81; B 4.78

2) 9.6 g (50.4%) of B-triisoamyl-N-triisobutylborazole, b.p. 126–128°/0.06 mm, m.p. 53–55°.

Found, %: C 70.21; 70.20; H 12.95; 12.94; B 7.36; 7.38
$C_{27}H_{60}B_3N_3$. Calculated, %: C 70.61; H 13.17; B 7.07

M found 458, calculated 459.
In the experiment, 26.5 g of isobutylamine hydrochloride was obtained.

5. Isoamyl-bis(diethylamino)boron

The experiment was carried out analogously to those described above. 14 g (0.09 mole) of isoamylboron dichloride and 30 g (0.41 mole) of diethylamine were taken. 17.1 g of diethylamine hydrochloride and 10.4 g (50%) of isoamyl-bis(diethylamino)boron were obtained, b.p. 103–104°/9 mm; d_4^{20} 0.8192; n_D^{20} 1.4488.

Found, %: C 68.59; 68.32; H 13.48; 13.51; B 5.14; 5.14
$C_{13}H_{31}BN_2$. Calculated, %: C 69.02; H 13.81; B 4.78

6. Isoamyl-bis(phenylamino)boron

To a solution of 46.9 g (0.504 mole) of aniline in 300 ml of ether, a mixture of 19.1 g (0.125 mole) of isoamylboron dichloride and 50 ml of ether was added with stirring over the course of one hour at 0°. The reaction mixture was then stirred at room temperature for 2 hours. The precipitate of aniline hydrochloride (31 g) was washed twice with ether and extracted many times with hot benzene. The solvents were distilled off from the filtrate and the residue was heated for one hour at 90°; the small amount of aniline hydrochloride precipitate that separated was filtered off, and the filtrate was subjected to fractional distillation. 18.8 g of isoamyl-bis(phenylamino)boron (46.6%) was obtained, with b.p. 142–143°/0.07 mm; d_4^{20} 0.9954; n_D^{20} 1.5700.

Found, %: C 76.88; 76.61; H 8.68; 8.59; B 4.07; 3.98
$C_{17}H_{23}BN_2$. Calculated, %: C 76.70; H 8.71; B 4.07

7. B-Triisoamyl-N-triphenylborazole

Isoamyl-bis(phenylamino)boron (11.1 g), placed in a flask with a descending condenser, was heated on a metal bath. At 300° distillation of aniline began; subsequently the temperature of the bath was gradually raised (over 2 hours) to 365°. 3 g of aniline distilled off. The residue, which crystallized at room temperature, was distilled in vacuum. 6 g (83.3%) of a yellow, rapidly solidifying substance was obtained, with b.p. 178–185°/0.03 mm. After redistillation, B-triisoamyl-N-triphenylborazole had b.p. 180–181°/0.03 mm, m.p. 93.5–95.5°.

Found, %: C 76.45; H 9.45; B 6.34
$C_{33}H_{48}B_3N_3$. Calculated, %: C 76.33; H 9.32; B 6.25

M found 475, calculated 519.
The substance is readily soluble in ether, benzene, and isopentane.

8. B-Triisoamylborazole

A stream of dry ammonia was passed through an ethereal solution of isoamylboron dichloride (6.8 g in 150 ml of ether), cooled to −50°. The reaction mixture was then stirred for one hour at room temperature; the precipitated ammonium chloride (4.4 g) was filtered off and washed with ether. The ether was distilled off from the filtrate, and the residue was distilled. 2.1 g (48.7%) of B-triisoamylborazole was obtained as a colorless liquid, with b.p. 114–115.5°/0.1 mm; d_4^{20} 0.8485; n_D^{20} 1.4538.

Found, %: C 62.07; 61.80; H 12.43; 12.61; B 10.84
$C_{15}H_{36}B_3N_3$. Calculated, %: C 61.93; H 12.47; B 11.16

M found 282, calculated 291.

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