ORGANIC AND BIOLOGICAL CHEMISTRY

ORGANOBORON COMPOUNDS

COMMUNICATION 162. INTERNAL-COMPLEX 3-AMINOPROPYLBORON COMPOUNDS*

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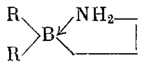
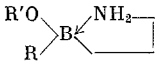
It is known that esters formed by boron acids with α- and β-amino alcohols have a chelate structure with an internal coordinate link B←N and therefore have enhanced stability [1]. We have recently prepared organoboron internal-complex compounds of a new type — dialkyl(3-aminopropyl)boranes (I) (by the hydroboration of allylamine with tetraalkyldiboranes or by the action of allylamine on trialkylboranes [2, 3]) and the related alkyl(3-aminopropyl)borinic acids and their esters (II) (by the action of water or glycols on alkylazaborolidines [4]).†

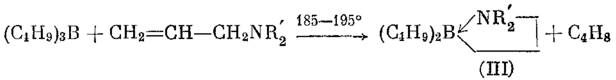




(II)

(Ia) $R = n\text{-}C_3H_7$; (Ib) $R = n\text{-}C_4H_9$.

In the present work we have prepared a number of new compounds of this type with the object of making a further study of their properties and, in particular, of determining the effect of substituents on the boron and nitrogen atoms on the stability of the coordinate link B←N. The reaction of N,N-dimethylallylamine and of N,N-diethylallylamine with tributylborane gives, respectively, dibutyl[3-(dimethylamino)propyl]borane (IIIa) and dibutyl[3-(diethylamino)propyl]borane (IIIb), the second of which we have already described [3].



$$(C_4H_9)_3B + CH_2{=}CH{-}CH_2NR'_2 \xrightarrow{185-195^\circ} (C_4H_9)_2B\overset{NR'_2}{\lessdot}\!\!] + C_4H_8 \qquad (1)$$

(III)

(IIIa) $R'{=}CH_3$; (IIIb) $R'{=}C_2H_5$.

Whereas (IIIa) was obtained in 77% yield, the yield of (IIIb) usually did not exceed 55-65%, and in the latter case, together with the main product, unchanged tributylborane and a high-boiling fraction with a higher nitrogen content than (IIIb) {probably butylbis[3-(dimethylamino)propyl]borane} were isolated. This points to the partial disproportionation of (IIIb) under the conditions of the experiment, though at a lower temperature this does not occur, and (IIIb) can be vacuum-distilled without change. (3-Aminopropyl)dibutylborane (Ib) [2] is stable to long keeping in air, (IIIa) slowly changes under these conditions, and (IIIb) is rapidly oxidized. Hence, with respect to stability to oxidation these compounds must be placed in the following series (IIIb) < (IIIa) < (Ib), whereas in their tendency to undergo disproportionation they fall in the reverse order. These data indicate a diminution in the stability of the coordinate link B←N along the series (Ib) > (IIIa) > (IIIb), probably as a result of steric hindrance due to the alkyl groups on the nitrogen atom. (IIIa) and (IIIb) were also prepared by the addition of an ethereal solution of tetrabutyldiborane to the corresponding allylamines

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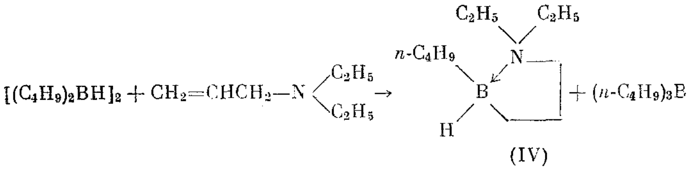
† [3-(Dimethylamino)propyl]borane has also been described: it was synthesized from trimethylamine-borane and N,N-dimethylallylamine [5].

$$\tfrac{1}{2}[(C_4H_9)_2BH]_2 + CH_2 = CHCH_2NR_2' \rightarrow (III) \qquad (2)$$

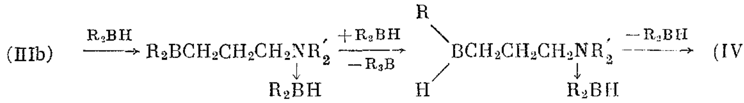
When tetrabutyldiborane and N,N-diethylallylamine were mixed in the reverse order, as main reaction products we unexpectedly isolated butyl[3-(diethylamino)propyl]borane (IV) in 62% yield and tributylborane, and



(3)

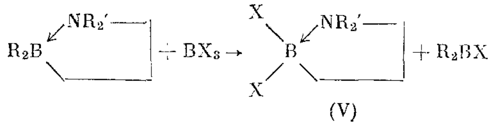
only a very small amount of (IIIb) was obtained. (IV) is a peculiar complex between dialkylborane and a tertiary amine. When (IV) is treated with alcohols and thiols, even at room temperature, hydrogen is liberated. The infrared spectrum of (IV) contains an intense absorption band with its maximum at 2312 cm^{-1} corresponding to the stretching vibrations of the B—H bond. The lowering of the vibration frequency of the B—H bond in (IV), as compared with the vibration frequency of the terminal B—H bond in alkyldiboranes, is to be explained by internal coordination between boron and nitrogen atoms.

The formation of (IV) may be explained as follows: (IIIb) is formed at first and then reacts, in accordance with the following scheme, with excess of tetraalkyldiborane, for the complex-forming power of trialkylboranes is less than that of alkylboranes:



(4)

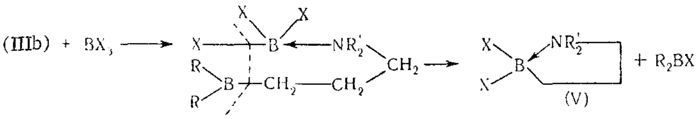
By the action of boron trichloride or tribromide on (III) we obtained the internal-complex [3-(dialkylamino)propyl]dihaloboranes (Va), (Vb), and (Vc):



(5)

(Va) $R=C_4H_9$ $R'=CH_3$; $X=Cl$; (Vb) $R=C_4H_9$; $R'=C_2H_5$; $X=Cl$; (Vc) $R=C_4H_9$, $R' = C_2H_5$; $X=Br$

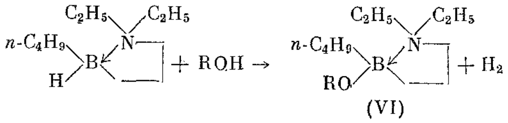
The reaction was conducted at room temperature by passing the boron halide into (III). A considerable amount of heat was liberated. It is probable that the boron halides, as the stronger Lewis acids, break the coordinate link between boron and nitrogen in (III) with formation of a complex, which then, when heated in a vacuum, breaks down into (V) and the dialkylhaloborane:



(6)

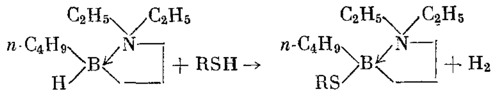
[3-(Dialkylamino)propyl]dihaloboranes are while crystalline substances which deliquesce in air.

Using (IV) as our starting substance we prepared other internal-complex boron compounds. Thus, by the action of alcohols and thiols (IV) was converted into butyl[3-(diethylamino)propyl]borinic esters (VI) and butyl[3-(diethylamino)propyl]thioborinic esters (VII):



(7)

$R = C_2H_5$

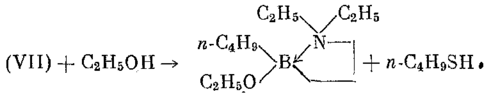


(VII)

(8)

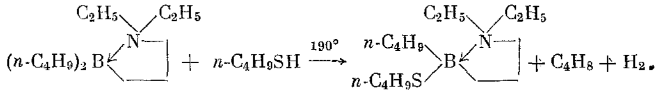
R = n-C_4H_9

When treated with ethanol, (VII) was converted into (VI) with elimination of 1-butanethiol:



(9)

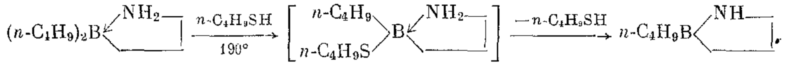
The presence of internal coordination in (VI) and (VII) is indicated by a number of properties of these substances: their relative stability to disproportionation, the noncorrespondence of the experimentally found molecular refraction with that calculated without taking account of the coordinate link B ← N, and their high refractive indices. (VII) was also prepared independently from (IIIb) and 1-butanethiol at 190°:



(10)

It is known that trialkylboranes react with thiols even at room temperature [9]. The high stability of (IIIb), which like trialkylboranes contains three B—C bonds, is to be explained by its stabilization by the internal coordination between the boron and nitrogen atoms.

(Ib) also reacts with thiols only at high temperature, but the intermediately formed (3-aminopropyl)butylthioborinic ester is immediately converted into 2-butyl-1,2-azaborolidine with elimination of 1-butanethiol:



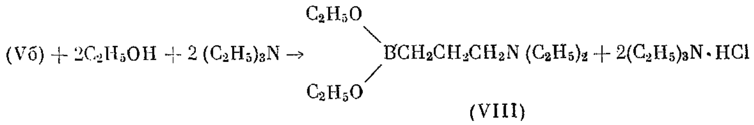
(11)

As will be seen from the scheme (11), to bring about this reaction only the presence of catalytic amounts of the thiol is necessary.

It may be supposed that in (VI) and (VII) the stability of the coordinate link is less than in (III) as a result of the diminution in the acceptor power of the boron atom. This is confirmed by the results of dipole moment measurements:

Compound	(Ib)	(IIIa)	(IIIb)	(VI)
Dipole moment, D	4.20	4.00	4.00	2.53

In keeping with the values of the dipole moments of coordination compounds of boron (4.0-6.5 D), the dipole moments of (Ib), (IIIa), and (IIIb) are 4.0-4.2 D. The much lower dipole moment of (VI) indicates a substantial weakening of the coordination. In the case of (VIII), which was prepared from (Vb) by the action of ethanol in presence of triethylamine [Eq. (12)], it is probable that internal coordination is absent, which



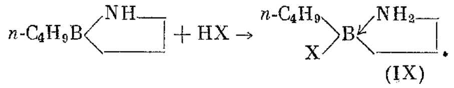
$$(Vb) + 2C_2H_5OH + 2(C_2H_5)_3N \rightarrow (C_2H_5O)_2BCH_2CH_2CH_2N(C_2H_5)_2 + 2(C_2H_5)_3N \cdot HCl \qquad (12)$$

(VIII)

is evidenced by the low value of the dipole moment (1.44 D). This shows itself in other properties of (VIII). For example, the boiling point of (VIII) is much lower than the boiling points of (Ib), (IIIa), and (IIIb), the refractive index (1.4243) differs greatly from the refractive indices of (Ib) (1.4672) and (IIIb) (1.4750), and the value found for the molecular refraction corresponds to the calculated value.

Hence, the stability of the internal coordinate link between the boron and nitrogen atoms is determined by the same factors as that of the usual coordinate link in complex compounds of boron. Actually, trialkylboranes, as is well known, have a higher complex-forming power than boron esters and thio esters, but the basicity of tertiary amines toward organoboron compounds falls with increase in the size of the alkyl groups attached to nitrogen.

As already stated, internal-complex compounds of the type under consideration may be prepared from alkylazaborolidines. As in the case of the action of water or alcohols [4], by the action of hydrogen chloride and of acetic acid on 2-butyl-1,2-azaborolidine the internal-complex compounds (3-aminopropyl)butylchloroborane (IXa) and acetoxy(3-aminopropyl)butylborane (IXb) are formed, respectively:

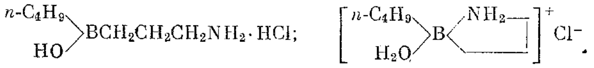


(13)

(IXa) X=Cl; (IXb) X=CH_3COO^-

The infrared spectrum of concentration solutions of (IXb) in CCl_4 contains a band with a maximum at 1588 cm^{-1} corresponding to the deformation vibrations of the NH_2 group and also bands with maxima at 3350, 3240, and 3350 cm^{-1} corresponding to the stretching vibrations of N—H bonds in free and associated molecules. On dilution of solutions of (IXb) in CCl_4 down to about 1% the absorption bands of associated N—H groups (3240 and 3355 cm^{-1}) disappear. The spectra of (IXa) and (IXb) are very similar to one another. The association which occurs here is probably due to the formation of intermolecular hydrogen bonds.

With water (IXa) forms a white crystalline substance corresponding in analysis to a 1 : 1 addition product. The structure of this adduct may correspond to one of the formulas cited:



EXPERIMENTAL

Dibutyl[3-(diethylamino)propyl]borane (IIIb). 25.4 g of N,N-diethylallylamine was added slowly to 37.7 g of tributylborane at 185°. The reaction mixture was then heated at this temperature until no more gas was liberated. In the distillation we obtained: 10.8 g of tributylborane, b.p. 65-67° (3.5 mm), n_D^{20} 1.4290; 27.2 g (55%) (IIIb), b.p. 117-120° (1.5 mm); n_D^{20} 1.4750; 8.8 g of a fraction of b.p. 125-165° (1.5 mm), from which we isolated a substance of b.p. 120-122° (0.1 mm) and n_D^{20} 1.4798 {probably butylbis[3-(diethylamino)propyl]borane}. Found %: N 9.87. $C_{18}H_{41}BN_2$. Calculated %: N 9.50.

11.6 g of tetrabutyldiborane was added dropwise with stirring to an ethereal solution of 8.3 g of N,N-diethylallylamine. In the distillation we obtained 11.5 g (66%) of (IIIb), b.p. 117-118° (1.5 mm), and also a lower-boiling fraction {a mixture of tributylborane and butyl[3-(diethylamino)propyl]borane}. By the oxidation of 12.1 g of (IIIb) with hydrogen peroxide in an alkaline medium we isolated 5 g of n-butyl alcohol of 97% purity [this indicates that (IIIb) contains not more than 3% of isomers containing s-butyl groups]. Products of the oxidation of the 3-(diethylamino)propyl group were not isolated.

Dibutyl[3-(dimethylamino)propyl]borane (IIIa). From 29.5 g of tributylborane and 13.8 g of N,N-dimethylallylamine at 185°, we obtained 26.3 g (77%) of (IIIa); b.p. 98-100° (2 mm); n_D^{20} 1.4658; d_4^{20} 0.8379. Found %: C 73.96; H 14.27; B 5.13. $C_{13}H_{30}RN$. Calculated %: C 73.92; H 14.32; B 5.12. 3.6 liters of butenes was isolated in the experiment.

28.7 g of tetrabutyldiborane was added dropwise with stirring to 19.7 g of N,N-dimethylallylamine in 70 ml of ether. The reaction mixture was then boiled for 1 h. In the distillation we obtained 36.8 g (76.6%) of (IIIa); b.p. 95-98° (2 mm); n_D^{20} 1.4655.

Butyl[3-(diethylamino)propyl]borane (IV). 22.2 g of N,N-diethylallylamine was added dropwise with stirring to an ethereal solution of 24.7 g of tetrabutyldiborane (70 ml). In the distillation of the reaction products we obtained: 10.5 g (58.5%) of tributylborane, b.p. 85-95° (7 mm); n_D^{20} 1.4260; 11.1 g (62%) of (IV), b.p. 93-100° (2 mm), which after redistillation had b.p. 98-100° (2 mm); n_D^{20} 1.4650; d_4^{20} 0.8469. Found %: C 72.60; H 14.25; B 5.99. $C_{11}H_{26}BN$. Calculated %: C 72.14; H 14.30; B 5.91. 9.0 g of a fraction of b.p. 125-135° (2 mm) and n_D^{20} 1.4689, which consisted mainly of (IIIb).

Dichloro[3-(diethylamino)propyl]borane (Vb). 27.0 g of boron trichloride was passed into 35.4 g of dibutyl[3-(diethylamino)propyl]borane (much heat was evolved). In the distillation of the reaction products we obtained 18.5 g (78%) of dibutylchloroborane, b.p. 65-67° (15 mm) and n_D^{20} 14231 {the literature [7] gives: b.p. 60° (12 mm); n_D^{20} 1.4243}, and 25.3 g (87%) of dichloro[3-(diethylamino)propyl]borane, b.p. 110-116° (0.2 mm), which solidified to a white crystalline mass. The crystals were transferred to a filter and washed with isopentane; m.p. 69-71.5°. Found %: C 42.99; H 8.39; B 5.68; Cl 36.14; mol.wt. 210 (cryoscopically in benzene). $C_7H_{16}BNCl_2$. Calculated %: C 42.89; H 8.18; B 5.52; Cl 36.21; mol.wt. 196.

Dibromo[3-(diethylamino)propyl]borane (Vc). With continuous stirring 27.4 g of boron tribromide was added dropwise to 23.1 g of (IIIb). The reaction mixture was then heated for 30 min at 40°. In the distillation we obtained 18.8 g (85.5%) of bromodibutylborane, b.p. 49-51° (1.5 mm) and n_D^{20} 1.4465, and 25.0 g (91%) of (Vc), b.p. 135-140° (0.1 mm); m.p. 111-118°. Found %: C 29.41; H 5.73; B 3.87; Br 56.24. mol.wt. 293. $C_7H_{16}BNBr_2$. Calculated %: C 29.51; H 5.67; B 3.80; Br 56.10; mol.wt. 285.

Dichloro[3-(dimethylamino)propyl]borane (Va). 24.4 g of boron trichloride was passed into 30.7 g of dibutyl[3-(dimethylamino)propyl]borane. The reaction mixture was heated in a vacuum, and dibutylchloroborane slowly distilled off (14.4 g, 62%); on redistillation it had b.p. 50° (9 mm). The crystalline residue of dichloro[3-(dimethylamino)propyl]borane (12.4 g, 51%) was transferred to a filter and carefully washed with isopentane. M.p. 176-182°. Found %: C 35.89; H 7.33; B 6.33; Cl 42.44. $C_5H_{12}BNCl_2$. Calculated %: C 35.75; H 7.20; B 6.44; Cl 42.27.

Butyl Butyl[3-(diethylamino)propyl]thioborinate (VII). 7.9 g of 1-butanethiol was added dropwise to 21.0 g of (IIIb) heated to 190°, and heating was continued at the same temperature until no more gases came off (hydrogen, butane, butene). In the distillation of the reaction products we obtained 13 g (55%) of (VII); b.p. 116-120° (0.1 mm); n_D^{20} 1.4968; d_4^{20} 0.9238. Found %: C 66.50; H 12.36. $C_{15}H_{24}BNS$. Calculated %: C 66.39; H 12.61.

9.6 g of 1-butanethiol was added dropwise at room temperature to 17.7 g of butyl[3-(diethylamino)propyl]borane. The temperature of the reaction mixture was raised slowly to 100°, and heating was continued until no more hydrogen came off (2.1 liters). In the distillation we obtained 21.2 g (81%) of (VII), b.p. 117 to 120° (0.1 mm), n_D^{20} 1.4980.

Action of 1-Butanethiol on (3-Aminopropyl)dibutylborane. With heating to 185°, 1-butanethiol was added dropwise to 20.0 g of (3-aminopropyl)dibutylborane. The temperature of the reaction mixture fell to 170°, after which the liberation of gas stopped (2 ml of 1-butanethiol was used). In the fractional distillation of the reaction mixture we obtained 5.7 g (42%) of 2-butyl-1,2-azaborolidine, b.p. 38-44° (7 mm) [8], and 7.2 g of unchanged (Ib), b.p. 98-104° (2 mm); n_D^{20} 1.4661.

Ethyl Butyl[3-(diethylamino)propyl]borinate (VI). 2 g of ethanol was added dropwise to 4.3 g of butyl[3-(diethylamino)propyl]borane. 540 ml of hydrogen was liberated. In the distillation we obtained 3.7 g (69.5%) of the ethyl ester, b.p. 86° (1 mm); n_D^{20} 1.4512; d_4^{20} 0.8576. Found %: C 68.67; H 13.29; B 4.90; MR_D 71.28; mol.wt. 218. $C_{13}H_{30}BNO$. Calculated %: C 68.72; H 13.31; B 4.76; MR_D 72.37; mol.wt. 227.

2.4 g of ethanol and 10.8 g of (VII) were mixed. On distillation we obtained 4.3 g of 1-butanethiol and 7.9 g (88%) of (VI).

Diethyl 3-(Diethylamino)-1-propaneboronate (VIII). 6.5 g of ethanol was added dropwise with constant stirring to a mixture of 11.4 g of (Vb) in 50 ml of benzene and 11.8 g of triethylamine. The reaction mixture was then heated for 1 h in a water bath at 60-70°. The crystalline precipitate of triethylamine hydrochloride was filtered off. Solvent was vacuum-distilled from the filtrate. In the distillation of the residue we obtained 6.5 g (52%) of the diethyl ester (VIII), b.p. 73-76° (3 mm); n_D^{20} 1.4243; d_4^{20} 0.8539. Found %: C 61.65; H 12.11; B 5.13; MR 64.30; mol.wt. 207. $C_{11}H_{26}BNO_2$. Calculated %: C 61.40; H 12.18; B 5.03; MR 64.29; mol.wt. 215.

(3-Aminopropyl)butylchloroborane (IXa). An ethereal solution of 7.8 g of HCl was added with stirring to 25.5 g of 2-butyl-1,2-azaborolidine [9]. Ether was driven off in a vacuum, and the viscous residue was distilled. We obtained 22.0 g (65.5%) of (IXa), b.p. 93-95° (2.5 mm); n_D^{20} 1.4898. The infrared spectrum contains an absorption band with a maximum at 1592 cm^{-1} corresponding to the deformation vibrations of the NH_2 group. Found %: C 52.26; H 10.49; B 6.77; Cl 21.59. $C_7H_{17}BNCl$. Calculated %: C 52.05; H 10.61; B 6.70; Cl 21.96.

Acetoxy(3-aminopropyl)butylborane (IXb). 5.5 g of glacial acetic acid was added slowly with stirring to 11.6 g of 2-butyl-1,2-azaborolidine. The reaction mixture was then heated at 60° in a water bath for 2 h. In the distillation we obtained 12.9 g (74%) of (IXb), b.p. 76-80° (0.2 mm); n_D^{20} 1.4601. Found %: C 59.19; H 11.08; B 5.69. $C_9H_{20}BNO_2$. Calculated %: C 58.40; H 10.89; B 5.85.

The dipole moments were determined from dielectric constant and density measurements carried out on an "Express Dipole" laboratory instrument (dielectric constants were measured by the beat method).

We thank A. N. Nikitina and V. Smorchkov for the determination of dipole moments.

CONCLUSIONS

1. A number of new organoboron compounds containing the 3-aminopropyl group were prepared.

2. The dipole moments of some of these compounds were measured to permit a comparative characterization of the stability of the internal coordinate link.

3. The replacement of hydrogen atoms on the nitrogen by alkyl groups lowers the stability of the coordinate link between boron and nitrogen atoms.

4. The introduction of a boron-attached alkoxy groups into the 3-aminopropyl compounds weakens the donor-acceptor interaction between boron and nitrogen atoms.

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