B. M. MIKHAILOV and V. A. DOROKHOV

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Abstract

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B. M. MIKHAILOV and V. A. DOROKHOV

ORGANOBORON COMPOUNDS

COMPLEX COMPOUNDS OF BORANE AND PHENYLBORANE WITH DIETHYLAMINE AND SOME OF THEIR TRANSFORMATIONS

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In the interaction of dimethylamine and diborane, Wiberg and co-workers (^{1}) obtained dimethylamine-borane, which on heating is converted into bis-(dimethylamino)-diborane. The same authors, by the action of diethylamine on diborane, isolated a colorless solid substance and assigned to it the structure of diethylamine-borane (^{1}). Recently, Berg and Good synthesized a series of complex compounds of borane with cyclic secondary amines and converted them into the corresponding aminoboranes (^{2}).

Investigating the reaction between diethylamine and diborane in an ether medium, we found that diethylamine-borane (I) is formed in 90% yield:

$$2(C_2H_5)_2NH + B_2H_6 \rightarrow 2(C_2H_5)_2NH \cdot BH_3.$$

(I)

Contrary to the data of Wiberg and co-workers (^{1}), I is not a crystalline substance, but a colorless liquid distilling in vacuum, stable at room temperature toward water and alcohols.

1,2-Diphenyldiborane behaves analogously with respect to diethylamine, being smoothly converted into diethylamine-phenylborane (II), which is considerably less thermally stable than I.

$$2(C_2H_5)_2NH + (C_6H_5BH_2)_2 \rightarrow 2(C_2H_5)_2NH \cdot H_2BC_6H_5.$$

(II)

Determination of the molecular weight of the obtained compounds I and II by the cryoscopic method indicates that in benzene solution they are associated. Probably, in the liquid state the association of these compounds is expressed to an even greater degree, as is indicated by the comparatively high boiling point of diethylamine-borane (I).

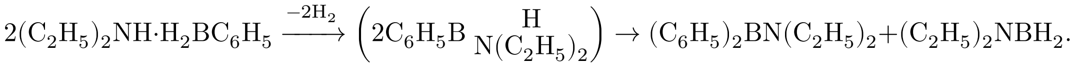
Diethylamine-borane (I) at 130–150° is smoothly converted, with liberation of hydrogen, into bis-(diethylamino)-diborane (III), which is a crystalline substance subliming in vacuum.

$$2(C_2H_5)_2NH\cdot BH_3 \rightarrow ((C_2H_5)_2NBH_2)_2 + 2H_2.$$

(I) (III)

III reacts hardly at all at room temperature with water and alcohols; above 60° it reacts at an appreciable rate.

Diethylamine-phenylborane (II), on heating (90–150°) in vacuum, is converted, with liberation of hydrogen, into a mixture of diphenyl-diethylamino-borane (V) and diethylamine-borane (VI):



$$2(C_2H_5)_2NH\cdot H_2BC_6H_5 \xrightarrow{-2H_2} \left(2C_6H_5B\begin{smallmatrix}H\\N(C_2H_5)_2\end{smallmatrix}\right) \rightarrow (C_6H_5)_2BN(C_2H_5)_2+(C_2H_5)_2NBH_2.$$

(II) (IV) (V) (VI)

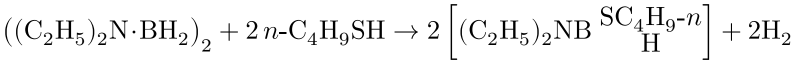
Diethylamine-borane (VI) was trapped in a receiver cooled to −70°, in the form of a mobile liquid which, on raising the temperature with warming, dimerizes into crystalline bis-(diethylamino)-diborane (III).

At the first stage of the pyrolytic process, evidently, phenyl-diethylamino-borane (IV) is formed, which then symmetrizes into (V) and (VI). The symmetrization reaction is reversible, and under conditions of removal of VI from the reaction sphere the equilibrium $IV \rightleftarrows V + VI$ is shifted completely to the right.

If pyrolysis of II is carried out at atmospheric pressure, then, along with diphenyldiethylaminoboron (V), a fraction is obtained that reacts vigorously with alcohol, with liberation of hydrogen. The same fraction is obtained on heating V and VI. According to analysis, this fraction is IV, probably with an admixture of III, from which it cannot be completely freed by distillation.

It is of interest that Burg and Boone investigated the disproportionation of methyldiethylaminoborane into dimethyl-(diethylamino)-boron and dimethylaminoborane and found that the process has an equilibrium character ([3]).

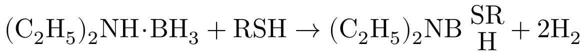
Bis-(diethylamino)-diborane reacts at 100° with *n*-butyl mercaptan to form *n*-butylmercapto-(diethylamino)-borane, which represents a new type of substituted borane.



$$((C_2H_5)_2N\cdot BH_2)_2 + 2\,n\text{-}C_4H_9SH \rightarrow 2\left[(C_2H_5)_2NB\begin{smallmatrix}SC_4H_9\text{-}n\\H\end{smallmatrix}\right] + 2H_2$$

(VIIa)

Alkylmercapto-(diethylamino)-boranes (VII) can be obtained in 85% yield directly by the action of mercaptans on diethylaminoborane at 100°.

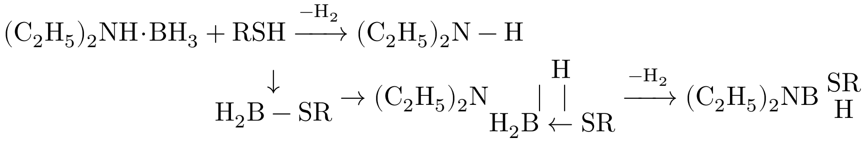


$$(C_2H_5)_2NH{\cdot}BH_3 + RSH \rightarrow (C_2H_5)_2NB\begin{array}{l}SR\\H\end{array} + 2H_2$$

(VII)

a) $R = n\text{-}C_4H_9$, b) $R = n\text{-}C_3H_7$.

Apparently, the process proceeds according to the following scheme:



$$(C_2H_5)_2NH{\cdot}BH_3 + RSH \xrightarrow{-H_2} (C_2H_5)_2N - H$$

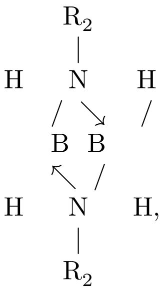
$$\downarrow$$

$$H_2B - SR \rightarrow (C_2H_5)_2N\begin{array}{c}\qquad H\\ | \quad |\\ H_2B \leftarrow SR\end{array} \xrightarrow{-H_2} (C_2H_5)_2NB\begin{array}{l}SR\\H\end{array}$$

(I) (VIII) (IX) (VII)

According to this, in the first stage of the reaction, with liberation of hydrogen, a complex of diethylamine with alkylmercaptoborane (VIII) arises, which is converted into a complex of diethylaminoborane with mercaptan (IX). The latter eliminates hydrogen, turning into VII.

Alkylmercapto-(diethylamino)-boranes (VII) are liquids with an unpleasant odor, rapidly oxidized in air and distilling in vacuum without decomposition. They exist in monomeric form, which accounts for their ability to react vigorously with alcohols with liberation of hydrogen, as is also the case with phenyldiethylaminoborane. By contrast, dimeric derivatives of borane with dialkylamino groups, such as, for example, bis-(dialkylamino)-diboranes, having the structure



are inert toward alcohols at room temperature.

Bis-(diethylamino)-diborane (III) adds to olefins at 120–130° in the presence of pyridine. In this way, di-*n*-butyldiethylaminoboron (IXa) and di-*n*-octyldiethylaminoboron (IXb) were obtained.

$$((C_2H_5)_2NBH_2)_2 + 2RCH = CH_2 \rightarrow (RCH_2CH_2)_2BN(C_2H_5)_2$$

(III) (IX)

a) $R = C_2H_5$; b) $R = C_6H_{13}$.

The addition of III to olefins proceeds with still greater difficulty and in lower yield than the addition in the case of tetraalkylmercaptodiboranes (4).

Experimental Part

All operations were carried out in an atmosphere of dry nitrogen. Diborane was obtained by the action of boron trifluoride etherate on sodium borohydride in ether, in 60–70% yield.

Diethylamine-borane (I). A solution of 18.2 g (0.25 mole) of diethylamine in 70 ml of abs. ether was stirred while 0.14 mole of diborane was passed through over 5 h. The ether was then distilled off in vacuo and the residue was distilled. Obtained: 20.1 g of diethylamine-borane (92%), b.p. 75–77° at 2.5 mm, m.p. -24 to $-20°$; d_4^{20} 0.7568; n_D^{20} 1.4358.

Found, %: C 55.74; H 16.22; B 12.62
$C_4H_{14}BN$. Calculated, %: C 55.24; H 16.10; B 12.44

Mol. wt. found 116.9; calculated 87.0.

Bis-(diethylamino)-diborane (III). In a flask equipped with a reflux condenser and connected to a gasometer, 13.9 g (0.16 mole) of diethylamine-borane was placed and heated on an oil bath at 130–150° for 7 h. In the process, 3300 ml of hydrogen was evolved. On cooling, the reaction product (13.0 g) crystallized. After purification by sublimation in vacuo, 12.1 g (89%) of bis-(diethylamino)-diborane was obtained, m.p. 42–44°.

Found, %: C 56.65; H 14.14; B 12.23
$C_8H_{24}N_2B_2$. Calculated, %: C 56.54; H 14.24; B 12.73

Mol. wt. found 159.1; 164.1; calculated 169.9.

Diethylamine-phenylborane (II). To a solution of 5.4 g (0.03 mole) of 1,2-diphenyldiborane (5) in 90 ml of abs. ether, cooled to $-30°$, a solution of 5.1 g (0.07 mole) of diethylamine in 18 ml of abs. ether was added dropwise. The ether was then distilled off in vacuo and the residue was kept in vacuo (2 mm Hg) to constant loss in weight (about 30 min). Obtained: 9.75 g of diethylamine-phenylborane as a viscous liquid, n_D^{20} 1.5290. The yield was almost quantitative.

Found, %: C 73.68; H 10.55; B 7.12
$C_{10}H_{18}BN$. Calculated, %: C 73.62; H 11.12; B 6.63

Mol. wt. found 184.5; 190.4; calculated 163.

Pyrolysis of diethylamine-phenylborane. a) Into a flask connected to a reflux condenser and to a trap cooled to −70°, 9.6 g (0.06 mole) of diethylamine-phenylborane was placed and heated in vacuo on an oil bath (80–110°) for 2.5 h. In the trap there was found 2.2 g of a liquid substance which, on warming to room temperature, rapidly crystallized with strong self-heating. The crystalline substance formed was bis-(diethylamino)-diborane (yield 88%), m.p. 41–44°.

Found, %: B 12.00
$C_8H_{24}N_2B_2$. Calculated, %: B 12.73

The residue in the reaction flask was subjected to fractional distillation, giving 5.6 g (80%) of diphenyl-diethylamino-boron, b.p. 128–132° at 2.5 mm, m.p. 38–39.5°. Lit. m.p. 36–37° (6).

Found, %: B 4.58
$C_{16}H_{20}BN$. Calculated, %: B 4.60

b) 10.9 g (0.067 mole) of diethylamine-phenylborane was heated in a flask connected to a gasometer at 90–150°. 1400 ml of hydrogen was evolved. The reaction products were subjected to fractional distillation. The following were isolated: a fraction with b.p. 58–63° at 2.5 mm in an amount of 4.9 g, and a fraction with b.p. 125–128° at 2.5 mm—4.0 g. On redistillation of the first

fraction had b.p. 48–50° at 1.5 mm; n_D^{20} 1.5015. It reacts vigorously with alcohol, evolving hydrogen.

Found, %: C 73.00; H 10.33; B 7.62

The second fraction, which crystallized in the receiver, was diphenyldiethylaminoboron, m.p. 38–39.5°.

n-Butylmercapto-(diethylamino)borane (VIIa).
a) A mixture of 6.1 g (0.036 mole) of bis(diethylamino)diborane and 6.8 g (0.075 mole) of n-butyl mercaptan was heated for 2 h at 90–110°. 1550 ml of hydrogen was evolved. Distillation gave 10.6 g (85%) of n-butylmercapto-(diethylamino)borane with b.p. 49–51° at 1.5 mm; d_4^{20} 0.849; n_D^{20} 1.4636.

Found, %: C 55.67; H 11.72; B 6.43; S 18.50
$C_8H_{20}BNS$. Calculated, %: C 55.52; H 11.65; B 6.25; S 18.52

Molecular weight found 176.3; 172.2; calculated 173.1.

b) A mixture of 10.2 g (0.117 mole) of diethylamine-borane and 11.3 g (0.125 mole) of n-butyl mercaptan was heated at 100–120° for 1.5 h. 5200 ml of hydrogen was evolved. Distillation gave 17.5 g of n-butylmercapto-(diethylamino)borane, b.p. 49–51° at 1.5 mm. Yield 86%.

n-Propylmercapto-(diethylamino)borane (VIIb).
A mixture of 7.7 g (0.088 mole) of diethylamine-borane and 7.0 g (0.092 mole) of n-propyl mercaptan was heated at 80–120° for 3.5 h. During heating, 3900 ml of hydrogen was evolved. As a result of distillation, 11.6 g (82%) of n-propylmercapto-(diethylamino)borane was obtained with b.p. 79–81° at 17 mm; d_4^{20} 0.848; n_D^{20} 1.4628.

Found, %: C 52.52; H 11.50; B 7.08; S 19.89
$C_7H_{18}BNS$. Calculated, %: C 52.84; H 11.40; B 6.80; S 20.15

Molecular weight found 166.5; calculated 159.1.

Addition of bis(diethylamino)diborane to butylene.
In a flask equipped with a thermometer and reflux condenser were placed 7.1 g (0.042 mole) of bis(diethylamino)diborane and 0.4 ml of pyridine. Butylene was passed through the mixture for 10 h at 120–130°. After fractional distillation, 7.8 g (48%) of dibutyldiethylaminoboron was obtained with b.p. 52–55° at 1.5 mm, d_4^{20} 0.781; n_D^{20} 1.4377.

Found, %: C 73.50; H 14.55; B 5.45
Calculated, %: C 73.10; H 14.30; B 5.48

In the experiment, a low-boiling fraction was also obtained containing a substance that reacts with alcohol with evolution of hydrogen. This fraction was not studied further in detail.

Addition of bis(diethylamino)diborane to octene.
A mixture of 4.0 g (0.024 mole) of bis(diethylamino)diborane, 10.8 g (0.096 mole) of octene-1, and 0.3 ml of pyridine was heated for 4 h at 110–130°. Fractional distillation yielded 4.3 g (30%) of dioctyldiethylaminoboron with b.p. 150–152° at 2 mm, d_4^{20} 0.8072; n_D^{20} 1.4502.

Found, %: C 78.04; H 14.32; B 3.46
Calculated, %: C 77.62; H 14.33; B 3.50

Institute of Organic Chemistry named after N. D. Zelinsky
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