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B. M. MIKHAILOV, L. S. VASIL'EV, E. N. SAFONOVA

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Abstract

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B. M. MIKHAILOV, L. S. VASIL' EV, E. N. SAFONOVA

TRANSFORMATIONS OF CYCLIC BORON COMPOUNDS UNDER THE ACTION OF METHYL BORATE

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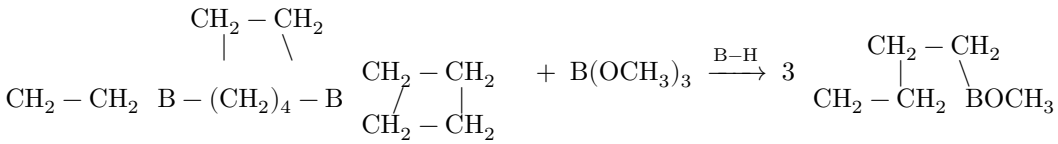
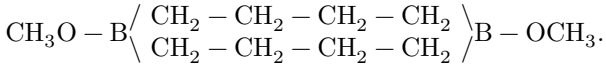
Earlier we showed ([1],[2]) that borotrialkyls and orthoborates, depending on their ratio, are smoothly converted under the influence of tetraalkyldiboranes into esters of alkyl- or dialkylboronic acids. In continuation of this work we studied the interaction of di-(boracycloalkyl)alkanes and 1-methoxyboracycloalkanes with methyl borate in the presence of tetraalkyldiboranes. It was found that di-1,4-(1-boracyclopentyl)butane (I), on moderate heating with an equimolecular amount of methyl borate, is converted into 1-methoxyboracyclopentane (II) in 80% yield, calculated according to the following equation:

(I)



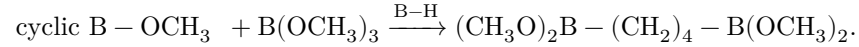
(II)

As a by-product of the reaction, a compound of composition $C_{10}H_{22}B_2O_2$ is obtained, probably representing 1,6-dimethoxy-1,6-diboracyclodecane (III)



(III)

1-Methoxyboracyclopentane (II) also reacts with methyl borate, giving the tetramethyl ester of butane-1,4-diboronic acid (IV) and, in small amount, a triboron compound—the methyl ester of di-(4-dimethoxyborylbutyl)boronic acid (V):

(II) 

(IV)

$$(CH_3O)_2B-(CH_2)_4-B-(CH_2)_4-B(OCH_3)_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OCH_3$$

(V)

Substances (IV) and (V) can be obtained directly from di-1,4-(1-boracyclopentyl)butane (I), if it is heated with 5 moles of methyl borate:

$$I + 4B(OCH_3)_3 \xrightarrow{B-H} 3\,(CH_3O)_2B-(CH_2)_4-B(OCH_3)_2.$$

(IV)

By transesterification of the tetramethyl ester of butane-1,4-diboronic acid (IV) with *n*-hexyl alcohol, the tetra-*n*-hexyl ester of butane-1,4-diboronic acid (VI) was obtained in 98% yield; at $\sim$ 300° it decomposes into 1-hexoxyboracyclopentane (VII) and hexyl borate:

$$\underset{\text{(VI)}}{(C_6H_{13}O)_2B-(CH_2)_4-B(OC_6H_{13})_2} \xrightarrow{\sim 300^\circ} \underset{\text{(VII)}}{(\quad B-OC_6H_{13})} + B(OC_6H_{13})_3.$$

1-Alkoxyboracyclopentanes (II) and (VII) polymerize on standing. The polymer, however, is unstable and depolymerizes on heating.

The second object of the investigation was di-1,4-(1-boracyclopentyl)hexane (VIII), formed as the sole product in the interaction of diborane and diallyl in a ratio of 2 : 3 ([3]).

We found that if the reaction between diborane and diallyl is carried out in a ratio of 1 : 4, then the dicyclic compound (VIII) and 6-(1-boracyclopentyl)hexene-1 (IX) are obtained in almost equimolecular amounts

$$\begin{array}{lll} CH_2-CH_2-CH_2 & & CH_2-CH_2-CH_2 \\ | \qquad\quad B-(CH_2)_6-B & & \quad | \\ CH_2-CH_2-CH_2 & & CH_2-CH_2-CH_2 \end{array}$$

(VIII)

$$\begin{array}{l} CH_2-CH_2-CH_2 \\ | \qquad\quad B-(CH_2)_4CH=CH_2. \\ CH_2-CH_2-CH_2 \end{array}$$

(IX)

On heating (VIII) with one mole of methyl borate in the presence of tetrapropyldiborane, 1-methoxyboracyclopentane (X) is obtained in 81% yield

$$\mathrm{VIII} + \mathrm{B(OCH_3)_3} \xrightarrow{\mathrm{B-H}} \begin{array}{l} \mathrm{CH_2-CH_2-CH_2} \\ | \qquad\qquad \mathrm{B-OCH_3}. \\ \mathrm{CH_2-CH_2-CH_2} \end{array}$$

(X)

With 5 moles of methyl borate in the presence of tetra-*n*-propyldiborane, (VIII) gives equimolecular amounts of 1-methoxyboracyclopentane (X) and the tetramethyl ester of hexane-1,6-diboronic acid (XI)

$$(\mathrm{CH_3O})_2\mathrm{B} - (\mathrm{CH_2})_6 - \mathrm{B(OCH_3)_2}$$

(XI)

1-Methoxyboracyclopentane also reacts with methyl borate, being converted into the tetramethyl ester of hexane-1,6-diboronic acid.

Experimental Part

All operations with organoboron compounds were carried out in an atmosphere of dry nitrogen. Di-1,4-(1-boracyclopentyl)butane was obtained by the interaction of butadiene and diborane in ether medium at $-20 \div (-30^\circ)$ ([4]). Tetraalkyldiboranes were obtained by the methods proposed by us earlier ([5]).

Interaction of di-1,4-(1-boracyclopentyl)butane and methyl borate. a) **In a ratio of 1:1.** Into a three-necked flask equipped with a thermometer, a nitrogen inlet, and a reflux condenser connected to a Tishchenko bottle with acetone, were placed 93.8 g (0.494 mole) of di-1,4-(1-boracyclopentyl)butane, 54.0 g (0.519 mole) methyl borate and 2.0 g (0.0102 mole) of tetra-*n*-propyldiborane. The reaction mixture is boiled for 1.5 hours (the b.p. thereby rises from 84 to 130°), then kept for another 1.5 hours at 130–135° and subjected to fractional distillation on a Hempel column. Obtained:

1) 116.7 g (yield 80.5%) of 1-methoxiboracyclopentane with b.p. 42–43°/87 mm. After redistillation the substance had b.p. 40.5–41.0°/83 mm; d_4^{20} 0.8421; n_D^{20} 1.4172.

Found, %:	C 61.27; 61.14; H 11.27; 11.39; B 11.15; 11.29
$\mathrm{C_5H_{11}BO}$. Calculated, %:	C 61.35; H 11.32; B 11.05

Molecular weight found 100.6, 101.2, calculated 97.96.

2) 22.3 g of 1,6-dimethoxy-1,6-diboracyclodecane with b.p. 77-79°/3 mm. After redistillation the ether had b.p. 69.5-70.0°/2.5 mm; d_4^{20} 0.9055; n_D^{20} 1.4538.

Found, %:	C 61.16; 61.00; H 11.25; 11.57; B 10.91; 10.81
$C_{10}H_{22}B_2O_2$. Calculated, %:	C 61.35; H 11.32; B 11.05

Molecular weight found 183.4, 184.3, calculated 195.9.

b) **In a ratio of 1:5.** 15.2 g (0.08 mole) of di-1,4-(1-boracyclopentyl)butane, 42.6 g (0.41 mole) of methyl borate, and 2.3 g (0.0068 mole) of tetraisoamyldiborane are boiled for 7 hours; the b.p. of the reaction mass thereby gradually rises from 73 to 104°. After addition of 2.5 ml of methanol to the reaction mass and fractional distillation on a Hempel column, the following were obtained:

1) 36.4 g (yield 75.2%) of the tetramethyl ester of butane-1,4-diboronic acid with b.p. 57-60°/2.5 mm; n_D^{20} 1.4170. After redistillation the ether had b.p. 53.0-53.5°/2 mm; d_4^{20} 0.9441; n_D^{20} 1.4185.

Found, %:	C 48.27; 48.33; H 9.99; 10.10; B 10.58; 10.75
$C_8H_{20}B_2O_4$. Calculated, %:	C 47.59; H 9.98; B 10.71

2) 3.6 g of the methyl ester of di-(4-dimethoxiborylbutyl)boric acid with b.p. 116-120°/2 mm; n_D^{20} 1.4370. After redistillation the ether had b.p. 115-116°/1.5 mm; d_4^{20} 0.9428; n_D^{20} 1.4358.

Found, %:	C 52.17; 52.44; H 10.02; 10.12; B 11.17; 11.02
$C_{13}H_{31}B_3O_5$. Calculated, %:	C 52.08; H 10.41; B 10.82

Molecular weight found 291.7, 298.2, calculated 299.84.

By transesterification of the tetramethyl ester of butane-1,4-diboronic acid with *n*-hexyl alcohol, the tetra-*n*-hexyl ester of butane-1,4-diboronic acid was obtained in 98.5% yield, with b.p. 198-200°/1.5 mm, d_4^{20} 0.8667; n_D^{20} 1.4402.

Found, %:	C 69.40; 69.33; H 12.32; 12.40; B 4.55; 4.84
$C_{28}H_{60}B_2O_4$. Calculated, %:	C 69.70; H 12.53; B 4.48

Reaction of 1-methoxiboracyclopentane and methyl borate. 20.6 g (0.210 mole) of 1-methoxiboracyclopentane, 27.9 g (0.268 mole) of methyl borate,

and 1.3 g (0.0066 mole) of tetra-*n*-propyldiborane are boiled for 3.5 hours; during this time the boiling temperature of the reaction mass rises from 76 to 102°. After addition of 1.5 ml of abs. methanol and fractional distillation on a Hempel column, the following were obtained:

1) 30.4 g (yield 71.5%) of the tetramethyl ester of butane-1,4-diboronic acid with b.p. 54–56°/2.5 mm, n_D^{20} 1.4175.

2) 2.8 g of the methyl ester of di-(4-dimethoxiborylbutyl)boric acid with b.p. 116–120°/2 mm, n_D^{20} 1.4360.

Pyrolysis of the tetrahexyl ester of butane-1,4-diboronic acid. 121.8 g (0.253 mole) of tetra-*n*-hexyl ester of butane-1,4-diboronic acid and heated at 270–310°; over 1.5 hours 1-*n*-hexoxyboracyclopentane distilled off, while tri-*n*-hexyl borate remained in the flask. Fractional distillation gave:

1) 30.7 g (yield 72.4%) of 1-hexoxyboracyclopentane, b.p. 44–45°/2 mm; d_4^{20} 0.8386; n_D^{20} 1.4382.

Found, %:	C 71.22; 71.08; H 12.46; 12.43; B 6.56; 6.24
$C_{10}H_{21}BO$. Calculated, %:	C 71.44; H 12.59; B 6.43

2) 71.1 g (yield 89.5%) of tri-*n*-hexyl borate, b.p. 129–133°/2.5 mm; n_D^{20} 1.4270.

3) 7.3 g of the starting tetra-*n*-hexyl ester of butane-1,4-diboronic acid, b.p. 195–203°/2.5 mm; n_D^{20} 1.4415.

Reaction of diborane and diallyl. Diborane (0.25 mole), prepared from 13.5 g of lithium hydride, 80 g of aluminum bromide, and 79 g of boron trifluoride etherate in 430 ml of ether, was passed into a solution of 82 g (1 mole) of diallyl in 250 ml of ether with water cooling. On the next day the solvent was distilled off, and the residue was fractionated in vacuo. Obtained: 1) 26.2 g (0.146 mole) of 6-(1-boracycloheptyl)-hexene-1, b.p. 57–59°/3 mm; d_4^{20} 0.8214; n_D^{20} 1.4630.

Found, %:	C 81.19; 80.78; H 12.66; 12.87; B 6.07; 6.57
$C_{12}H_{23}B$. Calculated, %:	C 80.91; H 13.01; B 6.07

Molecular weight found 175, calculated 178.12. 2) 44.4 g (0.16 mole) of di-1,6-(1-boracycloheptyl)-hexane, b.p. 141–142°/2 mm; n_D^{20} 1.4818 (literature data: b.p. 131–132°/1 mm [3]).

Reaction of di-1,6-(1-boracycloheptyl)hexane and methyl borate. a) **In a ratio of 1 : 1.** A mixture of 15.1 g (0.055 mole) of di-1,6-(1-boracycloheptyl)-hexane, 5.7 g (0.055 mole) of methyl borate, and 0.7 g (0.0036 mole) of tetrapropyldiborane was heated for 2 hours at 120–130°. Obtained:

1) 17.0 g (yield 81%) of 1-methoxyboracycloheptane, b.p. 42–43°/15 mm; d_4^{20} 0.864; n_D^{20} 1.4391.

Found, %:	C 67.01; 66.53; H 12.04; 12.20; B 9.06; 9.02
$C_7H_{15}BO$. Calculated, %:	C 66.72; H 12.00; B 8.59

2) 3.3 g of polymer.

b) **In a ratio of 1 : 5.** To a mixture of 13.9 g (0.051 mole) of di-1,6-(1-boracycloheptyl)-hexane and 2.2 g (0.011 mole) of tetrapropyldiborane, heated to 130°, 26.4 g (0.254 mole) of methyl borate was added over 2 hours. By the end of the addition the boiling temperature had dropped to 94°. The mixture was then boiled for 2 hours, during which the temperature rose to 102°. Distillation gave: 1) 8.9 g (0.07 mole) of 1-methoxyboracycloheptane, b.p. 42–43°/15 mm; n_D^{20} 1.4391. 2) 16.2 g (0.071 mole) of tetramethyl ester of hexane-1,6-diboronic acid, b.p. 82–84°/1.5 mm; d_4^{20} 0.9325; n_D^{20} 1.4252.

Found, %:	C 52.29; 52.51; H 10.41; 10.13; B 9.57; 9.71
$C_{10}H_{24}B_2O_4$. Calculated, %:	C 52.23; H 10.52; B 9.41

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