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B. M. MIKHAILOV and V. A. DOROKHOV

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Abstract

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B. M. MIKHAILOV and V. A. DOROKHOV

THE ACTION OF DIBORANE ON ESTERS OF DIARYL- AND ARYLBORONIC ACIDS

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Reactions between diborane and organoboron compounds have been little studied. Schlesinger and co-workers (^{1,2}) found that trialkylborons (trimethyl-, triethyl-, and tri-*n*-propylboron) react with diborane to form mono-, di-, tri-, and tetraalkyldiboranes. Wiberg, Evans, and Noth (^{3}) established that triphenylboron is also capable of reacting with diborane, but under more severe conditions (40—100°, 2—4 atm.), yielding 1,2-diphenyldiborane. The same compound was obtained by the authors by reduction of phenyldichloroborane with lithium borohydride (^{3}).

We have investigated reactions between diborane and butyl esters of diaryl- and arylboronic acids in an ether medium at room temperature. Esters of diarylboronic acids react with diborane under these conditions with formation of 1,2-diaryldiboranes according to the following equation:

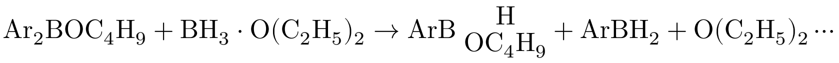
$$3\mathrm{Ar_2BOC_4H_9} + 2\mathrm{B_2H_6} = 3(\mathrm{ArBH_2})_2 + \mathrm{B(OC_4H_9)_3} \qquad (1)$$

$$\mathrm{Ar} = \mathrm{C_6H_5},\ n\text{-}\mathrm{ClC_6H_4},\ \alpha\text{-}\mathrm{C_{10}H_7}.$$

In this way 1,2-diphenyldiborane, 1,2-di-*n*-chlorophenyldiborane, and 1,2-di-α-naphthyldiborane were obtained in yields of 75—81%, calculated according to equation (1). It is very probable that in an ether medium diborane reacts not as such, but in the form of a complex compound of borane with ether, $\mathrm{BH_3 \cdot O(C_2H_5)_2}$. The ability of diborane to form borane etherates with simple ethers has been noted by various authors (^{4,5,6}). In favor of such an assumption is the fact that, in an ether medium, diborane enters, for example, into reactions with olefinic hydrocarbons with greater ease than in the absence of ethers. The first stage of the reaction between esters of diarylboronic acids and the borane etherate consists in replacement of the alkoxy group by hydrogen and formation of diarylborane and alkoxyborane

$$\mathrm{Ar_2BOC_4H_9} + \mathrm{BH_3 \cdot O(C_2H_5)_2} \rightarrow \mathrm{Ar_2BH} + \mathrm{C_4H_9OBH_2} + \mathrm{O(C_2H_5)_2} \cdots \qquad (2)$$

Another variant of the first stage of the reaction, providing for replacement in the ester of an aryl group by hydrogen and formation, as an intermediate compound, of arylalkoxyborane,



$$Ar_2BOC_4H_9 + BH_3 \cdot O(C_2H_5)_2 \rightarrow ArB\genfrac{}{}{0pt}{}{H}{OC_4H_9} + ArBH_2 + O(C_2H_5)_2 \cdots \quad (3)$$

is excluded on the grounds that the reactions of diborane with esters of arylboronic acids considered below, in which arylalkoxyboranes are formed in the first stage, lead to the production of 1,2-diaryldiboranes in significantly lower yields.

In the second stage of the process, the diarylborane formed reacts in turn with borane etherate, being converted into arylborane, which dimerizes to 1,2-diaryldiborane

$$Ar_2BH + BH_3 \cdot O(C_2H_5)_2 \rightarrow (ArBH_2)_2 + O(C_2H_5)_2 \cdots \quad (4)$$

The butoxyborane arising according to equation (2) is almost completely converted into tributyl borate. From the amount of hydrogen obtained on hydrolysis of the mother liquor after separation of 1,2-diaryldiborane (allowing for the 1,2-diaryldiborane remaining dissolved in it), it may be concluded that only 5-10% of the butoxyboranes ($C_4H_9OBH_2$ or $(C_4H_9O)_2BH$) remain unconverted into orthoborate. Most probably, butoxyborane is converted into orthoborate by disproportionation, an equilibrium being established between dibutoxyborane and butyl borate, strongly shifted to the right

$$4C_4H_9OBH_2 \rightarrow 2(C_4H_9O)_2BH + B_2H_6,$$

$$6(C_4H_9O)_2BH \rightleftarrows 4(C_4H_9O)_3B + B_2H_6 \cdots \quad (5)$$

Evidence in favor of this assumption is provided by data on the study of the action of methanol on diborane ([7]), according to which dimethoxyborane is obtained in the liquid state, rapidly converting at 0° into methyl borate. However, it is not excluded that butoxyborane may partly react with the initial ester of diarylboric acid according to the following equations:

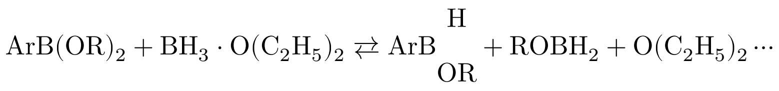
$$Ar_2BOC_4H_9 + C_4H_9OBH_2 = Ar_2BH + (C_4H_9O)_2BH,$$

$$Ar_2BOC_4H_9 + (C_4H_9O)_2BH = Ar_2BH + (C_4H_9O)_3B.$$

Under the action of diborane on esters of arylboric acids, 1,2-diaryldiboranes are also obtained, with the essential peculiarity, however, that their yield in this case is only about 50% (calculated according to equation (6)), and even when an excess of diborane is used, 20–25% of the initial ester invariably does not enter into the reaction.

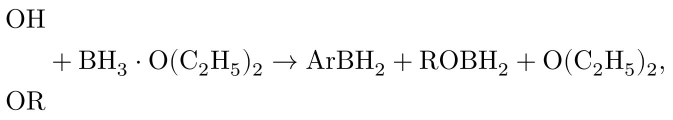
$$6\mathrm{ArB(OR)_2} + 4\mathrm{BH_3}\cdot\mathrm{O(C_2H_5)_2} = 3\mathrm{(ArBH_2)_2} + 4\mathrm{B(OR)_3} + 4\mathrm{O(C_2H_5)_2}. \quad (6)$$

Apparently, the first stage of process (7) is a reversible reaction,



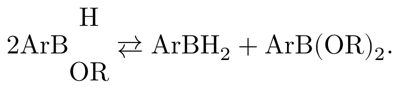
$$\mathrm{ArB(OR)_2} + \mathrm{BH_3}\cdot\mathrm{O(C_2H_5)_2} \rightleftarrows \mathrm{ArB}\begin{matrix}\mathrm{H}\\ \mathrm{OR}\end{matrix} + \mathrm{ROBH_2} + \mathrm{O(C_2H_5)_2}\cdots \quad (7)$$

and the alkoxyarylborane (I) formed in this way is converted into arylborane not by a further irreversible reaction with borane,



$$\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OR}\end{matrix} + \mathrm{BH_3}\cdot\mathrm{O(C_2H_5)_2} \rightarrow \mathrm{ArBH_2} + \mathrm{ROBH_2} + \mathrm{O(C_2H_5)_2}, \quad (8)$$

but by disproportionation (9), which is likewise a reversible process,



$$2\mathrm{ArB}\begin{matrix}\mathrm{H}\\ \mathrm{OR}\end{matrix} \rightleftarrows \mathrm{ArBH_2} + \mathrm{ArB(OR)_2}. \quad (9)$$

A shift of equilibrium (7) to the right cannot be achieved because diborane is only slightly soluble in diethyl ether and its concentration in the reaction mixture is constant and very small.

Pyridine complexes of arylboranes ([8a]) and diarylboranes ([8b]) were synthesized by Hothorn by reduction of esters of aryl- and diarylboric acids with lithium aluminum hydride in ethereal solution in the presence of pyridine. On reduction of phenylboron dichloride with lithium aluminum hydride in boiling dioxane, triphenylboron is formed ([9]).

Experimental Part

All operations were carried out in an atmosphere of dry nitrogen. Diborane was obtained in 80–85% yield by the method of Shapiro et al. ([10]), by adding dropwise a 0.8 molar ethereal solution of lithium aluminum hydride to a 2.5 molar ethereal solution of boron fluoride etherate.

Action of diborane on esters of diarylboric acids

0.047–0.071 mole of the butyl ester of a diarylboric acid was dissolved in 20–25 ml of dry ether, and a stream of diborane, prepared from 0.125–0.188 mole of lithium aluminum hydride and 0.125–0.188 mole of boron fluoride etherate, was passed through the solution for 1.5–2 hr. The crystalline precipitate that separated was filtered off and washed with dry ether. The yields, melting points, and analyses of the 1,2-diaryldiboranes obtained are given in Table 1.

Table 1

Ar_2BOR	Amount of Ar_2BOR, in moles	Yield $(ArBH_2)_2$, %	m.p., °C	Found B, %	Found Ar, %	Found mol. wt.	Calculated B, %	Calculated Ar, %	Calculated mol. wt.
$(C_6H_5)_2BOC_4H_9$-*n*	0.071	71	81–83*	–	–	–	–	–	–
(*n*-$ClC_6H_4)_2BOC_4H_9$-*i*	0.056	70	115–117	8.39	86.02	255.5	8.62	89.62	248.8
(*α*-$C_{10}H_7)_2BOC_4H_9$-*n*	0.047	81	117–119	7.40	86.66	299.3	7.73	90.82	280.0

* Lit. m.p. 82–85° (^{3}).

The 1,2-diaryldiboranes obtained are colorless crystalline substances. 1,2-Diphenyldiborane is readily soluble in benzene, somewhat less so in ether. 1,2-Di-*p*-chlorophenyldiborane and 1,2-di-*α*-naphthyldiborane are soluble in benzene and very poorly soluble in ether and isopentane.

Action of diborane on esters of arylboric acids

1. Interaction of diborane and di-*n*-butyl phenylboronate

Diborane, prepared from 0.25 mole of lithium aluminum hydride and 0.25 mole of boron fluoride etherate, was passed for 3–4 hr through a solution of 24.1 g (0.103 mole) of the *n*-butyl ester of phenylboric acid in 25 ml of dry diethyl ether. The solvent was removed in vacuo, and the precipitate that separated was filtered off and washed with a small amount of dry ether cooled to −50°. This gave 3.8 g of 1,2-diphenyldiborane, m.p. 80–83°. Yield 40% of theory. The filtrate was subjected to fractional distillation. The following fractions were obtained: 1) 35–70° at 2 mm −1.3 g; 2) 70–89° at 2 mm −7.9 g; 3) 89–108° at 2 mm −4.8 g, and a crystalline residue −2 g. The second fraction, consisting of tri-*n*-butyl borate, after redistillation had b.p. 71–72° at 2 mm; d_4^{20} 0.8551; n_D^{20} 1.4102. The third fraction—*n*-butyl ester of phenylboric acid—after redistillation had b.p. 92–97° at 2 mm, n_D^{20} 1.4748. The crystalline residue was dissolved in ether, and ammonia was passed through the solution. This gave 1.2 g of triphenylboron ammoniate, m.p. 226–230° (with decomposition).

2. **Reaction of diborane with the diisobutyl ester of *p*-chlorophenylboronic acid.** Diborane, prepared from 0.18 mole of lithium aluminum hydride and 0.18 mole of boron fluoride etherate, was passed into an ethereal solution of 19.6 g (0.072 mole) of the diisobutyl ester of *p*-chlorophenylboronic acid. 4.5 g (50%) of 1,2-di-*p*-chlorophenyldiborane with m.p. 115–117° was isolated. Fractional distillation of the filtrate gave the following fractions: 1) 50–65° at 2.5 mm —6.2 g; 2) 110–120° at 2 mm —4.4 g. The first fraction, which was triisobutyl borate, after redistillation had b.p. 59–60° at 2.5 mm; n_D^{20} 1.4041. The second fraction—the isobutyl ester of *p*-chlorophenylboronic acid—after redistillation had b.p. 110–112° at 2 mm.

Hydrolysis of 1,2-di-*p*-chlorophenyldiborane: 1.4 g of di-*p*-chlorodiphenyldiborane was dissolved in 50 ml of benzene, and the solution was shaken with water until evolution of hydrogen ceased. The benzene layer was separated, the benzene was distilled off, and the residue was washed with hexane. 1.3 g of *p*-chlorophenylboronic acid with m.p. 270–275° was obtained.

$C_6H_6O_2ClB$. Found %: B 7.21
Calculated %: B 6.92

3. **Reaction of diborane with the diisobutyl ester of α-naphthylboronic acid.** Diborane, prepared from 0.17 mole of lithium aluminum hydride and 0.17 mole of boron fluoride etherate, was passed into an ethereal solution of 14.9 g (0.052 mole) of the diisobutyl ester of α-naphthylboronic acid. 4.0 g (55%) of 1,2-di-α-naphthyldiborane with m.p. 117–119° (with decomposition) was obtained. Pyridine and then isopentane were added to the benzene solution of 1,2-di-α-naphthyldiborane. The precipitated pyridinate of 1,2-di-α-naphthyldiborane, after crystallization from a mixture of benzene and hexane, had m.p. 140.5–141.5°. Literature m.p. 140–141° ([86]).

From the filtrate, fractional distillation gave the following fractions: 1) 50–68° at 3 mm —4.6 g; 2) 140–150° at 2.5 mm —3.0 g. The first fraction, which was triisobutyl borate, on redistillation had b.p. 64–65° at 3 mm; n_D^{20} 1.4049. The second fraction—the isobutyl ester of α-naphthylboronic acid—had b.p. 142–147° at 2.5 mm; n_D^{20} 1.5225.

Hydrolysis of 1,2-di-α-naphthyldiborane: 1.5 g of di-α-naphthyldiborane was dissolved in 40 ml of benzene, and the solution was shaken with water until evolution of hydrogen ceased. The benzene layer was separated, the benzene was distilled off, and the residue was washed with isopentane. 1.25 g of α-naphthylboronic acid with m.p. 185–190° was obtained.

$C_{10}H_9O_2B$. Found %: B 6.06
Calculated %: B 6.29

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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