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Abstract

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Organoboron Compounds

Reactions of 1,2-Diaryldiboranes with Olefinic and Diene Hydrocarbons

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The method we have proposed for obtaining 1,2-diaryldiboranes from esters of aryl- or diarylboric acids and diborane ([1]) makes these interesting diborane derivatives accessible for study.

Their chemical properties have scarcely been investigated. It is known that 1,2-diphenyldiborane forms complex compounds with pyridine and trimethylamine, and, under the action of methyl alcohol, is converted into the dimethyl ester of phenylboric acid ([2]).

We have investigated the reactions of 1,2-diaryldiboranes with olefinic and diene hydrocarbons. With olefinic hydrocarbons—propylene or α-butylene—1,2-diphenyldiborane reacts in ethereal solution on cooling. The phenylbordialkyls formed in this process are unstable and, even at room temperature, comparatively rapidly undergo symmetrization to triphenylboron and borotrialkyls.

$$3(C_6H_5BH_2)_2 + 12\,CH_2{=}CH{-}R \rightarrow 6C_6H_5B\begin{matrix}/\,CH_2{-}CH_2{-}R\\ \backslash\,CH_2{-}CH_2{-}R\end{matrix} \rightarrow$$

$$\rightarrow 2(C_6H_5)_3B + 2B(CH_2{-}CH_2{-}R)_3$$

$$R = CH_3,\ C_2H_5$$

Thus, in an experiment with propylene, after the solvent had been distilled off in vacuo, a mixture of liquid with crystalline triphenylboron was obtained. On the following day, upon distillation, only tri-*n*-propylboron and triphenylboron were obtained. The reaction products between diphenyldiborane and α-butylene were separated immediately after completion of the experiment. After separation of triphenylboron, distillation of the liquid part of the mixture gave fractions with extended boiling ranges, higher than the boiling points of *n*-tributylboron, which indicated the presence in them of phenyl-di-*n*-butylboron. However, on further fractionation, symmetrization occurred and, as a result,

only triphenylboron and tri-*n*-butylboron were obtained. In this case it is not excluded that triphenylboron is formed in part by symmetrization of the initial 1,2-diphenyldiborane in the course of its reaction with olefinic hydrocarbons.

Reactions of 1,2-diaryldiboranes with diene hydrocarbons were carried out in benzene or toluene solution at −40–30°. As the starting 1,2-diaryldiboranes, 1,2-diphenyldiborane and the 1,2-di-*o*-tolyldiborane synthesized by us for the first time were used. The latter was obtained in 51% yield by passing diborane into an ethereal solution of isobutyl ester of di-*o*-tolylboric acid

$$3(o\text{-}CH_3C_6H_4)_2BOC_4H_9\text{-iso}+2B_2H_6 \rightarrow 3(o\text{-}CH_3C_6H_4BH_2)_2+(\text{iso-}C_4H_9O)_3B.$$

When 1,2-diphenyldiborane is allowed to act on butadiene, a cyclic compound with a boron atom in the ring—1-phenylboracyclopentane (I)—is formed in 51% yield:

$$(C_6H_5BH_2)_2 + 2CH_2{=}CH{-}CH{=}CH_2 \longrightarrow 2C_6H_5B \quad \begin{matrix} CH_2{-}CH_2 \\ | \quad | \\ CH_2{-}CH_2 \end{matrix}$$

(I)

Analogous addition of 1,2-diaryldiboranes to dienes also took place in other cases. Thus, when 1,2-diphenyldiborane was allowed to act on isoprene, 1-phenyl-3-methylboracyclopentane (II) was obtained, and from 1,2-di-*o*-tolyldiborane and butadiene, 1-*o*-tolylboracyclopentane (III) was synthesized:

$$C_6H_5B \quad \begin{matrix} CH_2{-}CH_2 \\ | \quad | \\ CH_2{-}CH_2 \\ \quad CH_3 \end{matrix} \qquad o\text{-}CH_3C_6H_4B \quad \begin{matrix} CH_2{-}CH_2 \\ | \quad | \\ CH_2{-}CH_2 \end{matrix}$$

(II) (III)

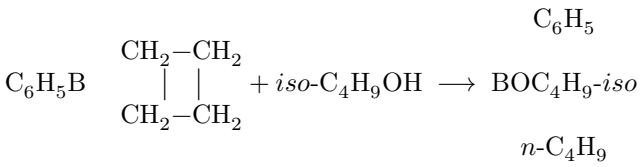
The transformations studied are also accompanied by the formation of borotriaryls, which indicates partial symmetrization of the initial 1,2-diaryldiboranes during the reaction.

1,2-Diphenyldiborane reacts at −40° with cyclopentadiene. In this case, a solid high-molecular-weight substance is obtained, insoluble in ether and very sparingly soluble in benzene.

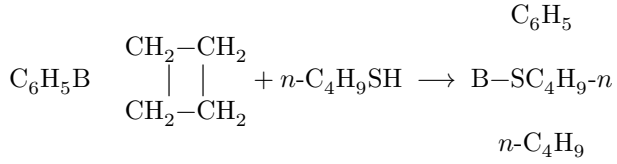
1-Phenylboracyclopentane had previously been obtained by the action of phenylboron difluoride on 1,4-dilithiobutane ([3]). The formation of the cyclic compound

1,1-diboracyclopentane-butane was observed by Köster upon the action of diborane on butadiene ([4]).

It was of interest to investigate the behavior of 1-arylboracyclopentanes toward compounds with active hydrogen. It turned out that 1-phenylboracyclopentane reacts with isobutyl alcohol more readily than borotrialkyls ([5]). In this process, with cleavage of the ring, the isobutyl ester of *n*-butylphenylboronic acid is formed:



Under the action of *n*-butyl mercaptan, 1-phenylboracyclopentane is converted into the *n*-butyl ester of *n*-butylphenylthioboronic acid, the first representative of esters of alkylarylthioboronic acids:



Experimental Part

All operations were carried out in an atmosphere of dry nitrogen.

1,2-Di-*o*-tolyldiborane. Into a solution of 20.6 g (0.077 mole) of the isobutyl ester of di-*o*-tolylboronic acid in 25 ml of ether, diborane was passed; the latter was obtained from 10.2 g of $NaBH_4$ and 35 ml of boron trifluoride etherate in ether. The ether was distilled off, and the residue was thoroughly washed with cooled–

ether and hexane. 8.2 g (51%) of 1,2-di-*o*-tolyldiborane was obtained as colorless crystals with m.p. 53–55°.

Found, %:	B 10.10; $CH_3C_6H_4$ 87.40
C_7H_9B. Calculated, %:	B 10.40; $CH_3C_6H_4$ 89.60.

1,2-Di-*o*-tolyldiborane is readily soluble in ether, hexane, and benzene. It reacts vigorously with alcohol, with evolution of hydrogen.

Reaction of 1,2-diphenyldiborane with propylene. Propylene was passed through a solution of 5.4 g (0.03 mole) of 1,2-diphenyldiborane in 80 ml of absolute ether, cooled to −20–−10°. The solvent was distilled off in vacuo.

On the following day the crystalline precipitate was filtered off and washed with isopentane. 2.8 g of triphenylboron was isolated, m.p. 137-145°. From the filtrate, upon distillation, 4.3 g of tripropylboron was obtained, b.p. 26-32° at 2 mm; n_D^{20} 1.4158. The crystalline residue, in an amount of 1.7 g, was triphenylboron, which after washing with hexane had m.p. 133-140°.

Reaction of 1,2-diphenyldiborane with butene-1. Butene-1 was passed through a solution of 4.4 g (0.024 mole) of 1,2-diphenyldiborane in 70 ml of absolute ether, cooled to −5-0°. The solvent was distilled off in vacuo; the crystalline precipitate was filtered off and washed with isopentane. 0.7 g of triphenylboron was obtained, m.p. 137-145°. On distillation of the filtrate, the following fractions were obtained: 1) 55-75° at 2.5 mm, 2.4 g; 2) 75-100° at 2.5 mm, 3.7 g; crystalline residue, 2.5 g. On redistillation, the first fraction distilled almost completely at 59-62° at 2 mm. The second fraction on redistillation had b.p. 59-70° at 2 mm, with a residue of 0.5 g of crystalline material. On subsequent distillation this fraction distilled completely at b.p. 59-61° at 2 mm; n_D^{20} 1.4268. Thus, all the liquid reaction products obtained are tributylboron. The crystalline residues were identified as triphenylboron, which after washing with hexane had m.p. 134-139°.

1-Phenylborocyclopentane (I). A four-necked flask fitted with a stirrer, two dropping funnels, and a condenser was immersed in a mixture of solid carbon dioxide and acetone, having a temperature of −25—−30°. The condenser was also cooled with a mixture of solid carbon dioxide and acetone. With stirring, a solution of 8.4 g (0.047 mole) of 1,2-diphenyldiborane in 90 ml of toluene and 6.5 g (0.12 mole) of butadiene were added dropwise simultaneously to the flask. After the addition was complete, the reaction mixture was allowed to reach room temperature and was kept at this temperature for 1 h. The solvent was then distilled off in vacuo. The precipitate that separated was filtered off and washed with isopentane. 1.3 g of triphenylboron was obtained, m.p. 125-138°.

Found, %: B 4.33. $C_{18}H_{15}B$. Calculated, %: B 4.47.

The ammoniate of triphenylboron had m.p. 226-228°.

The filtrate obtained after separation of triphenylboron was subjected to fractional distillation. 6.8 g (51%) of 1-phenylborocyclopentane was obtained, b.p. 58-62° at 2 mm. After additional distillation the substance had b.p. 50-51° at 1 mm; d_4^{20} 0.9239; n_D^{20} 1.5278; MR_D found 48.00; calculated 48.17*.

Found, %:	C 83.30; H 9.19; B 7.58
$C_{10}H_{13}B$. Calculated, %:	C 83.39; H 9.10; B 7.51.

The distillation residue (3.0 g) still contained a certain amount of triphenylboron.

1-*o*-Tolylborocyclopentane (III). The synthesis was carried out analogously to the preparation of 1-phenylborocyclopentane. 8.7 g (0.042

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* The refraction of the B—$C_{aliph.}$ bond was taken as 1.75, and that of B—$C_{arom.}$ as 2.96 [6].

mol) of di-*o*-tolyldiborane in 80 ml of toluene and 9 ml of butadiene. After removal of the solvent, the residue was subjected to fractional distillation. This gave 6.8 g (51%) of 1-*o*-tolylboracyclopentane, b.p. 65-70° at 1.5 mm. On redistillation the substance had b.p. 63-65° at 1 mm; d_4^{20} 0.9370; n_D^{20} 1.5429. MR_D found 53.08, calculated 52.83.

Found, %: C 83.47; H 9.75; B 6.98
$C_{11}H_{15}B$. Calculated, %: C 83.58; H 9.57; B 6.85.

1-Phenyl-3-methylboracyclopentane (II). A solution of 10.9 g (0.06 mol) of 1,2-diphenyldiborane in 60 ml of benzene and a solution of 8.5 g (0.125 mol) of isoprene in 12 ml of benzene were mixed gradually while cooling with ice water. After removal of the solvent, the residue was subjected to fractional distillation. This gave 7.6 g (40%) of 1-phenyl-3-methylboracyclopentane, b.p. 61-64° at 2 mm; d_4^{20} 0.9083; n_D^{20} 1.5205; MR_D found 52.95; calculated 52.83.

Found, %: C 83.10; H 9.56; B 6.82
$C_{11}H_{15}B$. Calculated, %: C 83.58; H 9.57; B 6.85.

Action of isobutyl alcohol on 1-phenylboracyclopentane. Isobutyl ester of *n*-butylphenylboronic acid. To 5.0 g (0.035 mol) of 1-phenylboracyclopentane was added dropwise 3.5 ml (0.040 mol) of isobutyl alcohol. The mixture was then boiled for 30 min. From the complex mixture of reaction products, on distillation, the isobutyl ester of *n*-butylphenylboronic acid was isolated in an amount of 2.4 g (30%), b.p. 92-93° at 2 mm, d_4^{20} 0.8870; n_D^{20} 1.4809, previously obtained by B. M. Mikhailov and P. M. Aronovich (7).

Action of *n*-butyl mercaptan on 1-phenylboracyclopentane. *n*-Butyl ester of *n*-butylphenylthioboronic acid. To 6.6 g (0.046 mol) of 1-phenylboracyclopentane was added dropwise 5.5 ml (0.052 mol) of *n*-butyl mercaptan, and the mixture was then heated for 15 min at 70-80°. By fractional distillation from the mixture of reaction products, a fraction with b.p. 107-111° at 1.5 mm was isolated in an amount of 4.4 g (39%). On redistillation, this fraction, which was the *n*-butyl ester of *n*-butylphenylthioboronic acid, had b.p. 107-108° at 1.5 mm; n_D^{20} 1.5252; d_4^{20} 0.9296.

Found, %: C 77.53; H 10.12
$C_{14}H_{23}SB$. Calculated, %: C 77.81; H 9.90.

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