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Abstract

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Organoboron Compounds

Allyl Derivatives of Boron

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Of the allyl compounds of boron, only triallylboron is known with certainty. The data of Rothstein and Saville [1] on the preparation of other compounds of this series should, as will be clear from the following account, be treated critically.

We have studied the chemical properties of triallylboron and, on its basis, obtained a number of new allyl derivatives of boron.

The triallylboron needed for the investigation was prepared by us by the action of allylmagnesium bromide on the etherate of boron fluoride, with a yield of 68%. The preparation had b.p. 155°, as did the triallylboron obtained in 33% yield from triallyl borate and allylmagnesium bromide [2]. A. V. Topchiev and co-workers [3] obtained triallylboron with a higher boiling point in one stage by adding a mixture of allyl bromide and boron fluoride etherate to magnesium.

The investigation showed that triallylboron possesses a considerably higher reactivity than trialkyl compounds of boron. In contrast to the latter, it reacts with water at room temperature, forming allylboronic acid, isolated in the form of its anhydride

$$\begin{gathered}(C_3H_5)_3B + 2H_2O = [C_3H_5B(OH)_2] + 2C_3H_6 \\ \downarrow \\ (C_3H_5BO)_3\end{gathered}$$

At the first stage of the reaction there is evidently formed diallylborinic acid, which undergoes further hydrolytic cleavage at the boron-carbon bond.

Triallylboron reacts at room temperature also with alcohols. On treating it with 1 mole of *n*-butyl alcohol, with evolution of propylene, the *n*-butyl ester of diallylborinic acid is obtained

$$(C_3H_5)_3B + n\text{-}C_4H_9OH = (C_3H_5)_2BOC_4H_9\text{-}n + C_3H_6.$$

The latter, in turn, is capable of reacting with alcohol; therefore, on the action of 2 moles of alcohol on triallylboron, the di-*n*-butyl ester of allylboronic acid is obtained

$$(C_3H_5)_3B + 2n\text{-}C_4H_9OH = C_3H_5B(OC_4H_9)_2 + 2C_3H_6.$$

When methyl alcohol acts on triallylboron at a reagent ratio of 1 : 1, not the methyl ester of diallylborinic acid but the dimethyl ester of allylboronic acid is obtained, and part of the initial triallylboron is recovered unchanged:

$$(C_3H_5)_3B + 2CH_3OH = C_3H_5\text{—}B(OCH_3)_2.$$

The esters of diallylborinic acid are very unstable toward water: under its action they hydrolyze in the cold to allylboronic acid.

Rothstein and Saville [1] stated that, on the action of allylmagnesium bromide on boron fluoride, followed by decomposition of the reaction products with water, the anhydride of diallylborinic acid is obtained. Since diallyl-

boric acid, from which its anhydride could have formed during distillation, is hydrolyzed by water to allylboronic acid; then, obviously, already under the conditions of the experiment the authors could not have obtained the indicated anhydride.

Triallylboron readily reacts with *n*-butylamine. The reaction proceeds at room temperature and, with an equimolar ratio of the reactants, leads to the formation of diallyl-*n*-butylaminoborane:

$$(C_3H_5)_3B + n\text{-}C_4H_9NH_2 = (C_3H_5)_2B - NHC_4H_9\text{-}n + C_3H_6.$$

We next studied the reaction between allylmagnesium bromide and trimethyl borate. If the reaction products are not decomposed with water, but, after removal of the ether, the residue is heated in vacuo, only a small amount of liquid can be distilled off. Fractional distillation established the presence in the distillate of the methyl ester of allylboronic acid and triallylboron. Decomposition of the dry voluminous residue with dilute hydrochloric acid and esterification of the reaction products with allyl alcohol gave the diallyl ester of allylboronic acid. In another experiment, the products of the Grignard reaction were decomposed directly with hydrochloric acid and esterified with *n*-butanol. As a result, the di-*n*-butyl ester of allylboronic acid was isolated in 45% yield.

$$B(OCH_3)_3 + C_3H_5MgBr \xrightarrow[\text{2) } C_4H_9OH]{\text{1) HCl, aq}} C_3H_5B(OC_4H_9)_2$$

According to Rotstein and Saville, the interaction of allylmagnesium bromide and methyl borate (1 : 1) gives the methyl ester of diallylborinic acid and a substance with b.p. 110°/0.4 mm, which, in the opinion of these authors, is the diallyl ester of allylboronic acid. The indicated compounds could certainly not have been obtained by the authors, since they treated the reaction products with water, whereas esters of allylborinic and diallylborinic acids are readily hydrolyzed by it to allylboronic acid. It should be noted that the substance taken by the authors to be the methyl ester of diallylborinic acid boiled higher (190°) than the *n*-butyl ester of diallylborinic acid obtained by us (b.p. 185°), while the diallyl ester of allylboronic acid has b.p. 82°/21 mm, and not 110°/0.4 mm.

It is of interest to study the reaction of allylmagnesium bromide with the ester of metaboric acid, with which arylmagnesium bromides react to form diarylborinic acids *(). It turned out that, on the action of allylmagnesium bromide on the* n-*butyl ester of metaboric acid, followed by decomposition of the reaction products with water and esterification with* n*-butyl alcohol, the dibutyl ester of allylboronic acid (24.8%) and a substance with b.p. 166°/2.5 mm are obtained, the latter having the same elemental composition as the dibutyl ester of allylboronic acid but double the molecular weight. The structure of this "dimer" has not been established.

Experimental Part

All operations were carried out in an atmosphere of nitrogen.

Triallylboron. To an ethereal solution of allylmagnesium bromide, prepared from 42.5 g (1.77 mole) of magnesium, 70.8 g (0.58 mole) of allyl bromide, and 470 ml of abs. ether, placed in a four-necked flask equipped with a stirrer, dropping funnel, reflux condenser, and inlet for nitrogen, an ethereal solution of 20.3 g (0.14 mole) of boron trifluoride etherate was added with vigorous stirring over 50 min. The reaction mixture was boiled with stirring for 3 hours and left overnight. The next day the ether was decanted from the solidified residue of salts, and the precipitate was washed by boiling with 100 ml of abs. ether. The ether was distilled off from the combined ethereal extracts. The residue was distilled in vacuo. This gave 12.7 g (68.1% of theory) of triallylboron with b.p. 44–46°/10 mm; d_4^{20} 0.7689; n_D^{20} 1.4500.

Found, %: C 80.85; 80.74; H 11.37; 11.39; B 8.13; 8.09
$C_9H_{15}B$. Calculated, %: C 80.65; H 11.28; B 8.07.

Allylboronic acid anhydride. To 8.6 g (0.064 mole) of triallylborane, cooled to −60°, with vigorous stirring, 1.15 g (0.064 mole) of water (oxygen-free) in 4 ml of abs. tetrahydrofuran was added over the course of 1.5 hours. Vigorous foaming was observed. The mixture was then stirred for 30 min at room temperature, the tetrahydrofuran was distilled off, and the residue was distilled in vacuum. There was obtained 2.64 g (61% of theory) of allylboronic acid anhydride with b.p. 86.5-91°/7 mm. After repeated distillation the substance had b.p. 60.5-61°/3 mm, d_4^{20} 0.9318; n_D^{20} 1.4435.

$(C_3H_5BO)_3$. Found %: C 52.95; 52.97; H 7.19; 7.33; B 16.14; 15.72; M 186.8
Calculated %: C 53.08; H 7.42; B 15.94; M 203.7.

Allylboronic acid anhydride is a mobile liquid that ignites in air and readily polymerizes on slow distillation.

Di-*n*-butyl ester of allylboronic acid. To 6.23 g (0.046 mole) of triallylborane, 6.84 g (0.092 mole) of abs. *n*-butyl alcohol was added over the course of an hour with vigorous stirring; warming occurred. In a trap cooled to −75°, 3.2 g of propylene condensed. On distillation of the reaction mass, 8.05 g (88.4%) of the di-*n*-butyl ester of allylboronic acid was obtained, with b.p. 98-100°/15 mm; d_4^{20} 0.8413; n_D^{20} 1.4230.

$C_{11}H_{23}BO_2$. Found %: C 66.60; 66.56; H 11.72; 11.65; B 5.03; 5.29
Calculated %: C 66.68; H 11.70; B 5.45.

The ester is soluble in benzene and ether and is readily hydrolyzed by water.

***n*-Butyl ester of diallylboronic acid.** To 8 g (0.059 mole) of triallylborane, 4.48 g (0.059 mole) of abs. *n*-butyl alcohol was slowly added. The reaction was accompanied by heating. Fractional distillation gave 5.9 g (60.2%) of the *n*-butyl ester of diallylboronic acid, with b.p. 60-66°/7 mm. After additional distillation the ester had b.p. 61-62°/6 mm; d_4^{20} 0.8092; n_D^{20} 1.4303.

$C_{10}H_{19}BO$. Found %: C 72.68; 72.48; H 11.28; 11.48; B 6.49; 6.45
Calculated %: C 72.32; H 11.53; B 6.51.

The substance is soluble in ether and benzene and is hydrolyzed by water to allylboronic acid.

In the experiment, in addition, 0.9 g (7.7%) of the *n*-butyl ester of allylboronic acid (n_D^{20} 1.4230) and propylene were obtained.

Dimethyl ester of allylboronic acid. To 14.53 g (0.108 mole) of triallylborane, 3.46 g (0.108 mole) of abs. methyl alcohol was slowly added with vigorous stirring. Heating of the reaction mixture occurred. In the trap (−70°), 3.46 g of propylene condensed.

On fractional distillation of the reaction products there were obtained:
1) 3.9 g of the dimethyl ester of allylboronic acid, with b.p. 42-43°/60 mm (31.7% based on triallylborane taken into the reaction), d_4^{20} 0.8671; n_D^{20} 1.4021.

$C_5H_{11}BO_2$. Found %: C 52.82; 52.70; H 9.68; 9.89; B 9.31; 9.28
Calculated %: C 52.70; H 9.73; B 9.49.

2) 3.5 g of triallylborane, with b.p. 76-80°/60 mm,

3) a fraction in the amount of 1.4 g with b.p. 117-119°/47 mm. (Not investigated.)

Diallyl-*n*-butylaminoborane. To 6 g (0.0448 mole) of triallylborane, 3.28 g (0.0448 mole) of *n*-butylamine was added over the course of 30 min. Heating of the mixture and foaming were observed. The mixture was then heated for 30 min at 100°. In the trap, 1.2 g of propylene was collected. On distillation, 5.5 g was obtained

(74.4%) diallyl-*n*-butylaminoborane with b.p. 85.5-86.5°/17 mm; d_4^{20} 0.8338; n_D^{20} 1.4697.

Found, %: C 72.83; 72.93; H 12.27; 12.00; B 6.06; 6.45
$C_{10}H_{20}BN$. Calculated, %: C 72.74; H 12.21; B 6.55.

The substance is soluble in benzene and ether and is readily hydrolyzed by water.

Action of allylmagnesium bromide on trimethyl borate. To a mixture of 52 g (0.5 mole) of trimethyl borate and 200 ml of ether, cooled to −75°, there was added over 6 hr an ethereal solution of allylmagnesium bromide prepared from 42.5 g of magnesium, 70.8 g (0.58 mole) of allyl bromide, and 470 ml of ether. The reaction mass was stirred for 2 hr and then left in a cooling bath overnight.

On the next day, ether was distilled off from the reaction mixture, which was a thick mass, and then the liquid products were distilled off in vacuo (18 mm). The condensate collected in a trap (−70°) was fractionated; 3.9 g (6.8%) of methyl allylboronate (b.p. 107-109°, n_D^{20} 1.4022) and 0.36 g of triallylborane were isolated.

The dry residue obtained after distillation of the reaction products was decomposed with 400 ml of 3.5% hydrochloric acid, the ether layer was separated, and the aqueous solution was extracted with 200 ml of ether. After distillation of the ether, the residue was esterified with 200 ml of allyl alcohol. After distillation of the azeotropic mixture of allyl alcohol with water and of the alcohol, the reaction product was distilled.

A yield of 26.3 g (31%) of diallyl allylboronate was obtained, with b.p. 81-84°/21 mm. After additional distillation the substance had b.p. 82-82.5°/21 mm; d_4^{20} 0.8931; n_D^{20} 1.4352.

Found, %: C 64.90; 64.81; H 9.22; 9.47; B 6.27; 6.17
$C_9H_{15}BO_2$. Calculated, %: C 65.10; H 9.11; B 6.52.

In the aqueous layer, 41.5% boric acid was found.

In another experiment, the reaction products were hydrolyzed with hydrochloric acid and then esterified with *n*-butanol. A yield of 45.2 g (45.6%) of di-*n*-butyl allylboronate was obtained, with b.p. 92-96°/11 mm (n_D^{20} 1.4230), and 12.5 g (10.7%) of tributyl borate with b.p. 104-109°/11 mm. In the aqueous layer, 36.7% boric acid was found.

Action of allylmagnesium bromide on the *n*-butyl ester of metaboric

acid. To a solution of 0.93 mole of allylmagnesium bromide in 725 ml of ether, with vigorous stirring, there was added 46.6 g (0.155 mole) of *n*-butyl metaborate diluted with 52 ml of benzene. After the spontaneous heating had ceased, the mixture was boiled for 2 hr on a water bath and then hydrolyzed with 500 ml of 7% hydrochloric acid. After distillation of the ether, the residue was esterified with *n*-butanol. A yield of 22.9 g (24.8%) of the *n*-butyl ester of allylboronic acid was obtained, with b.p. 90–94°/9.5 mm, and 17.6 g (19.1%) of the dimer of the *n*-butyl ester of allylboronic acid, with b.p. 165–166°/3 mm; d_4^{20} 0.8814; n_D^{20} 1.4388.

Found, %: C 66.55; 66.90; H 11.51; 11.75; B 5.48; 5.31; M 349.7
$(C_{11}H_{23}O_2)_2$. Calculated, %: C 66.69; H 11.70; B 5.46; M 396.2.

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