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Abstract

Full Text

Chemistry

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STUDIES IN THE FIELD OF BORON COMPOUNDS

NEW DERIVATIVES OF TRIALLYLBORON

The present work is a continuation of our investigations into the chemical properties of triallylboron (^{1}), in which the interaction of triallylboron with acetic acid, ethyl and allyl alcohols, acetaldehyde, bromine, and pyridine was studied. Known derivatives of triallylboron include: the anhydride, the dimethyl ester and di-*n*-butyl ester of allylboronic acid, the *n*-butyl ester of diallylboronic acid, diallyl-*n*-butylaminoboron, and certain others, obtained by B. M. Mikhailov and F. B. Tutorskaya (^{2}).

In the present work, triallylboron, obtained by the method developed by us (^{3}), was subjected to the action of alcohols, acids, and aldehydes. All reactions proceeded with strong heating of the reaction mixture.

The interaction of triallylboron at 20° with alcohols leads to the formation of the corresponding diesters of allylboronic acid:

$$(C_3H_5)_3B + ROH \rightarrow C_3H_5B(OR)_2 + C_3H_6.$$

The propylene liberated during the reaction was trapped with a bromine solution in carbon tetrachloride; in this process 1,2-dibromopropane was formed, the amount of which corresponded exactly to the propylene evolved. Reactions of triallylboron with *n*-propyl, *n*-amyl, and benzyl alcohols and with phenol were studied. The reactions of triallylboron were carried out with an excess of alcohol in order to ensure complete utilization of the former. The di-*n*-propyl ester of allylboronic acid, the di-*n*-amyl ester of allylboronic acid, the dibenzyl ester of allylboronic acid, and the diphenyl ester of allylboronic acid were obtained and characterized.

When triallylboron interacts with acids, diallylacyloxyboron is formed and propylene is liberated,

$$(C_3H_5)_3B + RCOOH \rightarrow (C_3H_5)_2BOCOR + C_3H_6,$$

where $R = C_6H_5;\ C_3H_7$.

In the interaction of triallylboron with benzoic acid, in addition to diallylbenzoyloxyboron, allyldibenzoyloxyboron was also obtained.

With aldehydes, triallylboron reacts with the formation of esters of allylboronic acid, propylene, and cyclohexadiene according to the scheme:

$$(C_3H_5)_3B + RCHO \rightarrow C_3H_5B(OCH_2R)_2 + C_6H_8 + C_3H_6,$$

where $R = C_3H_7;\ C_6H_5$.

In the reaction with propionaldehyde, the propyl ester of diallylboronic acid was obtained. The physicochemical properties of the synthesized organoboron compounds are given in Table 1.

Experimental Part

All experiments were carried out at 20° in an atmosphere of argon thoroughly purified from oxygen.

1. **Di-*n*-propyl ester of allylboric acid.** To 3.8 g of *n*-propyl alcohol, 4.3 g of triallylboron was added dropwise. The evolved gas was trapped in a bromine solution in CCl_4, which was rapidly decolorized. The resulting solution was then washed with soda solution and with water to neutral reaction and dried over ignited $CaCl_2$. After distillation, 1,2-dibromopropane was isolated, with b.p. 140.2°; n_D^{20} 1.5327 (literature data: b.p. 141.6°; n_D^{20} 1.5367).

From the reaction flask, under vacuum, a colorless transparent liquid was distilled off, boiling at 75–77°/35 mm, which was the di-*n*-propyl ester of allylboric acid (yield 87.5%); d_4^{20} 0.8657; n_D^{20} 1.4092.

Found %:	C 64.1; H 11.08; B 6.13
$C_3H_5B(OC_3H_7)_2$. Calculated %:	C 63.5; H 11.17; B 6.5

2. **Di-*n*-amyl ester of allylboric acid.** To 6.2 g of *n*-amyl alcohol, 4.73 g of triallylboron was added dropwise. Strong heating of the reaction mixture was observed. As a result of vacuum distillation, the di-*n*-amyl ester of allylboric acid was isolated (yield 76%)—a colorless transparent liquid with b.p. 132°/39 mm; d_4^{20} 0.8776; n_D^{20} 1.4223. The evolved propylene was trapped in a bromine solution.

Found %:	C 69.9; H 12.26; B 4.77
$C_3H_5B(OC_5H_{11})_2$. Calculated %:	C 69.1; H 11.94; B 4.8

3. **Dibenzyl ester of allylboric acid.** 5.45 g of triallylboron was added dropwise to 8.79 g of benzyl alcohol. On fractionation, a colorless liquid was distilled off, boiling at 143–145°/3 mm—the dibenzyl ester of allylboric

acid (yield 76.4%); d_4^{20} 1.0663; n_D^{20} 1.5368. During the reaction, propylene was evolved, which was trapped in a bromine solution in CCl_4.

Found %:	C 76.6; H 7.13; B 4.13
$C_3H_5B(OC_7H_7)_2$. Calculated %:	C 76.7; H 7.15; B 4.12

4. **Diphenyl ester of allylboric acid.** To 7.44 g of phenol, 5.3 g of triallylboron was added dropwise. The reaction mixture was then distilled under vacuum, yielding a colorless transparent liquid boiling at 135–137°/15 mm, which was the diphenyl ester of allylboric acid (yield 48%); d_4^{20} 1.0573; n_D^{20} 1.5373, and a dark-yellow residue, which was not investigated. During the experiment, intensive evolution of propylene was observed.

Found %:	C 75.19; H 6.59; B 4.57
$C_3H_5B(OC_6H_5)_2$. Calculated %:	C 75.6; H 6.3; B 4.62

5. **Interaction of triallylboron with benzoic acid.** To 5.56 g of benzoic acid, 6.1 g of triallylboron was added dropwise. The reaction proceeded with strong heating of the mixture. As a result of vacuum distillation, two fractions were isolated: a) 110–112°/6 mm, consisting of diallylbenzoyloxyboron (yield 42.8%), and b) boiling at 130°/6 mm—allyldibenzoyloxyboron (yield 23.9%). Both fractions are white crystals. After distillation, a yellow-orange polymer remains in the reaction flask; in air it rapidly oxidizes and darkens.

Found %:	C 72.71; H 7.05; B 4.72
$(C_3H_5)_2BOCOC_6H_5$. Calculated %:	C 77.89; H 7.01; B 5.14

Found %:	C 68.98; H 5.7; B 4.19
$C_3H_5B(OCOC_6H_5)_2$. Calculated %:	C 69.38; H 5.1; B 3.74

6. **Reaction of triallylboron with *n*-butyric acid.** In the interaction of 4 g of triallylboron and 2.7 g of *n*-butyric acid, diallylpropionyloxyboron was formed—a heavy colorless liquid boiling at 46–48°/5 mm (yield 66.2%); d_4^{20} 0.9679; n_D^{20} 1.4472. After distillation of the diallylpropionyloxyboron, a small amount of a dark-orange solid polymer remained in the reaction flask.

Found, %: C 67.12; H 9.99; B 5.74
$(C_3H_5)_2BOCOC_3H_7$. Calculated, %: C 66.66; H 9.44; B 6.11

7. **Reaction of triallylboron with propionaldehyde.** To 3.9 g of propionaldehyde, 9 g of triallylboron were added dropwise.

Table 1

Physicochemical properties of the synthesized organoboron compounds

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No.	Compound	B.p., °C/mm	M.p., °C	Yield, %	Molecular weight, calculated	Molecular weight, found	d_4^{20}	n_D^{20}
1	$C_3H_5B(OC_3H_7)_2$	75–77/35	–	87.5	170	168.8	0.8657	1.4092
2	$C_3H_5B(OC_5H_{11})_2$	132/10	–	76.0	226	224.6	0.8776	1.4223
3	$C_3H_5B(OC_7H_7)_2$	143–145/3	–	76.4	266	264.3	1.0663	1.5368
4	$C_3H_5B(OC_6H_5)_2$	135–137/15	–	48.0	238	235.3	1.0573	1.5373
5	$(C_3H_5)_2BOCOC_6H_5$	110–112/6	84	42.8	214	212.8	–	–
6	$C_3H_5B(OCOC_6H_5)_2$	130/6	92.3	23.9	294	292.4	–	–
7	$(C_3H_5)_2BOCOC_3H_7$	46–48/5	–	66.2	180	183.9	0.9679	1.4472
8	$(C_3H_5)_2BOC_3H_7$	91/4	–	86.2	152	152.3	0.8905	1.4372
9	$C_3H_5B(OC_4H_9)_2$	75–76/6	–	53.6	198	202.02	0.8866	1.4350

No.	Compound	Calculated C	Calculated H	Calculated B	Found C	Found H	Found B
1	$C_3H_5B(OC_3H_7)_2$	63.5	11.17	6.5	64.1	11.08	6.13
2	$C_3H_5B(OC_5H_{11})_2$	69.1	11.94	4.8	69.9	12.26	4.77
3	$C_3H_5B(OC_7H_7)_2$	76.7	7.15	4.12	76.6	7.13	4.13
4	$C_3H_5B(OC_6H_5)_2$	75.6	6.3	4.62	75.19	6.59	4.57
5	$(C_3H_5)_2BOCOC_6H_5$	72.89	7.01	5.14	72.71	7.05	4.72
6	$C_3H_5B(OCOC_6H_5)_2$	69.38	5.1	3.74	68.88	5.7	4.19
7	$(C_3H_5)_2BOCOC_3H_7$	66.66	9.44	6.11	67.12	9.99	5.74
8	$(C_3H_5)_2BOC_3H_7$	71.05	11.9	7.23	70.28	12.03	6.94
9	$C_3H_5B(OC_4H_9)_2$	62.12	11.62	5.55	62.84	10.87	5.99

The reaction mixture was observed to heat up, with liberation of cyclohexadiene, which collected in a trap at 0°, and of propylene, which was captured by a bromine solution in CCl_4. Distillation of the reaction mixture gave a colorless heavy oily liquid with b.p. 91°/4 mm, representing the propyl ester of diallylboric acid (yield 86.2%); d_4^{20} 0.8905; n_D^{20} 1.4372.

Found, %: C 70.28; H 12.03; B 6.94
$(C_3H_5)_2BOC_3H_7$. Calculated, %: C 71.05; H 11.9; B 7.23

8. **Reaction of triallylboron with benzaldehyde.** In the interaction of 5.49 g of triallylboron and 8.7 g of benzaldehyde, the mixture of reactants heated up and propylene was vigorously evolved, decolorizing the bromine

solution in CCl_4. Cyclohexadiene collected in a trap cooled to 0°. From the reaction product, the dibenzyl ester of allylboric acid was isolated, boiling at 154-156°/5 mm; d_4^{20} 1.0668; n_D^{20} 1.5368.

Found, %: C 69.7; H 12.38; B 4.71
$C_3H_5B(OC_7H_7)_2$. Calculated, %: C 69.1; H 11.94; B 4.8

9. **Reaction of triallylboron with butyraldehyde.** To 3.1 g of butyraldehyde, 5.75 g of triallylboron was added dropwise. Heating of the reaction mixture and evolution of cyclohexadiene and propylene were observed. As a result of vacuum fractionation, a colorless oily liquid boiling at 75-76°/6 mm was isolated—dibutyl ester of allylboronic acid (yield 53.6%); d_4^{20} 0.8966; n_D^{20} 1.4350.

Found, %:	C 62.84; H 10.87; B 5.99
$C_3H_5B(OC_4H_9)_2$. Calculated, %:	C 62.12; H 11.62; B 5.55

The synthesized esters of allylboronic acid are being tested as monomers in the preparation of boron-containing polymers.

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