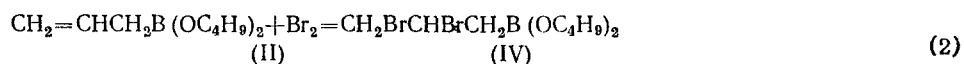
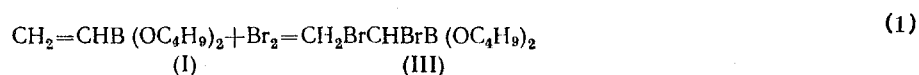


$\beta$  - DECOMPOSITION OF BUTYL ESTERS OF  $\alpha$ ,  $\beta$  - DI BROMOETHYLBORONIC  
AND  $\beta$ ,  $\gamma$  - DIBROMOPROPYLBORONIC ACIDS

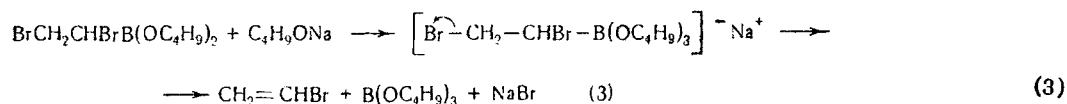
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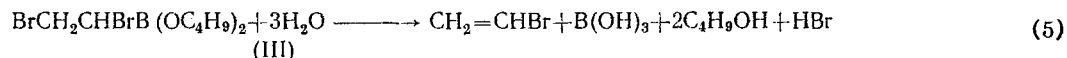
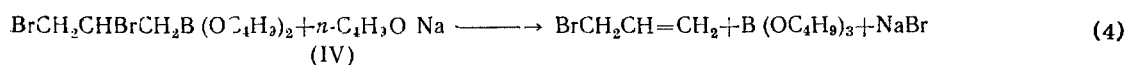
Continuing our earlier [1, 2] study of the properties of the esters of unsaturated organoboron acids, we accomplished the addition of bromine to the di-n-butyl esters of vinyl- (I) and allylboronic (II) acids, and in this way obtained the di-n-butyl esters of  $\alpha$ ,  $\beta$  -dibromoethylboronic (III) and  $\beta$ ,  $\gamma$  -dibromopropylboronic (IV) acids.



The unsaturated bromide is liberated when esters (III) and (IV) are treated with an alcoholic solution of alcoholate or with dilute acid or alkali solution. As a result, the esters of the dibromoethyl- and dibromopropylboronic acids undergo  $\beta$  -decomposition when treated with nucleophilic reagents. Taking into consideration the tendency displayed by organoboron compounds to form complexes, it is possible to assume that esters (III) and (IV) first form complexes with the reagent, after which the bromine (found in the  $\beta$  -position) is cleaved as negative ion and the B - C bond is ruptured. For example, the reaction of the dibromoethylboronic ester with alcoholate can be expressed by the scheme:

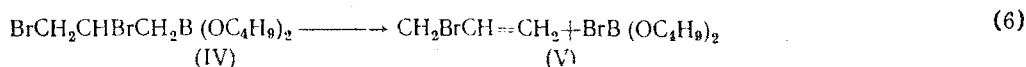


The following reactions probably also proceed by a similar mechanism:



According to Equation (5), half of the bromine contained in esters (III) and (IV) is determined by titration with silver nitrate solution.

Ester (IV), in which the bromine atoms are found in the  $\beta$ ,  $\gamma$  -positions with respect to the boron atom, decomposes more easily than does ester (III), where the bromine atoms are in the  $\alpha$  -  $\beta$  -positions. Thus, the latter remains unchanged after 6-hour heating at 140 - 150°, whereas the  $\beta$ ,  $\gamma$  -dibromopropylboronic ester decomposes partially even when distilled, forming tributyl borate, allyl bromide and butyl bromide. The primary product of the cleavage of ester (IV), besides allyl bromide, is probably the dibutyl ester of the bromoboronic acid (V), which decomposes further, according to the data of Bujwid, Gerrard and Lappert [3], to butyl bromide, tributyl borate and boric anhydride.



It should be mentioned that the decomposition of organoboron compounds, containing halogen in the  $\beta$ -position, was observed earlier for  $(\text{ClCH}=\text{CH})_2\text{BOH}$ ,  $\text{ClCH}=\text{CHB}=\text{CHB}(\text{OH})_2$  [4] and  $\text{ClCH}_2\text{CH}_2\text{BCl}_2 \cdot \text{O}(\text{CH}_3)_2$  [5].

#### EXPERIMENTAL

Di-n-butyl ester of  $\alpha, \beta$ -dibromoethylboronic acid (III). To a stirred mixture of 25.2 g (0.137 mole) of di-n-butyl vinylboronate [6] in 25 ml of n-hexane was added at  $-20$  to  $-30^\circ$ , in 20 min, 22.6 g (0.141 mole) of bromine, diluted with 15 ml of n-hexane. Then the mixture was stirred for 1 hr without cooling, the hexane and excess bromine were removed by vacuum-distillation, and the residue was distilled to give 44 g (93.5%) of the di-n-butyl ester of  $\alpha, \beta$ -dibromoethylboronic acid with  $142$ – $143^\circ$  (3 mm);  $d_4^{20}$  1.3391;  $d_D^{20}$  1.4730. Found: C 35.09, 35.28; H 5.94, 6.22; B 3.29, 2.94; Br 46.18, 46.03%.  $\text{C}_{10}\text{H}_{21}\text{O}_2\text{BBr}_2$ . Calculated: C 34.92; H 6.15; B 3.17; Br 46.47%.

Di-n-butyl ester of  $\beta$ - $\gamma$ -dibromopropylboronic acid (IV). Using the same conditions as above, 17.7 g (0.107 mole) of bromine was added to 20.6 g (0.104 mole) of the di-n-butyl ester of allylboronic acid [7]. On rapid distillation from a Claisen flask we obtained 4.1 g of mixed tributyl borate and di-n-butyl  $\beta, \gamma$ -dibromopropylboronate, b.p.  $72$ – $117^\circ$  (0.4 mm), and 28.6 g (77%) of the dibutyl ester of  $\beta, \gamma$ -dibromopropylboronic acid, b.p.  $117$ – $124^\circ$  (0.4 mm), and  $n_D^{20}$  1.4747. When redistilled, the ester had b.p.  $126$ – $128^\circ$  (0.5 mm);  $d_4^{20}$  1.3337;  $d_D^{20}$  1.4755. Found: C 37.24, 37.25; H 6.43, 6.67; B 3.17, 3.25; Br 44.53, 44.32%.  $\text{C}_{11}\text{H}_{23}\text{O}_2\text{BBr}_2$ . Calculated: C 36.90; H 6.48; B 3.02; Br 44.66%. Ester (IV) fumes strongly in the air. When 20 g of the ester was distilled through a short fractionating column at 6 mm we collected two fractions: fraction I, 11.2 g, b.p.  $80$ – $137^\circ$  (6 mm), and fraction II, 7.1 g of ester (IV) contaminated with tributyl borate, b.p.  $137$ – $140^\circ$  (6 mm);  $n_D^{20}$  1.4568. Redistillation of fraction I gave tributyl borate with b.p.  $87$ – $90^\circ$  (6 mm);  $n_D^{20}$  1.4112. Literature data [8]: b.p.  $105$ – $106^\circ$  (8 mm);  $n_D^{20}$  1.4080. During the distillation of ester (IV) we collected 3.2 g of liquid in the traps, from which we were unable to isolate any pure substances by distillation. After adding a solution of bromine in isopentane to the mixture, followed by distillation, we obtained 0.8 g of n- $\text{C}_4\text{H}_9\text{Br}$ , b.p.  $96$ – $99^\circ$ ;  $n_D^{20}$  1.4420 (literature data [9]: b.p.  $101.6^\circ$ ;  $n_D^{20}$  1.4398), and 3.25 g of 1, 2, 3-tribromopropane, b.p.  $111$ – $115^\circ$  (32 mm);  $n_D^{20}$  1.5795 (literature data [10]: b.p.  $102^\circ$  (18 mm);  $n_D^{20}$  1.5863). Consequently, the original mixture contained 1.4 g of allyl bromide.

Reaction of sodium butylate with the di-n-butyl ester of  $\alpha, \beta$ -dibromoethylboronic acid. To 17.2 g (0.05 mole) of the dibutyl ester of  $\alpha, \beta$ -dibromoethylboronic acid was added with stirring, in 20–30 min, a solution of sodium n-butylate in butyl alcohol, prepared from 1.15 g (0.05 mole) of sodium and 30 ml of absolute n-butyl alcohol. The reaction was exothermic, and the temperature of the mixture was held at  $15$ – $20^\circ$  by cooling with water. The mixture of liquid and precipitate was stirred for 2.5 hr at room temperature, after which the vinyl bromide was distilled at room temperature and 200 mm of pressure. In the traps (cooled to  $-70^\circ$ ) we collected 3.2 g (60%) of vinyl bromide, which vaporized completely at room temperature ( $22^\circ$ );  $n_D^{15}$  1.4335. Literature data [11]: b.p.  $15.8^\circ$ ;  $n_D^{20}$  1.4462. After removal of the vinyl bromide by distillation the reaction mixture was filtered, and the precipitate was washed with benzene and dried. We obtained 5.0 g (97%) of NaBr. Distillation of the filtrate gave 9.4 g (81.7%) of tributyl borate with b.p.  $82$ – $86^\circ$  (4 mm);  $n_D^{20}$  1.4105.

Reaction of sodium butylate with the di-n-butyl ester of  $\beta, \gamma$ -dibromopropylboronic acid. Using the same conditions as above, 15 g (0.042 mole) of the di-n-butyl ester of  $\beta, \gamma$ -dibromopropylboronic acid was reacted with 0.043 mole of sodium butylate in butanol, after which the precipitate (the volatile products were condensed in the cold traps) was filtered and washed with isopentane. The yield of sodium bromide was 4.2 g (97.5%). Distillation of the filtrate gave a mixture of allyl bromide and butanol, b.p.  $32$ – $58^\circ$  (180 mm), and tri-n-butyl borate, 8.8 g (91%), b.p.  $98$ – $102^\circ$  (8 mm);  $n_D^{20}$  1.4095. Distillation of the 1st fraction and the contents of the traps through a short column gave 3.24 g (64%) of allyl bromide with b.p.  $68$ – $74^\circ$ ;  $n_D^{20}$  1.4612. Literature data [12]: b.p.  $70^\circ$  (759 mm);  $n_D^{20}$  1.4697.

Action of 0.1 N sulfuric acid solution on the di-n-butyl ester of  $\alpha, \beta$ -dibromoethylboronic acid. To a mixture of 23.5 g (0.068 mole) of the dibutyl ester of  $\alpha, \beta$ -dibromoethylboronic acid and 20 ml of diethyl ether was added with stirring, at room temperature, in 10 min, 4 ml (0.222 mole of water) of 0.1 N sulfuric acid solution. After several minutes a precipitate began to deposit. The mixture was stirred for 4 hr at room temperature, and the precipitate was filtered, washed with ether, and dried in vacuo. We obtained 1.55 g of boric acid. The filtrate contained 5.15 g (0.0635 mole) of hydrogen bromide. Distillation of the filtrate gave: 1) 0.9 g of n-butanol with b.p.

35 – 38° (14 mm);  $n_D^{20}$  1.4002; 2) 5.2 g of tributyl borate with b.p. 81–88° (4 mm);  $n_D^{20}$  1.4145; and 3) 1.5 g of the dibutyl dibromoethylboronate with b.p. 132 – 139° (3 mm);  $n_D^{20}$  1.4695. The yield of boric acid (as such and as the tributyl ester), based on reacted ester (III), was 74.7% of the theoretical. All of the operations were carried out in an atmosphere of dry nitrogen.

#### SUMMARY

1. The dibutyl esters of the vinyl- and allylboronic acids add bromine smoothly.
2. The dibutyl esters of  $\alpha$ ,  $\beta$ -dibromoethylboronic acid and  $\beta$ ,  $\gamma$ -dibromopropylboronic acid easily undergo  $\beta$ -decomposition.

#### LITERATURE CITED

1. B. M. Mikhailov, P. M. Aronovich, and L. V. Tarasova, *Zhur. Obshchei Khim.* 30, 3624 (1960).
2. B. M. Mikhailov and P. M. Aronovich, *Vysokomolekulyarnye Soedineniya*, No. 6 (1961).
3. Z. J. Bujwid, W. Gerrard, and M. F. Lappert, *Chemistry and Industry* 1957, 1386.
4. A. E. Borisov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1951, 402.
5. M. F. Hawthorne, and J. A. Dupont, *J. Amer. Chem. Soc.* 80, 5830 (1958).
6. B. M. Mikhailov and F. B. Tutorskaya, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1959, 1865.
7. B. M. Mikhailov and F. B. Tutorskaya, *Doklady Akad. Nauk SSSR* 123, 479 (1958).
8. B. A. Arbuzov and V. S. Vinogradova, *Doklady Akad. Nauk SSSR* 55, 415 (1947).
9. C. P. Smyth and E. W. Engel, *J. Amer. Chem. Soc.* 51, 2649 (1929).
10. A. I. Vogel, *J. Chem. Soc.* 1948, 1850.
11. *Handbook of Chemistry and Physics*, Cleveland, 1951 – 1952.
12. J. H. Jeffery and A. I. Vogel, *J. Chem. Soc.* 1948, 669.

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