

# SYNTHESIS OF B-TRIALKYLBORAZOLES FROM ESTERS OF ALKYLTHIOBORIC ACIDS

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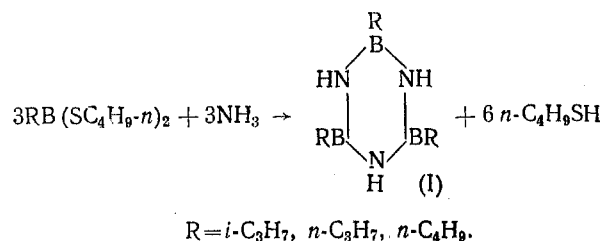
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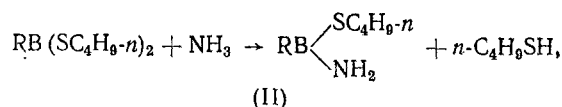
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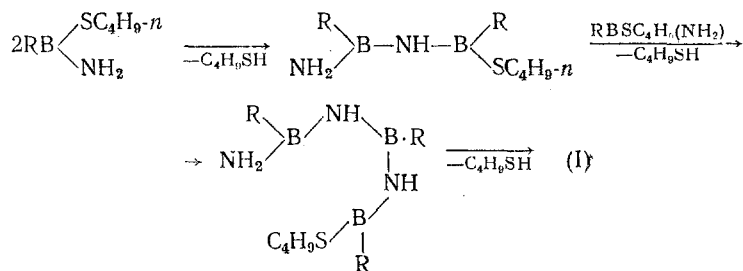
We established recently that the action of ammonia on the di-*n*-butyl ester of isoamylthioboric acid results in the formation of B-triisoamylborazole with a high yield [1]. Further investigation showed that *n*-butyl esters of other alkylthioboric acids also enter into reaction with ammonia. The reaction takes place at room temperature and leads to the formation of B-trialkylborazoles (I) with yields of 80-86%.



The mechanism of the reaction comprises formation in the first stage of an aminothioester (II)



which then apparently condenses into a borazole according to the following scheme:



The initial di-*n*-butyl esters of *n*-propyl and *n*-butylthioboric acids were synthesized by reacting *n*-butyl thiol with the corresponding alkylboron dibromides [1]. The di-*n*-butyl ester of isopropylthioboric acid was also prepared by us for the first time by reacting *n*-butyl thiol with isopropylboron dibromide, which had been synthesized from isopropylboric acid anhydride and boron tribromide by a method described earlier [2]. The B-trialkyl borazole derivatives B-trimethylborazole [3] and B-triethylborazole [1] had been prepared earlier by heating the corresponding boron trialkyls with ammonia in an autoclave at 330-450°.

## EXPERIMENTAL

All operations with organoboron compounds were carried out in an atmospheric of dry nitrogen.

**Isopropylboron dibromide.** By applying the method described earlier [2], 16 g of isopropylboric acid anhydride were reacted with 38.2 g of boron tribromide to prepare 28.5 g (58.3%) of isopropylboron dibromide with a b.p. of 109-113°. After repeated distillation the substance had b.p. 112-113°,  $d_4^{20}$ , 624;  $n_D^{20}$  1.4676. Found: B 5.05; 4.99; Br 73.71; 73.63%.  $\text{C}_3\text{H}_7\text{BBr}_2$ . Calculated: B 5.07; Br 74.78%.

Di-n-butyl ester of isopropylthioboric acid. After 21.8 g of isopropylboron dibromide had been boiled under reflux with 23.4 g of n-butyl thiol for 12 hr, 18.42 g (78%) of the di-n-butyl ester of isopropylthioboric acid were obtained. B.p. 128.5-129° (7 mm);  $d_4^{20}$  0.9079;  $n_D^{20}$  1.4940.

Found: C 56.99; 57.03; H 10.58; 10.73%.  $C_{11}H_{25}BS_2$ . Calculated: C 56.83; H 10.85%.

B-Triisopropylborazole. A stream of dry ammonia was passed at room temperature for 40 min, through 17 g of the di-n-butyl ester of isopropylthioboric acid. Slight heating of the reaction mixture took place. After the n-butyl thiol (11.65 g) had been distilled off in vacuum, distillation of the residue in vacuum yielded 4.12 g (82.4%) of B-triisopropylborazole with b.p. 87.5-88° (7 mm);  $d_4^{20}$  0.8453;  $n_D^{20}$  1.4478. Found: C 52.42; 52.49; H 11.55; 11.75; B 15.61; 15.54.  $C_9H_{24}B_3N_3$ . Calculated: C 52.27; H 11.70; B 15.70%.

B-Tri-n-propylborazole. By reacting similarly 14.5 g of the di-n-butyl ester of n-propylthioboric acid, 3.7 g (86%) of tri-n-propylborazole with b.p. 106.5° (6 mm) were prepared:  $d_4^{20}$  0.8493;  $n_D^{20}$  1.4500. Found: C 52.41; 52.34; H 11.74; 11.84; B 15.59; 15.20%.  $C_9H_{24}B_3N_3$ . Calculated: C 52.27; H 11.70; B 15.70%. 9.5 g of n-butyl thiol were separated from the reaction mixture.

B-Tri-n-butylborazole. Passing of dry ammonia for 40 min through 14.8 g of the di-n-butyl ester of n-butylthioboric acid resulted in a yield of 8.3 g of n-butyl thiol and of 4.0 g (80.3%) of B-tri-n-butylborazole with b.p. 135.5° (4 mm);  $d_4^{20}$  0.8506;  $n_D^{20}$  1.4540. Found: C 57.89; 57.80; H 11.91; 11.93; B 13.35; 13.14%.  $C_{12}H_{30}B_3N_3$ . Calculated: C 57.91; H 12.14; B 13.05%.

#### SUMMARY

It has been found that B-trialkylborazoles are formed smoothly by the reaction of ammonia with alkylthioboric acid esters.

#### LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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