TRIS(TRIORGANOSILYL)BORATES

N. F. Orlov, B. N. Dolgov, and M. G. Voronkov

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Silicoorganic derivatives of boron containing the Si-O-B bond have attracted the attention of a number of investigators in very recent times [1-20]. This interest is due above all to the possibility of utilization of borosilicoorganic compounds, for example as water-resistant [1], electrically insulating [2], and heat-resistant [3-4] coatings. Boric oxide [5], trialkyl borates [6, 7] and boric acid [8] are widely known as catalysts for polymerization of polysiloxanes based on the intermediate formation of compounds containing Si-O-B bonds. The use of boron compounds in syntheses of arylhalosilanes is also probably associated with the formation of silicoorganic derivatives of boron [9], and this theory is supported by the ability of tris(trimethylsilyl) borate to catalyze the arylation of hydrochlorosilanes [10, 11].

During the development of methods of synthesis of various silicoheteroorganic compounds (see for example [12, 13]) it seemed of interest to us to supplement the previously developed methods of preparation of triorganosilylesters of boric acid-tris(triorganosilyl) borates-[14-16]-by new methods. Krieble's patented claim [14, 15] of the possibility of synthesis of tris(trimethylsilyl) borate by reaction of boric acid with trimethylethoxysilane was not subsequently confirmed although a similar method had been used successfully [16] for preparation of higher tris(trialkylsilyl) borates. One of us has described [16] methods of preparation of tris(trialkylsilyl) borates by reaction of hexaalkyldisiloxanes with boron trioxide, by reaction of trialkylchlorosilanes with boric acid or with trialkyl borates, or by transesterification of trialkyl borates with trialkylsilanols. These methods give rather poor yields (20-30%). We developed new methods of synthesis of tris (triorganosilyl) borates that were notable for the excellent yields of 80-95% [12, 17]. The first two of these were based on reactions of triorganosilanols with boron trioxide or boric acid

$$3R_3SiOH + B (OH)_3 \longrightarrow (R_3SiO)_3 B + 3H_2O$$
 (1)

$$6R_3SiOH + B_2O_3 \longrightarrow 2 (R_3SiO)_3 B + 3H_2O$$
⁽²⁾

A third method of synthesis of tris(triorganosilyl) borates was based on reaction of triorganosilanes with boric acid in presence of colloidal nickel [12]

$$3R_3SiH + B (OH)_3 \longrightarrow (R_3SiO)_3 B + 3H_2$$
 (3)

Reactions (1) and (2) were realized by continuous azeotropic distillation of water from the mixture or triorganosilanols with boric acid or boron trioxide containing an inert solvent (benzene).* It is interesting that under these conditions there was no sign of the competing reaction of condensation of triorganosilanols to hexaorganodisiloxanes

^{*} After the main results of the present work had been published [12], references appeared in the literature to the possibility of effecting reactions (1) [18], (2) [19], and (3) [20]. Contrary to our procedure, the water of reaction in the synthesis of tris(triethylsilyl) borate by reaction (2) was removed by binding with anhydrous $CuSO_4$. Moreover the yield of $[(C_2H_5)_3SiO]_3B$ was only 40%.

| | B.p. deg C | | | | | Si, % | | B, % | Prepared |
|---|---------------|--------|--------------|----------|-----------------|-----------------------------|-----------------|------------|----------------|
| Compound | (pmm mercury) | a 20 | D_{D}^{20} | Yield | calcu- lated | found | calcu- lated | found | by reaction |
| [(CH ₃) ₂ C ₂ H ₅ SiO] ₃ B* | 93-94 (6) | 0,8598 | 1,40,2 | 47 | 26.29 | | 3 38 | 3 97- 3 96 | - |
| [(C ₂ H ₅) ₂ CH ₃ SiO] ₃ B | 138-140 (6) | 0,8773 | 1,4240 | 61 | 23,24 | 22,87; 22,78 | 2.98 | 2.99.2.86 | - ~ |
| fr(C-H-)-SiOI-B | 172-175 (6) | 0,8904 | 1,4378 | 84 | 20,83 | 20,56; 20,49 | 2,67 | 2,63; 2,58 | l ⊷ |
| | 154-155 (4) | 0.8915 | 1,43// | 92 61 | 20,83 | 20, 64; 20, 72 | 2,67 | 2,72; 2,69 | 2 |
| [(C2H5)2C6H5SiO]3B* | 250-255 (6) | 1,0125 | 1,5200 | 85 | 15.66 | 20,77; 20,68 14,91:15,03 | 2,61 | 2,65; 2,62 | m ≺ |
| [(C ₆ H ₅) ₂ CH ₃ SiO] ₃ B* | 320-325 (3) | 1,120 | 1,5850 | 77 | 12,95 | 12,46: 12.34 | 1.66 | 10, 10, 11 | |
| [(C ₆ H ₅) ₃ SiO] ₃ B* | Т. пл. 150- | 1 | I | 98,5 | 10,0я | 9,97; 9,89 | 1,29 | | • • |
| • New compound | | - | - | - | _ | | - | _ | |

(4)

which might have been expected to take place. Tris(triorganosilyl) borates were obtained in accordance with reaction (3) by heating of a mixture of triorganosilane and boric acid in presence of colloidal nickel, formed by reaction of nickel chloride, with triorganosilane.

By the three methods mentioned, we prepared six tris(triorganosilyl) borates (see table), four of which were previously unknown.

EXPERIMEN TAL

Triorganosilanols were prepared by the method described earlier [21]; their constants agree closely with the literature data; boric acid and boron trioxide ("pure for analysis") were used without further purification. Triethylsilane was synthesized by reaction of ethyldichlorosilane with ethylmagnesium bromide. It had b.p. $108^{\circ}(757 \text{ mm}), n_D^{\circ}$ 1.4113; d^{20}_4 0.7311.

The silicon in tris(triorganosilyl) borates was determined by mineralization with a mixture of oleum and nitric acid. The precipitated silicic acid was filtered and calcined at 900°. The boron content was found by titration of a weighed sample in aqueous dioxane with 0.1 N NaOH solution in presence of mannitol (phenolphthalein as indicator).

In illustration of the three new methods of synthesis we shall describe the preparation of tris(triethylsilyl) borate by schemes (1), (2), and (3). All of the remaining tris(triorganosilyl) borates were synthesized by the same methods. The physical constants of the substances after further purification, their yields, and analyses are set forth in the table.

Synthesis of $[(C_2H_5)_3SiO]_3B$ by reaction (1). A mixture of 3.1 g of H_3BO_3 (0.06 mole), 19.8 g (0.15 mole) of triethylsilanol and 70 ml of benzene was refluxed for an hour (the condenser was attached to a water collecting trap). After this operation, 2.4 ml of water had separated. The solvent was distilled from the reaction mixture and the residue fractionated in vacuo. There was obtained 17.0 g (84.0%) of tris(triethylsilyl) borate with b.p. 172-174° (6 mm), n²⁰ 1.4378.

Synthesis of $[(C_2H_5)_3SiO]_3B$ by reaction (2). A mixture of 3.5 g of B_2O_3 (0.05 mole), 39.6 g (0.3 mole) of triethylsilanol, and 80 ml of benzene was heated for 2 hr as indicated in the preceding experiment. After separation of 2.65 ml of water, the benzene was distilled, and the residue distilled in vacuo to give 37.0 g (92.0%) of tris(triethylsilyl) borate with b.p. 165-167° (5 mm), n_{D}^{20} 1.4377.

Synthesis of $[(C_2H_5)_3SiO]_3B$ by reaction (3). A mixture of 4.32 g (0.07 mole) of H_3BO_3 , 2.8 g (0.24 mole) of triethylsilane, and 0.01 g of colloidal nickel was refluxed for 14 hr. After this period the temperature of the reaction mixture had risen to 148° and 4.5 liters of hydrogen had been released. Fractional distillation in vacuo gave 17.0 g (61.0%) of tris(triethylsilyl) borate with b.p. 154-155° (4 mm); n_2^{20} 1.4373.

SUMMARY

Three new methods were developed for synthesis of tris(triorganosilyl) borates, based on reaction of triorganosilanols with boron trioxide or with boric acid, and on reaction of H_3BO_3 with triorganosilanes. These methods were employed for preparation of six compounds of this type, of which four were previously unknown.

LITERATURE CITED

- 1. W. I. Patnode, U. S. Patent 2434953 (1948); Chem. Abstrs 42, 2985 (1948).
- 2. K. Hizawa, and E. Nojimoto, Japanese Patent 4791 (1953); Chem. Abstrs 48, 11109 (1954).
- 3. E. Nijimoto, Japanese Patent 1441 (1952); Chem. Abstrs 47, 6179 (1953).
- 4. K. N. Nishikawa et. al., U. S. Patent 2375998 (1945); Chem. Abstrs. 48, 7932 (1954).
- R. R. McGregor, E. L. Warrick, U. S. Patent 2371068 (1945); Chem. Abstrs. 40, 245 (1946); U. S. Patent 2431878 (1947); Chem. Abstrs. 42, 1761 (1948).
- 6. E. G. Rochow, U. S. Patent 2371068 (1945); Chem. Abstrs 39, 4889 (1945).
- 7. J. Swiss and C. E. Arntzen, U. S. Patent 2595727 (1952); Chem. Abstrs 46, 7362 (1952).
- 8. S. Nitzshe and M. Wick, West German Patent 958702 (1957); Ref. Zhur. Khim. 27082 (1958).
- 9. G. N. Mal'nova, E. P. Mikheev, A. L. Klebanskii, S. A. Golubtsov, and N. P. Filimonova, Doklady Akad. Nauk SSSR 117, 623 (1957).
- 10. A. J. Barry, U. S. Patent 2611775 (1952); Chem. Abstrs 47, 8092 (1953).
- 11. British Patent 694526 (1953); Chem. Abstrs 48, 10765 (1954).
- N. F. Orlov, B. N. Dolgov, and M. G. Voronkov, Transactions of the Conference on Chemistry and Practical Application of Silicoorganic Compounds, Part 1 (Central Office of Technical Information, Leningrad, 1958), p. 161.
- 13. N. F. Orlov, B. N. Dolgov, and M. Voronkov, Doklady Akad. Nauk SSSR 122, 246 (1958).
- 14. R. H. Krieble, U. S. Patent 2440101 (1948); Chem. Abstrs 42, 6376 (1948).
- 15. British Patent 643298 (1950); Chem. Abstrs 45, 7819 (1951).
- 16. M. G. Voronkov and V. N. Vinogradova, Zhur. Obshchei Khim. 27, 1476 (1957).
- 17. N. F. Orlov and B. N. Dolgov, Author's Certificate 115167 (1958).
- 18. E. W. Abel and A. Singh, J. Chem. Soc. 690 (1959).
- 19. B. I. Yakovlev and N. V. Vinogradova, Zhur. Obshchei Khim. 29, 695 (1959).
- 20. B. N. Dolgov, Yu. I. Khudobin, and N. P. Kharitonov, Doklady Akad. Nauk SSSR 122, 607 (1958).
- 21. B. N. Dolgov and N. F. Orlov, Doklady Akad. Nauk SSSR 117, 617 (1957).

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