The reaction mixture was maintained at 0° for 24 hr., then poured into a mixture of equal volumes of 6 *N* hydrochloric acid and ether. The sulfonate ester was extracted with ether and the ether extract was washed with ice-cold 6 *N* hydrochloric acid. In order to remove traces of pyridine the ether extract was washed once with 10% cadmium chloride solution and dried over anhydrous magnesium sulfate. The ether was removed and the residue crystallized from a mixture of pentane–ether (10:1) at −70°. The isopinocampheyl methanesulfonate had m.p. ~10°. The compound was stable when kept below 0° for a long period of time.

Anal. Calcd. for $C_{11}H_{20}SO_3$: C, 56.90; H, 8.65. Found: C, 56.79; H, 8.73.

Neoisopinocampheyl Methanesulfonate.—Under similar experimental conditions as described above, 0.71 g. of neoisopinocampheol[5] [(5 mmoles, m.p. 45–47°, $[\alpha]^{20}$ +36° (*c* 3, benzene)] was converted to the neoisopinocampheyl methanesulfonate, m.p. ~0°. The compound is less stable as compared to the isopinocampheyl derivative.

Anal. Calcd. for $C_{11}H_{20}SO_3$: C, 56.90; H, 8.65. Found: C, 56.41; H, 8.07.

Rate Studies.—The reaction rates were followed by conventional titrimetric procedures. The first-order reaction constants obtained are summarized in Table I.

Organoboron Compounds. XVI. An Improved Method for the Preparation of Trialkylboroxines[1,2]

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The reaction of boric oxide with trialkylboranes was reported earlier[3] to provide a more convenient method for the preparation of trialkylboroxines than the previously used dehydration of alkylboronic acids. Because of the high temperatures and long heating times required, this reaction was restricted to the preparation of primary trialkylboroxines, since thermal isomerization[4] of secondary or tertiary alkyl groups to primary groups occurred during reaction and, as more recently observed,[1] partial conversion of primary alkyl groups to secondary alkyl groups also took place. Furthermore it was found on continued use of this reaction that it was difficult to obtain or prepare samples of anhydrous boric oxide with reproducible reaction characteristics. Incompletely dehydrated boric oxide causes some hydrolysis of trialkylboranes, and boric oxide thoroughly dehydrated at high temperature was found to be very unreactive, resulting in heating times as long as 60 hr. in some instances.

A modification of the method, involving the use of trimethoxyboroxine as a source of reactive boric oxide, with resultant decrease of time of reaction, lower reaction temperatures, and decreased thermal isomerization is reported in the present paper.

Trimethoxyboroxine, obtainable from the reaction of boric oxide with trimethoxyborane (and also available commercially from the Callery Company) is dissociated on attempted distillation[5-7] into boric oxide and trimethoxyborane.

Under controlled conditions it has been found that heating of mixtures of primary trialkylboranes and trimethoxyboroxine as low as 131° and for periods as short as 2 hr. results in 60–77% yields of isomer-pure, sharp-boiling trialkylboroxines. An essential feature of the reaction conditions is that the trimethoxyborane formed by decomposition of trimethoxyboroxine must be distilled as rapidly as it is formed. If the mixture is heated without rapid removal of the trimethoxyborane, the reaction products consist mostly of dialkylmethoxyboranes and alkyldimethoxyboranes resulting from the reaction of trimethoxyborane with trialkylboranes.[8]

In order to determine whether any of the alkyldimethoxyborane, obtained as a by-product in the preparative reaction, resulted from direct reaction between trimethoxyborane and trialkylboroxine, this possible reaction was attempted under the same conditions as used for the preparative reaction. It was found that under these conditions only a 6% yield of alkyldimethoxyborane was obtained.

Of the three reactions involved in the process, the most rapid is apparently the thermal decomposition of trimethoxyboroxine. This follows from the observation that trimethoxyborane can be removed from the reaction mixture in almost quantitative yield by distillation. This requires that reaction of trimethoxyborane with trialkylborane and reaction of boric oxide with trialkylborane be relatively slow. Of the latter two reactions, the trimethoxyborane–trialkylborane reaction appears to be the more rapid since the yield of esters is higher than the yield of trialkylboroxine when the trimethoxyborane is left in the reaction mixture.

The rapid formation of trialkylboroxines at relatively low temperature led to the expectation that isomer-pure secondary trialkylboroxines could be obtained by this method. This expectation was realized in the case of the preparation of tri-*sec*-butylboroxine although it was found that during the preparative reaction some isomerization of secondary to primary groups occurred. From the reaction mixture there was obtained a 35% yield of isomer-pure tri-*sec*-butylboroxine. The total yield of tributylboroxine was 69%. In the case of the treatment of triisopropylborane with trimethoxyboroxine heating for 1 hr. in the same temperature range as for tri-*sec*-butylborane and removal of trimethoxyborane resulted in the precipitation of solid boric oxide but no formation of tripropylboroxine. Heating of the reaction mixture for an additional hour resulted in dissolution of the boric oxide and formation of tripropylboroxine which consisted of an inseparable mixture of normal and isopropylboroxines. It appears that direct reaction of triisopropylborane with trimethoxyboroxine does not occur, while direct reaction of tri-*sec*-butylborane with trimethoxyboroxine does take place under essentially the same conditions. The reason for this difference in behavior is not immediately evident.

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[1] Previous paper: P. A. McCusker, F. M. Rossi, J. H. Bright, and G. F. Hennion, *J. Org. Chem.*, **28**, 2889 (1963).

[2] Contribution from the Radiation Laboratory operated by the University of Notre Dame under contract with the Atomic Energy Commission.

[3] G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5179 (1957).

[4] G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957).

[5] J. Goubeau and H. Keller, *Z. Anorg. Allgem. Chem.*, **267**, 1 (1951).

[6] G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **77**, 1578 (1955).

[7] M. F. Lappert, *J. Chem. Soc.*, 2790 (1958).

[8] R. Koster, *Angew. Chem.*, **71**, 31 (1959).

From the purified trialkylboroxines, alkylboronic acids may be prepared in high purity by simple addition of water.

Experimental

All operations were carried out in an atmosphere of dry nitrogen.

Preparation of Triisobutylboroxine from Triisobutylborane and Trimethoxyboroxine.—The preparation of triisobutylboroxine will be detailed as typical of the procedure used for all the boroxine preparations. Trimethoxyboroxine (78 g., 0.42 mole), obtained from Callery Chemical Co., was heated with triisobutylborane (76 g., 0.42 mole) at atmospheric pressure, and the resulting trimethoxyborane was removed as rapidly as it was formed by distillation through a 28-theoretical-plate, spinning-band column. Complete removal of the trimethoxyborane (0.39 mole) required 2.5 hr., during which time the temperature of the reaction mixture rose from 131 to 207°. Distillation of the remaining reaction mixture gave a few grams of a forerun containing isobutyldimethoxyborane and unchanged triisobutylborane, and 77 g. of crude triisobutylboroxine. Unchanged boric oxide (7.0 g.) remained as a residue. Redistillation of the crude material gave 68 g. (64% yield) of pure triisobutylboroxine, b.p. 90.1° at 3.6 mm., $n^{25}\text{D}$ 1.4117, d^{25} 0.8558; MR_D calcd.,[9] 73.13; MR_D obsd., 72.89.

In a separate experiment trimethoxyboroxine (47 g., 0.27 mole) was heated with triisobutylborane (59 g., 0.32 mole) except that the resulting trimethoxyborane was removed slowly over a period of 5 hr. Distillation of the resulting mixture gave the following spectrum of crude products: 0.05 mole of diisobutylmethoxyborane, 0.15 mole of triisobutylboroxine, 0.22 mole of unchanged triisobutylborane, and 0.06 mole of boric oxide.

Other Trialkylboroxines Containing Primary Alkyl Groups.—By entirely similar procedures tri-*n*-propylboroxine, tri-*n*-butylboroxine, and tri-*n*-amylboroxine were prepared in yields above 60%. Close boiling fractions, with physical properties in agreement with those previously reported,[10] were obtained.

Attempted Preparation of Triisopropylboroxine.—Trimethoxyboroxine (28 g., 0.16 mole) was heated with isomer-pure triisopropylborane at 133–210° and 0.14 mole of trimethoxyborane was rapidly removed by distillation over a period of 1 hr. During removal of the trimethoxyborane large amounts of white solid formed in the reaction mixture. Distillation resulted in the recovery of starting materials only. No triisopropylboroxine was obtained.

In a second experiment trimethoxyboroxine (17 g., 0.10 mole) was heated with triisopropylborane (18 g., 0.09 mole) in a temperature range of 138–191° over a 2-hr. period with removal of trimethoxyborane. After about 1 hr. the formation of a white solid was noted but continued heating resulted in the disappearance of the solid. After a total of 2 hr., distillation of the reaction mixture gave 20 g. of a fraction containing a mixture of tripropylboroxines, b.p. 57–67° at 4 mm.

Anal. Calcd. for $C_{19}H_{21}B_3O_3$: B, 15.45. Found: B, 15.15.

By oxidation and gas–liquid chromatography of the resulting alcohols, the mixture was found to contain *n*-propyl groups and isopropyl groups in a 57:43 ratio. The yield of mixed tripropylboroxines was essentially quantitative.

Preparation of Tri-*sec*-butylboroxine from Tri-*sec*-butylborane and Trimethoxyboroxine.—Trimethoxyboroxine (24 g., 0.14 mole) was heated with isomer-pure tri-*sec*-butylborane (24 g., 0.13 mole) with rapid removal of 0.14 mole of trimethoxyborane. The temperature of the reaction mixture ranged from 149 to 197° and the reaction was complete in 1 hr. Distillation resulted in two principal fractions. The first, 17 g., had the following properties: b.p. 70.5–75.1° at 1.35 mm., $n^{25}\text{D}$ 1.4159, d^{25} 0.8705.

Anal. Calcd. for $C_{12}H_{27}B_3O_3$: B, 12.9. Found: B, 12.9.

By g.l.c. the ratio of *sec*-butyl to *n*-butyl groups was 94:6. The second fraction (7 g.) had the following properties: b.p. 75.1–93.0° at 1.4 mm., $n^{25}\text{D}$ 1.4174, d^{25} 0.8717. (*Anal.* Found: B, 12.8.) The *sec*-butyl–*n*-butyl group ratio was 65:35. The combined yield of tributylboroxine was 69%. Redistillation of the lower boiling fraction gave 0.05 mole (35% yield) of pure tri-*sec*-butylboroxine, b.p. 59.1° at 0.6 mm.

Anal. Calcd. for C_4H_9BO: C, 57.2; H, 10.8; B, 12.9. Found: C, 55.6; H, 11.1; B, 12.8.

Preparation of Trimethoxyboroxine.—Metaboric acid (23 g., 0.52 mole), obtained from Fisher Scientific Co., was heated at 168° and 1 mm. for 12 hr. in a vacuum oven. Trimethoxyborane (42 g., 0.40 mole) was added to the resulting boric oxide and the mixture refluxed over a period of 6 hr. in the temperature range of 229–117°. Half of the excess trimethoxyborane was distilled and the resulting material was treated with tri-*n*-butylborane as in the above preparations. Tri-*n*-butylboroxine was obtained in yields comparable to those obtained when commercial trimethoxyboroxine was used.

Treatment of Trimethoxyborane with Tri-*n*-butylboroxine.—To tri-*n*-butylboroxine (28 g., 0.11 mole) at reflux temperature was added over a period of 3.5 hr. 25 g. (0.24 mole) of trimethoxyborane. During the addition, the reaction temperature dropped from 189 to 134°. Heating was continued for an additional 2 hr. Distillation of the reaction mixture resulted in the recovery of 0.20 mole of unchanged trimethoxyborane, 0.10 mole of unchanged tri-*n*-butylboroxine, and 4 g. of a material collected in a cold trap. From the trap material there was obtained on hydrolysis 0.02 mole of *n*-butylboronic acid. The estimated yield of *n*-butyldimethoxyborane was 6%.

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[9] R. G. Gillis, *Rev. Pure Appl. Chem.*, **10**, 1 (1960).

[10] P. A. McCusker, E. C. Ashby, and H. S. Makowski, *J. Am. Chem. Soc.* **79**, 5179 (1957).

Organoboron Compounds. XVII. Preparation and Hydrolytic Properties of Some Substituted Borazines Containing Fluorescent Groups[1]

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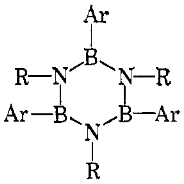
For the detection of neutrons by means of scintillation counters, compounds which have both high neutron cross sections and are strongly fluorescent are desirable. Interesting examples of such types of compounds can be obtained by introducing polyphenyl groups into the borazine molecule. In the present paper the preparation of four such compounds, B-tris(diphenylyl)-N-trimethylborazine (I), B-tris(diphenylyl)-N-triphenylborazine (II), B-tris(α-naphthyl)-N-trimethylborazine (III), and B-tris(p-terphenylyl)-N-trimethylborazine (IV), is described and their rates of hydrolysis are compared. The structural formulation of the compounds is given in Chart I.

CHART I



I, Ar = $C_6H_5C_6H_4$: R = CH_3
II, Ar = $C_6H_5C_6H_4$; R = C_6H_5
III, Ar = α-$C_{10}H_7$; R = CH_3
IV, Ar = p-$C_6H_5C_6H_4C_6H_4$; R = CH_3

Among the several methods reported for the preparation of borazine derivatives,[4] the more generally

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[1] Previous paper: P. A. McCusker and J. H. Bright, *J. Org. Chem.*, **29**, 2093 (1964).

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[3] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission.

[4] J. C. Sheldon and B. C. Smith, *Quart. Rev.* (London), **14**, 201 (1960).