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}_{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}_{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}_{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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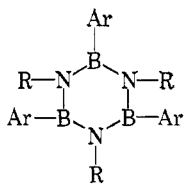
For the detection of neutrons by means of scintillation counters, compounds which have both high neutron cross sections and are strongly fluorescent are desirable. Interesting examples of such types of compounds can be obtained by introducing polyphenyl groups into the borazine molecule. In the present 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).

used are the method of Ruigh[5] which involves the reaction of organodichloroboranes with amines and the method of Harris, Ryschkewitsch, and Sisler[6] and Groszos and Stafiej[7] which consist of the reaction of Grignard reagents with substituted B-trichloroborazines. The availability of a convenient method for the preparation of the required B-trichloro-N-substituted borazines dictated our choice of the latter method for the preparation of the desired compounds.

Three of the four compounds to be prepared contain methyl groups attached to nitrogen and compounds of this type have been reported[7] to be readily hydrolyzed in contact with water. Completely anhydrous procedures were therefore used. It was found that much better results were obtained when lithium aryls were used rather than Grignard reagents. The yield of I was increased from 33 to 61% by using lithium aryl rather than Grignard reagent. In the case of IV the required Grignard is obtainable only with difficulty, while the lithium aryl was prepared conveniently by halogen exchange. The principal advantage of lithium aryls over Grignard reagents in these preparations lies in the relative ease of separation of lithium chloride from ether solutions compared to the separation of magnesium salts. The elimination of lithium chloride or its etherate from the residue, obtained by removal of most of the ether by distillation, was readily accomplished by successive treatments with dry benzene at reflux temperature, removal of ether by distillation, and separation of precipitated lithium chloride by filtration under anhydrous conditions.

No significant differences in the rates of reaction of the N-trimethyltrichloroborazine with the three different lithium aryls was observed, indicating that steric effects arising from the size of the aryl group did not seriously affect the reaction. The variation in the yields obtained is probably due to differences in the losses during crystallizations.

The products, obtained by recrystallization from a variety of solvents, were in the form of small white needles. Their identification was based on the reactions used and on elemental analysis. The infrared spectra all showed strong absorption in the B–N ring stretching region (1370–1410 cm.$^{-1}$) as well as the characteristic frequencies corresponding to the aryl groups.

The substituted borazines prepared in this work, although less sensitive to moisture than borazine itself, were found to undergo significant hydrolysis on storage as the result of occasional exposure to normal atmosphere. Elemental analysis of samples, stored for several months with occasional short exposure to the atmosphere, gave evidence of about 5% hydrolytic decomposition in the case of III and IV, and of about 15% decomposition in the case of I, accompanied by loss of volatile amine.

On contact with liquid water, there was extensive hydrolysis in a period of 30 min. in the case of B-tris(diphenylyl)-N-trimethylborazine (I), while the corresponding N-phenylborazine was only slightly hydrolyzed in the same period. This observation is in agreement with that of Groszos and Stafiej[7] on the relative rates of hydrolysis of N-methyl- and N-phenyl-substituted borazines. Two of the N-methyl-substituted borazines prepared in this work, III and IV, however, did not exhibit the property of ready hydrolysis on contact with liquid water. These latter two compounds were quite resistant to hydrolytic attack by liquid water and were comparable in this respect to the N-phenyl compound. It would appear that the large α-naphthyl and p-terphenylyl groups on the boron exert a steric effect which slows the attack by water.

More quantitative studies on relative hydrolysis rates were carried out on solutions containing 1.12 mg./ml. of the compounds in 22.5 wt. % dioxane in water. The rates of hydrolysis were followed by measurements of the conductivity of the solutions *vs.* time. The required relationships between conductivity and concentrations were obtained by measurements of the conductivities of various solutions of methylamine–phenylboronic acid in dioxane–water and of similar solutions of aniline–phenylboronic acid. Within a period of 2 min. at 25° I underwent 82% hydrolysis, while, in a 3-min. period, II was only 11% hydrolyzed. Slow hydrolysis of II proceeded, however, and reached 34% in about 18.5 hr. The data obtained on the rates of hydrolysis could not be fitted to any simple rate law. Since I and II have the same groups on boron and different groups on nitrogen, it would appear that, in this case, the nature of the group attached to nitrogen is a controlling factor in the rate of hydrolysis. The reduced rate of hydrolysis of an N-methylborazine when a diphenylyl group on boron is replaced by an α-naphthyl group, however, indicates that steric protection of boron can also reduce the rate of hydrolysis.

Experimental

Preparation of the Substituted Borazines.—The procedures used for the preparation of the several substituted borazines were, in general, quite similar. One of the preparations will be described in detail as typical of the general method used.

All operations, including filtrations, were carried out without exposure to air or moisture. Closed apparatus, using dry-nitrogen pressure, or a dry-nitrogen filled drybox was used. All solvents were thoroughly dried.

Preparation of B-Tris(diphenylyl)-N-trimethylborazine (I).—B-Trichloro-N-trimethylborazine was prepared by the method of Brown and Laubengayer.[8] A solution of 4.65 g. of B-trichloro-N-trimethylborazine in 100 ml. of dry ether was added dropwise with stirring to 90 ml. of a 0.685 M solution of diphenyllithium[9] in ethyl ether. A rapid exothermic reaction occurred and a white precipitate separated. The addition was complete in 20 min. and stirring and refluxing were continued for an additional hour. The ether was distilled off until a thick paste remained. Dry benzene (200 ml.) was then added and the solvent was distilled to near dryness. Additional benzene was added and the resulting suspension was filtered while hot and washed with hot benzene. These operations were repeated until a filtrate free of chloride was obtained. The solid remaining after evaporation of benzene was recrystallized from ethyl ether solution (saturated at reflux temperature and slowly cooled to −78°) giving 7.2 g. of crude product (yield, 61%), m.p. 214–219°. Several additional recrystallizations from ethyl ether gave white needles, m.p. 222–223°.

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[5] W. L. Ruigh, Research on Boron Polymers, WADC Report 55-26, part I–III (1955–1956).

[6] J. J. Harris, C. E. Ryschkewitsch, and H. H. Sisler, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept., 1957, 9S; *J. Am. Chem. Soc.*, **80**, 4515 (1958).

[7] S. J. Groszos and S. F. Stafiej, Abstracts, 131st National Meeting of the American Chemical Society, Miami, Fla., April, 1957, 53-O; *J. Am. Chem. Soc.*, **80**, 1359 (1958).

[8] C. A. Brown and A. W. Laubengayer, *ibid.*, **77**, 3699 (1955).

[9] H. Gilman, E. H. Zoellner, and W. M. Selby, *ibid.*, **54**, 1957 (1932).

Anal. Calcd. for $C_{39}H_{36}B_3N_3$: C, 80.81; H, 6.21; B, 5.61; N, 7.21. Found: C, 78.11; H, 6.41; B, 5.81; N, 7.31.

Preparation of B-Tris(diphenylyl)-N-triphenylborazine (II).—Following the general procedure described above, 44 g. of B-trichloro-N-triphenylborazine[7] reacted with 450 ml. of 0.725 *M* diphenyllithium in ethyl ether to give 38.2 g. of crude product (47% yield), m.p. 292–298°. The product was purified by several recrystallizations from a 1:6 by volume mixture of benzene and petroleum ether (b.p. 35–55°), saturating at reflux temperature and slowly cooling to −30°.. The purified product was in the form of white needles, m.p. 222–223°.

Anal. Calcd. for $C_{54}H_{42}B_3N_3$: C, 84.7; H, 5.5; B, 4.2; N, 5.5. Found: C, 84.8; H, 5.6; B, 4.7; N, 5.4.

Preparation of B-Tris(α-naphthyl)-N-trimethylborazine (III).—B-Trichloro-N-trimethylborazine (22.5 g.) reacted with 215 ml. of 1.41 *M* α-naphthylmagnesium bromide in ethyl ether. The combined crude products from three crystallizations from benzene totaled 28.1 g. (66% yield), m.p. 290–292°. Recrystallizations from a 1:5 by volume mixture of benzene and petroleum ether gave white crystals, m.p. 291-292.

Anal. Calcd. for $C_{33}H_{30}B_3N_3$: C, 79.1; H, 6.0; B, 6.5; N, 8.4. Found: C, 80.6; H, 5.9; B, 6.1; N, 7.7.

Preparation of B-Tris(*p*-terphenylyl)-N-trimethylborazine (IV).—Attempts to prepare *p*-terphenyllithium by direct reaction of *p*-terphenyl bromide with lithium gave very low yields. Better results were obtained when the *p*-terphenyllithium was prepared by a displacement reaction between *n*-butyllithium and *p*-terphenyl bromide.

B-Trichloro-N-trimethylborazine (22.7 g.) reacted as above with 0.3 mole of *p*-terphenyllithium. An 11-g. yield of crude product was obtained (15% yield based on *p*-terphenyl bromide), m.p. 245–250°. Recrystallizations from a 1:4 by volume mixture of benzene and petroleum ether gave a product, m.p. 255–256°.

Anal. Calcd. for $C_{57}H_{48}B_3N_3$: C, 84.8; H, 6.0; B, 4.0; N, 5.2. Found: C, 82.8; H, 5.9; B, 3.9; N, 5.0.

Hydrolysis Studies.—For the qualitative hydrolysis experiments, weighed samples (50–100 mg.) were treated with 20 ml. of water in a small flask at room temperature and in one case at reflux temperature. After various time intervals, the suspensions were filtered through sintered glass crucibles and the insoluble materials dried under vacuum, weighed, and their identity checked by melting point. The filtrates were analyzed for boron. The results of these experiments are given in Table I. In addition, samples of I and II were treated for several hours with hot concentrated KOH and hydrolysis was found to be complete. Similar treatment of III resulted in only 30% hydrolysis.

TABLE I

HYDROLYSIS OF SUBSTITUTED BORAZINES

Compound	Time, hr.	% recovery	B analysis of filtrate	M.p., °C., of recovered solid
I	0.5	52	Pos.	199–202
II	0.5	95	Neg.	Unchanged
II	0.5[a]	91	Pos.	Unchanged
III	24	95	Neg.	Unchanged

[a] At reflux temperature.

The data obtained on the rates of hydrolysis of I and II in dioxane–water solutions are listed in Table II. Less complete studies on the hydrolysis of III under comparable conditions indicated that the rate of hydrolysis of III was roughly comparable to that of II.

TABLE II

RATES OF HYDROLYSIS IN DIOXANE–WATER SOLUTIONS AT 25°

Compound I		Compound II	
Time, min.	% hydrolysis	Time, min.	% hydrolysis
2	82	3	11
8	87	5	13
27	90	15	16
157	93	53	20
1013	97	83	22
		1112	34

Decarboxylative Deamination of Amino Acids

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Reactions of aliphatic α-amino acids with isoamyl nitrite (γ-methylbutyl nitrite) in various solvents have been studied and the volatile hydrocarbon products have been analyzed by v.p.c. (Table I). In addition to these volatile hydrocarbon components, nitrogen, carbon dioxide, nitrous oxide, and nitric oxide are products of the reactions. The yield of nitrogen is apparently quantitative based on initial amino acid, but, since these inorganic gases also arise from thermal decomposition of isoamyl nitrite,[1] their yields are not necessarily meaningful. The hydrocarbon fraction constitutes less than 1% of the total amino acid consumed in the reaction. Preliminary studies of the nonvolatile products indicate that several products are formed (see Experimental). These have not been characterized. Control reactions have definitely established that the volatile hydrocarbon products do not arise from thermal decomposition of isoamyl nitrite, nor are they formed when isoamyl nitrite is not present in the reaction mixture.

TABLE I

VOLATILE HYDROCARBON PRODUCTS FROM REACTION OF ISOAMYL NITRITE AND α-AMINO ACIDS[a]

Hydrocarbons[d]	Valine–dioxane	Valine–DMF[b]	Valine–EtOH–H_2O[c]	α-Amino-butyric acid–dioxane	Alanine–DMF[b]
Methane	—[e]	—	—	2	3
Ethylene	—	—	3	3	94
Ethane	—	—	—	—	—
Propylene	5	1	—	87	3
Propane	—	—	—	—	0
Cyclopropane	—	0	—	5	—
Isobutane	—	—	—	—	0
Isobutene[f] 1-butene	76	88	82	2	*g*
trans-2-Butene	6	6	15	1	*g*
Methylcyclopropane	12	2	0	0	*g*
cis-2-Butene	≈1	3	0	0	*g*

[a] At 63°; values for products given in per cent. [b] Dimethylformamide. [c] 70% ethyl alcohol–water; room temperature. [d] Given in per cent of the total volatile (<C_5) hydrocarbon fraction (<1% of initial amino acid). [e] — indicates trace amount observed. [f] Not separated under the experimental conditions (see Experimental). [g] The presence of these components was not checked.

This study was originally undertaken to ascertain whether diazotization of α-amino acids under aprotic conditions[2] would lead to the formation of carbenoid species by simultaneous or stepwise loss of nitrogen and carbon dioxide from I. The extremely low yields (*vide supra*) of hydrocarbon products in these reactions, which might be derived from such a reaction, certainly negate any preparatory value.

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(1) D. H. Szulczewski and T. Higuchi, *Anal. Chem.*, **29**, 1541 (1957); see also N. Kornblum and E. P. Oliveto, *J. Am. Chem. Soc.*, **71**, 226 (1949).

(2) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).