146. *Alkyltin Route to Alkylboron and Alkyltin Halides and Compounds Prepared therefrom.*

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Alkylboron halides (Cl, Br) are conveniently prepared on a molar scale by reaction of a boron trihalide and a tetra-alkyltin; in contrast with the phenyl system, not more than two of the alkyl groups attached could be transferred from tin to boron. Some of the other products were identified or isolated. Representative esters, including 1,3-dioxa-2-boroles, have been prepared directly from the alkylboron halides to demonstrate the procedure, to provide additional evidence of constitution, and to provide materials for spectroscopy (to be reported elsewhere).

A number of dialkoxydialkyltins and bis-8-hydroxyquinolinates have been prepared from the dialkyltin dihalides for similar reasons.

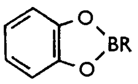
ALKYL- AND ARYL-BORON HALIDES are important reagents for which direct preparation on a molar scale by ordinary techniques is desirable.[1] This was achieved for arylboron halides by the use of tetraphenyltin [2] and arylmercury halides,[3] and we now describe the alkyltin–boron trichloride procedure for preparation of alkylboron halides.

The use of alkyltins arose from the observation by Brinckman and Stone [4] that vinylboron halides could be made from tetravinyltin and boron trihalide. Their work involved conventional high-vacuum systems and millimole quantities. Tetramethyltin and boron trifluoride gave methylboron difluoride and trimethyltin tetrafluoroborate in a sealed tube.[5]

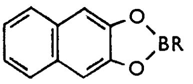
Tetra-alkyltins react readily with boron trichloride to form alkylboron chlorides and even trialkylboron, according to the proportions used; but in contrast to the phenyl system [2] not more than two alkyl groups are transferable from tin to boron, even when boron trichloride is used in excess and in a sealed tube. Boron tribromide behaved similarly.

$$R_4Sn + 2BCl_3 \longrightarrow R_2SnCl_2 + 2RBCl_2 \tag{1}$$

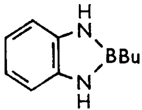
In each system there were several products, and their complete separation was extremely protracted; stannous chloride was isolated. In the tetra n-butyltin–boron tribromide system, butane, but-1-ene, and *trans*- and *cis*-but-2-ene were identified, and stannous bromide was isolated. In the tetra-n-octyltin–boron chloride system, octenes were identified and stannous chloride was isolated. Nevertheless, the procedure appears to be the most convenient for the preparation of alkylboron dihalides (Cl, Br) and dialkylboron halides on a molar scale by ordinary techniques.



(I : R = Et, Pr^n, Bu^n, n-C_8H_{17})



(II : R = Pr^n, Bu^n, n-C_8H_{17})



(III)

Certain esters have now been prepared by interaction of the alkylboron halide and the hydroxy-compound; other procedures were used previously.[6] Examples of the 1,3-dioxa-2-boroles obtained are (I) and (II); the 1,3-diaza-2-boroline (III) has also been obtained. From the alkylboron dichloride and ammonia, *B*-trialkylborazoles [$(RB{\cdot}NH{\cdot})_3$; R = Pr^n and Bu^n] have been prepared.

From the dialkyltin dihalides a number of dialkoxydialkyltins were prepared (Table 1).

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[1] Gerrard, " The Organic Chemistry of Boron," Academic Press, Inc., New York, 1961.

[2] Burch, Gerrard, Howarth, and Mooney, *J.*, 1960, 4916.

[3] Gerrard, Howarth, Mooney, and Pratt, *J.*, 1963, 1582.

[4] Brinckman and Stone, *Chem. and Ind.*, 1959, 254; *J. Amer. Chem. Soc.*, 1960, **82**, 6218.

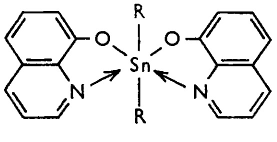
[5] Burg and Spielman, *J. Amer. Chem. Soc.*, 1961, **83**, 2667.

[6] Maitlis, *Chem. Rev.*, 1962, **62**, 223.

Several organotin alkoxides have been mentioned,[7] but few properly characterised. The following have been made from the organotin halide and sodium alkoxide: $Me_3Sn{\cdot}OEt$, $Et_3Sn{\cdot}OEt$,[8] $Ph_2Sn(OEt)_2$,[9] $Bu^n{}_3Sn{\cdot}OMe$, $Ph_3Sn{\cdot}OMe$, and $Bu^n{}_2Sn(OMe)_2$.[10] From the perfluorovinyltin compound the following were prepared: $Et_2Sn(OEt)_2$, $Bu^n{}_2Sn(OEt)_2$ (by alcoholysis), and $Bu^n{}_3Sn{\cdot}OEt$ (by sodium ethoxide).[11] In the present work the dialkoxides were prepared as in reaction (2) (R'OH as solvent) at 0°:

$$R_2SnX_2(Cl, Br) + 2NaOR' \longrightarrow R_2Sn(OR')_2 + 2NaX \qquad (2)$$

They are viscous liquids, except for $Me_2Sn(OMe)_2$ which was a low-melting solid; all are very easily hydrolysed.


(IV)

From the organotin dihalides 8-hydroxyquinolinate compounds (IV) were prepared (Table 2) by reported procedures[12] and, unlike the simple dialkoxides are stable to moisture, presumably because the lone-pair electrons on each nitrogen use the vacant 5*d*-orbitals of tin, and give a stable compound of octahedral (sp^3d^2) configuration.

Infrared, nuclear magnetic resonance, and other studies of the tin and boron compounds will be reported elsewhere.

EXPERIMENTAL

Preparation of Alkylboron Halides.—Operations were conducted in apparatus flushed with nitrogen. Boron trihalide and tetra-alkyltin were heated under a reflux condenser filled with a mixture of acetone and solid carbon dioxide. The time of heating is given below in parentheses. Several products were obtained, and their complete separation would have involved protracted operations. Distillation afforded in the main a condensate (−80°), examined by vapour-phase chromatography (v.p.c.) (R.T. = relative retention times), and infrared spectroscopy. Higher fractions of alkylboron halides were not easily separated into pure specimens; the yields recorded are for the stated specimen, and more was present in the unresolved fractions. The specimens were characterised by chemical analysis, infrared spectroscopy, and preparation of derivatives. The distilled dialkyltin dihalide was recrystallised from n-pentane, and characterised by elemental analysis and infrared spectroscopy.

The ^{11}B nuclear magnetic resonance of some of the boron dihalides have been measured on a Perkin-Elmer nuclear magnetic resonance spectrometer at 12·833 Mc./sec. and the chemical shifts, designated ($\delta^{11}B$), are in p.p.m. to low field of Me_2O,BF_3 as external standard, no susceptibility correction has been applied.

Tetra-n-butyltin (A) (173·6 g., 1 mol.) and boron trichloride (4 mol.) (16 hr.) gave a condensate (−80°) (boron trichloride, 1·9 mole) and a liquid (13·9 g.), b. p. 72—106·5°, containing n-butyl chloride (2·78 g., R.T. 0·67), s-butyl chloride (1·2 g., R.T. 0·48) (both arising from di-n-butyl ether present in (A), and n-butylboron dichloride (9·9 g., R.T. 0·20). n-Butylboron dichloride (45·7 g.), b. p. 106—108° (Found: B, 7·4; Cl, 49·9. Calc. for $C_4H_9BCl_2$: B, 7·8; Cl, 51·1%) ($\delta^{11}B$ 63·8), and di-n-butyltin dichloride (99·6 g.), m. p. 43° (Found: C, 31·6; H, 6·1; Cl, 23·0; Sn, 38·3. Calc. for $C_8H_{18}Cl_2Sn$: C, 31·6; H, 6·0; Cl, 23·3; Sn, 39·1%) were also obtained. A condensate (−80°) (31·5 g.) was formed during distillation. The v.p.c. involved a 5% w/w squalane–Celite column at 40°, with 1·9 l. of N_2/hr., at an inlet pressure (55·5 cm. and outlet pressure 39·0 cm. Hg. (iso-octane = 1·00).

With tetra-n-butyltin (A) (296 g., 1 mol.) and boron trichloride (2·1 mol.) (14 hr.) there was a similar pattern of results; crude n-butylboron dichloride (94·1 g., 40% yield), b. p. 101—110° (Found: B, 7·6; Cl, 49·3%) and di-n-butyltin dichloride (234·3 g.), b. p. 104—108°/0·7 mm., giving white crystals (215·3 g., 83%) were isolated. With 1 mol. of boron trichloride and 1·0 mol. (642 g.) of tetra-n-butyltin (16 hr.), di-n-butylboron chloride (52·8 g., 17·9%), b. p. 68—69°/20 mm. (Found: B, 6·7; Cl, 22·5. Calc. for $C_8H_{18}BCl$: B, 6·8; Cl, 22·1%), was also formed.

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[7] Ingham, Rosenberg, and Gilman, *Chem. Rev.*, 1960, **60**, 459.

[8] Ladenburg, *Annalen*, *Suppl.*, 1872, **8**, 79; *Ber.*, 1870, **3**, 353.

[9] Aronheim, *Annalen*, 1878, **194**, 145.

[10] Alleston and Davies, *J.*, 1962, 2050.

[11] Seyferth, Raab, and Brändle; *J. Org. Chem.*, 1961, **26**, 2934.

[12] Blake, Coates, and Tate, *J.*, 1961, 756.

Increasing the ratio of (A) (604 g., 3 mol.) to boron trichloride (2 mol.) (13 hr.) gave crude di-n-butylboron chloride (103·2 g.), b. p. 60°/15 mm. to 70°/10 mm., tri-n-butylboron (31·2 g., 29·6%), b. p. 87—90°/9 mm. (Found: C, 78·9; H, 14·9; B, 5·7. Calc. for $C_{12}H_{27}B$: C, 79·1; H, 14·9; B, 5·9%), and a mixture (478·8 g.) of tri-n-butyltin chloride and di-n-butyltin dichloride.

Boron tribromide (1·1 mol.) and tetra-n-butyltin (A) (319 g., 1 mol.) (55 hr.) gave a condensate (33 g.) of butane (51%), but-1-ene (26%), *trans-* (17%) and *cis*-but-2-ene (6%). Addition of n-pentane (100 ml.) to the residue gave stannous bromide (43 g.) (Found: Br, 58·6: Sn, 42·2. Calc. for Br_2Sn: Br, 57·4; Sn, 42·6%), and the pentane filtrate afforded di-n-butylboron bromide (110 g., 58·4%), b. p. 73—75·5°/13 mm. (Found: B, 5·2; Br, 39·2. Calc. for $C_8H_{18}BBr$: Br, 5·3; B, 39·0%), di-n-butyltin dibromide (151 g.), b. p. 157—160°/13 mm., m. p. 22·0° (Found: C, 24·3; H, 4·5; Br, 39·3; Sn, 27·8. Calc. for $C_8H_{18}Br_2Sn$: C, 24·4; H, 4·6; Br, 40·7; Sn, 30·2%), and fractions containing n-butylboron dibromide. V.p.c. was by a 12 ft. 35% w/w tetrahydrodimethylthiophen dioxide (dimethylsulpholane)–Celite column at 20°.

Tetra-n-propyltin (291 g., 1 mol.) and boron trichloride (2·1 mol.) (8 hr.) gave, *inter alia,* n-propylboron dichloride (111 g.), b. p. 78—80° (Found: B, 8·2; Cl, 54·5. Calc. for $C_3H_7BCl_2$: B, 8·7; Cl, 56·9%), ($\delta^{11}B$ 63·5), and di-n-propyltin dichloride (209 g.), m. p. 79·5—80·5° (Found: C, 26·0; H, 5·2; Cl, 25·7; Sn, 43·0. Calc. for $C_6H_{14}Cl_2Sn$: C, 26·1; H, 5·1; Cl, 25·7; Sn, 43·0%).

Tetra-n-octyltin (315·6 g., 1 mol.) and boron trichloride (2 mol.) (8 hr.) gave *n-octylboron dichloride* (91 g.), b. p. 77—78°/8 mm. (Found: B, 5·4; Cl, 36·3. $C_8H_{17}BCl_2$ requires B, 5·5; Cl, 36·4%) ($\delta^{11}B$ 64·0), a less pure specimen (44 g.), b. p. 74—76°/8 mm., crude di-n-octyltin dichloride (172 g.) [91 g. of m. p. 46—47° (Found: C, 46·1; H, 8·1; Cl, 17·2; Sn, 28·2. Calc. for $C_{16}H_{34}Cl_2Sn$: C, 46·1; H, 8·2; Cl, 17·0; Sn, 28·5%) after repeated crystallisation from isopentane], and stannous chloride (41 g.).

Tetraethyltin (108 g., 1 mol.) and boron trichloride (2 mol.) (6 hr.) gave, *inter alia,* ethylboron dichloride (54·5 g.), b. p. 49—54° (Found: B, 9·8; Cl, 62·5. Calc. for $C_2H_5BCl_2$: B, 9·8; Cl, 64·0%), and crude diethyltin dichloride (1·162 g.), which gave white needles (82 g.), m. p. 84·5—86·0° (Found: C, 19·3; H, 4·2; Cl, 28·7; Sn, 48·0. Calc. for $C_4H_{10}Cl_2Sn$: C, 19·4; H, 4·1; Cl, 28·7; Sn, 47·9%) after three crystallisations from benzene.

Tetramethyltin (173 g., 1 mol.) and boron tribromide (2 mol.) (3 hr.) gave methylboron dibromide (225 g.), b. p. 59—62° (Found: B, 5·5; Br, 85·0. Calc. for CH_3BBr_2: B, 5·8; Br, 86·1%), dimethylboron bromide (26·5 g.), b. p. 30—32° (Found: Br, 64·6. Calc. for C_2H_6BBr: Br, 66·2%), and white crystals of dimethyltin dibromide (212 g.) (from benzene–n-pentane), m. p. 73·5—74·5° (Found: C, 7·7; H, 2·0; Br, 51·6; Sn, 38·4. Calc. for $C_2H_6Br_2Sn$: C, 7·8; H, 2·0; Br, 51·8; Sn, 38·4%).

Compounds Derived from Alkylboron Chlorides.—Diethyl-n-propylboronate (71%), b. p. 130—132°, n_D^{20} 1·3891 (Found: C, 58·3; H, 11·9; B, 7·5. $C_7H_{17}BO_2$ requires C, 58·4; H, 11·9; B, 7·5%), was obtained by adding ethanol (23·7 g., 2·34 mol.) to n-propylboron dichloride (1 mol.) in benzene. *Diethyl n-butylboronate,* b. p. 154—159°, n_D^{20} 1·3972 (Found: C, 60·5; H, 11·9; Br, 6·8. $C_8H_{19}BO_2$ requires C, 61·2; H, 11·5; B, 6·9%). and *diethyl n-octylboronate,* b. p. 110—114°/16 mm., n_D^{20} 1·4168 (Found: C, 67·2; H, 12·6; B, 4·9. $C_{12}H_{27}BO_2$ requires C, 67·3; H, 12·7; B, 5·0%) were prepared as above. *Ethyl dimethylborinate* (61%), b. p. 44—46°, n_D^{20} 1·3650 (Found: C, 55·1; H, 12·7; B, 12·4. $C_4H_{11}BO$ requires C, 55·9; H, 12·9; B, 12·6%), was obtained from dimethylboron bromide (25·5 g.). Ethyl di-n-butylborinate (72%), b. p. 79—82°/17 mm., n_D^{20} 1·4121 (Found: C, 70·5; H, 13·5; B, 6·1. Calc. for $C_{10}H_{23}BO$: C, 70·6; H, 13·6; B, 6·4%), was likewise obtained from di-n-butylboron chloride (20·8 g.).

2-*Propylbenzo*-1,3-*dioxa*-2-*borole* (72%), b. p. 95·5—96°/15 mm., n_D^{20} 1·4964 (Found: C, 66·8; H, 6·7; B, 6·5. $C_9H_{11}BO_2$ requires C, 66·7; H, 6·8; B, 6·7%), was likewise obtained from n-propylboron dichloride (24·2 g., 1 mol.) and pyrocatechol (21·4 g., 1 mol.). 2-*Butylbenzo*-1,3-*dioxa*-2-*borole* (78%), b. p. 52°/0·05 mm., n_D^{20} 1·4942 (Found: C, 67·9; H, 7·5; B, 6·0. $C_{10}H_{13}BO_2$ requires C, 68·2; H, 7·5; B, 6·1%), was obtained from n-butylboron dichloride (34 g., 1 mol.) and catechol (1 mol.) in methylene chloride (200 ml.) 2-*n-Propylnaphtho*[2,3-d]-1,3-*dioxa*-2-*borole* (62%), m. p. 68·5—70° (Found: C, 73·6; H, 6·3; B, 5·0. $C_{13}H_{13}BO_2$ requires C, 73·6; H, 6·2; B, 5·1%) (two crystallisations from isopentane), was obtained from n-propylboron dichloride (15·6 g., 1 mol.) and naphthalene-2,3-diol (1 mol.) in benzene (100 ml.). Likewise the 2-*n-butyl compound* (80%), m. p. 75·5—77° (Found: C, 74·2; H, 6·8; B, 4·7.

$C_{14}H_{15}BO_2$ requires C, 74·3; H, 6·7; B, 4·8%), was obtained. The 2-*n-octyl compound* (66%) m. p. 42—43° (Found: C, 76·2; H, 8·3; H, 3·8. $C_{18}H_{23}BO_2$ requires C, 76·5; H, 8·2; B, 3·8%) (crystallisation from methylene dichloride), was obtained from n-octylboron dichloride (10·6 g., 1 mol.). 2-n-Butylbenzo-1,3-diaza-2-borole (66·5%), m. p. 80—82° (Found: C, 68·8; H, 8·5; B, 6·0; N, 16·2. Calc. for $C_{10}H_{15}BN_2$: C, 69·0; H, 8·7; B, 6·2; N, 16·1%) [crystallised as white plates from n-pentane–isopentane (1 : 1)], was obtained from the boron dichloride (13·1 g., 1 mol.) and *o*-phenylenediamine (1 mol.) in benzene. The m. p. is reported as 61—62° [13] and 86—86·5°.[14]

TABLE 1.

Dialkoxydialkyltins.

No.	R in $R_2Sn(OR')_2$	R′ in $R_2Sn(OR')_2$	B. p.°/mm. (m. p.)	n_D^{20}	Yield (%)	NaCl g.	NaCl (%)
1	Me	Me	(46·5—47·5°)	—	74·7	6·55	85·5
2	,,	Et	81°/0·1	1·4775	56·2	7·50	98·0
3	,,	Pr^n	100°/0·1	1·4711	41·0	5·19	67·7
4	,,	Bu^n	130—131°/0·5	1·4720	42·6	5·30	69·1
5	Et	Me *	102—104°/0·05 †	1·5019	49·3	5·91	77·1
6	,,	Et *	90°/0·3 ‡	1·4845	55·6	7·04	91·8
7	,,	Pr^n	88°/0·01	1·4811	48·8	7·04	91·8
8	,,	Bu^n	112°/0·03	1·4778	36·8	6·18	80·6
9	Pr^n	Me	105—107°/0·1	1·4925	49·3	6·39	83·4
10	,,	Et	84°/0·03	1·4820	56·1	6·74	88·0
11	,,	Pr^n	90—92°/0·05	1·4782	49·7	6·96	91·0
12	,,	Bu^n	100°/0·05	1·4772	48·3	7·22	94·3
13	Bu^n	Me *	126—130°/0·05 §	1·4880	46·0	6·65	86·8
14	,,	Et *	96—97°/0·2 ¶	1·4790	59·9	7·59	99·0
15	,,	Pr^n	99—100°/0·1	1·4782	53·9	6·60	86·1
16	,,	Bu^n	136—138°/0·05	1·4721	40·7	4·37	57·1
17	n-C_8H_{17}	Me	167—168°/0·05	1·4802	64·0	6·74	88·0
18	,,	Et	170°/0·07 to 175°/0·1	1·4772	63·3	6·73	87·8
19	,,	Pr^n	174°/0·02 to 180°/0·4	1·4753	55·7	7·29	95·0
20	,,	Bu^n	182—188°/0·05	1·4735	52·3	5·71	74·6

No.	Found (%) C	Found (%) H	Found (%) Sn	Formula	Required (%) C	Required (%) H	Required (%) Sn
1	22·6	5·5	56·6	$C_4H_{12}O_2Sn$	22·8	5·7	56·2
2	30·2	6·9	50·1	$C_6H_{16}O_2Sn$	30·2	6·8	49·6
3	35·9	7·6	45·0	$C_8H_{20}O_2Sn$	36·0	7·6	44·4
4	40·6	8·3	40·6	$C_{10}H_{24}O_2Sn$	40·7	8·2	40·2
5	30·2	6·9	50·2	$C_6H_{16}O_2Sn$	30·1	6·8	49·6
6	35·8	7·6	44·9	$C_8H_{20}O_2Sn$	36·0	7·6	44·4
7	40·6	8·1	40·2	$C_{10}H_{24}O_2Sn$	40·7	8·2	40·2
8	44·6	8·8	36·8	$C_{12}H_{28}O_2Sn$	44·6	8·7	36·7
9	36·1	7·6	44·5	$C_8H_{20}O_2Sn$	36·0	7·6	44·5
10	40·6	8·1	40·2	$C_{10}H_{24}O_2Sn$	40·7	8·2	40·2
11	44·7	8·7	36·5	$C_{12}H_{28}O_2Sn$	44·6	8·7	36·7
12	47·8	9·1	34·0	$C_{14}H_{32}O_2Sn$	47·9	9·2	33·8
13	40·8	8·3	40·2	$C_{10}H_{24}O_2Sn$	40·7	8·2	40·2
14	44·5	8·7	36·7	$C_{12}H_{28}O_2Sn$	44·6	8·8	36·7
15	47·7	9·0	33·7	$C_{14}H_{32}O_2Sn$	47·9	9·2	33·8
16	50·9	9·5	30·8	$C_{16}H_{36}O_2Sn$	50·7	9·6	31·3
17	53·2	9·9	28·5	$C_{18}H_{40}O_2Sn$	53·1	9·9	29·1
18	55·2	10·2	27·6	$C_{20}H_{44}O_2Sn$	55·1	10·2	27·2
19	57·0	10·5	25·7	$C_{22}H_{48}O_2Sn$	57·1	10·5	25·6
20	58·7	10·7	24·1	$C_{24}H_{52}O_2Sn$	58·6	10·6	24·1

* Known compound. † A patent [15] reports b. p. 124—126°/3 mm., n_D^{20} 1·4206. ‡ Seyforth *et al.*[11] report b. p. 78°/0·1 mm., n_D^{25} 1·4828. § Alleston and Davies [10] report b. p. 126—128°/0·05 mm., n_D^{25} 1·4852. ¶ Seyferth *et al.*,[11] report b. p. 95°/0·15 mm.

n-Butylboron dichloride (119·9 g., 3 mol.) was dissolved in benzene (250 ml.) and treated

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[13] Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 831.
[14] Letsinger and Hamilton, *J. Amer. Chem. Soc.*, 1958, **80**, 5411.
[15] Mack and Parker, U.S.P. 2,700,675.

with gaseous ammonia under reflux (−80° condenser). The mixture was stirred for 8 hr. The cold system was filtered from ammonium chloride which was then heated with benzene for 3 hr. to extract adhering borazole. *B*-Tri-n-butylborazole (41·2 g., 57·7%), b. p. 102—105°/0·2 mm. (Found: C, 57·7; H, 12·3; B, 12·6; N, 16·8. Calc. for $C_{12}H_{30}B_3N_3$: C, 57·9; H, 12·2; B, 13·0; N, 16·9%), was obtained. Similarly *B*-tri-n-propylborazole (10·9 g., 51·5%), b. p. 70°/0·6 mm. (Found: C, 52·2; H, 11·6; B, 15·3; N, 19·6. Calc. for $C_9H_{24}B_3N_3$: C, 52·3; H, 11·7; B, 15·7; N, 20·3%), was obtained from n-propylboron dichloride (38 g., 3 mol.).

n-Propylboronic acid (3·55 g.), m. p. 105—106° (Found: C, 40·9; H, 10·1; B, 12·3. Calc. for $C_3H_9BO_2$: C, 41·0; H, 10·2; B, 12·3%), was obtained by the reaction of n-propylboron dichloride (10·9 g.) with water in ether. The acid (1·72 g.) gave the ester of diethanolamine (2·04 g.), m. p. 155—157·5° (Found: C, 53·8; H, 10·4; B, 6·8; N, 8·8. Calc. for $C_7H_{16}BNO_2$: C, 53·6; H, 10·3; B, 6·9; N, 8·9%), by the azeotropic removal of water from a benzene solution. The ester recrystallised from benzene–pentane (1 : 1). n-Octylboronic acid (8·82 g.), m. p. 83—84° (Found: C, 61·0; H, 12·2; B, 6·7. Calc. for $C_8H_{19}BO_2$: C, 60·8; H, 12·1; B, 6·8%), was similarly prepared from n-octylboron dichloride (13·75 g.) and was (5·3 g.) converted into the *diethanolamine ester* (5·14 g.), m. p. 97·5—98·5° (Found: C, 63·7; H, 11·4; B, 4·6; N, 6·1. $C_{12}H_{26}BNO_2$ requires C, 63·5; H, 11·5; B, 4·8; N, 6·2%).

Compounds Derived from Dialkyltin Dihalides.—The dialkoxydialkyltins (Table 1) were prepared as described for the n-butyl compound. Di-n-butyltin dichloride (20·0 g., 1·0 mol.) in anhydrous butan-1-ol (22·0 ml.) was added dropwise to a stirred solution of sodium n-butoxide (2·0 mol.) in the same solvent at 0° under dry nitrogen. The mixture was stirred for 3 hr., and the finely divided precipitate (4·84 g.) containing sodium chloride (4·37 g., 57·1%) was then centrifuged off in the absence of moisture. The solvent was removed from the supernatant liquid at 20°/0·1 mm. to give *di-n-butoxydi-n-butyltin* (10·19 g., 40·7%), b. p. 136—138°/0·05 mm., n_D^{20} 1·4721 (Found: C, 50·9; H, 9·5; Sn, 30·8. $C_{16}H_{36}O_2Sn$ requires C, 50·7; H, 9·6; Sn, 31·3%).

Dialkyltin bis-8-hydroxyquinolinate derivatives (Table 2) were prepared by the described procedure.[12]

TABLE 2.

Dialkyltin bis-8-hydroxyquinolinates.

R	M. p.	Yield (%)	Found (%)				Formula	Required (%)			
			C	H	N	Sn		C	H	N	Sn
Me	236·5—238°	71·7	54·7	4·3	6·3	27·4	$C_{20}H_{18}N_2O_2Sn$	54·9	4·2	6·4	27·1
Et	177—178	88·0	56·5	5·0	5·8	25·7	$C_{22}H_{22}N_2O_2Sn$	56·8	4·8	6·0	25·5
Pr^n	162—163	68·8	58·4	5·5	5·6	24·1	$C_{24}H_{26}N_2O_2Sn$	58·5	5·3	5·7	24·1
Bu^n *	155—156	79·5	60·1	5·9	5·4	22·5	$C_{26}H_{30}N_2O_2Sn$	59·9	5·8	5·4	22·8
Bu^i	188—189	32·8	59·7	5·9	5·1	23·0	,,	59·9	5·8	5·4	22·8
n-C_8H_{17} ...	78—79	53·6	64·2	7·1	4·4	18·9	$C_{34}H_{46}N_2O_2Sn$	64·4	7·3	4·4	18·8
$C_6H_5\cdot CH_2$...	118—120	67·0	65·3	4·5	4·6	19·7	$C_{32}H_{26}N_2O_2Sn$	65·3	4·5	4·8	20·2

* See ref. 12.

Gas-chromatographic Separation of Alkyltin Chlorides.—In the procedure described herein, the alkyltin chlorides appear as by-products; but they are usually obtained by the mutual exchange of alkyl and chlorine between two atoms of tin, $R_4Sn + SnCl_4 \longrightarrow R_3SnCl + RSnCl_3$, etc. Separation by fractional distillation is often protracted, and a simple method was required to analyse a reaction product. The apparatus consisted of a 1 ft. glass column, of 4 mm. bore, containing a 16 cm. length of Celite impregnated with 5% " Embaphase " silicone as stationary phase. A Pye argon detector was used, but with a radium D source in place of strontium-90. The column and detector were placed inside a 14″ length of 5″ blown-blank wound with 22 S.W.G. Staybrite wire and thermostatically controlled at 90° by means of a Fielden Bikini controller. A pre-column flash-heater, at 170°, was used to ensure complete vaporisation of the sample. Of naphthalene (b. p. 218°), biphenyl (b. p. 254°), acenaphthene (b. p. 277°), dimethyl phthalate (b. p. 282°), anthracene (b. p. 351°), and benzyl biphenyl (b. p. ~285°/110 mm.), only acenaphthene was suitable as a marker, since for the others either the retention time was too short or the peak coincided with that of one of the components. The relative retention times for the butyltin system are shown in Table 3, columns I and II give the retention times for each component separately, and III and IV those for a mixture of all four components (the retention time of acenaphthene, added to the mixture as a solution in chloroform, is taken as 1·00).

TABLE 3.

	B. p./mm. (found)	Relative retention times I	II	III	IV
n-Butyltin trichloride	94°/10	0·21		0·22	0·20
Di-n-butyltin dichloride	104—108°/0·7	1·35	1·33	1·36	1·34
Tri-n-butylin chloride	172°/25	3·78		3·78	3·78
Tetra-n-butyltin	149°/12	5·42	5·21	5·26	5·23

The use of a conventional 4 ft. Pye argon column caused too great disproportionation and decomposition; no decomposition was observed on the short column. Tetra-n-octyltin (b. p. 268°/10 mm.), tetraisopropyltin, and tetra-n-propyltin were also analysed.

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