Synthesis and Reactions of Some New 1,3-Dioxa-2-bora Heterocycles Derived from *o*-Hydroxybenzyl Alcohol

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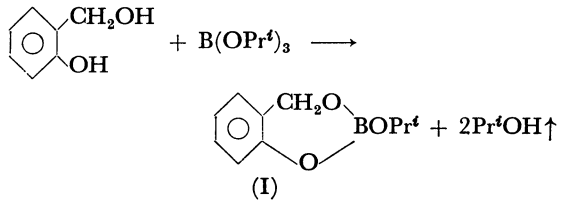
2-Isopropoxy-4*H*-1,3,2-benzodioxaborin(I), obtained from isopropyl borate and *o*-hydroxybenzyl alcohol, reacts with a variety of hydroxy compounds (*viz.*, *t*-butyl alcohol, phenol, ethane-1,2-diol, 2-aminoethanol, *o*-amino phenol) and acetic anhydride to give the corresponding 2-substituted heterocycles. Reactions of (I) as well as other 1,3-dioxa-2-bora heterocycles with bases (*viz.*, ammonia, triethylamine, pyridine, dimethylformamide) show that the electrophilicity of boron decreases in the order: 2-alkoxy-1,3,2-benzodioxaborole>2-phenoxy-4*H*-1,3,2-benzodioxaborin>(I)>2-alkoxy-1,3,2-dioxaborinane.

Codisproportionation reaction between bis(4*H*-1,3,2-benzodioxaborin-2-yl)oxide (obtained directly from boric acid and *o*-hydroxybenzyl alcohol) and triorganotin hydroxide or oxide yields 2-triorganostannoxy-4*H*-1,3,2-benzodioxyborin. Cleavage and insertion reactions of these compounds have been studied.

Boron heterocycles containing two oxygen atoms, *e.g.*, 1,3,2-dioxaborolanes,[1] -borinanes[2] and 1,3,2-benzodioxaboroles[3] have been extensively studied. The effect of ring size on the stability[4] as well as the electrophilic nature of boron[5] in such derivatives have also been investigated. The higher reactivity of benzodioxaborole derivatives in comparison to dioxaborinanes and dioxaborolanes can be easily understood in terms of greater electron deficient character of boron in the former class of compounds. Boron heterocycles derived from *o*-hydroxybenzyl alcohol form a mixed system and have been synthesized only recently by the reactions of this ligand with tris(dimethylamino)borane, tris(ethanethiolato)borane and phenylboric acid.[6] Azeotropic removal of water from a mixture of *o*-hydroxybenzyl alcohol, boric acid and an alcohol leads to the formation of the corresponding 2-alkoxy-4*H*-1,3,2-benzodioxaborin. In the present paper we report a detailed study of the synthesis and reactions of various 2-substituted-4*H*-1,3,2-benzodioxaborins. Attempts have also been made to compare the electrophilic nature of boron in these and in other types of 1,3-dioxa-2-bora heterocycles.

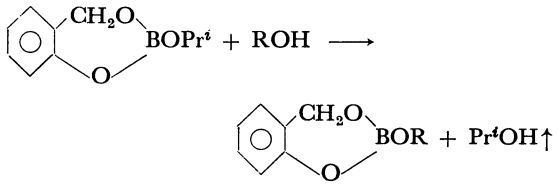
Results and Discussion

2-Isopropoxy-4*H*-1,3,2-benzodioxaborin (I) is obtained as a colourless volatile liquid by the interaction of isopropyl borate with *o*-hydroxybenzyl alcohol in refluxing benzene, with azeotropic removal of the liberated isopropanol.



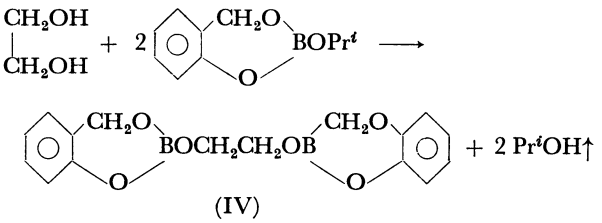
(I)

The isopropoxy group of the boron heterocycle (I) could be easily replaced by other alkoxy and phenoxy groups by simple alcohol interchange technique in benzene. The progress of the reaction could be followed by estimating the amount of isopropanol in azeotrope. It has been observed qualitatively that these reactions are comparatively slower than those of 2-isopropoxy-1,3,2-benzodioxaborole.



(II), R=Bu^t; (III), R=Ph

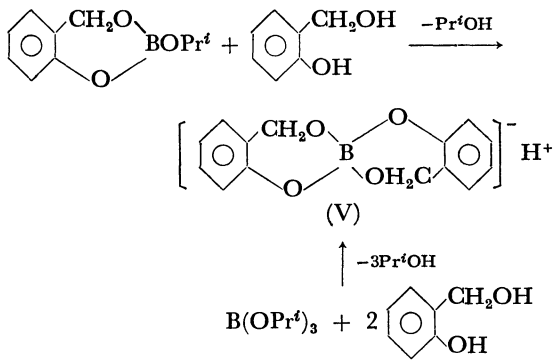
Reaction of I with ethylene glycol affords 2,2′-ethylenedioxybis(4*H*-1,3,2-benzodioxaborin) (IV) as a white solid.



(IV)

It is noteworthy that the reaction of I with *o*-hydroxybenzyl alcohol in 2:1 molar ratio does not proceed to completion and only half of the calculated amount of isopropanol is obtained in the azeotrope. The resulting semisolid on distillation yields, some unreacted 2-isopropoxyborin (I) and decomposed residue. Similar results are obtained when reaction of isopropyl borate with *o*-hydroxybenzyl alcohol in 2:3 molar ratio is carried out. It appears that the product in these reactions is an equimolar mixture of I and bis(*o*-benzomethylenedioxy)borate (V). 2,2′-(*o*-Benzomethylenedioxy)bis(4*H*-1,3,2-benzodioxaborin) is not obtained in these reactions even under forcing conditions. This may be due to steric reasons. Molecular models show that two 4*H*-1,3,2-benzodioxaborin-2-yl moieties present on the two oxygen atoms of *o*-benzomethylenedioxy moiety cannot rotate freely.

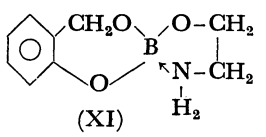
Compound V is obtained in quantitative yields as a viscous semisolid by the following routes:



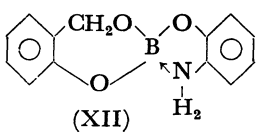
Attempts to synthesize the sodium salt of V by crystallisation from an aqueous solution of boric acid, *o*-hydroxybenzyl alcohol and sodium hydroxide were unsuccessful. The ammonium salt $[(C_7H_6O_2)_2B]^-[NH_4]^+$ (VI), however, is immediately precipitated on passin gammonia to a benzene solution of V.

Reactions of 2-phenoxy- and 2-isopropoxy-4*H*-1,3,2-benzodioxaborin with nitrogen donors have been studied. The phenoxy derivative (III) forms stable 1:1 complexes with triethylamine and pyridine (VII and VIII respectively) exothermally whereas with dimethylformamide, no reaction appears to take place. I also does not give an adduct with dimethylformamide but on mixing with pyridine, heat is evolved and liquid complex (IX) is formed which loses pyridine slowly under high vacuum, leaving behind a highly viscous semisolid, insoluble in benzene and carbon tetrachloride. This semisolid yielded I on distillation under reduced pressure. The structure of the semisolid could not be studied further. Unlike pyridine, ammonia forms a stable 1:1 complex (X) with I. Attempts to prepare a salt of the type $[C_6H_4<^{O}_{CH_2O}>B(OPr^i)_2]^-[NH_4]^+$ by passing ammonia to an equimolar mixture of I and isopropanol in benzene were unsuccessful. The addition complex (X) was precipitated in these cases also. It may be pointed out in this context that 2-isopropoxy-1,3,2-benzodioxaborole forms addition complexes with various donors including dimethylformamide whereas 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane does not show any tendency of complex formation.[7] Thus, the electrophilicity of boron in 1,3-dioxa-2-bora heterocycles appears to decrease in the order: 2-isopropoxy-1,3,2-benzodioxaborole>III>I>2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane.

Reactions of I with 2-aminoethanol and *o*-aminophenol in refluxing benzene give insoluble solid products XI and XII in which there is internal coordination from nitrogen to boron. In contrast to I and III, the derivatives XI and XII do not show any tendency to form complexes with nitrogen donors.

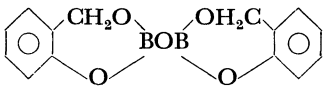


(XI)

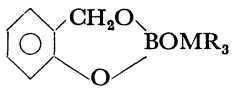


(XII)

Azeotropic removal of water with benzene from an equimolar mixture of boric acid and *o*-hydroxybenzyl alcohol yields bis(4*H*-1,3,2-benzodioxaborin-2-yl)oxide (XIII) which reacts further with bis(tributyltin)oxide and triphenyltin hydroxide giving 2-tributylstannoxy- and 2-triphenylstannoxy-4*H*-1,3,2-benzodioxaborin, XIV and XV, respectively. These are new examples of stannoboroxanes.[8] The facile cleavage of Sn–O–B bond in XV by trimethylchlorogermane and -silane affords the corresponding trimethylgermoxy (XVI) and trimethylsiloxy (XVII) derivatives which are easily separated from triphenyltin chloride by fractional distillation.

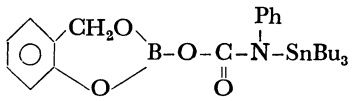


(XIII)

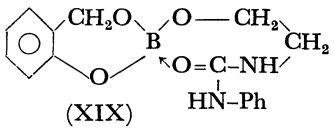


(XIV) $MR_3=SnBu_3$
(XV) $MR_3=SnPh_3$
(XVI) $MR_3=GeMe_3$
(XVII) $MR_3=SiMe_3$

The higher reactivity of Sn–O bond in comparison to B–O bond in stannoboroxanes has been demonstrated previously by the study of their cleavage and insertion reactions.[9] Insertions of unsaturated substrates across Sn–O bond are very facile. On the other hand, the only reported example of insertion across B–O bond appears to be the extremely slow reaction (24% yield in 30 days at room temperature) of 2-butoxy-1,3,2-benzodioxaborole with phenyl isocyanate.[10] The present studies show that whereas I, as expected, does not show any tendency to react with phenyl isocyanate, the corresponding 2-tributylstannoxy derivative (XIV) reacts immediately and exothermally to give the insertion product (XVIII). Aminoethoxy derivative (XI) also reacts with phenyl isocyanate presumably at the amino group and based on earlier studies,[11] the addition compound has been tentatively assigned structure XIX, in which the carbonyl group of the substituted urea moiety coordinates with boron.



(XVIII)



(XIX)

IR and PMR Spectra. The common peaks present in the IR spectra of all the derivatives (I—XIX) are; (i) a sharp and strong peak at 755 cm^{-1} (out of plane aromatic C–H bending); (ii) peaks of medium intensity at 1030, 1115 and 1160 cm^{-1} (inplane C–H bending), (iii) strong intensity peaks at 1080 and 1255 ± 5 cm^{-1} (due to aliphatic and aromatic C–O stretching vibrations respectively) and (iv) a weak intensity band at 3050 ± 10 cm^{-1} (due to aromatic C–H stretching). The region 1300—1500 cm^{-1} shows four to five strong peaks and an attempt to assign ν_{B-O}

Table 1. Reactions of 2-isopropoxy-4*H*-1,3,2-benzodioxaborin (I) with hydroxy compounds

S. No.	Wt of borin (I) (g) (mmol)	Hydroxy compound (g) (mmol)	Pr^iOH in azeotrope (g) Found Calcd	Product molecular formula Nature	Yield (g) (%)	Bp (°C/mmHg) (Mp, °C)	Boron (%) Found Calcd	Nitrogen (%) Found Calcd	PMR (CCl_4) peaks (τ)
1	2.12 (11.0)	*t*-Butyl alcohol 3.0	0.59 0.68	$C_{11}H_{15}BO_3$ Colourless liquid (II)	1.80 (80)	68/0.01 —	5.21 5.34	—	2.8—3.7 (m, 4H, aromatic), 5.16 (s, 2H, CH_2), 8.85 (s, 9H, Bu^t).
2	2.16 (11.3)	Phenol 1.15 (12.2)	0.49 0.69	$C_{13}H_{11}BO_3$ Semisolid (III)	2.20 (87)	135/0.01 —	4.76 4.87	—	2.55—3.6 (m, 9H, aromatic), 4.96 (s, 2H, CH_2).
3	2.36 (12.3)	Ethyleneglycol 0.40 (6.5)	0.65 0.76	$C_{16}H_{16}B_2O_6$ White solid (IV)	2.03 (97)	— (70)	6.57 6.75	—	2.6—3.45[a] (m, 8H, aromatic), 4.95 (s, 4H, CH_2) 5.96 (s, 4H, CH_2CH_2).
4	7.10 (36.4)	Ethanolamine 2.25 (36.8)	2.06 2.16	$C_9H_{12}BNO_3$ White solid (XI)	6.89 (97)	165/4.0 (120)	5.67 5.61	7.10[b] 7.15	
5	1.75 (9.1)	*o*-Aminophenol 1.0 (9.2)	0.46 0.54	$C_{13}H_{12}BNO_3$ Grey solid (XII)	2.20 (100)	— (137)	4.63 4.56	5.67[b] 5.82	

a) In $CDCl_3$. b) Insoluble in CCl_4 and $CDCl_3$.

with any amount of certainty is rather difficult. $\nu_{B-OC(aliphatic)}$ and $\nu_{B-OC(aromatic)}$ will absorb at different positions, the latter being at higher wave number and the two peaks present in 1350—1420 cm^{-1} region may tentatively be assigned to these vibrations.

In the derivative XIV, the presence of tributylstannoxy group[12] is shown by the appearance of $\nu_{as\ SnC_3}$ at 670 and 600 cm^{-1}, $\nu_{s\ SnC_3}$ at 515 cm^{-1} and ν_{B-O-Sn}[9] at 1280 cm^{-1}. Similarly compound (XVII) shows the characteristic peaks[13,14] of B–OSiMe$_3$ group at 840 cm^{-1} ($\rho_{as\ CH_3}$), 660 cm^{-1} ($\nu_{as\ SiC_3}$), 620 cm^{-1} ($\nu_{s\ SiC_3}$) and 1325 cm^{-1} ($\nu_{as\ B-O-Si}$). The corresponding peak positions for BOGeMe$_3$ group in derivative XVI are 830 cm^{-1} ($\rho_{as\ CH_3}$), 615 cm^{-1} ($\nu_{as\ GeC_3}$), 575 cm^{-1} ($\nu_{s\ GeC_3}$) and 1300 cm^{-1} ($\nu_{as\ B-O-Ge}$).[15] The symmetric deformation of Si–CH_3 and Ge–CH_3 groups, generally appearing at 1240—1260 cm^{-1} are masked by the strong ν_{C-O} band.

ν_{N-H} appears as a sharp weak peak at 3180 cm^{-1} in the *o*-aminophenoxy derivative (XII) but in the 2-aminoethoxy derivative (XI) it is present as a broad shoulder at 3100—3200 cm^{-1}. In the insertion product XIX of the latter compound with phenyl isocyanate, the ν_{NH} peak moves to a higher frequency at 3300 cm^{-1} and the $\nu_{C=O}$ peak is present at 1630 cm^{-1}. The $\nu_{C=O}$ peak in the ureido compound (XVIII) appears at 1610 cm^{-1}.

The purity of most of the new heterocycles (I—XIX) was checked by their PMR spectra in CCl_4. The specific peak positions are reported in the experimental section. The common peaks due to *o*-O–C_6H_4–CH_2–O-moiety, present in all the PMR spectra are a complex multiplet at 2.5—3.7 τ due to aromatic protons and a sharp singlet near 5.0 τ due to CH_2 protons. The position of the latter peak appears to be influenced by the coordination number of boron. Thus, the methylene singlet is present at 4.97 and 4.96 τ in 2-isopropoxy and 2-phenoxy-4*H*-1,3,2-benzodioxaborins respectively. In the corresponding 1 : 1 pyridine complexes, this peak shifts to 5.2 and 5.4 τ respectively. This increased shielding of the methylene protons probably reflects decreased p→pπ bonding from oxygen to born when the latter goes from three-coordinate to four-coordinate state.

Experimental

o-Hydroxybenzyl alcohol (Fluka) was used as supplied. Benzene (B.D.H., L.R.) was kept overnight on sodium wire and distilled, and was finally dried azeotropically with ethanol. Molecular weights were determined ebulliometrically in benzene using thermistor sensing.

Boron was estimated by Thomas' method.[16] Isopropanol in the azeotrope was estimated by oxidation method.[17] Infrared spectra were recorded on Perkin-Elmer model 337-grating spectrometer. PMR spectra were recorded on Perkin-Elmer R12B spectrometer.

2-Isopropoxy-4H-1,3,2-benzodioxaborin. Fractionation of a mixture of isopropyl borate (3.55 g, 18.8 mmol) and *o*-hydroxybenzyl alcohol (2.27 g, 18.3 mmol) in benzene (≈60 ml) yielded isopropanol (2.06 g, calcd 2.26 g) in the azeotrope and the desired product (I) (3.03 g, 88%) at 72 °C/0.01 mmHg as a colourless liquid. (Found: B, 5.63; M, 185. Calcd for $C_{10}H_{13}BO_3$: B, 5.73%; M, 192).

PMR (CCl_4): τ 2.7—3.3 (m, 4H, aromatic), 4.97 (S, 2H, CH_2). 5.5 (Septet, 1H, J=6 Hz), 8.83 (d, 6H, CH_3, J=6 Hz).

Bis(o-benzomethylenedioxy)borate and Its Ammonium Salt.

(a) On refluxing isopropyl borate (2.77 g, 14.7 mmol) with *o*-hydroxybenzyl alcohol (3.65 g, 29.4 mmol) in benzene (≈60 ml) for one hour followed by fractionation, isopropanol (2.66 g, calcd 2.71 g) was obtained in the azeotrope. On removing excess of solvent under reduced pressure, the desired product (V) (3.68 g, 99.2%) was obtained as viscous semisolid. (Found: B, 4.18. Calcd for $C_{14}H_{13}BO_4$: B, 4.24%).

PMR (CCl_4): τ 2.9—3.45 (m, 8H, aromatic), 5.2 (s, 4H, CH_2).

(b) A mixture of 2-isopropoxy-4*H*-1,3,2-benzodioxaborin (1.92 g, 10.0 mmol) and *o*-hydroxybenzyl alcohol (1.24 g, 10.0 mmol) in benzene (≈40 ml), on fractionation, gave isopropanol (0.50 g, calcd 0.60 g) in the azeotrope. After removal of excess benzene *in vacuo*, the product (V) (2.55 g,

100%) was obtained as a viscous semisolid (Found: B, 4.15. Calcd for $C_{14}H_{13}BO_4$: B, 4.24%).

By passing ammonia to a solution of V (3.38 g) in benzene (≈60 ml), the ammonium salt was immediately precipitated (VI) (3.48 g, 96.7%) mp 210—213 °C (Found: B, 3.82; N, 4.46. Calcd for $C_{14}H_{16}BNO_4$: B, 3.96; N, 4.83%).

Attempted Preparation of 2,2'-(o-Benzomethylenedioxy)bis(4H-1,3,2-benzodioxaborin). *(a)*: A mixture of isopropyl borate (2.89 g, 15.3 mmol) and *o*-hydroxybenzyl alcohol(2.78 g, 22.4 mmol) in benzene (≈60 ml) was refluxed for 3 h and fractionated (Found: isopropanol 2.20 g, calcd for 46 mmol 2.76 g) Removal of excess benzene under vacuum, yielded a semisolid (3.36 g) which on distillation under reduced pressure gave 2-isopropoxy-4*H*-1,3,2-benzodioxaborin(1.07 g) at 62 °C/0.05 mmHg (authentic IR and PMR spectra) and a light yellow solid (1.36 g) as undistilled residue (Found: B, 5.40%).

(b): Reaction of compound I (2.04 g, 12.5 mmol) and *o*-hydroxybenzyl alcohol (0.66 g, 5.3 mmol) in benzene (≈60 ml) yielded isopropanol (0.30 g, calcd 0.64 g) and a viscous product (2.35 g, calcd 2.06 g) (Found: B, 4.88%).

Reactions of 2-Isopropoxy-4H-1,3,2-benzodioxaborin with Hydroxy Compounds. A mixture of I and the hydroxy compound in benzene was refluxed and fractionated. After complete removal of the liberated isopropanol azeotropically, the solvent was distilled. The product was finally freed of solvent *in vacuo*. The details of these reactions are summarised in Table 1.

Addition Complexes of 2-Isopropoxy-4H-1,3,2-benzodioxaborin.

(a): Heat was evolved on adding pyridine (1.08 g) to 2-isopropoxy-4*H*-1,3,2-benzodioxaborin (1.92 g). Excess of pyridine was removed *in vacuo* leaving 1: 1 complex (2.70 g) as a viscous product. PMR (CCl_4): τ 1,3—3.1 (m, 5H, pyridine), 3.1—3.6 (m, 4H, aromatic), 5.2 (s, 2H, CH_2), 5.75 (Septet, 1H, C*H*Me$_2$), 8.95 (d, 6H, CH*Me*$_2$). This complex lost pyridine very slowly (20 h/0.01 mmHg) giving a highly viscous semisolid (2.16 g, Found: B, 5.05%). This on distillation gives I (0.78 g) at 82 °C/0.01 mmHg leaving an undistilled residue (1.14 g).

(b): A solid product X (1.44 g, 100%) mp 205—208 °C, was precipitated immediately on passing ammonia to a solution of compound I (1.32 g) in benzene(≈40 ml) (Found: B, 5.25; N, 6.69. Calcd for $C_{10}H_{16}BNO_3$: B, 5.27; N, 6.70%).

The above complex X (0.92 g, mp 205—208 °C) was also precipitated on passing ammonia to a mixture of compound I (0.86 g) and isopropanol (0.42 g) in benzene (≈50 ml). Unreacted isopropanol (0.4 g) was obtained from the filtrate by azeotropic distillation.

Addition Complexes of 2-Phenoxy-4H-1,3,2-benzodioxaborin.

(a): A solid 1: 1 complex (VII) (0.58 g, 90%) mp 135—138 °C was precipitated on adding triethylamine (0.34 g) to a benzene solution of 2-phenoxy-4*H*-1,3,2-benzodioxaborin (0.44 g)(Found: B, 3.36. Calcd for $C_{19}H_{26}BNO_3$: B, 3.46%).

(b): Heat was evolved on adding pyridine (0.20 g) to 2-phenoxy-4*H*-1,3,2-benzodioxaborin (0.40 g). Excess of pyridine was removed *in vacuo*, leaving 1: 1 complex (VIII) (0.54 g, 100%) as a solid, mp 120 °C (Found: B, 3.53. Calcd for $C_{18}H_{16}BNO_3$: B, 3.55%). PMR(CCl_4): τ 1.3—3.1 (m, 5H, pyridine), 3.1—3.7 (m, 9H, aromatic), 5.4 (s, 2H, CH_2).

(c): No reaction appeared to take place on adding dimethylformamide (0.40 g) to the 2-phenoxy derivative (III) (1.12 g); unchanged (III) was obtained on removing dimethylformamide *in vacuo*.

2-Acetoxy-4H-1,3,2-benzodioxaborin. A mixture of acetic anhydride (0.59 g, 5.8 mmol) and 2-isopropoxy-4*H*-1,3,2-benzodioxaborin (0.97 g, 5.1 mmol) was kept at room temperature for several days. The liberated ester was removed *in vacuo* yielding the product (0.97 g, 100%) as viscous semisold (Found: B, 5.81; $OCOCH_3$, 27.53. Calcd for $C_9H_9BO_4$: B, 5.73; $OCOCH_3$, 28.63%).

Bis(4H-1,3,2-benzodioxaborin-2-yl)oxide. On removal of water azeotropically from a mixture of boric acid (1.17 g, 18.9 mmol) and *o*-hydroxybenzyl alcohol (2.34 g, 18.9 mmol) in benzene (≈60 ml), followed by drying the product under reduced pressure, bis(4*H*-1,3,2-benzodioxaborin-2-yl)oxide (XIII) (2.66 g, 100%) was obtained as a viscous semisolid which solidified slowly on keeping at low temperature, (mp 160—164 °C)(Found: B, 7.80. Calcd for $C_{14}H_{12}B_2O_5$: B, 7.64%).

2-Tributylstannoxy-4H-1,3,2-benzodioxaborin. A mixture of bis(4*H*-1,3,2-benzodioxaborin-2-yl)oxide (3.98 g, 14.1 mmol) and bis(tributyltin)oxide (8.41 g, 14.9 mmol) in benzene was refluxed for 2 h. The product was freed from solvent *in vacuo* to yield the desired product (XIV) (11.77 g, 95.3%) as a colourless liquid, bp 178—180 °C/0.9 mmHg. (Found: B, 34; Sn, 26.94; M, 430. Calcd for $C_{19}H_{33}BO_3Sn$; B, 2.37; Sn, 27.06%; M, 439).

PMR (CCl_4): τ 2.65—3.35 (m, 4H, aromatic), 5.0 (s, 2H, CH_2), 7.7—9.5 (m, 27H, Bu_3Sn).

2-Triphenylstannoxy-4H-1,3,2-benzodioxaborin. Water was removed azeotropically from a mixture of bis(4*H*-1,3,2-benzodioxaborin-2-yl)oxide (2.14 g, 7.6 mmol) and triphenyltin hydroxide (5.51 g, 15.0 mmol) in benzene. Removal of excess benzene gave the product (7.49 g, 100%) as a viscous semisolid (XV) (Found: B, 2.18; Sn, 23.60. Calcd for $C_{25}H_{21}BO_3Sn$: B, 2.20; Sn, 23.68%).

2-Trimethylsiloxy-4H-1,3,2-benzodioxaborin. Trimethylchlorosilane (1.53 g, 14.4 mmol) reacted exothermally with 2-triphenylstannoxy-4*H*-1,3,2-benzodioxaborin (7.49 g, 15.0 mmol). Distillation under reduced pressure yielded 2-trimethylsiloxy-4*H*-1,3,2-benzodioxaborin (XVII) (2.50 g, 85.1 %) as a colourless liquid, bp 80 °C/0.8 mmHg. leaving triphenyltinchloride (6.90 g) as an undistilled residue (Found: B, 4.91; Si, 12.40; M, 214. Calcd for $C_{10}H_{15}BO_3Si$: B, 4.95; Si, 12.47%; M, 222).

PMR (CCl_4): τ 2.6—3.45 (m, 4H, aromatic), 5.06 (s, 2H, CH_2), 8.85 (s, 9H, Me_3Si).

2-Trimethylbermoxy-4H-1,3,2-benzodioxaborin. On adding trimethylchlorogermane (2.40 g, 15.7 mmol) to 2-triphenylstannoxy-4*H*-1,3,2-benzodioxaborin (7.49 g, 15.0 mmol) heat was evolved. Distillation yielded the desired compound (XVI) (3.52 g, 88.2%), bp 125 °C/1.0 mmHg as a colourless liquid (Found: B, 4.11%; M, 261. Calcd for $C_{10}H_{15}BGeO_3$: B, 4.12%; M, 267).

PMR (CCl_4): τ 2.9—3.35 (m, 4H, aromatic), 5.0 (s, 2H, CH_2), 9.52 (s, 9H, Me_3Ge).

Reaction between 2-Tributylstannoxy-4H-1,3,2-benzodioxaborin and Phenyl Isocyanate in 1: 1 Molar Ratio. Phenyl isocyanate (0.31 g, 2.6 mmol) reacted exothermally with 2-tributylstannoxy-4*H*-1,3,2-benzodioxaborin (1.14 g, 2.6 mmol) in benzene (≈5 ml) giving the adduct as a light brown viscous liquid (XVIII) (1.45 g, 100%) which showed no free isocyanate peak in the IR spectrum (Found: B, 1.93; Sn, 20.77. Calcd for $C_{26}H_{38}BNO_4Sn$: B, 1.94; Sn, 20.91%). The compound distils with slight decomposition at 210 °C/1.0 mmHg.

PMR (CCl_4): τ 2.5—3.5 (m, 9H, aromatic), 5.0 (s, 2H, CH_2), 7.9—8.5 (m, 27H, Bu_3Sn).

Reaction between 2-(2-Aminoethoxy)-4H-1,3,2-benzodioxaborin and Phenyl Isocyanate in 1: 1 Molar Ratio. To a suspension of 2-aminoethoxy-4*H*-1,3,2-benzodioxaborin (1.52 g, 7.9 mmol) in benzene (≈10 ml), phenyl isocyanate (0.95 g, 7.9 mmol) was added. The mixture was refluxed for 2 h giving a white crystalline solid (XIX) (2.46 g, 100%) (mp 160—165 °C) which was filtered and dried at 30 °C/0.01 mmHg (Found: B, 3.51; N, 7.20%. Calcd for $C_{16}H_{17}BN_2O_4$: B, 3.53; N,

7.26%).

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