Boron Heterocycles. Part VII.[1] Halogeno-, Methyl-, Phosphino-, and Amino-Derivatives of 1,3,2-Dioxaborolan and 1,3,2-Dithiaborolan Ring Systems

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Selected derivatives of the rings $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}-$ and $\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}-$ are reported. Derivatives of the latter system appear to be more stable thermally and with the exception of $[\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}\cdot CH_3]_2$ and $[\underline{S\cdot CH_2\cdot CH_2S\cdot B}\cdot P\cdot(CH_3)_2]_2$ are monomers in solution. Derivatives of $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}-$ are monomers in solution except for $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl$ which is associated, having an apparent molecular weight which is concentration dependent. Its boron-11 n.m.r. spectra in solution correlated with molecular-weight data suggest a chain-like species containing ternary and quaternary boron. Tensiometric titrations reveal that $P(CH_3)_3$ and $P(CH_3)_2H$ react with $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl$ in 1:3 rather than 1:1 molar ratios. The products $[\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl]_3P(CH_3)_3$ and $[\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl]_3P(CH_3)_2H$ are crystalline solids.

SIMPLE derivatives of the 1,3,2-dioxaborolan and 1,3,2-dithiaborolan ring systems have been relatively neglected with the exception of the parent compounds $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}H$ [2] and $\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}H$ [3] and their

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[1] Part VI, G. L. Brubaker and S. G. Shore, *Inorg. Chem.*, 1969, **8**, 2804.

[2] S. H. Rose and S. G. Shore, *Inorg. Chem.*, 1962, **1**, 744.

[3] B. Z. Egan, S. G. Shore, and J. E. Bonnell, *Inorg. Chem.*, 1964, **3**, 1024.

chloro-analogues.[4,5] Other halogen derivatives are unreported. Essentially no information is available concerning methyl and methylphosphino-substituents on boron. While methylamino-derivatives have been reported,[5,6] their properties are unknown. As part of a general study, we have been interested in the effect of substituent atoms and groups on the physical and chemical nature of the $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}$– and $\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}$– ring systems. The present investigation represents an attempt to provide syntheses and information concerning general properties of the derivatives indicated above.

RESULTS AND DISCUSSION

*2-Halogeno-*1,3,2*-dioxaborolan and 2-Halogeno-*1,3,2*-dithiaborolan.*—The general reaction of a boron halide with ethylene glycol or ethanedithiol in a 1 : 1 molar ratio was used in attempts to prepare the halogen derivatives

$$BX_3 + HYCH_2\cdot CH_2\cdot YH \longrightarrow \underline{YCH_2\cdot CH_2\cdot YB}X + 2HX$$

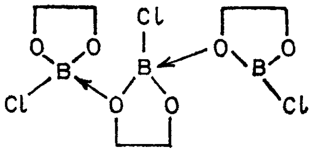
$$X = F, Cl, Br, I \qquad Y = O, S$$

This reaction proved to be successful for the preparation of the following derivatives of 1,3,2-dithiaborolan and 1,3,2-dioxaborolan: $\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}Cl$, $\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}Br$, $\underline{S\cdot CH_2\cdot CH_2\cdot S\cdot B}I$, and $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl$. Viscous, glassy materials of non-stoicheiometric composition were obtained in attempts to prepare the bromo- and iodo-derivatives of 1,3,2-dioxaborolan. Consistent with an earlier attempt to prepare $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}F$,[7] no apparent reaction was observed of BF_3 with $HO\cdot CH_2\cdot CH_2\cdot OH$ or BF_3 with $HS\cdot CH_2\cdot CH_2\cdot SH$. However, we have obtained evidence for the existence of the fluoro-derivatives using a less direct preparative procedure.[8]

With the exception of $\underline{O\cdot CH_2\cdot CH_2\cdot OB}Cl$ all the halogeno-derivatives are monomeric in solution with essentially concentration-independent apparent molecular weights.

Finch and Gardner[4] report that the apparent molecular weight of $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl$ is concentration dependent and that an earlier study[5] which claimed it to be a dimer simply involved a fortuitous choice of concentration for the molecular-weight determination. We have been able to confirm fully Finch and Gardner's molecular-weight studies. The apparent molecular weight can extend well below and well above the value for a dimeric formulation.

Perhaps the most reasonable structural formulation is the following one involving chain-like, intermolecular association with the average chain-length depending upon the concentration in solution.[4] Pure $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl$ is a viscous syrup at room temperature, suggesting significant association. Boron-11 n.m.r. spectra which we have obtained are consistent with this formulation in that two types of boron are



observed which can be assigned to the quaternary and ternary borons required by the above structural formulation. Identical spectra were obtained in methylene chloride and in benzene. The lower field peak ($\delta = -31\cdot 2$ p.p.m. relative to BF_3,Et_2O) is assigned to ternary boron, the higher field peak ($\delta = -23\cdot 5$ p.p.m.) is assigned to quaternary boron. As the concentration and hence association of $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}Cl$ increased, the peak assigned to quaternary boron increased in prominence.

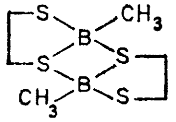
*2-Methyl-*1,3,2*-dioxaborolan and 2-Methyl-*1,3,2*-dithiaborolan.*—With methyl-lithium as an alkylating agent, the following reaction was observed.

$$\underline{YCH_2\cdot CH_2\cdot YB}Cl + LiCH_3 \longrightarrow \underline{YCH_2\cdot CH_2\cdot YB}\cdot CH_3 + LiCl$$

$$Y = O, S$$

The only previous reference[9] to the preparation of methyl derivatives cites the synthesis of $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}\cdot CH_3$ from the reaction of trimethylborane with ethanediol at 340° for a period of 14 h. Its properties were not discussed. We have found that $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot B}\cdot CH_3$ is a volatile liquid which is soluble in most common organic solvents. It is monomeric in benzene and in the vapour phase. The boron-11 n.m.r. spectrum consists of a single peak.

2-Methyl-1,3,2-dithiaborolan is a crystalline solid. It is dimeric in benzene and its mass spectrum indicates the presence of dimeric species in the vapour phase. The boron-11 n.m.r. spectrum is a singlet. Solubility is somewhat limited in ethers but sufficient in methylene chloride and benzene for n.m.r. and molecular-weight studies. The probable structure in solution is



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[4] A. Finch and P. J. Gardner, *J. Inorg. Nuclear Chem.*, 1963, **25**, 927; J. S. Blau, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1957, 4116; A. Finch, P. J. Gardner, and E. J. Pearn, *Rec. Trav. chim.*, 1964, **83**, 1314; A. Finch and E. J. Pearn, *Tetrahedron*, 1964, **20**, 173.

[5] R. J. Brotherton and A. L. McClosky, *J. Org. Chem.*, 1961, **26**, 1668; B.P. 790,090/1958.

[6] R. H. Cragg, *J. Inorg. Nuclear Chem.*, 1968, **30**, 395.

[7] H. G. Meerwein and J. W. Pannwitz, *J. prakt. Chim.*, 1934, **141**, 123.

[8] Unpublished data.

[9] D. Ulmschneider and J. Goubeau, *Chem. Ber.*, 1957, **90**, 2733.

Reactions with Trimethylphosphine and Dimethylphosphine.—From tensiometric titrations in n-butyl ether at 25°, it was shown that $P(CH_3)_3$ and $P(CH_3)_2H$ react with $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl$ in 1 : 3 molar ratios rather than the expected 1 : 1 ratios

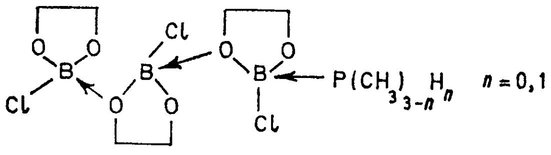
$$P(CH_3)_{3-n}H_n + 3O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl \longrightarrow [O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl]_3P(CH_3)_{3-n}H_n$$

$n = 0, 1$

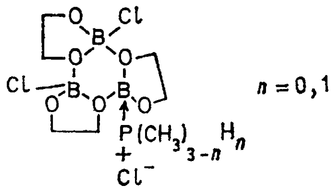
Titration curves for both systems were essentially identical. A typical curve is shown in the Figure. The excess of phosphine beyond the 1 : 3 ratio could be recovered. The products $[O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl]_3$-$P(CH_3)_3$ and $[O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl]_3P(CH_3)_2H$ are crystalline solids which are stable *in vacuo*. They have been prepared in a number of solvents: CH_2Cl_2, Et_2O, $Bu^n{}_2O$, and benzene. The boron-11 n.m.r. spectrum of each compound consists of a singlet and a doublet in the area ratio 2 : 1. The singlet occurs at $\delta = -23{\cdot}1$ p.p.m. for both compounds. This singlet is assigned to quaternary boron which is bound to four oxygen atoms. Its chemical shift is very close to that peak similarly assigned in the spectrum of polymeric $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl$. The doublet which is up-field of the singlet, arises from ^{31}P—^{11}B spin coupling. Boron-11 n.m.r. spectra of solutions in which molar ratios of reactants were 1 : 1 were identical to those spectra obtained from solutions in which the molar ratio of reactants was 1 : 3, thereby providing additional evidence that the phosphines and $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl$ do not react in 1 : 1 molar ratios.

The electrical conductivity of $[O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl]_3$-$P(CH_3)_2H$ in CH_3CN suggests that ionic species are present in solution; however, because the solute reacts with the solvent, meaningful treatment of the data could not be carried out.

For the present, we cannot distinguish between two types of structure which seem reasonable for the 3 : 1 adduct. One possibility would be a chain-like structure similar to that proposed for $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl$ in solution, with the alkyl phosphine bound to boron at the end of the chain.



A second possibility is a fused polycyclic structure.



Since the compounds are stable crystalline solids, and since the stoicheiometry of the reaction is fixed at 1 mole of alkyl phosphine per 3 moles of heterocycle, we prefer the second structure because it seems more likely to be invariant with respect to composition. In the solid state and in an ionizing solvent, it is presumed to consist of ion pairs, while in benzene, it is presumed to be molecular, behaviour analogous to that of phosphorus-(v) halides.

The reaction of dimethylphosphine and trimethylphosphine with 2-chloro-1,3,2-dithiaborolan yields the expected adducts

$$S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BCl + P(CH_3)_{3-n}H_n \longrightarrow S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP(CH_3)_{3-n}H_n$$

$n = 0, 1$

These compounds are crystalline solids which are stable *in vacuo* at room temperature. There is no apparent tendency for the formation of 1 : 3 adducts analogous to those obtained with $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl$. However, if an excess of $P(CH_3)_2H$ is used in the preparation of $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP(CH_3)_2H$, some dehydrohalogenation occurs. Small amounts of $P(CH_3)_2H_2Cl$ are found in the reaction mixture (identified from its *X*-ray powder diffraction pattern). The boron-11 n.m.r. spectrum of $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP(CH_3)_3$ and of $S{\cdot}CH_2{\cdot}CH_2S{\cdot}BClP$-$(CH_3)_2H$ consists of a doublet which arises from ^{31}P–^{11}B spin-coupling.

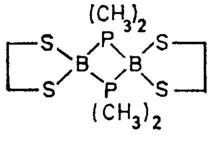
Addition of a tertiary amine to $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP$-$(CH_3)_2H$ leads to the removal of HCl.

$$S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP(CH_3)_2H + R_3N \longrightarrow 1/2[S{\cdot}CH_2CH_2{\cdot}S{\cdot}BP(CH_3)_2]_2 + R_3NHCl$$

$R = Me, Et$

Best results were obtained using trimethylamine. The product 2-dimethylphosphino-1,3,2-dithiaborolan is sufficiently soluble in CH_2Cl_2 and benzene for spectroscopic studies (n.m.r. and i.r.). In benzene solution it is a dimer.

The boron-11 n.m.r. spectrum is consistent with the dimeric structure drawn below:



The spectrum is a broad triplet of area ratio 1 : 2 : 1 which arises from ^{31}P–^{11}B spin-coupling. This dimer melts at *ca.* 188° with no detectable decomposition. It does not react with any of the following Lewis acids at room temperature: BF_3, BCl_3, and B_2H_6.

Reactions with Amines.—Addition of trimethylamine to 2-chloro-1,3,2-dioxaborolan and 2-chloro-1,3,2-dithiaborolan produces stable crystalline adducts

$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BClN(CH_3)_3}$ and $\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClN(CH_3)_3}$ which show no tendency to decompose at room temperature *in vacuo*. There is no evidence for reaction stoicheiometry other than a 1 : 1 molar ratio of reactants.

Amino-substituted boron heterocycles were prepared from the following general reactions with amines.[10]

$$\mathrm{YCH_2{\cdot}CH_2{\cdot}YBCl + 2NH_{3-\mathit{n}}(CH_3)_{\mathit{n}} \longrightarrow Y{\cdot}CH_2{\cdot}CH_2{\cdot}YB{\cdot}NH_{2-\mathit{n}}(CH_3)_{\mathit{n}} + NH_{4-\mathit{n}}(CH_3)_{\mathit{n}}Cl}$$

$\mathrm{Y = O, S}$
$n = 0, 1, 2$

It is believed that $\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}NH_2}$ and $\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}NHCH_3}$ are stable entities; however, they could not be isolated from the reaction of $\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BCl}$ with $\mathrm{NH_3}$ and with $\mathrm{NH_2CH_3}$ due to our inability to find a suitable solvent.

All the amino-derivatives are monomers in solution. Cragg[6] reports that $\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}N(CH_3)_2}$ is a monomer in the vapour phase, but a tetramer in benzene. We have found, however, that it is a monomer in both the vapour phase and benzene, in good agreement with an earlier report of Brotherton and McClosky.[5]

2-Amino-1,3,2-dioxaborolan is an amorphous solid which does not undergo apparent thermal decomposition at temperatures up to 150°. It does not sublime *in vacuo* at this temperature. Due to its low volatility and amorphous character, it is believed to be polymeric. However, in dimethyl sulphoxide it is monomeric. Diglyme was found to be the only other substance which dissolves significant amounts of this material.

Transamination reactions were also used to prepare amino-derivatives. This procedure proved to be the best synthesis in the following case:

$$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}N(CH_3)_2 + NH_3 \longrightarrow O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NH_2 + NH(CH_3)_2}$$

Attempts to prepare $\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}NH_2}$ and $\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}NHCH_3}$ through transamination procedures yielded non-stoicheiometric solids which could not be purified by extraction procedures.

Table 1 summarizes properties of the boron heterocycles which were prepared and isolated. In general the sulphur substituted ring systems are significantly more stable than their oxygen-containing counterparts.

TABLE 1

Properties of some boron heterocycles

Heterocycle	State at room temp.	Vap. press.	M.p.	Stability	Molecular weight Theory	Molecular weight Found (solvent)
$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl}$	Viscous liq.	10 mm 69°		Discolours slowly at room temp.		Conc. dependent benzene
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BCl}$	Liq.	20 mm 62°	−40°	Apparently stable at room temp. over periods of months	139	139 (benzene)
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BBr}$	Liq.	4 mm 30°	−25	Apparently stable at room temp. over periods of months	183	189 (benzene)
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BI}$	Liq.	1 mm 25°	−20	Discolours within 1 h at room temp.	230	232 (benzene)
$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NH_2}$	Solid	<1 mm		No apparent decomposition at 150°		
$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NHCH_3}$	Solid	18 mm 25°			101	102 (benzene)
$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}N(CH_3)_2}$	Liq.	11 mm 30°	−35	Apparently stable at room temp. over periods of months	115	120 (benzene)
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}N(CH_3)_2}$	Liq.	10 mm 87°	−20		147	147 (benzene)
$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}CH_3}$	Liq.				85·90	87·2 (vapour density)
$\mathrm{[S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BCH_3]_2}$	Solid				236	234 (benzene) 236 (mass spec.)
$\mathrm{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BClN(CH_3)_3}$	Solid		105—125 dec.			
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClN(CH_3)_3}$	Solid					
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP(CH_3)_3}$	Solid		164—180 dec.			
$\mathrm{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClP(CH_3)_2H}$	Solid		60		200·6	197 (benzene)
$\mathrm{[S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BP(CH_3)_2]_2}$	Solid		188		326·8	335 (benzene)
$\mathrm{[O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl]_3P(CH_3)_3}$	Solid					
$\mathrm{[O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl]_3P(CH_3)_2H}$	Solid		82			

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[10] G.P. 1,108,235/1961.

N.m.r. Spectra.—Table 2 presents boron-11 and proton n.m.r. spectra of the heterocyclic boron compounds reported in this study.

Boron-11 chemical shifts for the halogeno-derivatives of $S\cdot CH_2\cdot CH_2\cdot S\cdot B$– occur at increasing field as halogen substitution goes from Cl to Br to I. This trend in chemical shifts is the reverse of that observed in the boron trihalides.[11]

A second point of interest involves the proton shifts for CH_3 in the compounds $S\cdot CH_2\cdot CH_2\cdot S\cdot B\cdot N(CH_3)_2$, $O\cdot CH_2\cdot CH_2\cdot O\cdot B\cdot N(CH_3)_2$, $S\cdot CH_2\cdot CH_2\cdot S\cdot BClN(CH_3)_3$, and $O\cdot CH_2\cdot CH_2\cdot O\cdot BClN(CH_3)_3$. The methyl protons in the sulphur-containing compounds are deshielded compared to those in the oxygen-containing rings. In the case of the first pair of compounds, it can be argued that since sulphur is less effective than oxygen in relieving the electron deficiency of boron, the π-bond between boron and nitrogen in the sulphur compound is enhanced over that in its oxygen-containing counterpart, thereby causing relative deshielding of the methyl protons. In the case of the second pair of compounds, the deshielded methyl group reflects the fact that the dative B–N bond in the dithiaborolan adduct is stronger than that in the dioxaborolan adduct.[12]

TABLE 2

N.m.r. chemical shifts

Compound [a]	B^{11} [b]	H^1 [c]
$O\cdot CH_2\cdot CH_2\cdot O\cdot BCl$	−31·2 (ternary) −23·5 (quaternary)	1·15
$S\cdot CH_2\cdot CH_2\cdot S\cdot BCl$	−61·4	1·88
$S\cdot CH_2\cdot CH_2\cdot S\cdot BBr$	−58·9	1·90
$S\cdot CH_2\cdot CH_2\cdot S\cdot BI$	−50·0	1·95
$O\cdot CH_2\cdot CH_2\cdot O\cdot B\cdot NH\cdot CH_3$	−25·5	
$O\cdot CH_2\cdot CH_2\cdot O\cdot B\cdot N(CH_3)_2$	−25·2	CH_2, 1·28; CH_3, 2·78
$S\cdot CH_2\cdot CH_2\cdot S\cdot B\cdot N(CH_3)_2$	−45·3	CH_2, 2·33; CH_3, 2·57
$O\cdot CH_2\cdot CH_2\cdot O\cdot B\cdot CH_3$	−34·9	CH_2, 1·19; CH_3, 4·93
$[S\cdot CH_2\cdot CH_2\cdot S\cdot BCH_3]_2$	−67·4	CH_2, 2·08; CH_3, 4·38
$O\cdot CH_2\cdot CH_2\cdot O\cdot BClN(CH_3)_3$	−5·9	CH_2, 1·43; CH_3, 2·68
$S\cdot CH_2\cdot CH_2\cdot S\cdot BClN(CH_3)_3$	−17·1	CH_2, 2·23; CH_3, 2·43
$S\cdot CH_2\cdot CH_2\cdot S\cdot BClP(CH_3)_3$	−3·8 J_{BP} = 138 Hz	
$S\cdot CH_2\cdot CH_2\cdot S\cdot BClP(CH_3)_2H$	−1·8 J_{BP} = 111 Hz	CH_2, 2·29; CH_3, 3·75
$[S\cdot CH_2\cdot CH_2\cdot S\cdot B\cdot P(CH_3)_2]_2$	+8·5 J_{BP} = 90 Hz	CH_2, 2·45; CH_3, 4·05
$[O\cdot CH_2\cdot CH_2\cdot O\cdot BCl]_3P(CH_3)_3$	−23·1 −6·5 J_{BP} = 186 Hz	
$[O\cdot CH_2\cdot CH_2\cdot O\cdot BCl]_3P(CH_3)_2H$	−23·1 −1·6 J_{BP} = 156 Hz	

[a] CH_2Cl_2 used as solvent. [b] $(C_2H_5)_2OBF_3$ reference. [c] CH_2Cl_2 internal reference.

EXPERIMENTAL

Materials.—Reagent grade chemicals were used in all preparations. Ethylene glycol and ethane-1,2-dithiol were dried over sodium and fractionally distilled under reduced pressure. Methylene chloride, diethyl ether, and benzene were dried by refluxing them over CaH_2. Dimethyl sulphoxide was warmed in the presence of KOH and distilled under dry nitrogen. Glyme and diglyme were refluxed over $LiAlH_4$.

Dimethylphosphine was prepared by the reduction of $(CH_3)_4P_2S_2$ with $LiAlH_4$.[13] The $(CH_3)_4P_2S_2$ was prepared by the action of CH_3MgI on $PSCl_2$.[14] Trimethylphosphine was prepared and stored according to previously described procedures.[15,16]

Molecular-Weight Determinations.—A specially designed cryoscopic cell which could be flushed with dry nitrogen prior to each run was used for determining the molecular weights of these compounds because of their sensitivity to moisture. All samples were dissolved in benzene using dry-box techniques and typical cooling curves were obtained from temperature *vs.* time data, except in the case of 2-amino-1,3,2-dioxaborolan where the limited solubility in benzene made this impossible. In this case the determinations were run in dimethyl sulphoxide and warming curves were obtained.

Spectra.—N.m.r. spectra were obtained on Varian HR-60 and A-60 spectrometers.

Preparation of 2-*Halogeno*-1,3,2-*dioxaborolan and* 2-*Halogeno*-1,3,2-*dithiaborolan.*—$O\cdot CH_2\cdot CH_2\cdot O\cdot BCl$ *and* $S\cdot CH_2\cdot CH_2\cdot S\cdot BCl$. Boron trichloride (0·43 mol) was condensed into a flask containing CH_2Cl_2 (50 ml). Depending upon the heterocycle to be prepared either $HOCH_2CH_2OH$ or $HSCH_2CH_2SH$ (0·41 mol) was added during 15 min to the well-stirred BCl_3 solution. The hydrogen chloride formed in the reaction was removed by a slow stream of nitrogen which was blown through the apparatus. The clear solution was then allowed to warm to room temperature with stirring and after 1 h the solvent was removed under reduced pressure. The heterocycle was distilled slowly under reduced pressure at *ca.* 65°. It was collected and stored under dry nitrogen at −78°. For $O\cdot CH_2\cdot CH_2\cdot O\cdot BCl$, Found: B, 10·25; Cl, 35·0. Calc. for $C_2H_4BClO_2$: B, 10·35; Cl, 33·5%. For $S\cdot CH_2\cdot CH_2\cdot S\cdot BCl$, Found: C, 24·75; B, 7·75. Calc. for $C_2H_4BClS_2$: C, 25·6; B, 7·8%.

$S\cdot CH_2\cdot CH_2\cdot S\cdot BBr$ *and* $S\cdot CH_2\cdot CH_2\cdot S\cdot BI$. Boron tri-

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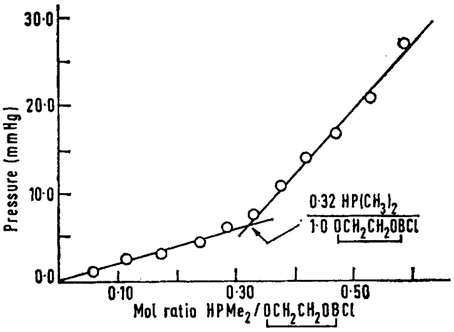
bromide (28·3 mmol) was condensed into a reaction vessel followed by CH_2Cl_2 (*ca.* 30 ml). An equimolar amount of $HSCH_2CH_2SH$, diluted in CH_2Cl_2 (*ca.* 10 ml) was added dropwise during 20 min at −40 °C. The solution was treated with Zn dust and Hg in order to remove coloured impurities. Solvent was removed by vacuum distillation of the filtered solution. The heterocycle was purified by vacuum distillation at *ca.* 40°. The synthesis of $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}I$ paralleled that of the bromo-analogue except that the reaction was carried out at −50° and solvent was distilled away at −30°. The heterocycle is a clear, probably colourless liquid. Solutions were colourless, but apparently thermal decomposition introduced impurities into the isolated product causing a pink colour. The iodo-derivative darkens noticeably within an hour at room temperature. For $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}Br$, Found: C, 13·1; B, 5·85; S, 32·0. Calc. for $C_2H_4BBrS_2$: C, 13·15; B, 5·9; S, 35·0%. For $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}I$, Found: B, 4·7; I, 52·3. Calc. for $C_2H_4BIS_2$: B, 4·75; I, 55·1%.

2-*Methyl*-1,3,2-*dioxaborolan and* 2-*Methyl*-1,3,2-*dithiaborolan*.—Essentially the same procedure was used to prepare both of these compounds. Under anhydrous conditions, CH_3Li (5 mmol) in ether (*ca.* 7 ml) was syringed into a tube containing either $\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}Cl$ or $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}Cl$ (5 mmol) in diethyl ether. The transfer was performed in a dry box. The tube was fitted with a stopcock and a side-arm which was fitted with a serum cap. Formation of LiCl (later identified by *X*-ray diffraction) was immediately apparent. In the preparation of $\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}CH_3$ all the volatile materials were distilled from the tube at room temperature. Ether was pumped away at −60° from this distillate, leaving behind $\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}CH_3$. In the case of $[\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}CH_3]_2$, ether was distilled away from the reaction mixture at −60°. The remaining solid was then put in an extractor and $[\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}CH_3]_2$ was extracted with CH_2Cl_2.

Addition of an excess of HCl to $\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}CH_3$ and $[\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}CH_3]_2$ yielded, in each case, amounts of CH_4 which were within 3% of theory.

Reactions with $P(CH_3)_3$ *and* $PH(CH_3)_2$.—The products $[\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}Cl]_3P(CH_3)_3$, $[\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}Cl]_3PH(CH_3)_2$, $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}ClP(CH_3)_3$, and $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}ClPH(CH_3)_2$ were first identified by means of tensiometric titrations which established the molar ratios of reactants involved. These titrations consisted of condensing small increments (0·3 mmol) of methyl substituted phosphine into a reaction vessel which contained a known quantity of heterocycle (*ca.* 2 mmol) in n-butyl ether (*ca.* 3 ml). The mixture was allowed to warm to 25° after each addition and the equilibrium vapour pressure in the system was recorded following a sufficient interval of time for equilibrium to be achieved. The titration curve consisted of a plot of equilibrium vapour pressure *versus* molar ratio of methyl substituted phosphine to heterocycle up to a value of 2·0/1·0. A break in each titration curve represented the molar ratio of reactants in the adducts: $P(CH_3)_3/\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}Cl$ = 1·0/3·0; $PH(CH_3)_2/\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}Cl$ = 0·96/3·0; $P(CH_3)_3/\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}Cl$ = 0·98/1·0; $PH(CH_3)_2/\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}Cl$ = 1·0/1·0. A typical titration curve is shown in the Figure. By pumping on the systems, excess of methyl substituted phosphine was recovered. The measured amount of recovered base further established reaction stoicheiometries indicated by the titration curves.

The adducts listed above were also prepared in CH_2Cl_2, $(C_2H_5)_2O$, and C_6H_6. Benzene proved to be the least desirable solvent because the products obtained were gummy. Diethyl ether, in general, appeared to afford the purest products.



Tensiometric titration of 2-chloro-1,3,2-dioxaborolan with dimethylphosphine (25 °C, n-butyl ether solvent)

In a typical reaction, a quantity (*ca.* 12 mmol) of either $\underline{O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B}Cl$ or $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}Cl$, in solvent (*ca.* 10 ml) [$(C_2H_5)_2O$ or CH_2Cl_2] was cooled to −196° in a tube on the vacuum line and the appropriate amount of either $P(CH_3)_3$ or $PH(CH_3)_2$, was condensed into the reaction tube. The temperature was allowed to warm to −80°, at which point the mixture was stirred for several minutes by means of a magnetic stirrer. The cold bath was removed and the solution was allowed to warm to ambient temperature with continuous stirring in order to permit complete reaction. The tube was then cooled to −60° and solvent was distilled away, leaving behind the non-volatile product.

Preparation of $[\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}{\cdot}P(CH_3)_2]_2$.—Dehydrohalogenation of $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}ClPH(CH_3)_2$ using either $(CH_3)_3N$ or $(C_2H_5)_3N$ produces $[\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}{\cdot}P(CH_3)_2]_2$. Purest product was obtained when $(CH_3)_3N$ was used to remove HCl because $(CH_3)_3NHCl$ was easier to separate from the product than $(C_2H_5)_3NHCl$.

In a typical preparation, $\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}ClPH(CH_3)_2$ (*ca.* 10 mmol) was placed in a reaction tube on the vacuum line and dry CH_2Cl_2 (15 ml) was condensed onto it. Trimethylamine (15 mmol) was then condensed into the tube and the mixture was warmed to 0 °C and stirred continuously for 5 h. Volatile materials were then pumped away at −45° and the remaining solid was placed in an extractor and extracted with dry benzene at ambient temperature. Benzene was pumped away leaving $[\underline{S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B}{\cdot}P$-

$(CH_3)_2]_2$. This product was then placed on a fritted glass filter and washed with dry pentane.

When $(C_2H_5)_3N$ was used to remove HCl, the reaction was run in benzene at room temperature with continuous stirring for *ca.* 24 h. Volatile materials were pumped away at room temperature and $[S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}P(CH_3)_2]_2$ was extracted and washed in the manner indicated above (Found: C, 29·3; H, 6·15; P, 18·9. Calc. for $C_{10}H_{26}B_2P_2S_4$: C, 29·3; H, 6·15; P, 18·85%).

Reactions with Amines

Trimethylamine Adducts.—Tensiometric titrations in CH_2Cl_2 in procedures similar to those used in the preparation of $P(CH_3)_3$ and $PH(CH_3)_2$ adducts were used to establish the compositions of $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BClN(CH_3)_3$ and $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BClN(CH_3)_3$. These materials are crystalline solids which are stable *in vacuo*. With the exception of boron-11 and proton n.m.r., no attempt was made to study these compounds further.

Amination Reactions.—Essentially identical procedures were used to prepare $O{\cdot}CH_2{\cdot}CH_2O{\cdot}B{\cdot}N(CH_3)_2$ and $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}N(CH_3)_2$. In a typical preparation $(CH_3)_2NH$ (0·37 mol) was condensed into a flask containing $(C_2H_5)_2O$ (90 ml) at −78°. The solution was warmed to −5° and either $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl$ or $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}BCl$ (0·18 mol) in $(C_2H_5)_2O$ (20 ml) was added dropwise during 20 min with stirring. Care was taken to exclude moisture from the reaction mixture. After warming to room temperature and stirring for 2 h the $(CH_3)_2NH_2Cl$ was filtered off and the filtrate and washings were collected for removal of solvent at room temperature *in vacuo*.

The product was $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}N(CH_3)_2$, a colourless liquid. It was purified by distillation at 29—32° and 11 mmHg (Found: B, 9·2; N, 12·25. Calc. for $C_4H_{10}BNO_2$: B, 9·4; N, 12·9%).

When the desired product was $S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}B{\cdot}N(CH_3)_2$, it was purified by distillation under reduced pressure at 86—88° and collected as a white solid at −78°. It is a colourless liquid at room temperature (Found: B, 7·2; N, 9·5. Calc. for $C_4H_{10}BNS_2$: B, 7·35, N, 9·5%).

Transamination Reactions.—Although $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NH{\cdot}CH_3$ can be prepared by the procedure described above, it is also readily prepared through the following transamination reaction.

A sample of $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}N(CH_3)_2$ (0·1 mol) was syringed into a reaction tube in a dry box. The heterocycle was frozen at −78° and the tube was evacuated. Approximately 1·0 mol of CH_3NH_2 was condensed onto the heterocycle at −78° and allowed to warm with continuous stirring to *ca.* −10° during *ca.* 1 h. The system was then cooled to −45° and the excess of amine was pumped away. The remaining white solid, $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NH(CH_3)$, was pumped on for several hours at −45° and briefly at room temperature to insure removal of excess of amine. This solid has a vapour pressure of 17·5 mmHg at 2·5° (Found: B, 9·9; N, 14·2. Calc. for $C_3H_8BNO_2$: B, 10·7; N, 13·9%).

The best preparation of $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NH_2$ involved transamination similar to the procedure described above except that 0·5 mol of NH_3 was added to 0·10 mol of $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}N(CH_3)_2$ at −78° and the system was warmed to and maintained at −45° for 2 h with continuous stirring. Volatile materials were then pumped away at this temperature, leaving $O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B{\cdot}NH_2$, a soft white solid which is amorphous (Found: B, 12·5; N, 15·35. Calc. for $C_2H_6BNO_2$: B, 12·45; N, 16·1%).

Infrared and X-Ray Diffraction Data.—These data for the compounds prepared in this work are deposited with the N.L.L. as Supplementary Publication No. SUP 20335 (6 pp., 1 microfiche).*

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