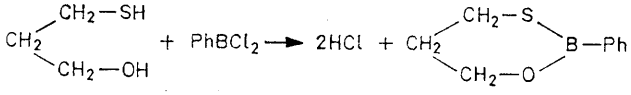
Organoboron Compounds. Part VIII.[1] Synthesis and Properties of Some 2-Substituted 1,3,2-Oxathiaborinans

By **R. Harry Cragg** and **Manije Nazery**, The Chemical Laboratory, University of Kent at Canterbury, Canterbury CT2 7NH, Kent

2-Substituted derivatives of the new heterocycle (O·[CH$_2$]$_3$·S·BX) (X = Ph, OR, NHR, NR$_2$, and SR) have been prepared. The properties of these compounds are described and the mass spectra of some are discussed.

ORGANOBORON heterocyclic derivatives of propane-1,3-diol [2] and propane-1,2-dithiol [3] have been fully investigated and a publication reporting two organoborane derivatives of propane-1,3-dithiol [4] has appeared. Although there has been considerable interest recently in heterocyclic organoboranes,[5,6] mixed oxygen–boron–sulphur heterocyclic compounds have been almost completely ignored. With the exception of a recent communication [7] and the patent literature [8] there has been no information concerning the chemistry and properties of these compounds. We therefore report our studies concerning heterocyclic derivatives of 1,3,2-oxathiaborinans.

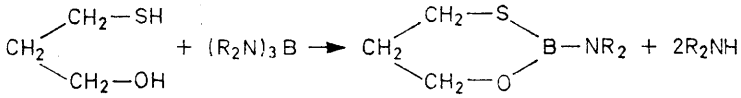
Although the standard method for the preparation of 3-mercaptopropanol involves the reaction of 3-acetylthiopropanol and aqueous sodium hydroxide under nitrogen, it is usually difficult to obtain [9] a pure product.



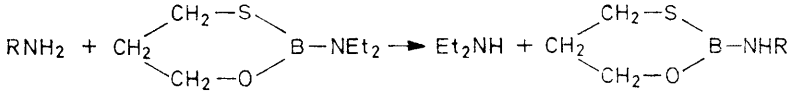
We therefore decided to use a new route for the synthesis of 3-mercaptopropanol *via* the interaction of thiourea with 3-bromopropanol followed by the addition of alkali to break up the complex. Acidification of this mixture gave the required product. Although yields using this method were relatively low (*ca.* 30%) nevertheless pure 3-mercaptopropanol could be obtained.

Trisdialkylaminoboranes reacted readily with 3-mercaptopropanol to give the corresponding 2-dialkylamino-1,3,2-oxathiaborinans, which are further examples of stable trigonal boranes in which the boron is attached to three different ligands. Transamination reactions, between a primary amine and 2-diethylamino-1,3,2-oxathiaborinan, resulted in the formation of the corresponding 2-alkylamino-1,3,2-oxathiaborinans. For each compound a band in the i.r. spectrum in the region 3401—3380 cm^{-1}, due to the NH stretching frequency, in the region characteristic for a monomeric alkylaminoborane,[10] was observed.

Trisethylthioborane reacted with 3-mercaptopropanol resulting in the formation of the corresponding 2-ethylthio-1,3,2-oxathiaborinan. Although the analyses for this compound were low due to (*a*) the hydrolytic instability of the compound and (*b*) the difficulty of separation from 3-mercaptopropanol due to its similarity in boiling point, mass spectral analysis showed the compound to be correct and this was further demonstrated by its reaction with tris-n-butoxystibine resulting in the formation of 2-n-butoxy-1,3,2-oxathiaborinan. This type of reaction could possibly have general application in the synthesis of alkoxyboranes especially in those cases where there is the possibility of decomposition of the required product.[11] The driving force of the reaction can be attributed to the high affinity of boron for oxygen and the high affinity of antimony for sulphur. Also in this type of reaction there are no products, such as hydrogen halides, which could cause decomposition of the alkoxyborane.



R = Me, Et.



R = Et, Pr^i, Bu^n, Bu^t

Dichlorophenylborane reacted readily with 3-mercaptopropanol to give a high yield of the corresponding 2-phenyl-1,3,2-oxathiaborinan.

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[2] A. Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn, *J. Chem. Soc.*, 1962, 1428.
[3] R. H. Cragg, J. P. N. Husband, and A. F. Weston, *J.C.S. Dalton*, 1973, 568.
[4] A. Finch and J. Pearn, *Tetrahedron*, 1964, **20**, 173.
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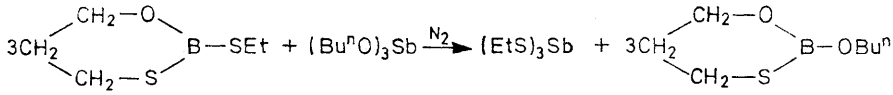
[8] G. W. Conklin and R. C. Morris, B.P. 790,090/1958.
[9] J. S. Harding and L. N. Owen, *J. Chem. Soc.*, 1954, 1536.
[10] M. F. Lappert, M. K. Majumder, and B. P. Tilley, *J. Chem. Soc.* (*A*), 1966, 1591.
[11] R. H. Cragg, M. Nazery, and A. F. Weston, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 497.

All the compounds prepared were mobile liquids which, although stable to distillation, and under an atmosphere of nitrogen, were hydrolytically unstable. None of the compounds appeared to associate and even after long periods of time the alkylamino-derivatives did not change their appearance, *i.e.* solidify. Molecular weights,



determined by mass spectrometry, showed the derivatives of 1,3,2-oxathiaborinan to be monomeric in the gaseous phase.

Infrared Spectra.—The i.r. spectra of the 1,3,2-oxathiaborinans were found to be rather complex and it is therefore difficult to assign bands, with the exception of those due to the NH stretching frequency, with any certainty. However the i.r. spectra were consistent with the formulation of the compounds and i.r. bands in the regions 1512—1483, 1325—1295, and 1110—940 cm^{-1} are tentatively assigned to B–N, B–O, and B–S stretching frequency bands.

Main ions of interest in the mass spectra of 2-substituted-1,3,2-oxathiaborinans

Substituent	$P(m/e)$	%	m/e (74%	base (m/e)	m/e (101%)	I_T
Ph	178	97·2	100	74	<1	28·2
NMe_2	145	67·0	4·7	144	2·1	58·0
NEt_2	173	15·6	<2	$P-15$	3·6	59·0
NHEt	145	18·2	3·9	$P-15$	3·6	57·0
$NHPr^i$	159	13·1	<2	$P-15$	1·3	56·1
$NHBu^n$	173	20·9	4·7	$P-43$	2·8	45·2
$NHBu^t$	173	8·3	2·4	$P-15$	4·8	
OBu^n	174	26·9	38·4	57	17·3	
SEt	162	100	67·7	162	42·7	

Mass Spectra.—Having prepared a new class of compounds we were in a position to study their mass spectra in order to compare their mass spectral fragmentation patterns with those that have previously been reported for similar systems. The Table lists the main ions of interest in the mass spectra of 1,3,2-oxathiaborinans.

2-Phenyl-1,3,2-oxathiaborinan.—The base peak in the spectrum is at m/e 74 and can be assigned to the propylene sulphide ion. The spectrum was found to be very similar to that reported for 2-phenyl-1,3,2-oxathiaborolan,[12] containing a multitude of peaks in the fragmentation pattern, with the exception that the ion m/e 91, assignable to the tropylium ion, is only of 4·1% abundance compared to the base peak.

Other Compounds.—As can be seen from the Table, with the exception of the phenyl compound the ion m/e 74 is of little importance. The results in general support the suggestion that given the opportunity the positive charge will reside on an atom in an exocyclic position in preference to one in the ring. As a consequence of this one observes fragmentation of the exocyclic group and an increase in stability, although in many cases only weak, of the bivalent borenium ion m/e 101, and propylene sulphide can be lost as a neutral fragment. We therefore observe that when the exocyclic group is an amino- or dialkylamine group the ion m/e 74 is of little importance and that fragmentation patterns are relatively simple with three or four ions accounting for something like 50% of the total ionisation, and these are all boron-containing ions (see Table).

However in the case where the phenyl group is the exocyclic substituent the positive charge resides on an atom in the ring and hence one observes many ions due to ring fragmentation with ion m/e 74 as the base peak and although this ion is the base peak it only accounts for *ca.* 11% of the total ionisation.

Two general conclusions can be made: first, where possible the positive charge will be localised on an atom in an exocyclic position in preference to a cyclic position and this causes boron-containing ion to carry a considerable percentage of the total ionisation. Secondly, when the charge resides on an atom in the ring one observes non-boron-containing ions to carry a high percentage of the total ionisation.

EXPERIMENTAL

Dichlorophenylborane,[13] trisdimethylaminoborane,[14] trisdiethylaminoborane,[15] and trisethylthioborane [16] were prepared by literature methods. All the prepared compounds readily hydrolysed and gave off an unpleasant odour, consequently reactions were carried out in dry apparatus and contact of the compounds with the atmosphere was kept at a minimum. In general sodium-dried benzene or light petroleum (b.p. 40—60°) were used as solvents. All mass spectra were recorded using an A.E.I. MS 902 mass spectrometer at 70 eV and 170° and i.r. spectra were recorded using a PE 457 spectrometer.

Preparation of 3-Mercaptopropanol.—Thiourea (36·1 g, 0·47 mol), dissolved in water (23·7 ml, 1·31 mol), was added to 3-bromopropanol (50 g, 0·35 mol). The mixture was refluxed and stirred and after *ca.* 2 h darkened to a brown liquid. After refluxing for a further period of up to 2 h the mixture was cooled and a solution of sodium hydroxide (10% solution) was added. This mixture was refluxed for 3 h and after cooling acidified to pH 4 by the slow addition of dilute sulphuric acid. The 3-mercaptopropanol was extracted with ether and the ether solution was filtered and after removal of the ether under vacuum the residue, on distillation, afforded 3-mercaptopropanol (24·1 g, 27·6%), b.p. 78—80°, 0·2 mmHg (Found: C, 38·9, H, 8·7%; *M*, 92. Calc. for C_3H_8OS: C, 39·1; H, 8·69%; *M*, 92).

[12] R. H. Cragg, G. Lawson, and J. F. J. Todd, *J.C.S. Dalton*, 1972, 878.
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[14] K. Niedenzu and J. W. Dawson, *Inorg. Synth.*, 1967, **10**, 135.
[15] W. Gerrard, M. F. Lappert, and C. A. Pearce, *J. Chem. Soc.*, 1957, 381.
[16] J. Brault and J. M. Lalancette, *Canad. J. Chem.*, 1964, **42**, 2093.

Preparation of 2-*Phenyl*-1,3,2-*oxathiaborinan*.—3-Mercaptopropanol (2·314 g, 0·025 mol) was added dropwise to dichlorophenylborane (4·0 g, 0·025 mol) in dichloromethane (50 ml) at 0°. The mixture was refluxed until the elimination of hydrogen chloride had ceased. The solvent was removed under vacuum and the residue on distillation afforded 2-*phenyl*-1,3,2-*oxathiaborinan* (3·1 g, 69%), b.p. 89—90°, 0·5 mmHg, n_D^{27} 1·5751 (Found: C, 60·75; H, 6·15%; *M*, 178. $C_9H_{11}BOS$ requires C, 60·60; H, 6·17%; *M*, 178).

Preparation of 2-*Diethylamino*-1,3,2-*oxathiaborinan*.—Tris-diethylaminoborane (14·74 g, 0·07 mol) was added slowly to 3-mercaptopropanol (6·0 g, 0·07 mol) in sodium-dried benzene (80 ml) at room temperature. The mixture was refluxed for three days after which no further elimination was found to occur. The solvent was removed under vacuum and the residue afforded, on distillation, 2-*diethylamino*-1,3,2-*oxathiaborinan* (10·15 g, 89·9%), b.p. 52—54°, 0·1 mmHg, n_D^{19} 1·4932 (Found: C, 47·95; H, 8·95; N, 7·6%; *M*, 173. $C_7H_{16}BNOS$ requires C, 48·5; H, 9·24; N, 8·09%; *M*, 173).

Using the above method, 2-*dimethylamino*-1,3,2-*oxathiaborinan* (75%), b.p. 54—56°, 0·2 mmHg, n_D^{22} 1·5049 (Found: C, 40·85; H, 8·0; N, 9·35%; *M*, 145. $C_5H_{12}BNOS$ requires C, 41·30; H, 8·27; N, 9·65%; *M*, 145) was obtained.

Preparation of 2-*Isopropylamino*-1,3,2-*oxathiaborinan*.—2-Diethylamino-1,3,2-oxathiaborinan (3·0 g, 0·02 mol) was added dropwise to a solution of isopropylamine (10 ml, 0·17 mol) in light petroleum (50 ml) at 0°. The mixture was refluxed for 12 h after which the solvent and volatile materials were removed under reduced pressure and the residue, on distillation, afforded 2-*isopropylamino*-1,3,2-*oxathiaborinan* (2·70 g, 98·4%), b.p. 50—52°, 0·5 mmHg, n_D^{24} 1·4842 (Found: C, 45·75; H, 8·95; N, 8·8%; *M*, 159. $C_6H_{14}BNOS$ requires C, 45·20; H, 8·80; N, 8·80%; *M*, 159).

Using the above method 2-*ethylamino*-1,3,2-*oxathiaborinan* (81·1%), b.p. 56—58°, 0·5 mmHg, n_D^{24} 1·4952 (Found: C, 41·7; H, 7·0; N, 9·15%; *M*, 145. $C_5H_{12}BNSO$ requires C, 41·30; H, 8·27; N, 9·65%; *M*, 145), 2-*n-butylamino*-1,3,2-*oxathiaborinan* (64·4%), b.p. 62—63°, 0·5 mmHg, n_D^{26} 1·4898 (Found: C, 47·8; H, 9·05; N, 7·35%; *M*, 173. $C_7H_{16}BNOS$ requires C, 48·5; H, 9·2; N, 8·1%; *M*, 173), and 2-*t-butylamino*-1,3,2-*oxathiaborinan* (65·7%), b.p. 66—67°, 0·8 mmHg, n_D^{25} 1·4901 (Found: C, 46·65; H, 9·4; N, 7·66%; *M*, 173. $C_7H_{16}BNOS$ requires C, 48·5; H, 9·24; N, 8·09%; *M*, 173) have been obtained.

Preparation of 2-*Ethylthio*-1,3,2-*oxathiaborinan*.—3-Mercaptopropanol (6·0 g, 0·07 mol) was added to a benzene solution (100 ml) of trisethylthioborane (12·65 g, 0·07 mol) at room temperature. The mixture was refluxed for two days after which the solvent and volatile materials were removed under reduced pressure and passed through a lead acetate solution where any ethanethiol was precipitated as the lead thiolate. The residue on distillation afforded 2-*ethylthio*-1,3,2-*oxathiaborinan* (7·92 g, 75%), b.p. 70—71°, 0·1 mmHg, n_D^{24} 1·5460 (Found: C, 31·9; H, 5·95%; *M*, 162. $C_5H_{11}BOS_2$ requires C, 37·0; H, 6·79%; *M*, 162). The analysis is low due to the extreme hydrolytic instability of the compound. However the mass spectrum of the compound showed it to be pure.

Preparation of 2-*n-Butoxy*-1,3,2-*oxathiaborinan*.—2-Ethylthio-1,3,2-oxathiaborinan (3·0 g, 0·018 mol) was slowly added to tri-n-butoxystibine (2·10 g, 0·006 mol) at 0°. The reaction was carried out in an atmosphere of nitrogen. The reaction was exothermic and after 30 min the resulting mixture was distilled, under reduced pressure, affording 2-*butoxy*-1,3,2-*oxathiaborinan* (2·82 g, 88%), b.p. 55—60°, 0·01 mmHg, n_D^{23} 1·4765 (Found: C, 49·5; H, 8·6%; *M*, 174. $C_7H_{15}BO_2S$ requires C, 48·20; H, 8·62%; *M*, 174) and trisethylthiostibine (0·82 g, 43%), b.p. 94—100°, 0·01 mmHg (Found: C, 23·4; H, 5·15%; *M*, 306. Calc. for $C_6H_{15}S_3Sb$: C, 23·60; H, 4·91%; *M*, 306).

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