

ORGANOBORON COMPOUNDS

XII *. SYNTHESIS AND PROPERTIES OF SOME 2-SUBSTITUTED-1,3,2-OXATHIABOROLANS

R. HARRY CRAGG **, JOHN DUDMAN and JOHN P.N. HUSBAND

The Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent (Great Britain)

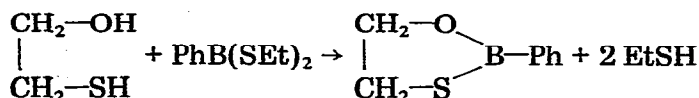
(Received March 5th, 1976)

Summary

The preparation and properties of some new boron heterocycles of formula

$$\begin{array}{c} \text{CH}_2\text{—O} \\ | \quad \diagup \\ \text{CH}_2\text{—S—B—X} \end{array} \quad (\text{X} = \text{Ph, SR, NR}_2 \text{ and NHR}) \text{ are described.}$$

Organoboron heterocyclic derivatives of ethane-1,2-diol and ethane-1,2-dithiol have been fully investigated [2]. In contrast heterocyclic derivatives of 2-mercaptoethanol have been ignored. Mixed oxygen—boron—sulphur heterocycles have been mentioned in a review [3], in the patent literature [4] and in a gas chromatographic study of heterocyclic organoboranes [5]. Recently we reported the results of a study on the synthesis and properties of oxathiaborinans [6] and now describe our recent work on heterocyclic derivatives of 1,3,2-oxathiaborolans. 2-Phenyl-1,3,2-oxathiaborolan was obtained in high yield from the interaction of 2-mercaptoethanol and bis(ethanethio)phenylborane.



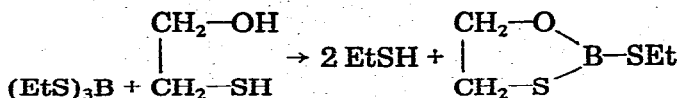
2-Phenyl-1,3,2-oxathiaborolan was also obtained, but in lower yield, from the interaction of dichlorophenylborane with 2-mercaptoethanol.

One general procedure in studying the chemistry of a heterocyclic organoborane is to study the substitution reactions of the corresponding chloroborane. All our attempts to prepare 2-chloro-1,3,2-oxathiaborolan from trichloroborane and 2-mercaptoethanol were unsuccessful. However its instability did not prevent our investigation of the derivatives of this system since the 2-mercapto com-

* For part XI see ref. 1.

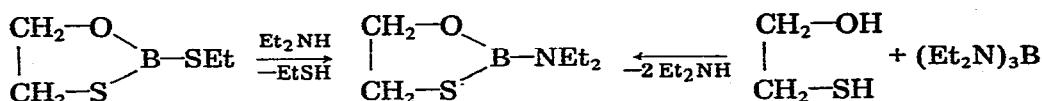
** To whom correspondence should be addressed.

pound, which was obtained from the interaction of tris(ethanethio)borane and 2-mercaptoethanol, was thermally stable.

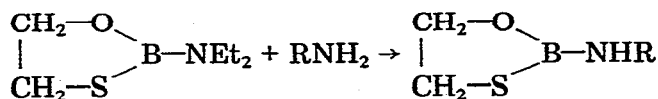


Hydrogen chloride reacted with the 2-mercapto derivative but instead of the 2-chloro compound, a polymeric material was formed.

Compounds containing boron–sulphur bonds react very readily with amines, and the interaction of diethylamine with the 2-ethanethio compound gave the corresponding 2-diethylamino-1,3,2-oxathiaborolan in high yield. An alternative method for its synthesis involved the interaction of 2-mercaptoethanol and tris(diethylamino)borane.



Transamination, between a primary amine and 2-diethylamino-1,3,2-oxathiaborolan, gave the corresponding 2-alkylamino-1,3,2-oxathiaborolans. The alkylamino and dialkylamino compounds are further examples of thermally stable unsymmetrical organoboranes having three different groups attached to boron.



R = n-Bu + t-Bu

In the case of the two alkylamino compounds a band in the infrared spectrum in the region 3400–3360 cm⁻¹, due to N–H stretching frequency was observed in the region characteristic for a monomeric alkylaminoborane [7].

Infrared spectra

The infrared spectra of the 1,3,2-oxathiaborolans were found to be complex, and except for those due to the N–H stretching frequency it is difficult to assign bands with any certainty. The infrared spectra were consistent with the formulation of the compounds and infrared bands in the regions 1515–1470,

TABLE 1

MAIN IONS OF INTEREST IN THE MASS SPECTRA OF 2-SUBSTITUTED-1,3,2-OXATHIABOROLANS

Substituent	Parent ion		Base peak	Parent ion — substituent	
	m/e	%	m/e	m/e	%
Ph	164	93	74	87	<1
NEt ₂	159	23	144	87	1.1
NHBu-n	159	18.8	116	87	<1
NIIBu-t	159	15	144	87	1.3
SEt	148	91.3	136	87	17.3

1330–1295 and 1035–970 cm^{-1} are tentatively assigned to B–N, B–O and B–S stretching frequency bands.

Mass spectra

The mass spectra of this new series of compounds have been studied and Table 1 lists the main ions of interest in the mass spectra of 1,3,2-oxathiaborolans. Full details of the mass spectrum of 2-phenyl-1,3,2-oxathiaborolan have been previously published [8].

Experimental

Dichlorophenylborane [9], bis(ethanethio)phenylborane [10], tris(ethanethio)borane [11] and tris(diethylamino)borane [12] were prepared by methods established in the literature. All the compounds prepared readily hydrolysed and gave off an unpleasant odour, consequentially the usual precautions were taken for handling air sensitive materials and contact with the atmosphere was kept to a minimum. The molecular weight determinations and mass spectra were obtained using an AEI MS902 mass spectrometer at 70 eV., infrared spectra were recorded using a PE 457 spectrometer and the ^{11}B NMR spectra were recorded using a PER 10 spectrometer. Chemical shifts are quoted with respect to trimethoxyborane as an external standard.

Preparation of 2-phenyl-1,3,2-oxathiaborolan

2-Mercaptoethanol (0.52 g, 0.006 mol) was slowly added from a syringe into bis(ethanethio)phenylborane (1.38 g, 0.006 mol) at -78°C . The mixture was allowed to reach room temperature and the ethane thiol was removed under vacuum to leave a residue which on distillation afforded 2-phenyl-1,3,2-oxathiaborolan (0.83 g, 77%), b.p. $81\text{--}84^\circ\text{C}/1.5\text{ mmHg}$, n_D^{25} 1.5764, ^{11}B NMR -31 ppm . (Found: C, 58.66; H, 5.62; Mol.wt., 164. $\text{C}_8\text{H}_9\text{OSB}$ calcd.: C, 58.51; H, 5.52%; Mol.wt., 164).

The reaction was repeated using dichlorophenylborane, and 2-phenyl-1,3,2-oxathiaborolan (55%) was obtained.

Preparation of 2-ethanethio-1,3,2-oxathiaborolan

2-mercaptoethanol (1.21 g, 0.016 mol) was added to tris(ethanethio)borane (2.99 g, 0.0166 mol) at -78°C . The reaction mixture was allowed to attain room temperature and after removal of ethane thiol under vacuum the residue on distillation afforded 2-ethanethio-1,3,2-oxathiaborolan (1.94 g, 84%) b.p. $73^\circ\text{C}/4.2\text{ mmHg}$, n_D^{25} 1.5403, ^{11}B NMR -32 ppm (Found: C, 32.04; H, 6.16%; Mol.wt., 148. $\text{C}_4\text{H}_9\text{OS}_2\text{B}$ calcd.: C, 31.81; H, 6.11%; Mol. wt., 148).

Preparation of 2-diethylamino-1,3,2-oxathiaborolan

Diethylamine (0.47 g, 0.006 mol) was added to 2-ethanethio-1,3,2-oxathiaborolan (0.94 g, 0.006 mol) at -20°C . The mixture was allowed to attain room temperature and after removal of ethane thiol under vacuum the residue on distillation afforded 2-diethylamino-1,3,2-oxathiaborolan (0.86 g, 76%), b.p. $58\text{--}60^\circ\text{C}/4\text{ mmHg}$, n_D^{25} 1.4810, ^{11}B NMR -16 ppm , (Found: C, 44.82; H, 8.76; N, 9.08%, Mol.wt., 159. $\text{C}_6\text{H}_{14}\text{NOSB}$ calcd.: C, 45.41; H, 8.81; N, 8.81%, Mol. wt., 159).

2-Diethylamino-1,3,2-oxathiaborolan was also obtained from the interaction of tris(diethylamino)borane and 2-mercaptoethanol.

Preparation of 2-n-butylamino-1,3,2-oxathiaborolan

n-Butylamine (2.2 g, 0.03 mol) and 2-diethylamino-1,3,2-oxathiaborolan (2.15 g, 0.014 mol) were refluxed in benzene for 4 h. After removal of the diethylamine and benzene under reduced pressure the residue on distillation afforded 2-n-butylamino-1,3,2-oxathiaborolan (1.32 g, 61.4%), b.p. 42–45°C/0.15 mmHg, (Found: C, 44.158; H, 8.73; N, 8.46%; Mol.wt., 159. $C_6H_{14}NOSB$ calcd.: C, 45.41; H, 8.81; N, 8.81%; Mol.wt., 159).

2-t-Butylamino-1,3,2-oxathiaborolan (65%) b.p. 36–38°C/0.1 mmHg, (Found: C, 45.92; H, 9.11; N, 8.93%, Mol.wt., 159. $C_6H_{14}NOSB$ calcd.: C, 45.41; H, 8.81; N, 8.81%; Mol.wt., 159) was also obtained from the interaction of t-butylamine and 2-diethylamino-1,3,2-oxathiaborolan.

Attempted synthesis of 2-chloro-1,3,2-oxathiaborolan

(a) 2-Ethanethio-1,3,2-oxathiaborolan was dissolved in petroleum ether and the mixture cooled to 0°C. Hydrogen chloride, from a cylinder, was bubbled through the solution for 30 min. The solvent, ethane thiol and excess hydrogen chloride were removed under vacuum and a white intractable solid remained.

(b) A 10% molar excess of trichloroborane was distilled into 2-mercaptoethanol at –80°C. On warming a vigorous reaction occurred resulting in the formation of a white unidentified solid.

References

- 1 R.H. Cragg and M. Nazery, *J. Organometal. Chem.*, **99** (1975) 42.
- 2 S.G. Shore, J.L. Crist, B. Lockman, J.R. Long and A.D. Coon, *J. Chem. Soc. Dalton*, (1972) 1123.
- 3 D. Seyferth and R.B. King, *Annual Surveys of Organometallic Chemistry*, Elsevier, Amsterdam, 1966, Vol. 2, p. 84.
- 4 G.W. Conklin and R.C. Morris, *Brit. Pat.*, 1958, 790, 090.
- 5 D. Barnes, W.G. Henderson, E.F. Mooney and P.C. Uden, *J. Inorg. Nucl. Chem.*, **33** (1971) 2799.
- 6 R.H. Cragg and M. Nazery, *J. Chem. Soc. Dalton*, (1974) 1438.
- 7 M.F. Lappert, M.K. Majumdar and B.P. Tilley, *J. Chem. Soc. (A)*, (1966) 1591.
- 8 R.H. Cragg, G. Lawson and J.F.J. Todd, *J. Chem. Soc. Dalton*, (1972) 878.
- 9 J.E. Burch, W. Gerrard, M. Howarth and E.F. Mooney, *J. Chem. Soc.*, (1960) 4916.
- 10 R.H. Cragg, M.F. Lappert and B.P. Tilley, *J. Chem. Soc. (A)*, (1967) 947.
- 11 J. Brault and J.M. Lalancette, *Can. J. Chem.*, **42** (1964) 2093.
- 12 W. Gerrard, M.F. Lappert and C.A. Pearce, *J. Chem. Soc.*, (1957) 381.