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PREPARATION AND STABILITY OF SULPHUR CONTAINING BORON HETEROCYCLES

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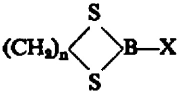
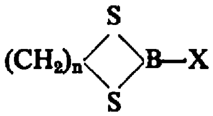
Abstract—Preparation and properties of some new boron containing heterocycles of general formula



are described.

Few organo-sulphur derivatives of boron have been reported[1,2] and little information is available on compounds of type A. Four compounds of this type (Table I) have



been prepared in high yields by the addition of the appropriate dithiol to boron trichloride or phenyl boron dichloride in dichloromethane solvent, at −80°. No reaction was found to occur until the mixture was warmed to room temperature, whereas during the preparation of the analogous oxygen compounds, hydrogen chloride is readily evolved at −80°.[3,4] The phenyl derivative (IV) could not be prepared via reaction of phenyl boronic anhydride and propane 1,3 dithiol.

Table 1

Compound	b.p.	n_D^{25}	% Yield
I—$S(CH_2)_2S$—B—Cl 2-chloro-1,3,2-dithioborolan	24–25°/ 0·5 mm	1·5778	88
II—$S(CH_2)_3S$—B—Cl 2-chloro-1,3,2-dithioborinan	52°/ 0·1 mm	1·5862	80
III—$S(CH_2)_2$—S—B—ϕ 2-phenyl-1,3,2-dithoborolan	90–92°/ 0·05 mm	1·6346	92
IV—$S(CH_2)_3$—S—B—ϕ 2-phenyl-1,3,2-dithioborinan	110–111°/ 0·05 mm	1·6375	90

The boiling points of the chloro-derivatives (I and II) when compared with the reported values for 2-chloro-1,3,2-dioxaborolan (V) (44°/0·2 mm) and 2-chloro-1,3,2-dioxaborinan (VI) (20–22°/0·05 mm) suggest that unlike V, 2-chloro-1,3,2-dithioborolan is not highly associated in the liquid state. In the oxygen series, V is a highly

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[1] M. F. Hawthorn, *J. Amer. Chem. Soc.* **83**, 1345 (1961).

[2] J. A. Blau, W. Gerrard and M. F. Lappert, *J. Chem. Soc.* 667 (1960).

[3] J. A. Blau, W. Gerrard and M. F. Lappert, *J. Chem. Soc.* 4116 (1957).

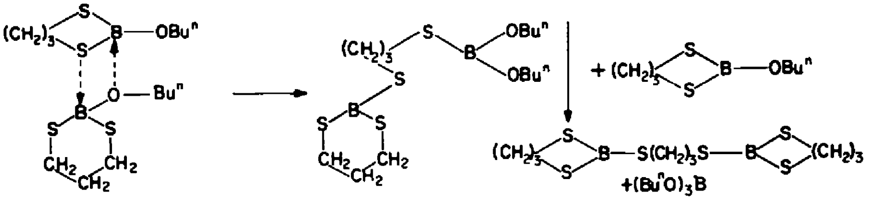
[4] A. Finch, J. C. Lockhart and E. J. Pearn, *J. Org. Chem.* **26**, 3250 (1961).

viscous liquid at room temperature whereas VI is mobile. Such a difference does not occur in the sulphur compounds, both I and II being mobile liquids at room temperature. Molecular weight determinations on compounds I–IV have shown that they are unassociated in dilute benzene solution.[5] The high strain in the dioxaborolan system can be relieved through association.[6] Molecular models suggest than both 5- and 6-membered sulphur rings are relatively free from strain and this may be correlated with the lack of association in dilute benzene solution.

Compounds I–IV were easily hydrolysed and also they appear to be sensitive to oxygen, a transparent film forming in an atmosphere of dry-air but not in one of dry nitrogen.

All compounds were thermally stable at room temperature and no decomposition was detected in I and II after heating for 65 hours and 24 hours respectively at 100°, again in contrast to the behaviour of the analogous oxygen compounds.

The ester (A, n = 3, X = SBu^n) was not isolated in a pure form from the reaction between II and n-butane thiol. An attempt to prepare a mixed ester (A, n = 3, X = OBu^n) suggests that on distillation disproportionation occurs with the formation of tri-n-butyl borate. This probably occurs as follows:



Disproportionation of this type has been reported for the dioxaborolan[6] and and dioxaborinan[7] esters.

The IR spectra of compounds I–IV (Table 2) show the characteristic absorption peaks associated with the B-S stretching vibration in the 900–1000 cm^{-1} region.[2] Further work is in progress on the IR spectra of boron heterocycles of type A, where X = Ph, Cl, SR, NR_2 and n = 2,3. A comparative study of these spectra with those of the oxygen analogues should be of interest.

EXPERIMENTAL

Reaction between boron trichloride and ethane dithiol. Ethanol dithiol (24·5 g, 0·26 mole n_D^{25} = 1·5569) was added dropwise to boron trichloride (25·0 g; 0·21 mole) in dichloromethane (40 ml) in a N_2 atm. under a −80° reflux and vigourous stirring. No HCl was evolved at −80°; but some evolved slowly as the mixture warmed to room temp. The mixture was pumped at 15–20 mm under a −80° reflux and HCl (Found 15·0 g, calc. 15·5 g) was trapped at −196°. The solvent was pumped off and the golden, yellow liquid (31·3 g) residue was analysed. (Found, e.h.c. 24·5; B, 8·5; $C_2H_4BS_2Cl$ requires: e.h.c. 25·6; B, 7·82%). A portion of this crude yield (12·4 g) on distillation (leaving no residue) gave 2-chloro-1,3,2-dithioborolan as a colourless liquid (10·1 g) b.p. 24–25°/0·1 mm n_D^{25} = 1·5778. (Found, C, 17·5; H, 3·37; S, 45·6; B, 7·69; Cl, 25·3; $C_2H_4S_2B.Cl$ requires C, 17·3; H, 2·91; S, 46·3; B, 7·82; Cl, 25·6 mol.wt. determined in benzene over a concentration range up to 0·4 M was 141, Calc. 138). The IR spectrum was recorded in 0·125 M CCl_4 solution.

Reaction between boron trichloride and propane 1,3 *dithiol.* Propane 1,3-dithiol (23·1 g, 0·22 mole n_D^{25} = 1·5375 Lit. n_D^{25} = 1·5380) in dichloromethane (20 ml) were reacted as in the previous experiment, HCl (15·0 g req. 15·5 g) was removed leaving a colourless, clear residue (33·0 g) which was

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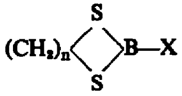
[5] A. Finch and P. J. Gardner, *J. Inorg. and Nuc. Chem.* **25**, 927 (1963)

[6] J. Dale, *J. Chem. Soc.* 910 (1961).

[7] A. Finch, P. J. Gardner, J. C. Lochart and E. J. Pearn, *J. Chem. Soc.* 1428 (1962).

TABLE 2. THE IR SPECTRA OF COMPOUNDS WITH THE GENERAL FORMULA



	No. 2. X = Cl	X = Ph		No. 3. X = Cl	X = Ph
		1595 m			1595 m
	1428 s	1440 s		1428 s	1440 s
		1345 m/sh		1342 v.w	1348 m/sh
	1282 s	1282 s		1282 s	1285 s
	1250 m	1232 v.v.s		1242 m	1220 m
	1200 v.v.w	1187 w		1190 mw	1205 v.v.s
		1162 w			1160 w
	1115 m.w			1115 m.w	1120 w
				1050 m.w	1075 w
	1010 v.s	1005 w		1020 v.s	1005 s
Triplet form	990/970 v.s	990 v.w		978 v.s	971 v.s
		952 m.s		940 m.s	921 m
		935 m	Triplet	915 s	909 s
		915 s	Triplet	895 v.s	900 v.s
		909 v.s		860 s	865 s
	848 s	848 s		826 m	826 m
	728 w	754 v.s			752 v.s
		696 v.s			698 s
	664 w			672 w	675 m
				650 w	
				445 w	

analysed. (Found, e.h.c. 27·1; B, 7·1; Calc. for $C_3H_6S_2B{\cdot}Cl$: e.h.c. 23·2; B, 7·1%). A portion of this product (10·1 g) yielded on distillation a dark red residue (1·2 g) and 2-chloro-1,3,2-dithioborinan 7·0 g; b.p. 56–58°/0·2 mm, n_D^{25} = 1·5862. (Found, C, 23·1; H, 3·8; S, 39·9; B, 7·19; Cl, 23·4; $C_3H_6S_2B{\cdot}Cl$ requires: C, 23·6; H, 3·9; S, 42·0; B, 7·12; Cl, 23·3%; Mol. wt. determined in benzene over a concentration range to 0·4 M, was 165, Calc. 152). The IR spectrum was determined in CCl_4 solution (0·125 M).

In a second preparation, omitting the solvent, propane 1,3-dithiol (28·8 g 0·21 mole) and boron trichloride (25·0 g, 0·21 mole) were mixed under a −80° reflux. Distillation gave 2-chloro-1,3,2-dioxaborinan (25·0 g, 80%) b.p. 50–52°/0·1 mm (e.h.c. 23·2; mol. wt. over the range 0·0–0·4 M in benzene 165).

Reaction between 2-chloro-1,3,2-dithioborinan and n-butylalcohol. 2-Chloro-1,3,2-dithioborinan (10·0 g, 0·06 mole.) in dichloromethane (25 ml) was mixed with n-butylalcohol (4·9 g, mole) in a N_2 atm. at 0° and vigorous stirring. No HCl was evolved and the mixture allowed to warm to room temp. The solvent was pumped off at 20 mm and the residue (14·5 g) on distillation gave a volatile fraction (2·0 g) which was pumped off at room temp and 0·01 mm; (HCl reqd. 2·4 g) and a second fraction (6·8 g) b.p. 46°/0·1 mm, n_D^{25} = 1·4330 was collected. (Found and B, 4·95; $C_7H_{15}S_2BO$ requires: B, 5·71; Calc. for $(BuO)_3B$, 4·77%).

The temp of the oil bath was raised but no further fraction collected. At an external temp of 180° the residue in the flask was a white solid (4·6 g). Redistillation of the second fraction (leaving no residue) 22–46°/0·1 mm yielded a colourless liquid, n_D^{25} = 1·4335 and B, 5·05%.

Reaction between 2-chloro-1,3,2-dithioborinan and n-butane thiol. 2-Chloro-1,3,2-dithioborinan (10·0 g, 0·06 mole) in dichloromethane (25 ml) was treated with n-butane thiol (6·0 g, 0·05 mole) at room temp under a water reflux in a N_2 atm. The solvent was pumped off and the yellow residue (12·0 g) on distillation of 10·0 g gave a volatile fraction (1·5 g) at 0·1 mm, a second fraction (6·4 g) b.p. 48°/0·1 mm, n_D^{25} = 1·5688 (B, 5·94, $C_7H_{15}S_3B$ requires: B, 5·26%), a high boiling fraction, (0·5 g) b.p. 110°/0·1 mm, and a solid yellow residue (0·9 g). The second fraction was redistilled, b.p. 50–52°/0·1 mm, n_D^{25} = 1·5750 (B, 6·00%). This fraction gave a slight precipitate with conc. HNO_3/$AgNO_3$ showing presence of hydrolysed chlorine.

Preparation of 2-phenyl-1,3,2-dithioborolan. Ethane dithiol (3·3 g, 0·035 mole) was added dropwise to phenyl boron dichloride (5·5 g, 0·035 mole) in dichloromethane (20 ml) at room temp under a N_2 atm, and vigorous stirring until the pink colour of the solution disappeared forming a yellow solution. Hydrogen chloride was collected [Found 1·8 g, reqd. 2·5 g yield, 73%] and the solvent was removed. The crude product [7·0 g] was a pale yellow colour and on distillation gave a colourless liquid (5·9 g) b.p. 97–98°/0·1 mm. Redistillation gave a water white liquid b.p. 90–92°/0·05 mm n_D^{25} = 1·6346. This compound, 2-phenyl-1,3,2-dithioborolan did not decolourize on standing. A white film appeared when the light was exposed to air. (Found, C, 51·6; H, 4·85; S, 35·4; $C_8H_9S_2B$ requires; C, 53·3; H, 5·00; S, 35·6%; mole. wt. in benzene, on concentration up to 0·4M; Found 179, Calc. 180).

Preparation of 2-phenyl-1,3,2-dithioborinan. Propane-1,3-dithiol (5·1 g, 0·047 mole) was added dropwise to phenyl boron dichloride (7·0 g, 0·044 mole) in dichloromethane (20 ml) at room temp in a N_2 atm. and vigorous stirring until the pink colour of the solution disappeared. Solvent and HCl were removed. (Found: HCl 2·7 g reqd. 3·2 g). The residue (9·5 g) on distillation gave a fraction (8·1 g, b.p. 116–120°/0·1 mm), which on redistillation gave a water, white liquid becoming slightly yellow on standing (7·0 g) b.p. 109–110°/0·05 mm n_D^{25} = 1·6375. A white film appeared on the surface if exposed to air. (Found C, 54·2; H, 5·45; S, 31·7; $C_9H_{11}S_2N$ requires: C, 55·6; H, 5·67; S, 33·0%; Mol. wt. determined in benzene in concentrations up to 0·4M, Found 196, Calc. 194).

Reaction between phenyl boronic anhydride and propane 1,3 dithiol. Propane-1,3-dithiol (13·5 g, 0·125 mole) and phenyl boronic anhydride (13·0 g, 0·04 mole) were mixed with benzene (50 ml) under a N_2 atm and heated for 15 hr in a Dean and Stark apparatus. No water collected, the benzene was then removed and the mixture heated strongly for a further 3 hr. After cooling, more benzene was added and again a water separation was attempted. On removing the benzene, a white solid remained from which no original di-thiol could be separated.

Pyrolysis of 2-chloro-1,3,2-dithioborolan at 100°. 2-Chloro-1,3,2-dithioborolan (2·62 g) was heated for 65 hr at 100° under a N_2 atm, in a loosely stoppered flask. The compound turned black but an IR of the pyrolysate was identical with the IR of the freshly prepared compound. No weight loss was found after heating. Distillation gave only 2-chloro-1,3,2-dithioborolan (2·2 g) b.p. 24–25°/0·1 mm, n_D^{25} = 1·5778 (e.h.c. 25·3) and a small amount of residue (0·2 g).

An attempt was made to pyrolyse this compound at 270–280° but the compound refluxed too vigorously at this temp and the experiment was abandoned.

Pyrolysis of 2-chloro-1,3,2-dithioborinan at 100°. 2-Chloro-1,3,2-dithioborinan (3.39 g) was heated at 100° for 24 hr under a N_2 atm, in a loosely stoppered flask. The compound immediately turned yellow but did not darken further. No weight loss occurred and distillation afforded the starting material (2·73 g) and some residue (0·46 g) which was similar to that obtained when distilling the freshly prepared material.

IR spectra were recorded as liquid films, using a Unicam S.P. 100 IR spectrometer equipped with NaCl and KBr optics.

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