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ORGANOBORON COMPOUNDS

XIII *. PREPARATION AND PROPERTIES OF SOME 2-SUBSTITUTED 1,3,2-DITHIABORINANS

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Summary

The preparation and properties of some boron heterocycles of the general formula  (where X = Ph, SR, NR_2, NHR and NHNPh) are described and the general features of their mass spectra discussed.

Introduction

Studies of heterocyclic organoboranes containing sulphur have been very limited composed with those of the corresponding compounds containing oxygen or nitrogen. The recent literature reports some general aspects of boron—sulphur chemistry [2] and cyclic boron—sulphur compounds [3] and our interest in this area has been prompted by their potential use in the synthesis of organoboron [4] and sulphur compounds [5].

Results and discussion

2-Phenyl-1,3,2-dithiaborinan was obtained via the interaction of dichlorophenylborane and 1,3-propanedithiol at —80°C. Although the compound was stable to distillation and in an inert atmosphere nevertheless it was found to be less stable than the corresponding 2-phenyl-1,3,2-dioxaborinan as demonstrated by the following reaction. On addition of 1,3-propanediol to 2-phenyl-1,3,2-dithiaborinan, in benzene, an exothermic reaction took place and after refluxing the

* For part XIII see ref. 1.

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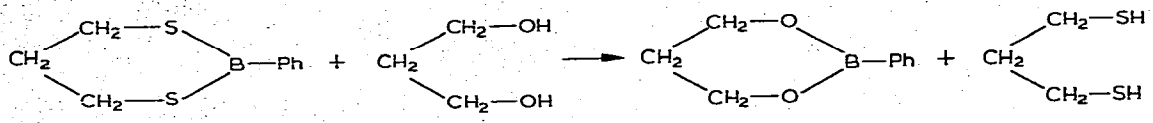
TABLE 1

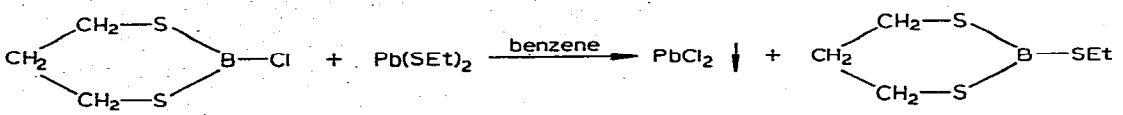
MAJOR IONS OF INTEREST IN THE MASS SPECTRA OF 2-SUBSTITUTED 1,3,2-DITHIABORINANS

2-Substituent (R)	Base peak (*m/e*)	Parent (*m/e*)	% Base	P — R (*m/e*)	% Base	*m/e* 74%	*m/e* 152%	*m/e* 120%	*m/e* 91%
Ph	41	194	81.0	117	8.1	84.0	27.0	64.9	18.9
Et_2N	174	189	19.3	117	3.5	6.4	—	—	—
BuNH	146	189	31.6	117	5.9	32.2	—	—	—
EtS	178	178	100	117	26.4	38.4	—	—	—

mixture for one hour the solvent was removed and the residue on distillation afforded 1,3-propanedithiol and 2-phenyl-1,3,2-dioxaborinan, both compounds being characterised by infrared and mass spectrometry. The reaction between

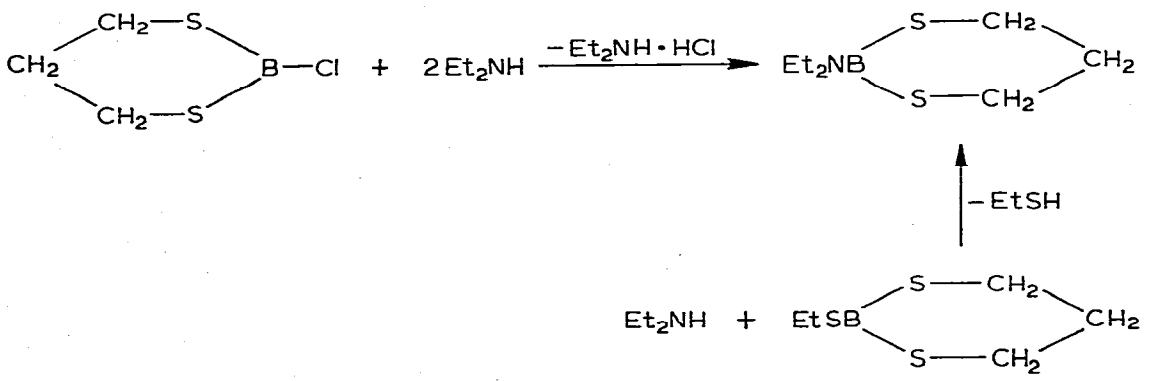


trisethanethioborane and 1,3-propanedithiol resulted in the formation of 2-ethanethio-1,3,2-dithiaborinan which was also obtained from the interaction of 2-chloro-1,3,2-dithiaborinan and the corresponding lead thiolate.



Attempts to prepare compounds of this type, by the interaction of butane thiol and 2-chloro-1,3,2-dithiaborinan, failed [6] and one would suggest that had lead butanethiolate been used instead of butane thiol then the reaction would have been succesful.

2-Diethylamino-1,3,2-dithiaborinan was obtained from the reaction of diethylamine with either 2-chloro-1,3,2-dithiaborinan or 2-ethanethio-1,3,2-dithiaborinan. The usual method of synthesis of aminoboranes is via the interaction of



a chloroborane with an amine. However in many cases it is difficult to obtain the aminoborane free from small amounts of aminehydrochloride. We would therefore suggest that when this is a problem then the reaction of the amine with a thioborane is to be recommended.

2-n-Butylamino-, 2-i-propylamino- and 2-phenylhydrazino-1,3,2-dithiaborinans were obtained by the well established transamination reaction. All the compounds

(R = i-Pr, n-Bu, PhNH)

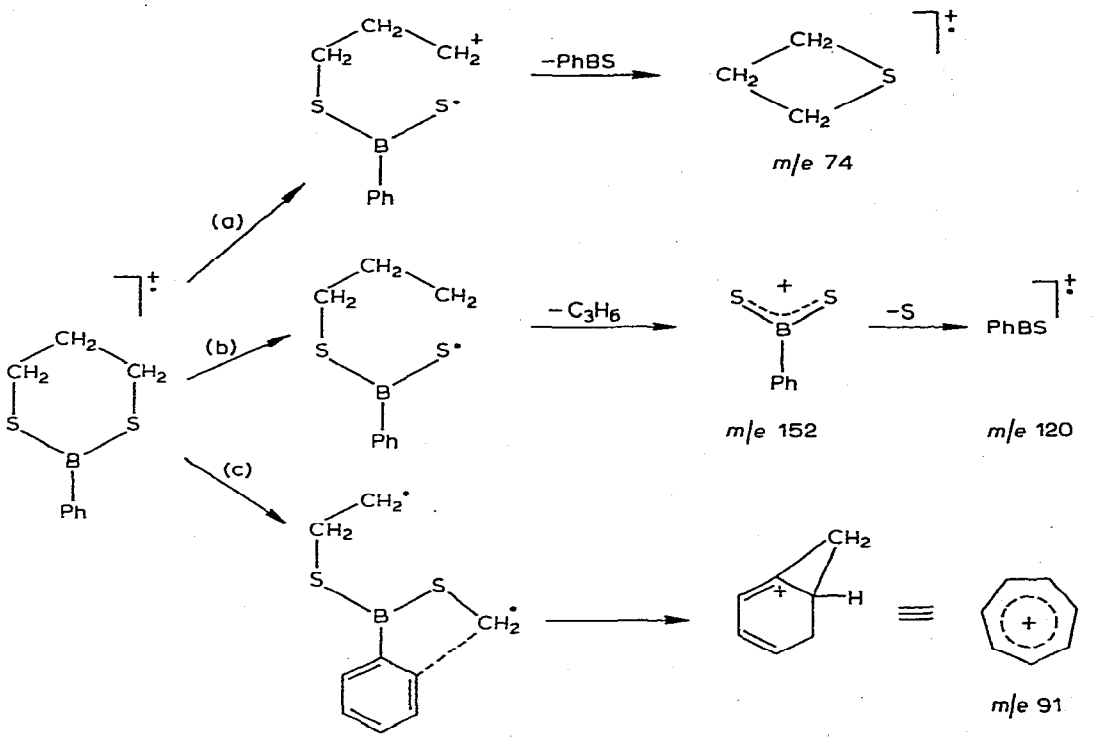
are thermally stable towards distillation but are readily hydrolysed. In the infrared spectra they all show peaks in the 1000—900 cm^{-1} region characteristic of

the asymmetric stretching modes of the $^{10}B^{32}S$ and $^{11}B^{32}S$ groups respectively [7] and the 2-i-propylamino, 2-n-butylamino and 2-phenylhydrazino compounds have peaks at 3438 cm^{-1}, 3372 cm^{-1} and 3372 cm^{-1} respectively characteristic of the NH stretching vibration [8].

Mass spectra

All compounds were found to be monomeric in the vapour phase. The principle ions of interest for each class of compounds are given in Table 1. In the mass spectrum of 2-phenyl-1,3,2-dithiaborinane three major fragmentation routes are observed (Scheme 1): (a) formation of sulphur hydrocarbon fragments (b) boron-sulphur fragments and (c) formation of hydrocarbon fragments.

SCHEME 1



Other compounds

As can be seen from Table 1 there are two features of interest: (a) all compounds fragment to give a relatively high percentage of the propylene sulphide ion *m/e* 74 and (b) in the mass spectrum of 2-ethanethio-1,3,2-dithiaborinan the cyclic borenium ion (*m/e* 117) appears to have considerable stability (26.4% cf. base peak).

Experimental

General procedures. Solvents were dried over sodium wire and distilled before use. The mass spectra were recorded using an AEI MS902 mass spectrometer at

70 eV. The source was maintained at 170°C and the compounds were introduced as neat liquids using an unheated direct-insertion probe.

Preparation of 2-phenyl-1,3,2-dithiaborinan Propane-1,3-dithiol (3.41 g, 0.03 mol) was added dropwise to dichlorophenylborane (5.00 g, 0.03 mol) at room temperature, using petroleum ether as the solvent. Hydrogen chloride was evolved after which the solvent was removed under vacuum and the residue, on distillation, afforded 2-phenyl-1,3,2-dithiaborinan (4.95 g, 81.1%), b.p. 130—134°C/0.1 mmHg, n_D^{25} 1.6274, Mol.wt. 194. (The b.p. established in the literature [6] 109—110°C/0.05 mmHg.)

Reaction of 2-phenyl-1,3,2-dithiaborinan with 1,3-propanediol. 1,3-Propanediol was slowly added to a benzene solution of 2-phenyl-1,3,2-dithiaborinan and the mixture refluxed for 3 h. The benzene was removed and the residue on distillation gave 1,3-propanedithiol and 2-phenyl-1,3,2-dioxaborinan, both compounds characterised by their infrared and mass spectra.

Preparation of 2-chloro-1,3,2-dithiaborinan. Propane-1,3-dithiol (28.8 g, 0.26 mol) was added dropwise to trichloroborane (25 g, 0.21 mol) at —78°C, the mixture being vigorously stirred. As the reaction proceeded, hydrogen chloride was evolved and a white solid which was initially formed disappeared with further addition of propane-1,3-dithiol. On removal of the hydrogen chloride the residue, on distillation, yielded 2-chloro-1,3,2-dithiaborinan (27.6 g, 85%), b.p. 54—58°C/0.2 mmHg, n_D^{23} 1.4756, Mol.wt. 152. (The b.p. reported in the literature [6] 56—58°C/0.2 mmHg.)

Preparation of 2-ethanethio-1,3,2-dithiaborinan. Lead ethanethiolate (11.87 g, 0.03 mol) was added slowly to a stirred solution of 2-chloro-1,3,2-dithiaborinan (11.0 g, 0.07 mol) in petroleum ether - b.p. 40/60 (230 ml). After the addition was completed the mixture was refluxed for 24 h. The white lead chloride was filtered off and on removal of the solvent, at reduced pressure, the residue on distillation afforded 2-ethylthio-1,3,2-dithiaborinan (4.48 g, 34.8%) b.p. 90—92°C/0.01 mmHg, n_D^{23} 1.6011. (Found: C, 33.8; H, 6.0; Mol.wt. 178. $C_5H_{11}BS_3$ calcd.: C, 33.7; H, 6.2%; Mol.wt. 178.)

Preparation of 2-diethylamino-1,3,2-dithiaborinan. Excess diethylamine (30 g, 0.4 mol) in petroleum ether (100 ml) was slowly added to 2-chloro-1,3,2-dithiaborinane (21.3 g, 0.12 mol) in petroleum ether (70 ml) at —78°C after which the mixture was allowed to attain room temperature. The insoluble amine hydrochloride was filtered off and on removal of the solvent under reduced pressure, the residue on distillation afforded 2-diethylamino-1,3,2-dithiaborinan (16.53 g, 63%) b.p. 96°C/8.0 mmHg, n_D^{27} 1.5425. (Found: C, 44.6; H, 8.3; N, 6.3; Mol.wt. 189. $C_7H_{16}BNS_2$ calcd.: C, 44.6; H, 8.4; N, 7.4%; Mol.wt. 189.)

Also obtained from the interaction of diethylamine and 2-ethanethio-1,3,2-dithiaborinan.

Preparation of 2-i-propylamino-1,3,2-dithiaborinan. 2-Diethylamino-1,3,2-dithiaborinan (3.0 g, 0.015 mol) was added slowly to a flask containing excess i-propylamine (10 ml, 0.1 mol) in petroleum ether (130 ml) at —78°C. After the addition, the mixture was allowed to attain room temperature and then refluxed for 12 h. After cooling, the solvent was removed under reduced pressure and the residue, on distillation, afforded 2-i-propylamino-1,3,2-dithiaborinan (2.1 g, 75.8%), b.p. 38—40°C/0.3 mmHg, n_D^{25} 1.5262. (Found: C, 40.91; H, 8.50; N, 8.20; Mol.wt. 175. $C_6H_{14}BNS_2$ calcd.: C, 41.11; H, 8.01; N, 8.01%; Mol.wt. 175.)

Preparation of 2-n-butylamino-1,3,2-dithiaborinan. 2-Diethylamino-1,3,2-dithiaborinan (2.3 g, 0.01 mol) and n-butylamine (0.88 g, 0.01 mol) were refluxed in benzene (40 ml) for one day. On cooling the solution the volatiles were removed under reduced pressure and the residue on distillation afforded 2-n-butylamino-1,3,2-dithiaborinan (1.50 g, 65%), b.p. 108—110°C/2.0 mmHg, n_D^{25} 1.5354. (Found: C, 44.18; H, 8.30; N, 6.16; Mol.wt. 189. $C_7H_{16}BNS_2$ calcd.: C, 44.41; H, 8.40; N, 7.40%; Mol.wt. 189.)

Preparation of 2-phenylhydrazino-1,3,2-dithiaborinan. Phenylhydrazine (2.01 g, 0.01 mol) and 2-diethylamino-1,3,2-dithiaborinan (1.14 g, 0.01 mol) were refluxed in benzene (30 ml) for about two days. On cooling the solution the volatiles were removed under reduced pressure and the residue on recrystallising (diethyl ether/petroleum ether mixture) afforded 2-phenylhydrazino-1,3,2-dithiaborinan (0.9 g, 38%), m.p. 151—155°C. (Found: C, 48.41; H, 6.1; N, 12.51. $C_9H_{13}BN_2S_2$ calcd.: C, 48.21; H, 5.8; N, 12.52%.)

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