Organoboron Compounds. Part VII.[1] Boron Derivatives of *o*-Hydroxybenzyl Alcohol

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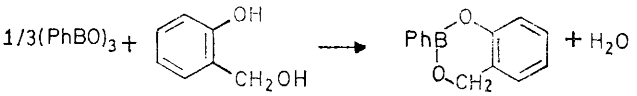
The synthesis and properties of a series of 2-substituted 4*H*-1,3,2-benzodioxaborins (where the substituents are Ph, R_2N, RNH, RO, and RS) are described. The i.r. and mass spectra of some of these compounds are discussed.

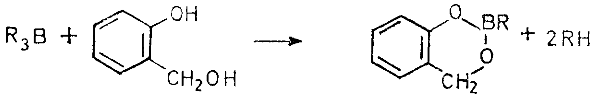
RECENTLY there has been renewed interest in the study of heterocyclic organoboranes. For example the results of a study concerning the synthesis and properties of dioxa- and dithia-borolans have recently been published[2] and we have just completed a study on the heterocyclic borane derivatives of cysteamine.[1] Although the chemistry and properties of dioxaborinans[3] and *o*-phenylene derivatives[4] have been fully investigated we could find no record of studies on a mixed system such as organoboron derivatives of *o*-hydroxybenzyl alcohol. We were interested in organoboron derivatives of this compound for two reasons, first to compare their properties with those of the dioxaborinan and *o*-phenylene systems, and secondly to compare the mass spectra of these compounds with those we have previously obtained for the dioxaborolan and borinan systems.

2-Phenyl-4*H*-1,3,2-benzodioxaborin was readily obtained by refluxing a mixture of phenylboroxine and *o*-hydroxybenzyl alcohol in benzene until the stoicheiometric amount of water had been eliminated. Using an alcohol (ethanol, n-propanol, or isopropyl alcohol)



and boric oxide, in place of phenylboroxine, resulted in the formation of 2-alkoxy-4*H*-1,3,2-benzodioxaborin.

Trisdialkylamino- and trisalkylthio-boranes readily reacted with *o*-hydroxybenzyl alcohol, in refluxing benzene, to give the analogous 2-dialkylamino- and 2-alkylthio-derivatives.



R = Me_2N, EtN, EtS

2-Alkylamino-4*H*-1,3,2-benzodioxaborins were obtained from the interaction of a primary amine with a

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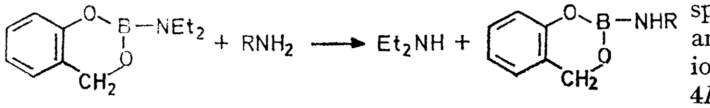
[1] Part VI, R. H. Cragg and A. F. Weston, *J.C.S. Dalton*, 1973, 1054.

[2] S. G. Shore, J. L. Crist, B. Lockman, J. R. Long, and A. D. Coon, *J.C.S. Dalton*, 1972, 1123.

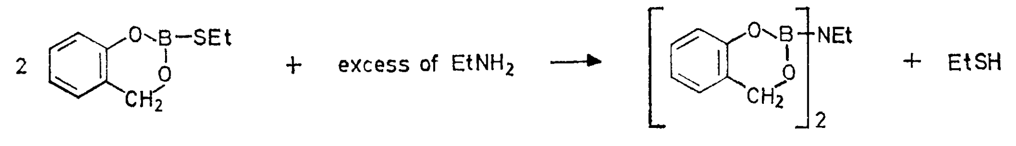
[3] A. Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn, *J. Chem. Soc.*, 1962, 1428.

[4] W. Gerrard, M. F. Lappert, and B. Mountfield, *J. Chem. Soc.*, 1959, 1529.

2-dialkylamino-derivative. The four 2-alkylamino-derivatives appear to be monomeric in the liquid state, the i.r. spectra containing a characteristic NH stretching frequency band in the region of 3428—3408 cm^{-1}. In contrast, the reaction of ethylamine and 2-ethylthio-4*H*-1,3,2-benzodioxaborin resulted in the formation of ethylbis(4*H*-1,3,2-benzodioxaborin-2-yl)amine.



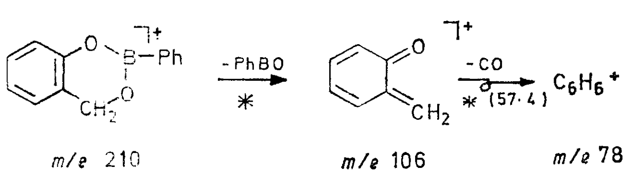
R = Me$_2$N, EtN, EtS

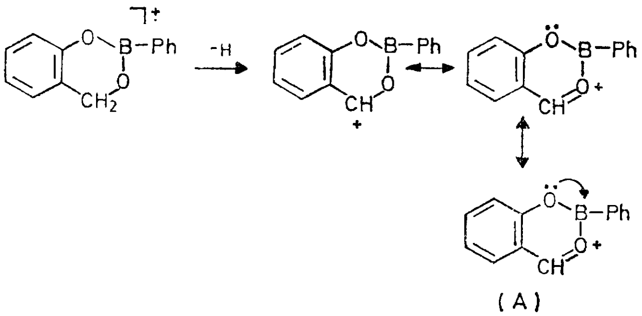


This compound was characterised by analysis and also by the absence of a band, in the NH region, in the i.r. spectrum. Molecular weights, determined by mass spectrometry show the compounds to be monomeric in the gas phase. All but the phenyl- and ethylamino-compounds were mobile liquids. By comparison with the *o*-phenylene and dioxaborin compounds the benzodioxaborins were more hydrolytically unstable, so much so that in some cases it was impossible to obtain accurate analytical figures, where characterisation, in the case of the ethoxy- and dimethylamino-compounds, was by precise mass determination of the molecular ion.

Mass Spectra.—All the compounds were introduced into the mass spectrometer using an unheated direct-insertion probe, and their contact with air was kept to a minimum. The purity of the compounds was checked by a detailed analysis of the spectra in which peaks, assignable to hydrolysis products, were absent.

We have recently been especially interested in the electron impact induced rearrangement processes of phenylorganoboranes which yield hydrocarbon (mainly tropylium) ions.[5-7] We therefore expected that this type of process would also be significant in the case of 2-phenyl-4*H*-1,3,2-benzodioxaborin. However this compound, which gave the tropylium ion in only 1% intensity (compared to the base peak), appears to be the first example of a compound which contains a $-CH_2O-$ group attached to boron, in a phenylorganoborane, where this process is not significant. Instead the two processes which are significant are as follows. First, the loss of PhBO to give an ion *m/e* 106, which then fragments in an analogous way to that for the corresponding ion in *o*-hydroxybenzyl alcohol.[8] Secondly, and more important, is the fragmentation of the $P-1$ ion. The base peak in the mass spectrum of 2-phenyl-4*H*-1,3,2-benzodioxaborin was at *m/e* 209 (*i.e.* $P-H$). The spectrum also contained a doubly charged ion at *m/e* 104·5, which had an intensity of 14% that of the base peak. This indicates that the ion *m/e* 209 has considerable stability and could possibly have pseudo-aromatic character. If one assumes that the positive charge in this ion is located on the oxygen atom and also that *pπ–pπ* bonding is also present between the second oxygen atom and the boron atom, as in (A), then the ion can be said to have pseudo-aromatic character and consequently would have considerable stability. There has recently been considerable interest concerning the structures of ions, in the gas phase, from organoboranes. One paper in particular [9] provided evidence for the non stability of borenium ions in the gas phase in the spectra of five-membered heterocyclic organoboranes. However, there is one reported case for the existence in the fragmentation of six-membered heterocyclic organoboranes.[10]





(A)

Ions of interest in the mass spectra of 2-substituted 4*H*-1,3,2-benzodioxaborins

2-Substituent (R)	Base peak (*m/e*)	Parent (*m/e*)	% Base	$P-R$ (*m/e*)	% Base
Ph	209	210	70·5	133	1·1
Me_2N	176	177	55·8	133	23·5
Et_2N	190	205	17·9	133	15·3
Pr^nHN	162	191	20·5	133	23·5
Pr^iHN	175	191	31·1	133	22·2
Bu^nHN	162	205	24·5	133	13·6
Bu^tHN	190	205	19·9	133	16·7
EtO	78	178	36·8	133	28·9
Pr^nO	191	192	86·3	133	55·2
Pr^iO	45	192	47·9	133	44·1
EtS	194	194	100	133	20·0

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[5] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 336.

[6] R. H. Cragg, D. A. Gallagher, J. P. N. Husband, G. Lawson, and J. F. J. Todd, *Chem. Comm.*, 1970, 1562.

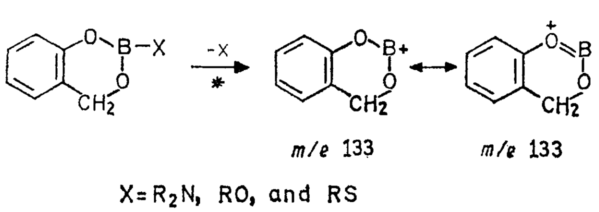
[7] R. H. Cragg, G. Lawson, and J. F. J. Todd, *J.C.S. Dalton*, 1972, 878.

[8] J. S. Shannon, *Austral. J. Chem.*, 1962, **15**, 265.

[9] J. C. Kotz, R. J. V. Zanden, and R. G. Cooks, *Chem. Comm.*, 1970, 923.

[10] R. C. Dougherty, *Tetrahedron*, 1968, **24**, 6755.

With the exception of the phenyl compound all the organoborane derivatives of *o*-hydroxybenzyl alcohol examined by mass spectrometry had a peak at *m/e* 133 which ranged from 8·1 to 28·9% intensity compared to the base peak for the respective compound (see Table). The peak at *m/e* 133 was characterised by precise mass determination of the ion (Found: 133·04557. $C_7H_6BO_2$ requires 133·04608). This strongly suggests that the borenium ions are significant in the mass spectra of organoborane derivatives of *o*-hydroxybenzyl alcohol.



Infrared Spectra.—The i.r. spectra of the 2-substituted 4*H*-1,3,2-benzodioxaborin were found to be rather complex and difficult to assign, with the exception of the NH stretching frequency bands. Tentative assignments for the B–O and B–N stretching modes are 1326—1235 cm^{-1} and 1535—1500 cm^{-1} respectively.

EXPERIMENTAL

All solvents were dried over sodium wire and distilled before use. Mass spectra were recorded, using an A.E.I. MS 902 mass spectrometer at 70 eV. The source was maintained at 170 °C and the compounds were introduced as neat liquids or solids using an unheated direct-insertion probe. The i.r. spectra were recorded on a Perkin-Elmer 457 spectrometer. The usual precautions were taken as is usual for air sensitive starting materials and products. All analyses were determined by Weiler and Strauss of Oxford. Trisdimethylaminoborane,[11] trisdiethylaminoborane,[12] and trisethanethioborane [13] were prepared by established methods.

Preparation of 2-*Phenyl*-4H-1,3,2-*benzodioxaborin*.—Phenylboroxine (1·49 g, 0·01 mol) and *o*-hydroxybenzyl alcohol (1·78 g, 0·01 mol) were refluxed in benzene (100 ml), using a Dean–Stark apparatus, until the stoicheiometric amount of water had been eliminated. The solvent was removed under vacuum and the residue afforded on distillation 2-phenyl-4*H*-1,3,2-benzodioxaborin (2·0 g, 66%), b.p. 120—124 °C, 0·05 mmHg, n_D^{22} 1·5901 (Found: C, 73·8; H, 5·05. $C_{13}H_{12}BO_2$ requires C, 74·2; H, 5·25%).

Preparation of 2-*Ethoxy*-4H-1,3,2-*benzodioxaborin*.—Boric oxide (0·83 g, 0·012 mol), ethanol (1·112 g, 0·024 mol), and *o*-hydroxybenzyl alcohol (3·0 g, 0·024 mol) were refluxed in benzene (120 ml), using a Dean–Stark apparatus, until the stoicheiometric amount of water had been eliminated. The solvent was removed under vacuum and the residue afforded on distillation 2-ethoxy-4*H*-1,3,2-benzodioxaborin (2·363 g, 54·8%), b.p. 69—71 °C, 0·01 mmHg, n_D^{22} 1·5086 (Found: C, 59·0; H, 5·95. $C_9H_{11}BO_3$ requires C, 60·6; H, 6·15%). The compound hydrolysed too rapidly for accurate analytical data to be obtained and was therefore characterised by a precise mass determination of the molecular ion (Found: 178·08011. $C_9H_{11}O_3B$ requires 178·07936). Using the above method 2-n-propoxy-4*H*-1,3,2-benzodioxaborin (43·3%), b.p. 90—91 °C, 0·1 mmHg, n_D^{23} 1·5008 (Found: C, 61·9; H, 6·7. $C_{10}H_{13}O_3B$ requires C, 62·5; H, 6·75%) and 2-isopropoxy-4*H*-1,3,2-benzodioxaborin (53·3%), b.p. 72—74 °C, 0·05 mmHg, n_D^{25} 1·4968 (Found: C, 61·6; H, 6·7. $C_{10}H_{13}O_3B$ requires C, 62·5; H, 6·75%) were obtained. Both compounds were very susceptible to hydrolysis.

Preparation of 2-*Diethylamino*-4H-1,3,2-*benzodioxaborin*.—Trisdiethylaminoborane (12·0 g, 0·05 mol) and *o*-hydroxybenzyl alcohol (6·555 g, 0·05 mol) were refluxed in benzene for four days. The solvent and volatile materials were removed under vacuum and the residue, on distillation, afforded 2-diethylamino-4*H*-1,3,2-benzodioxaborin (7·472 g, 68·9%), b.p. 100—102 °C, 0·8 mmHg, n_D^{24} 1·5119 (Found: C, 63·85; H, 8·1; N, 6·5. $C_{11}H_{16}BNO_2$ requires C, 64·4; H, 7·8; N, 6·8%).

Preparation of 2-*Dimethylamino*-4H-1,3,2-*benzodioxaborin*.—Trisdimethylaminoborane (4·61 g, 0·032 mol) and *o*-hydroxybenzyl alcohol (4·0 g, 0·032 mol) were refluxed in benzene (50 ml) until no more dimethylamine was evolved (*ca*. 6 h). The solvent was removed under vacuum and the residue, on distillation, afforded 2-dimethylamino-4*H*-1,3,2-benzodioxaborin (2·194 g, 38·4%), b.p. 82—83 °C, 0·2 mmHg, n_D^{23} 1·5259. The compound hydrolysed too rapidly for accurate analytical data to be obtained and was therefore characterised by a precise mass determination of the molecular ion (Found: 177·09610. $C_9H_{12}BNO_2$ requires 177·09555).

Preparation of Ethylbis(4H-1,3,2-*benzodioxaborin*-2-*yl*)-*amine*.—2-Ethylthio-4*H*-1,3,2-benzodioxaborin (3·262 g, 0·01 mol) was added slowly to an excess of ethylamine (7·95 g, 0·1 mol) in light petroleum (120 ml) at −78°. The mixture was allowed to attain room temperature and then refluxed for a few hours. A white precipitate, formed during this time, was filtered off, washed a few times with solvent, and was found to be ethylbis(4*H*-1,3,2-benzodioxaborin-2-yl)amine (1·00 g, 34%), m.p. 200—206 °C (Found: C, 62·35; H, 6·55; N, 4·65. $C_{16}H_{17}B_2NO_4$ requires C, 62·15; H, 5·55; N, 4·55%).

Preparation of 2-*Ethylthio*-4H-1,3,2-*benzodioxaborin*.—Trisethylthioborane (10 g, 0·05 mol) was slowly added to *o*-hydroxybenzyl alcohol (6·399 g, 0·05 mol) in benzene (100 ml). The mixture was refluxed for five days, the eliminated ethanethiol being captured by a solution of lead acetate. On removal of the solvent the residue afforded, on distillation 2-ethylthio-4*H*-1,3,2-benzodioxaborin (3·984 g, 39·8%), b.p. 74—75 °C, 0·3 mmHg. The compound was so hydrolytically unstable that satisfactory analytical data could not be obtained. A mass spectrum of the compound showed it to be pure with a molecular ion at *m/e* 194.

Preparation of 2-*Isopropylamino*-4H-1,3,2-*benzodioxaborin*.—An excess of isopropylamine (10 ml, 0·1 mol) and 2-diethylamino-4*H*-1,3,2-benzodioxaborin (3·0 g, 0·01 mol) were mixed in benzene (50 ml) at 5° and the temperature was then allowed to rise slowly to room temperature. The mixture was refluxed for two days after which the solvent and volatile products were removed under vacuum and the residue afforded, on distillation, 2-isopropylamino-4*H*-1,3,2-benzodioxaborin (0·84 g, 30%), b.p. 104 °C,

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[11] K. Niedenzu and J. W. Dawson, *Inorg. Synth.*, 1967, **10**, 135.

[12] W. Gerrard, M. F. Lappert, and C. A. Pearce, *J. Chem. Soc.*, 1957, 381.

[13] B. M. Mikhailov and Yu. N. Bubnov, *Izvest. Akad. Nauk S.S.S.R., Otdel, khim. Nauk*, 1962, 1378.

1·0 mmHg, n_D^{23} 1·5146 (Found: C, 62·45; H, 7·5; N, 7·15. $C_{10}H_{14}BNO_2$ requires C, 62·8; H, 7·3; N, 7·3%).

Using the above method 2-n-propylamino-4*H*-1,3,2-benzodioxaborin (91·1%), b.p. 88—89 °C, 0·01 mmHg, n_D^{24} 1·5181 (Found: C, 61·3; H, 7·35; N, 6·8. $C_{10}H_{14}BNO_2$ requires C, 62·8; H, 7·3; N, 7·3%), 2-n-butylamino-4*H*-1,3,2-benzodioxaborin (47·2%), b.p. 102—104 °C, 0·1 mmHg, n_D^{24} 1·5132 (Found: C, 64·2; H, 8·1; N, 6·75. $C_{11}H_{16}BNO_2$ requires C, 64·4; H, 7·8; N, 6·8%), and 2-t-butylamino-4*H*-1,3,2-benzodioxaborin (54%), b.p. 80—82 °C, 0·1 mmHg, n_D^{23} 1·5099 (Found: C, 63·7; H, 7·85; N, 6·65. $C_{11}H_{16}BNO_2$ requires C, 64·4; H, 7·8; N, 6·8%) have been obtained.

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