Organoboron Compounds. Part IX.[1] Synthesis and Properties of some 2-Phenyl-1,3,2-oxazaborolans

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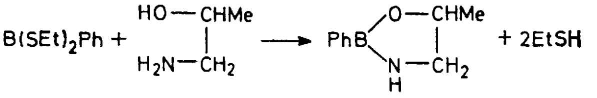
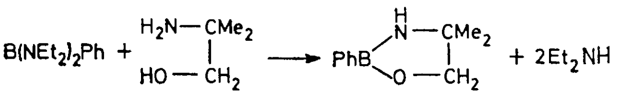
The synthesis and properties of some 2-phenyl-1,3,2-oxazaborolans are described and the i.r. spectra and general mass-spectral features of these compounds are discussed.

RECENTLY there has been renewed interest in the synthesis and properties of heterocyclic organoboranes. For example the 2-substituted 1,3,2-diazaboracycloalkanes have been reviewed [2] and work concerning the dioxa- and dithia-borolans and borinans has been published.[3] We have been interested in heterocyclic organoboranes for some time [4-7] and were surprised to find that with few exceptions [8] the 1,3,2-oxazaborolans appear to have been ignored. We therefore report our results concerning the preparation and properties of these compounds.

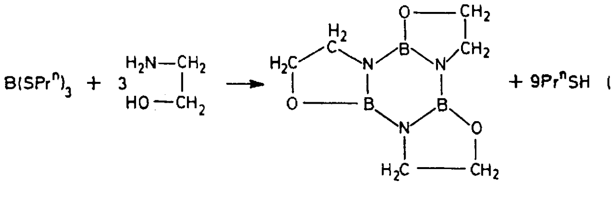
RESULTS AND DISCUSSION

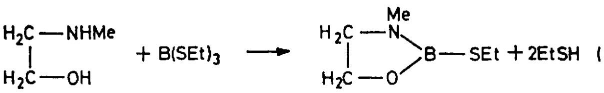
Two general methods were used for the synthesis of the 2-phenyl-1,3,2-oxazaborolans: (*a*) reaction of an aminoalcohol with bis(ethylthio)phenylborane; and (*b*) reaction of an aminoalcohol with bis(diethylamino)-phenylborane. In both cases, one of the products of the reaction is volatile and this leads to a very smooth synthesis of the boron heterocycles. For example 5-methyl-2-phenyl-1,3,2-oxazaborolan was obtained from the interaction of 1-methyl-2-aminoethanol and bis-(ethylthio)phenylborane in benzene solution [equation (1)]. The reaction was stopped when the volatile products passed into an aqueous lead(II) acetate solution failed to give any precipitation of lead(II) hydrogen-sulphide. In a similar way the interaction of bis-(diethylamino)phenylborane and 2-amino-2-methyl-propanol gave 4,4-dimethyl-2-phenyl-1,3,2-oxazaborolan [equation (2)]. Using method (*a*), nine 2-phenyl-1,3,2-oxazaborolans were prepared. Also 2-phenyl-1,3,2-oxazaborinan was prepared to enable us to compare the properties of the five- and six-membered heterocyclic systems. The physical properties and analytical data for these compounds are given in the Table.


(1)


(2)

The 2-phenyl-1,3,2-oxazaborolans were all obtained as distillable liquids; compounds (VI) and (VII) solidified on standing. Attempts to prepare 2-alkylthio-1,3,2-oxazaborolans were unsuccessful. For example the interaction of tris(n-propylthio)borane with 2-amino-ethanol resulted in formation of a polycyclic borazine without the isolation of any intermediate compound [equation (3)]. In contrast the interaction of tris-(ethylthio)borane and 2-methylaminoethanol resulted in formation of the corresponding heterocyclic compound [equation (4)].


(3)


(4)

I.r. Spectra.—The i.r.- and mass-spectral properties of 2-phenyl-1,3,2-diazaborolans and borinans have been discussed by Niedenzu [2] and assignments made were ν(N–H) at 3 465 cm^{-1} and ν(B–N) at 1 500 ± 10 cm^{-1}. The appearance of a shoulder on the ν(N–H) peak was interpreted as being due to some association in these compounds. This effect has also been observed for 2-phenyl-1,3,2-azathiaborolidine which we discussed in an earlier paper.[7] In the present compounds the effect is not so pronounced. The unsubstituted borolan and borinan showed only a slight shoulder. Those with substituents at the C(5) position, *i.e.* the carbon next to the oxygen atom, showed a slightly greater effect. The ν(N–H) band in compound (IV) was intermediate between those of (III) and (V). In contrast compounds with substituents at the C(4) position, *i.e.* the carbon adjacent to the nitrogen atom, showed a more pronounced effect, for example (V). In this case the two peaks were separated.

The effect of C(5) substitution was to lower ν(B–O) and the effect of C(4) substitution was to lower ν(B–N). Substitution of $PhCH_2$ for H on the nitrogen atom caused a significant increase in ν(C–N) in the borolan system. The ν(B–O) and ν(B–N) ring vibrations were consistent throughout, demonstrating that substitution had little effect on the stereochemistry of the ring.

The following tentative assignments are made for the

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[1] R. H. Cragg and M. Nazery, *J.C.S. Dalton*, 1974, 1438.

[2] K. Niedenzu and C. D. Miller, *Fortschr. Chem. Forsch.*, 1970, 191.

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

[4] R. H. Cragg, *J. Inorg. Nuclear Chem.*, 1968, **30**, 395.

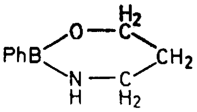
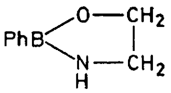
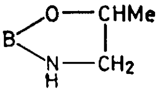
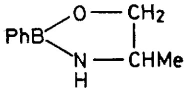
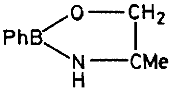
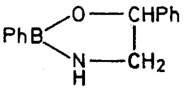
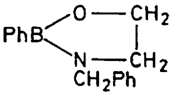
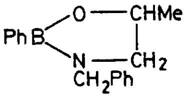
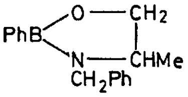
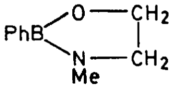
[5] R. H. Cragg, *Chem. Comm.*, 1969, 832.

[6] R. H. Cragg, J. P. N. Husband, and A. F. Weston, *J.C.S. Dalton*, 1973, 568.

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

[8] G. M. Anthony, G. J. W. Brooks, I. Maclean, and I. Sangster, *J. Chromatog.*, 1969, **7**, 623.

Analyses, yields, and b.p.s for 2-phenyl-1,3,2-oxazaborolans

			Analyses/%					
Compound	B.p. (θ_c/°C), P/mmHg	Yield/ %	Found			Calc.		
			C	H	N	C	H	N
(I) 	85, 0·1	87	67·15	7·5	8·55	67·1	7·5	8·70
(II) 	64, 0·15	56	65·25	6·7	9·35	65·3	6·8	9·50
(III) 	82, 0·4	86	65·95	7·7	8·35	67·1	7·5	8·70
(IV) 	70, 0·15	45	67·15	7·7	8·65	67·1	7·5	8·70
(V) 	84, 0·9	50	68·6	8·0	8·00	68·4	8·0	7·80
(VI) 	130, 0·1	70	74·75	6·6	6·15	75·3	6·3	6·30
(VII) 	128, 0·2	71	75·65	6·9	5·95	75·95	6·8	5·90
(VIII) 	122, 0·1	71	76·3	7·3	5·65	76·5	7·2	5·60
(XI) 	130, 0·1	69	75·0	7·5	5·70	76·5	7·2	5·60
(X) 	103, 5	86	67·0	7·7	8·85	67·15	7·5	8·70

borolan and borinan ring systems; the various wavenumbers (cm^{-1}) can be found within the quoted limits.

	Borolan	Borolan + borinan
ν(N–H)	3 450 ± 30	3 450 ± 30
ν(B–N)	1 503 ± 7	1 503 ± 8
ν(B–Ph)	1 453 ± 7	1 457 ± 11
ν(B–O)	1 321 ± 9	1 334 ± 22
ν(C–N)	1 223 ± 37	1 227 ± 42
ν(C–O)	1 099 ± 22	1 105 ± 28
ν(B–O) (ring)	698 ± 2	698 ± 2
ν(B–N) (ring)	650 ± 5	650 ± 5
	636 ± 3	636 ± 3

Mass Spectra.—*m*/*e* Values and relative intensities, in multi-isotopic form, of the ions of most interest in the fragmentation of a series of 2-phenyl-1,3,2-oxazaborolans and 2-phenyl-1,3,2-oxazaborinan are to be found in Supplementary Publication No. SUP 21188 (2 pp.).* With the exception of (V), all the compounds showed an intense P — 1 peak formed *via* loss of a proton from C(4). In some cases this was the base peak. Compound (V) has both C(4) positions methylated and hence no proton loss can take place by C–H bond β cleavage with respect to the annular nitrogen atom and in this compound the base peak was at *m*/*e* 160, *i.e.* P — CH_3: a C–C bond β cleavage with respect to the N atom. Doubly charged ions formed from the parent were in the majority of cases less than 1% of the total ion abundance.

In our mass-spectral studies on phenylorganoboranes we have observed electron-impact-induced rearrangements to give hydrocarbon fragments for example the tropylium ion.[9-11] The 2-phenyl-1,3,2-oxazaborolans

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

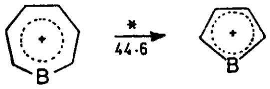
[9] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.

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

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

and borinan follow the general pattern. In the three compounds with a benzyl group attached to nitrogen, intense peaks at *m/e* 91, *i.e.* the tropylium ion, were observed. Methylation of the carbon atom adjacent to the nitrogen atom, in these borolans, enhanced tropylium-ion formation. The C(5) phenyl-substituted compound also showed a peak 33% of the base, assignable to the tropylium ion, and 2-phenyl-1,3,2-oxazaborolan showed an intense peak due to the tropylium ion which was 43% of the base peak. The monomethyl-substituted borolans and the borinan all showed peaks, assignable to the tropylium ion, of *ca.* 10% intensity compared to the base peak, whilst dimethyl substitution reduced the intensity of the peak to *ca.* 4%. Hence methylation reduced tropylium-ion formation, irrespective of the position of substitution, by approximately the same amount and dimethylation reduced it even further. The borinan also formed much less tropylium ion than the borolan.

The mass spectra of compounds (I), (III), and (IV) all showed peaks at *m/e* 105, which was shown by precise mass measurements to be due to $C_8H_9^+$ ion, in 24·3, 13·57, and 1·71% abundance compared to the base peak. There were $C_5H_5^+$ ions present in all spectra in such ratios to the $C_7H_7^+$ ions that all *m/e* peaks can be taken as completely $C_7H_7^+$ in tropylium-ion form, and the metastable ions at 46·4 associated with fragmentation of tropylium ion to cyclopentadienylium were observed in each case. All the compounds had peaks in their mass spectra at *m/e* 89 and 63. We find that these peaks, by precise mass measurements and metastable scanning, are due to the boratropylium and boracyclopentadienylium ions.[12] Although the boratropylium ion has previously been reported for three compounds,[13,14] its fragmentation to the corresponding boracyclopentadienylium ion appears to be a general process in the mass spectra of 2-phenyl-1,3,2-oxazaborolans.



m/e 89 *m/e* 63

EXPERIMENTAL

Solvents were dried over sodium wire and distilled before use. The mass spectra were recorded using an A.E.I. MS902 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. I.r. spectra were recorded using a Perkin-Elmer 457 spectrometer. Bis(diethylamino)phenylborane,[15] bis(ethylthio)phenylborane,[16] and tris(ethylthio)borane [17] were prepared by established methods.

2-Phenyl-1,3,2-*oxazaborolan*.—2-Aminoethanol (1·30 g, 0·02M) was added slowly to bis(diethylamino)phenylborane (4·27 g, 0·018M) in benzene (10 cm^3). The mixture was heated under reflux for 2 h. After removal of the solvent and volatile materials the residue, on distillation, afforded 2-*phenyl*-1,3,2-*oxazaborolan* (1·39 g, 56%), b.p. 64 °C (0·15 mmHg) (Found: C, 65·15; H, 6·6; N, 9·3. Calc. for $C_8H_{10}BNO$: C, 65·3; H, 6·8; N, 9·5%).

3-*Benzyl*-2-*phenyl*-1,3,2-*oxazaborolan*.— 2-Benzylaminoethanol (1·06 g, 0·007M) was added slowly to bis(ethylthio)phenylborane (1·5 g, 0·007M) in benzene (10 cm^3). The mixture was heated under reflux for 3 h after which the solvent and any remaining ethane thiol were removed *in vacuo*. The ethane thiol was passed into an aqueous lead(II) acetate solution where it was precipitated as the lead(II) hydrogensulphide. The residue on distillation afforded 3-*benzyl*-2-*phenyl*-1,3,2-*oxazaborolan* (1·22 g, 71%), b.p. 128 °C (0·2 mmHg), m.p. 40 °C (Found: C, 75·65; H, 6·90; N, 5·95. Calc. for $C_{15}H_{16}BNO$: C, 75·95; H, 6·75; N, 5·9%).

Reaction between Bis(*ethylthio*)*phenylborane and* DL-2-*aminopropan*-1-*ol*.—DL-2-Aminopropan-1-ol (1·02 g, 0·014M) was added to a solution of bis(ethylthio)phenylborane (2·85 g, 0·014M) in benzene. The mixture was heated under reflux for 3 h. The volatiles were removed *in vacuo* and the residue was washed with light petroleum and on filtration yielded an unidentified white solid, m.p. 124 °C. On removal of the solvent from the washings the residue afforded, on distillation, 4-*methyl*-2-*phenyl*-1,3,2-*oxazaborolan* (0·98 g, 45%), b.p. 70 °C (0·15 mmHg) (Found: C, 67·15; H, 7·70; N, 8·65. Calc. for $C_9H_{12}BNO$: C, 67·1; H, 7·45; N, 8·7%).

The reaction of L-2-aminopropan-1-ol with bis(ethylthio)phenylborane was carried out in the above manner. As all the other 2-phenyl-1,3,2-oxazaborolans and 2-phenyl-1,3,2-oxazaborinan were obtained by the above methods, their physical properties and analyses are given in the Table.

1,2;3,4;5,6-*Tris*(*ethyleneoxy*)*borazine*.— Tris(n-propylthio)borane (1·73 g, 0·028M) and 2-aminoethanol (6·85 g, 0·029M) were heated under reflux in benzene for 3 h. On removal of the solvent a residue was obtained which on sublimation [100 °C (0·5 mmHg)] afforded 1,2;3,4;5,6-*tris*-(*ethyleneoxy*)*borazine* (1·84 g, 92%), m.p. 150 °C (Found: C, 33·8; H, 8·95; N, 19·45; *M*, 207. Calc. for $C_6H_{12}B_3N_3O_3$: C, 34·8; H, 8·80; N, 20·3%; *M*, 207).

2-*Ethylthio*-3-*methyl*-1,3,2-*oxazaborolan*.— Tris(ethylthio)borane (2·23 g, 0·012M) and 2-methylaminoethanol (0·86 g, 0·012M) were heated under reflux in benzene for 3 h. On removal of the volatiles under reduced pressure the residue afforded on distillation 2-*ethylthio*-3-*methyl*-1,3,2-*oxazaborolan* (1·39 g, 3%), b.p. 60—63 °C (6 mmHg), n_D^{25} 1·4817 (Found: C, 41·4; H, 8·35; N, 9·75. Calc. for $C_5H_{12}BNOS$: C, 41·4; H, 8·30; N, 9·65%).

[3/2330 *Received*, 13*th November*, 1973]

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* 1 eV ≈ 1·60 × 10^{-19} J, 1M = 1 mol dm^{-3}.

[12] R. H. Cragg, J. F. J. Todd, R. B. Turner, and A. F. Weston, *J.C.S. Chem. Comm.*, 1972, 206.

[13] C. Cone, M. J. S. Dewar, R. Golden, F. Maseles, and P. Rona, *Chem. Comm.*, 1971, 1522.

[14] C. J. W. Brooks, B. S. Middleditch, and G. M. Anthony, *Org. Mass Spectrometry*, 1969, **2**, 1023.

[15] K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, 1962, **1**, 738.

[16] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.* (*A*), 1967, 947.

[17] J. Brault and J. M. Lalancette, *Canad. J. Chem.*, 1964, **42**, 2093.