Organoboron Compounds. Part 17.[1] Preparation and Properties of some 2,4-Diphenyl- and 2-Diethylamino-4-phenyl-1,3,5,2-oxadiazaboroles

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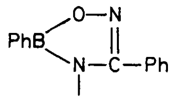
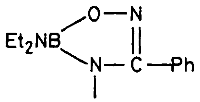
The preparation and properties of some 2,4-diphenyl- and 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaboroles are reported and some features of their ^{1}H n.m.r. and mass spectra are discussed. Their reactions with organic isocyanates are described briefly.

THE interaction between an organic isocyanate and an aminoborane, in which the $>B-N<$ group is incorporated in a heterocyclic ring, has resulted in the synthesis of novel large ring heterocyclic organoboranes.[2-6] Examples of this type of ring expansion are rather limited and we have therefore been extending our work to new systems. A review of the literature indicated only a few examples of heterocyclic organoboron derivatives of amidoximes[7,8] and we now report our results on the preparation and properties of some 2,4-diphenyl- and 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaboroles and their reaction with organic isocyanates. Two series of heterocycles were prepared. Type (1) was obtained from the interaction, in refluxing benzene, of bis(dimethylamino)phenylborane or bis(diethylamino)phenylborane and the corresponding amidoxime and type (2) from the interaction, in refluxing benzene, of tris(diethylamino)borane and the corresponding amidoxime.



(1) R = H, Me, Et, Pr^n, or Bu^n



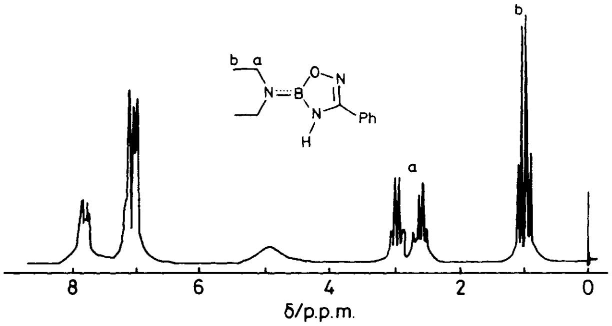
(2) R = H or Pr^n

RESULTS AND DISCUSSION

The heterocycles were all obtained in high yields and purified by distillation or recrystallisation from a benzene–petroleum mixture. Brief details of the preparation of (1; R = Me) and (2; R = H) are given in the Experimental section whilst Table 1 records the properties and analytical details of the compounds prepared.

Of special interest are the properties of 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaborole. The compound was remarkably stable and no elimination of diethylamine was observed even on vacuum sublimation (180 °C at 0.1 mmHg).† The ^{1}H n.m.r. spectrum recorded in C_6D_6 (see Figure) showed interesting features in that the methylene resonance is split into two quartets, separated by *ca.* 50 Hz, with a smaller splitting of the methyl resonance. This strongly suggests restricted rotation about the Et_2N-B bond which is surprising in that it would have been expected that the other two boron substituents would have satisfied the electron deficiency of the boron atom.

Mass Spectra of 3-Alkyl-2,4-diphenyl-1,3,5,2-oxadiazaboroles.—The major ions of importance in the mass spectra of this class of compound are given in Table 2.



^{1}H N.m.r. spectrum of 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaborole

In all cases (except where R = H) the parent ion and ion *m*/*e* 235 are very intense. Both peaks are assigned to ions containing an intact ring, demonstrating its considerable stability. A fragmentation scheme, which is applicable to all compounds in this series, is proposed for the 3-n-butyl compound. Precise mass determination of *m*/*e* 180 was carried out in order to determine its identity (Found: 180.081 389 9. $C_{13}H_{10}N$ requires 180.081 319 8; error 0.3 p.p.m.).

Interaction of Aryl Isocyanates with 2,4-Diphenyl-1,3,5,2-oxadiazaboroles.—The interaction of 2,4-diphenyl-1,3,5,2-oxadiazaborole with phenyl isocyanate or toluene-*p*-sulphonyl isocyanate resulted in the formation of 1 : 1 complexes for which the carbonyl-stretching frequencies were observed at 1 700 and 1 775 cm^{-1} respectively. In contrast, when a series of 3-alkyl-2,4-diphenyl-1,3,5,2-oxadiazaboroles were refluxed in toluene for several weeks with phenyl isocyanate or toluene-*p*-sulphonyl isocyanate the starting materials were obtained unchanged.

The lack of reaction between the alkyl boroles and isocyanates may be due to their pseudoaromatic character resulting from extensive delocalisation of π-electron density from the two phenyl groups into the boron heterocycle leading to a very stable ring.

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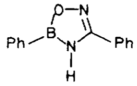
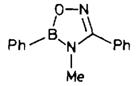
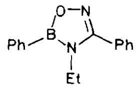
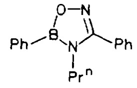
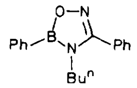
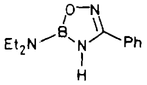
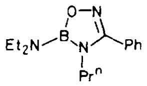
† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

TABLE 1

Analytical data for 2,4-diphenyl- and 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaboroles

Compound	Yield/%	M.p./°C	Analysis/% Found C	Found H	Found N	Required C	Required H	Required N
	90	164 *	70.2	5.0	12.6	70.3	5.0	12.6
	90	151—152	71.3	5.3	11.6	71.2	5.5	11.9
	85	102	72.3	6.0	11.2	72.0	6.0	11.2
	80	87—88	71.9	6.3	10.4	72.7	6.4	10.6
	80	76—77	73.2	6.7	9.8	73.4	6.8	10.1
	70	110	59.9	8.3	18.6	60.8	7.4	19.4
	40	165—165.5	63.8	8.5	15.6	64.9	8.5	16.2

* From ref. 8, m.p. 164 °C.

TABLE 2

Mass spectral data (percentage abundances) for 3-alkyl-2,4-diphenyl-1,3,5,2-oxadiazaboroles

R	*m/e* Parent ion	235	180	131	105 $PhBOH^+$	104 $PhBO^+$	77 Ph^+	51 $C_4H_5^+$
H *	45				100		90	
Me	71	42	6	20	27	100	55	29
Et	89	37	29	51	71	57	100	37
Pr^n	100	90	42	61	31	42	67	23
Bu^n		90	40	65	24	20	72	18

* Other ion at *m/e* 121, 75%.

Mass spectral evidence of the ring stability of these compounds has been discussed earlier.

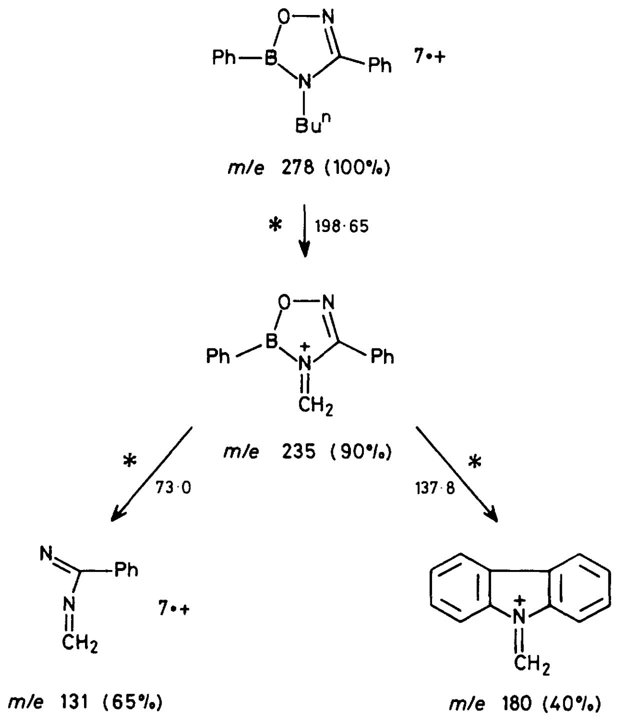
It is unlikely that the B–N bond in these systems is inert on steric grounds as insertion products have been isolated for 1,3-dialkyl-2-phenyl-1,3,2-diazaboroles [9] and we suggest that the inability to undergo insertion reactions under the reaction conditions described can be attributed mainly to electronic factors.

EXPERIMENTAL

The *N*-alkylbenzamidoximes were prepared by established methods *via* the interaction of chlorobenzaldoxime and a primary amine.[10] 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 solids using an unheated direct-insertion probe. The ^1H n.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer.

Bis(dimethylamino)phenylborane,[11] bis(diethylamino)-phenylborane,[11] and tris(diethylamino)borane [12] were prepared by established methods.

Preparation of 3-Methyl-2,4-diphenyl-1,3,5,2-oxadiazaborole.—*N*-Methylbenzamidoxime (3.0 g, 0.02 mol) was dissolved in benzene and bis(dimethylamino)phenylborane (3.52 g, 0.02 mol) added. The mixture was refluxed for 5 h and, after removal of the volatiles under reduced pressure, the residue, on recrystallisation from benzene–light petroleum (b.p. 60—80 °C), gave 3-methyl-2,4-diphenyl-1,3,5,2-oxadiazaborole (4.25 g, 90%).



Proposed fragmentation scheme for 3-n-butyl-2,4-diphenyl-1,3,5,2-oxadiazaborole (* metastable observed)

Preparation of 2-*Diethylamino*-4-*phenyl*-1,3,5,2-*oxadiazaborole*.—Benzamidoxime (2.7 g, 0.02 mol) was dissolved in benzene and tris(diethylamino)borane (4.5 g, 0.02 mol) was added. The mixture was refluxed for 5 h and, after removal of the volatiles under reduced pressure, the residue, on recrystallisation from benzene–light petroleum (b.p. 60—80 °C), gave 2-diethylamino-4-phenyl-1,3,5,2-oxadiazaborole (3.0 g, 70%), m.p. 110 °C.

Reactions of 2,4-*Diphenyl*-1,3,5,2-*oxadiazaboroles with Aryl Isocyanates*.—2,4-Diphenyl-1,3,5,2-oxadiazaborole (2.22 g, 0.01 mol) and phenyl isocyanate (1.19 g, 0.01 mol) were dissolved in toluene and the mixture refluxed for 1 d. On removal of the solvent the residue, after purification, yielded a 1 : 1 adduct (2.89 g, 85%), m.p. 142—144 °C (Found: C, 70.0; H, 5.0; N, 12.4. $C_{19}H_{16}BN_3O_2$ requires C, 70.4; H, 4.7; N, 12.3%).

2,4-Diphenyl-1,3,5,2-oxadiazaborole and toluene-*p*-sulphonyl isocyanate interacted to give a 1 : 1 adduct (88%), m.p. 122—126 °C (Found: C, 60.1; H, 4.9; N, 9.9. $C_{21}H_{19}BN_3O_4S$ requires C, 60.1; H, 4.3; N, 10.0%).

3-Methyl-2,4-diphenyl-1,3,5,2-oxadiazaborole and phenyl isocyanate were refluxed in benzene for 4 d. On removal of the benzene the residue, on distillation, afforded the starting materials. Similar observations were made for the 3-ethyl, 3-n-propyl, and 3-n-butyl compounds after refluxing with an aryl isocyanate in toluene for several weeks.

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