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ORGANOBORON COMPOUNDS

XIX *. ALKOXYDIALKYLAMINOPHENYLBORANES

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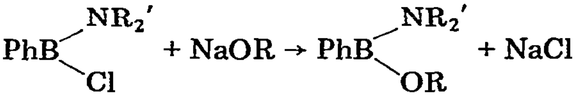
Summary

The preparation and properties of a series of alkoxydialkylaminophenylboranes are reported and their ^1H and ^{13}C NMR spectra discussed. The spectra indicate that there is restricted rotation about the boron—nitrogen bond in each compound studied.

Over the last few years we have been investigating the factors influencing p_π—p_π bonding in aminoboranes especially the application of ^{13}C to this problem. We have reported our results on fluorodialkylaminophenylboranes [2], alkylamino- and dialkylamino-diphenylboranes [3] and alkylaminodialkylaminophenylboranes [4]. In this present paper we report the results of our studies on alkoxydialkylaminophenylboranes. With the exception of the ^1H NMR spectrum of dimethylaminomethoxyphenylborane [5,6] there have been no NMR data published on this class of compound. Four methods of synthesis have been investigated for the preparation of alkoxydialkylaminophenylboranes.

High yields of the required product were obtained from the reaction between a chlorodialkylaminophenylborane and a sodium alkoxide



$$\mathrm{PhB}\begin{matrix}\nearrow \mathrm{NR_2'} \\ \searrow \mathrm{Cl}\end{matrix} + \mathrm{NaOR} \rightarrow \mathrm{PhB}\begin{matrix}\nearrow \mathrm{NR_2'} \\ \searrow \mathrm{OR}\end{matrix} + \mathrm{NaCl}$$

Alcoholysis of a bis(dialkylamino)phenylborane was successfully utilised to

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* For part XVIII see Ref. 1.

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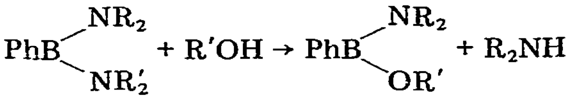
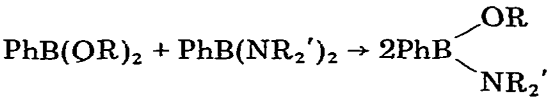
give alkoxydialkylaminophenylboranes in yields of 65—75%.



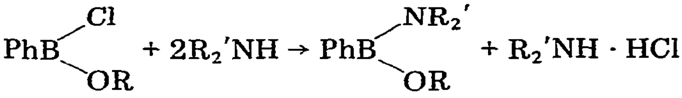
$$\mathrm{PhB}\begin{matrix}\diagup \mathrm{NR_2}\\ \diagdown \mathrm{NR_2'}\end{matrix} + \mathrm{R'OH} \rightarrow \mathrm{PhB}\begin{matrix}\diagup \mathrm{NR_2}\\ \diagdown \mathrm{OR'}\end{matrix} + \mathrm{R_2NH}$$

A further method utilises the well established redistribution reaction and involves the interaction of equimolar quantities of a bis(alkoxy)phenylborane and a bis(dialkylamino)phenylborane.



$$\mathrm{PhB(OR)_2} + \mathrm{PhB(NR_2')_2} \rightarrow 2\mathrm{PhB}\begin{matrix}\diagup \mathrm{OR}\\ \diagdown \mathrm{NR_2'}\end{matrix}$$

Finally alkoxydialkylaminophenylboranes were obtained in yields of 70—80% from the interaction of an alkoxychlorophenylborane and a secondary amine.



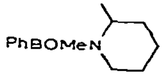
$$\mathrm{PhB}\begin{matrix}\diagup \mathrm{Cl}\\ \diagdown \mathrm{OR}\end{matrix} + 2\mathrm{R_2'NH} \rightarrow \mathrm{PhB}\begin{matrix}\diagup \mathrm{NR_2'}\\ \diagdown \mathrm{OR}\end{matrix} + \mathrm{R_2'NH \cdot HCl}$$

In all reactions dry conditions were utilised due to the ease of hydrolysis of the alkoxydialkylaminophenylboranes. All four methods gave good yields of the required compound. An example of each method is given in the experimental section and all yields, analysis data and boiling points for each compound are given in Table 1.

Alkoxydialkylaminophenylboranes were observed to undergo an insertion

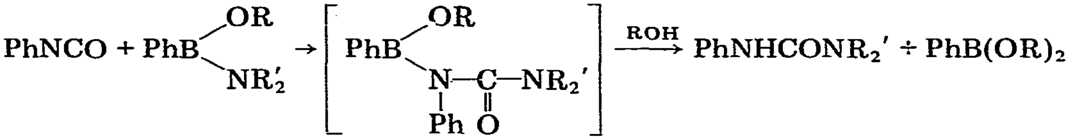
TABLE 1

ALKOXYDIALKYLAMINOPHENYLBORANES

Compound	Yield (%)	B.P. (°C/mmHg)	Analysis (Found (calcd.) (%))			Ref.	Ref.
			C	H	N		
$\mathrm{PhBOMeNMe_2}$	85	40/1	66.4 (66.3)	8.8 (8.6)	8.1 (8.6)	5	70/4.5
$\mathrm{PhBOMeN(i\text{-}Pr)_2}$	75	60/0.3	70.6 (71.2)	9.0 (10.1)	6.1 (6.4)	—	—
$\mathrm{PhBOMeN(n\text{-}Bu)_2}$	65	90/0.1	72.5 (72.9)	10.4 (10.5)	5.3 (5.7)	—	—
$\mathrm{PhBOMeN(s\text{-}Bu)_2}$	70	80/0.1	73.3 (72.9)	9.8 (10.5)	5.8 (5.7)	—	—
	60	90/0.01	70.7 (71.9)	8.7 (9.2)	5.4 (6.5)	—	—
	60	90/0.01	71.2 (71.9)	9.3 (9.2)	5.6 (6.5)	—	—
$\mathrm{PhBOEtNEt_2}$	70	60/0.1	69.7 (70.2)	10.1 (9.8)	6.8 (6.8)	8	104/10
$\mathrm{PhBO\text{-}i\text{-}PrNEt_2}$ [a]	65	62/0.1	—	—	—	—	—

[a] Characterised by precise mass (see text).

reaction with phenylisocyanate. The product of the reaction on alcoholysis gave the corresponding urea demonstrating that the relative migratory optitude is $R_2'N > RO$ or Ph.



^{1}H NMR

At ambient temperature the ^{1}H NMR spectra of the alkoxydialkylaminophenylboranes exhibit isomer shifts. However p_π—p_π bonding between oxygen and boron was significant enough as to reduce the degree of p_π—p_π bonding between nitrogen and boron to such an extent that in some instances the peaks in the NMR spectra were either broad or about to coalesce. Figure 1 contrasts the ^{1}H NMR spectra of chlorodimethylaminophenylborane with that of dimethylaminomethoxyphenylborane. The methyl resonances corresponding to a methyl group *cis* and *trans* to a phenyl group, are very sharp and well resolved in the spectrum of chlorodimethylaminophenylborane but show considerable broadening in dimethylaminomethoxyphenylborane. Also in the case of diisopropylaminomethoxyphenylborane the methyl resonances are quite close to coalescence. The ^{1}H NMR spectra demonstrate how p_π—p_π bonding from oxygen to boron and branching of the amino group result in a decrease of p_π—p_π bonding in the boron—nitrogen bond. The ^{1}H NMR isomer shifts for the alkoxydialkylaminophenylboranes are given in Table 2.

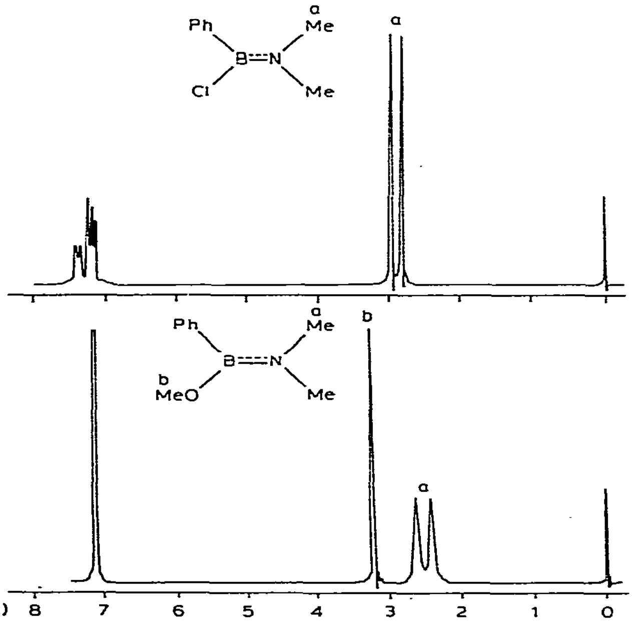
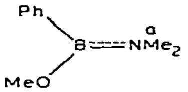
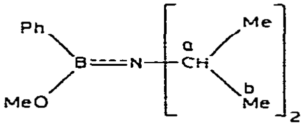
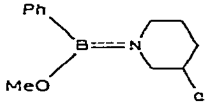
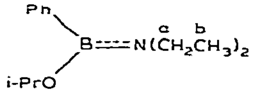
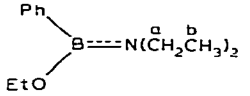


Fig. 1. Comparison of the ^{1}H NMR of $PhBNMe_2Cl$ and $PhBNMe_2OMe$.

TABLE 2

^{1}H NMR ISOMER SHIFTS FOR ALKOXY(DIALKYLAMINO)PHENYLBORANES

Compound	Isomer shifts (Hz)	
	a	b
	24	
	Broad	Broad ~90
	20	
	~80	
	~80	~40

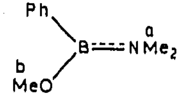
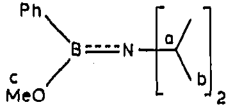
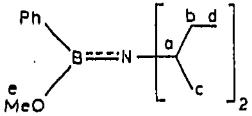
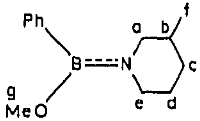
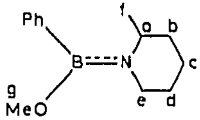
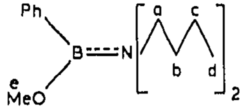
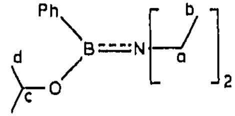
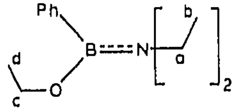
^{13}C NMR

The ^{13}C assignments for the alkoxyldialkylaminophenylboranes are given in Table 3. The assignment of resonances in the proton noise fully decoupled spectra was achieved without difficulty. The resonances assigned to the carbon atom directly bonded to boron were observed on recording the spectrum of the compound in the absence of a solvent [7]. In all cases evidence was observed in support of p_π—p_π bonding about the boron—nitrogen bond. However where the doublets were broad or had coalesced it was necessary to record the spectrum at a low temperature in order to resolve all non-equivalence. The spectrum of diisopropylaminomethoxyphenylborane (Fig. 2), fully illustrates the effect of temperature.

Experimental

NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer. The ^{1}H NMR spectra were recorded in the continuous wave mode while ^{13}C NMR spectra were recorded using the F.T. mode. Tetramethylsilane was used as an internal standard and the compounds were studied as solutions in CCl_4, $CDCl_3$ or as neat samples. Chemical shifts quoted are correct to ±0.05 ppm. An internal DMSO capillary lock was used when measuring the ^{13}C NMR spectra of neat

TABLE 3. ^{13}C NMR DATA OF ALKOXY(DIALKYLAMINO)PHENYLBORANES

Compound	T (°C)	C(1)	*o*	*m*	*p*	a	b	c	d	e	f	g
	−15	136.7	132.0	127.8	127.8	37.9	54					
						34.6						
		0	0	0	0	83	0					
	−49	138.8	130.3	127.1	126.8	47.9	23.1	52.8				
						42.9	21.2					
		0	0	0	0	125	40	0				
	−60	138.7	130.7	127.2	126.8	54.2	30.0	20.5	12.0	52.8		
						49.2	27.3	19.9	11.5			
		0	0	0	0	126.0	68.0	14.0	24.0	0		
	−47	136.6	132.0	127.9	127.9	54.7	33.1	34.2	27.9	47.3	19.9	54.2
						51.3	32.6		27.2	43.8	19.5	
		0	0	0	0	86.0	12.0	0	18.0	89.0	9.0	0
	−47	137.1	132.0	127.9	127.9	47.7	31.9	19.8	28.4	41.0	17.8	54.2
			131.5			44.1	31.4		27.8	37.1	17.6	
		0	12.2	0	0	92.0	12.0	0	15.0	97.0	6.0	0
	23	137.6	131.8	127.7	127.7	47.0	32.0	20.1	14.1	53.9		
						43.8						
		0	0	0	0	80.0	0	0	0	0		
	−5	137.8	130.7	127.2	127.2	41.0	15.4	65.9	24.4			
						38.2	15.0					
		0	0	0	0	70.0	10.0	0	0			
	−15	137.9	130.7	127.2	127.2	40.7	15.3	60.4	17.4			
						37.9	14.4					
		0	0	0	0	70.0	23.0	0	0			

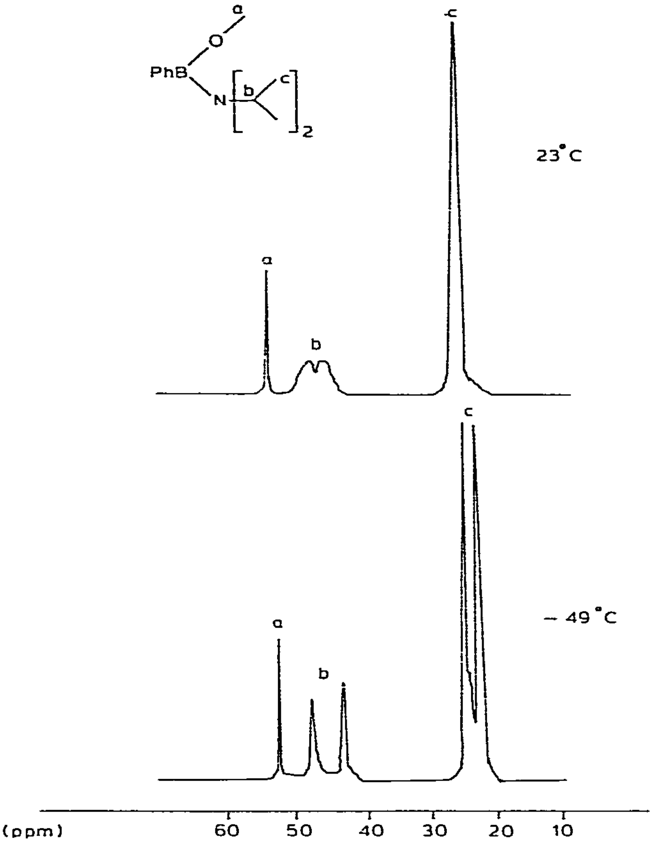


Fig. 2. The ^{13}C NMR spectra of $PhB(OMe)N(i\text{-}Pr)_2$.

samples and the temperature of the sample was varied by passing a stream of heated air or cold nitrogen over the probe.

Preparation of dimethylamino(methoxy)phenylborane

Bis(dimethylamino)phenylborane (3.52 g, 0.02 mol) and bis(methoxy)-phenylborane (3.00 g, 0.02 mol) were mixed together and set aside for 3 h. The mixture was then distilled under reduced pressure to give dimethylamino-(methoxy)phenylborane (2.77 g, 85%), b.p. 40°C/1 mmHg. (Found: C, 66.4; H, 8.8; N, 8.1. $C_9H_{14}NOB$ calcd.: C, 66.3; H, 8.6; N, 8.6%).

Preparation of diethylamino(i-propoxy)phenylborane

Bis(diethylamino)phenylborane (4.6 g, 0.02 mol) was cooled to —78°C and dry isopropanol (1.2 g, 0.02 mol) was added slowly with stirring. The mixture was set aside to attain room temperature and then gently warmed. Diethylamine (1.46 g, 100%) was evolved. Distillation of the residue under reduced pressure gave diethylamino(i-propoxy)phenylborane, (2.85 g, 65%), b.p. 62°C/0.1 mmHg. The precise mass of the parent ion was determined. (Found: 219.1794223. $C_{13}H_{22}NOB$ calcd.: 219.1794362. Error 0.06 ppm).

Preparation of diisopropylamino(methoxy)phenylborane

Di-i-propylamine (10.1 g, 0.1 mol) was dissolved in 40/60 petroleum ether (150 cc) and cooled to −78°C. Chloro(methoxy)phenylborane (4.64 g, 0.03 mol), dissolved in 40/60 petroleum ether (50 cc), was added dropwise with stirring. The mixture was refluxed for 3 h. Di-i-propylammonium chloride (4.13 g, 100%) was filtered off and the solvent removed from the filtrate to yield a clear mobile liquid. Distillation of this gave di-iso-propylamino(methoxy)-phenylborane (6.93 g, 75%), b.p. 60°C/0.3 mmHg. (Found: C, 70.6; H, 9.0; N, 6.1. $C_{13}H_{22}NOB$ calcd.: C, 71.2; H, 10.0; N, 6;4%).

Preparation of diethylaminoethoxyphenylborane

Chlorodiethylaminophenylborane (5.8 g, 0.03 mol) in petroleum ether (60 cc 40/60) was added slowly to sodium ethoxide (2.04 g, 0.03 mol) in petroleum ether (30 cc) with stirring. The mixture was refluxed for 3 h after which sodium chloride (1.68 g, 94%) was filtered off. The solvent was removed from the filtrate and the residue on distillation afforded diethylaminoethoxyphenylborane (4.35 g, 70%) b.p. 60°C/0.1 mmHg. (Found: C, 69.7; H, 10.1; N, 68. $C_{12}H_{20}NOB$ calcd.: C, 70.2; H, 9.8; N, 6.8%).

Interaction of dimethylaminomethoxyphenylborane and phenylisocyanate

Dimethylaminomethoxyphenylborane (1 mol) and phenylisocyanate (1 mol) were refluxed in benzene for 3 h. The product of the reaction was not isolated but on alcoholysis, with n-butylalcohol, afforded 1,1-dimethyl-3-phenyl urea m.p. 127°C (lit. 127—128°C). The identity of the urea was confirmed by ^1H NMR and a mixed melting point with an authentic sample.

Acknowledgement

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