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ORGANOBORON COMPOUNDS

XVIII. CHLORODIALKYLAMINOPHENYLBORANES

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Summary

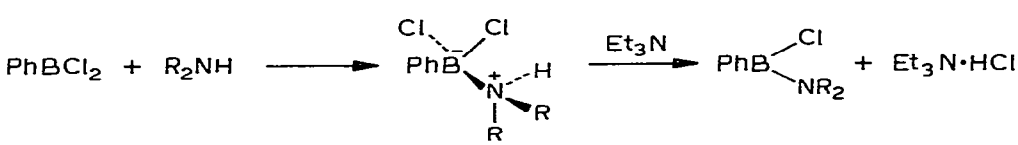
The synthesis and properties of a series of chlorodialkylaminophenylboranes, $PhB(NR_2)Cl$, are reported and their ^1H and ^{13}C NMR spectra discussed.

Introduction

Over the last few years we have been involved in an evaluation of the use of ^{13}C NMR spectroscopy as a means of obtaining information concerning the factors affecting the boron—nitrogen bond in aminoboranes [1—3]. The application of ^{13}C NMR spectroscopy to the study of phenylorganoboranes has been very limited, which is surprising in view of its advantage over ^1H NMR spectroscopy [4].

This present paper discusses the synthesis and properties of a series of chlorodialkylaminophenylboranes and illustrates the advantage of ^{13}C NMR over ^1H NMR in studying the nature of the boron—nitrogen bond in these compounds. In addition chlorodialkylaminophenylboranes were found to be precursors in the synthesis of unsymmetrical bis(dialkylamino)phenylboranes and their synthesis and properties are also discussed.

Two methods were employed for the synthesis of chlorodialkylaminophenylboranes. The first involved dissolving dichlorophenylborane in benzene and adding one mole of the required secondary amine slowly with stirring, at 40°C, to obtain a 1/1 complex. The complex was then decomposed using triethylamine to yield the desired product. Alternatively on mixing dichlorophenyl-



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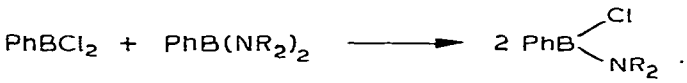
borane and a bis(dialkylamino)phenylborane a redistribution reaction occurs to yield a chlorodialkylaminophenylborane. Table 1 lists the analysis and boiling points of the chlorodialkylaminophenylboranes obtained by the above methods.



Chlorodialkylaminophenylboranes have been found to be useful reagents for the synthesis of organoboranes. Some idea of their value can be seen from the reactions shown in Fig. 1. Of interest is the reaction between a chlorodialkylaminophenylborane and phenylisocyanate which demonstrates that the boron—nitrogen bond is the most reactive to insertion. Reactions with antimony tri-

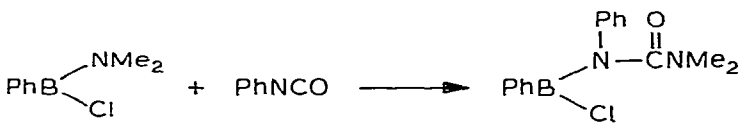
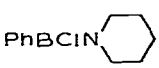
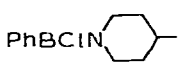
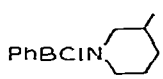
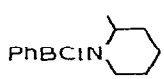


TABLE 1

CHLORO(DIALKYLAMINO)PHENYLBORANES

Compound	Yield (%)	B.p. (°C/mmHg)	Analysis (Found calcd.(%))			B.p. Ref.	Lit. (°C/mmHg)
			C	H	N		
$PhBClNMe_2$	90	40/1	—	—	—	10—12	51/2
$PhBClNEt_2$	75	50/0.1	—	—	—	12	67/2
$PhBClN(n\text{-}Pr)_2$	70	60/0.1	—	—	—	13	82/2
$PhBClN(i\text{-}Pr)_2$	75	64/0.1	—	—	—	12, 8	94/4
$PhBClN(s\text{-}Bu)_2$	65	75/0.1	—	—	—	9, 13	101/0.1
$PhBClN(i\text{-}Pent)_2$	60	85/0.1	68.6 (68.7)	9.8 (9.7)	4.9 (5.0)	—	—
$PhBClN(allyl)_2$ [a]	60	55/0.1	—	—	—	—	—
PhBClNH-t-Bu	80	40/0.1	61.4 (61.4)	7.8 (7.7)	6.9 (7.2)	—	—
	75	70/0.1	—	—	—	12	82/2
	65	75/0.1	65.0 (65.0)	7.4 (7.7)	6.4 (6.3)	—	—
	65	75/0.1	63.9 (65.0)	8.5 (7.7)	6.2 (6.3)	—	—
	65	75/0.1	64.8 (65.0)	7.6 (7.7)	6.3 (6.3)	—	—
PhBClNEtPh	50	110/0.1	68.5 (69.0)	6.7 (6.2)	5.7 (5.8)	12	105/2
PhBClN-s-BuPh	45	125/0.2	69.6 (70.7)	7.5 (7.0)	5.2 (5.2)	—	—
$PhBClN(n\text{-}Bu)_2$	65	75/0.1	—	—	—	13	98/0.1

[a] Characterised by precise mass analysis. (Found: 219.0951128. $C_{12}H_{15}NBCl$ calcd.: 219.0986029. Error 15.9 ppm).

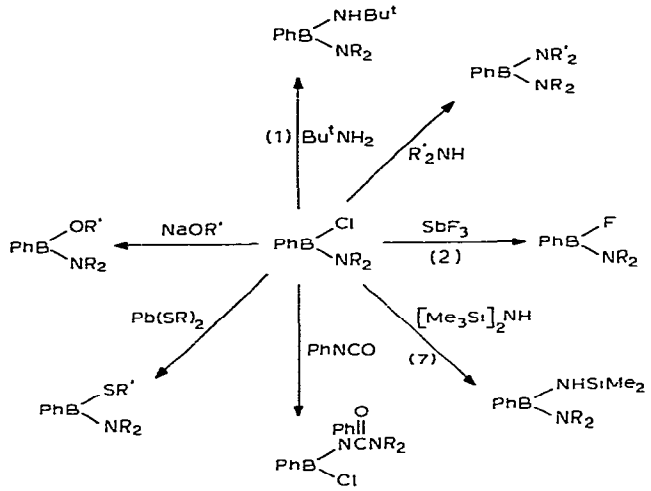


Fig. 1. Reactions of chlorodialkylaminophenylboranes.

fluoride, lead thiolates and sodium alkoxides have resulted in the synthesis of the corresponding fluoro-, alkylthio- and alkoxy-dialkylaminophenylboranes. The interaction with a secondary amine resulted in the formation of unsymmetrical bis(dialkylamino)phenylboranes which apart from $MeB(NMe_2)$-$\dot{N}C{=}CC{=}\dot{C}$ [5] appear to be a new class of compounds [6].

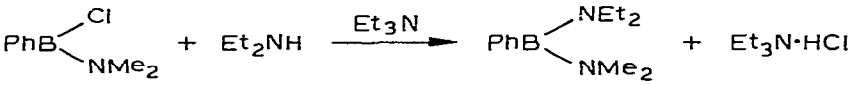
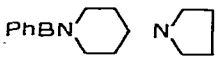


Table 2 lists the analyses and boiling points of the unsymmetrical bis(dialkylamino)phenylboranes obtained from the above method.

TABLE 2

UNSYMMETRICAL BIS(DIALKYLAMINO)PHENYLBORANES

Compound	Yield (%)	B.P. (°C/mmHg)	Analysis (Found calcd. (%))		
			C	H	N
$PhBNMe_2NEt_2$	75	65/0.1	70.3 (70.6)	10.4 (10.3)	13.5 (13.7)
$PhBNEt_2N(n\text{-}Pr)_2$	70	85/0.3	73.8 (73.9)	11.7 (11.2)	10.2 (10.8)
$PhBNMe_2N(s\text{-}Bu)_2$	70	95/0.2	73.2 (73.9)	10.1 (11.2)	10.7 (10.8)
	70	115/0.13	74.5 (74.4)	10.4 (9.5)	10.7 (11.6)

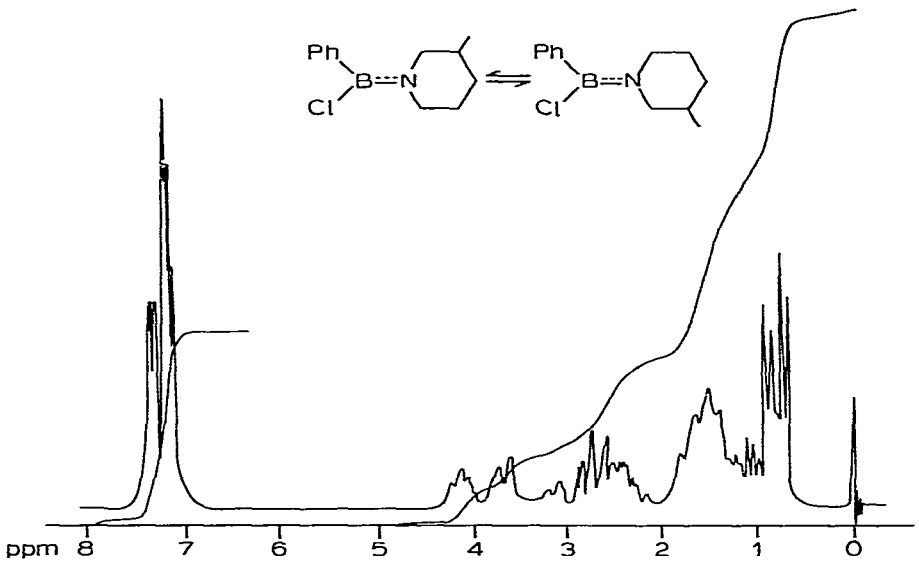


Fig. 2. The ^{1}H NMR spectrum of chloro(3-methylpiperidino)phenylborane.

^{1}H NMR spectra

(a) Chlorodialkylaminophenylboranes

In the majority of cases the spectra were too complex for any valuable information to be obtained and it is therefore only possible to give isomer shifts in favourable cases. The ^{1}H NMR spectrum of chloro-(3-methylpiperidino)phenylborane (Fig. 2) is complicated by considerable overlap of peaks, but it is possible to give an isomer shift for the methyl group. This would in the absence of

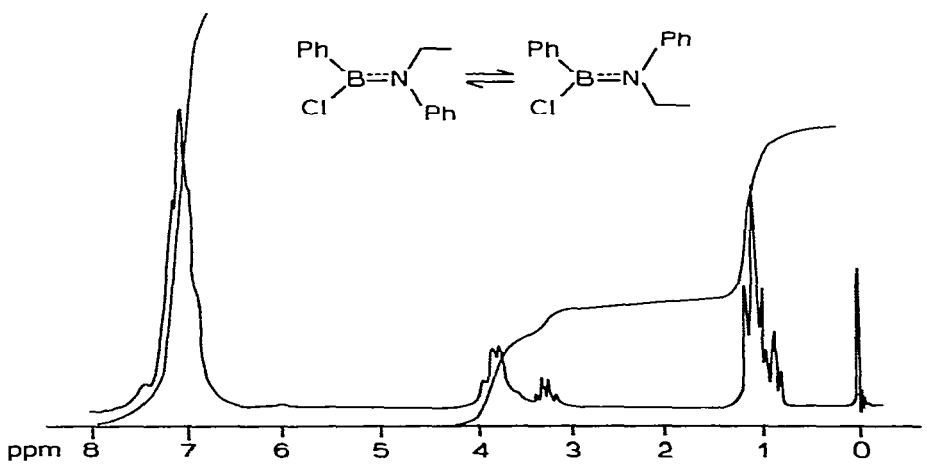
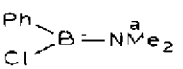
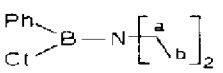
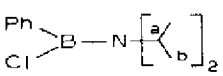
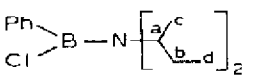
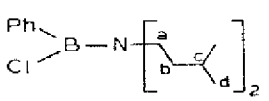
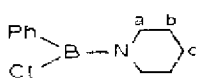
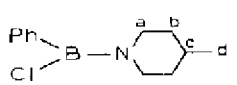
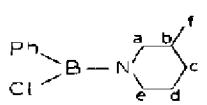
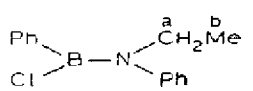


Fig. 3. The ^{1}H NMR spectrum of PhB(NEtPh)Cl.

restricted rotation, appear as a doublet due to spin—spin coupling with the vicinal proton of the piperidino ring. However two doublets are clearly resolved, one for the rotomer with the methyl group *cis* to Cl and the other for the rotomer with the methyl group *cis* to Ph. In nearly all cases of compounds discussed there is a 50/50 distribution of *cis* + *trans* rotomers as evidenced by the integration of the proton NMR. However, when the amino group is unsymmetrical a larger proportion of one rotomer obtains. The ^{1}H NMR spectrum of chloro-*N*-ethylaminophenylborane is a good illustration (Fig 3) The rotomer having 2 bulky phenyl groups *cis* predominates and the integration of the spectrum indicates that the compound exists as 80% in this form Other reports on similar

TABLE 3

^{1}H NMR ISOMER SHIFTS OF CHLORODIALKYLAMINOPHENYLBORANES

Compound	Isomer shift (Hz)					
	a	b	c	d	e	f
	16					
	40	5				
	40	36				
	45					
				20		
	16					
	50					
	50					14
	50	20				

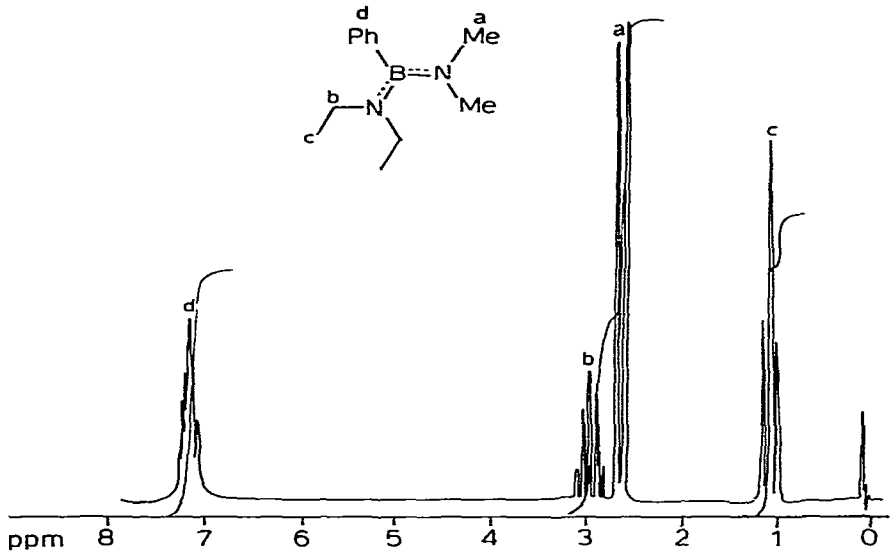


Fig. 4. The ^{1}H NMR spectrum of $PhB(NMe_2)NEt_2$.

systems indicate an isomer distribution of 90/10 [9]. The compounds isomer shifts of those compounds whose spectra were easily assigned are given in Table 3.

(b) Unsymmetrical bis(dialkylamino)phenylboranes

When both amino groups are secondary, and very similar, restricted rotation is observed about both B—N bonds. The ^{1}H NMR spectrum of $PhBNEt_2NMe_2$ shows the dimethylamino group as a perfect 1/1 doublet ($\Delta\nu$, 5 Hz). While the methylene protons of the diethylamino group appear as 2 quartets of equal intensity ($\Delta\nu$, 6 Hz) (Fig. 4). Unfortunately the ^{1}H NMR spectra of other members of this series are not so informative because of their complexity due to overlapping peaks.

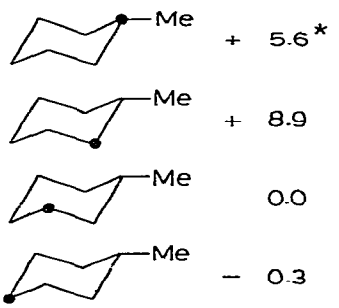
^{13}C NMR spectra

There has been some confusion regarding the assignment of *ortho, meta* and *para* carbon resonances in phenylboranes. Niedenzu [8] did not specify the criteria by which he assigned the resonances of the *ortho* and *meta* carbon atoms and our assignments conflict with his. Our assignments have been confirmed by off resonance decoupled and selectively decoupled $^{13}C(^1H)$ and by undecoupled ^{13}C spectral measurements [9]. These assignments were confirmed by Wrackmeyer who has used gated ^{1}H decoupled ^{13}C NMR to assign aromatic resonances [4]. The C(1) resonances were easy to assign since they were absent in the solution spectra but emerged on running a spectrum of the neat sample [9].

Aliphatic Carbons

Simple dialkylamino groups were easy to assign using established rules but the methylpiperidino compounds were more difficult and methyl substituent parameters had to be used.

The assignment of doublets in the ^{13}C NMR spectra of 2-, 3-, and 4-methyl piperidino-(X)-phenylboranes was made on the basis of results published by Dalling [15] and Morishima [16]. The chemical shifts of carbons in a series of methyl cyclohexanes have been unequivocally assigned using spin coupling techniques [15] and methyl substituent parameters have been determined. It was found that an equational methyl group deshields the carbons closest to it by the following amounts (ppm):



*+ means increased chemical shift, i.e. deshielding

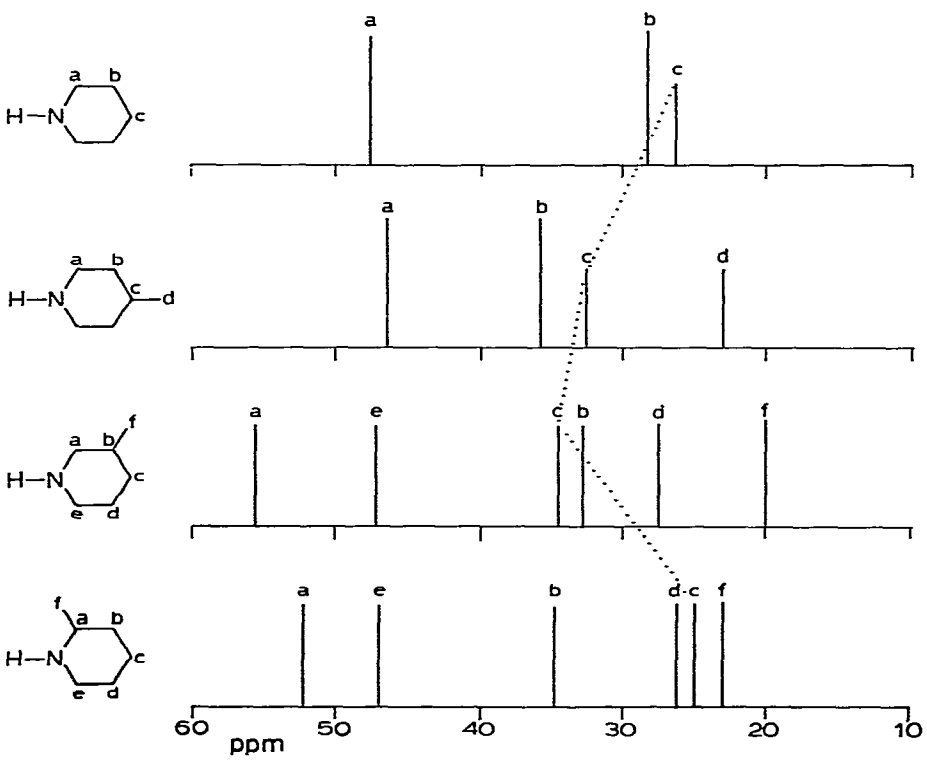


Fig. 5. ^{13}C assignments for piperidine and methylpiperidines.

A stick diagram (Fig. 5) for the ^{13}C NMR of piperidine, 2-, 3- and 4-methylpiperidine illustrates that these substituent parameters are applicable. In 4-methylpiperidine C(c) is deshielded by 5.3 ppm relative to piperidine, C(b) is deshielded by 8 ppm while C(a) is shielded by —1 ppm. In 3-methylpiperidine C(b) is deshielded by 4.8 ppm, C(a) by 7.8 ppm and C(c) by 8.6 ppm. The other carbons are relatively unaffected by the methyl group and stay unshifted. In 2-methylpiperidine C(a) is deshielded by 4.6 ppm and C(b) by 7.1 ppm. The other carbons are unshifted. Hence the carbon atom directly attached to the methyl group is deshielded by ~5 ppm, the vicinal carbon atom is deshielded by ~8 ppm and carbon atoms further removed are only marginally shifted. This behaviour is clearly shown by C(c) (Fig. 5 and 6).

Chlorodialkylaminophenylboranes

There are no reports in the literature of ^{13}C NMR data for this class of compound. Isomer shifts are much more readily obtained from these spectra than the corresponding ^{1}H NMR spectra. For example, in the aliphatic region of the ^{13}C NMR spectrum of chloro(3-methylpiperidino)phenylborane (Fig. 7) there are 6 clear 'doublets' corresponding to the 6 unique carbon atoms of the *cis* and *trans* rotomers. This compares strikingly with the complex mass of overlapping peaks observed in the ^{1}H NMR spectrum (Fig. 2) and illustrates the superior advantage of ^{13}C NMR for investigating restricted rotation.

The ^{13}C NMR spectrum of $PhBN(s\text{-}Bu)_2Cl$ shows additional features. One would expect to see 4 doublets in the aliphatic region of the spectrum, one set of signals arising from the s-butyl group *cis* to Cl and the other from the s-butyl

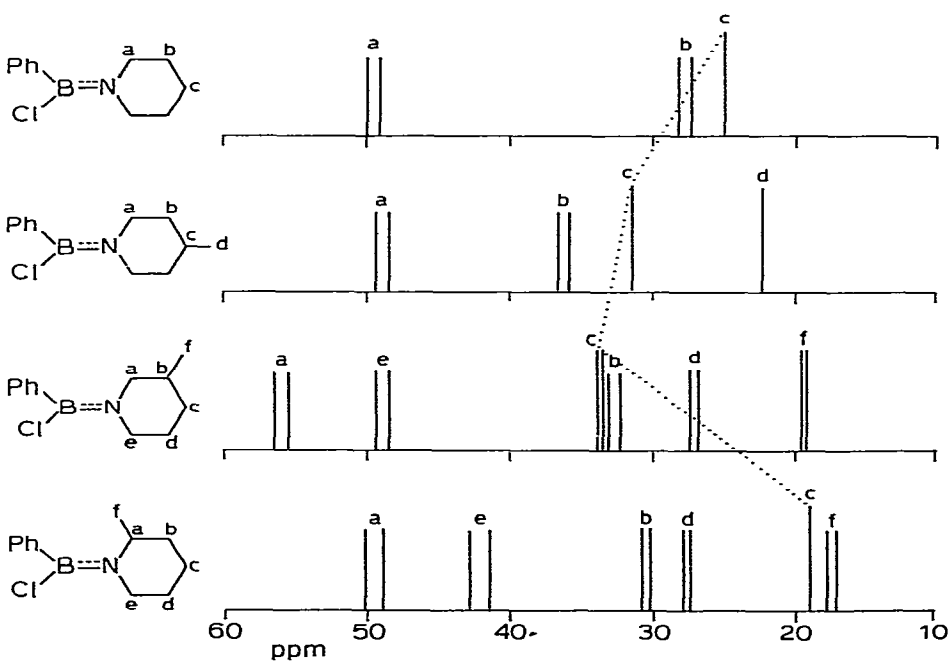


Fig. 6. ^{13}C assignments for chloropiperidinophenylboranes.

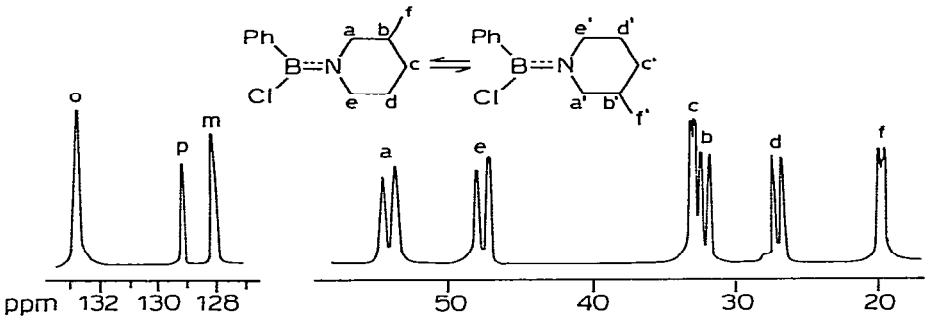


Fig. 7. ^{13}C NMR spectrum of chloro(3-methylpiperidino)phenylborane.

group *trans* to Cl. However, although 4 doublets were observed there is additional fine structure in some doublets (Fig. 8).

The fine structure observed in each doublet results from the chirality of the asymmetric carbon atom of the di-s-butylamino group. There are optical isomers in addition to rotational isomers. ^{13}C NMR data for this class of compounds are given in Table 4.

Unsymmetrical bis(dialkylamino)phenylboranes

At ambient temperature both amino groups show small 'splittings' and the *ortho* carbon atoms of the phenyl group are also split. This infers restricted rotation about all three bonds which is surprising in that simultaneous back donation from all three bonds resulting in a flat molecule which is unlikely on steric grounds. The ^{13}C NMR spectrum of $PhB(NMe_2)NEt_2$ illustrates these points (Fig. 9). Assignments for the ^{13}C NMR are given in Table 5.

In conclusion both ^1H and ^{13}C NMR spectra indicate restricted rotation about the boron—nitrogen bond in chlorodialkylaminophenylboranes and unsymmetrical bis(dialkylamino)phenylboranes however ^{13}C NMR has considerable advantages over ^1H NMR.

(Continued on p. 213)

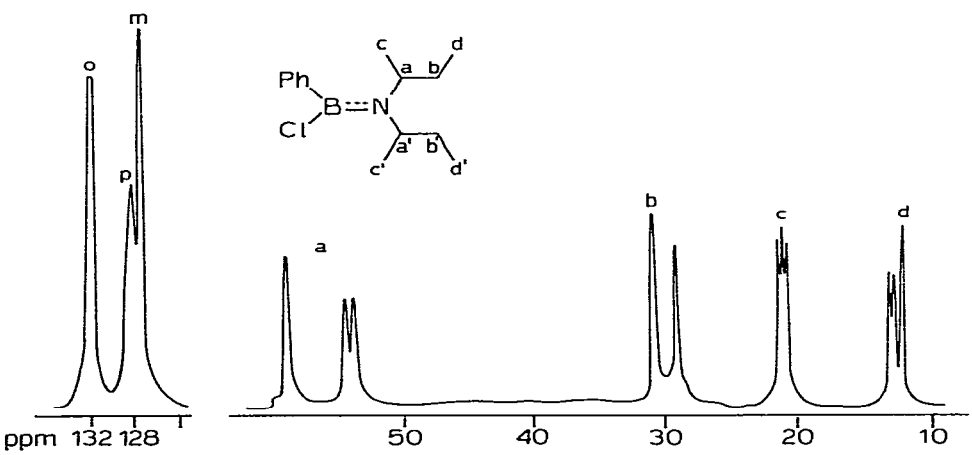
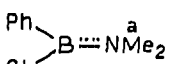
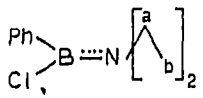
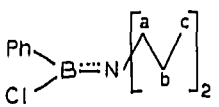
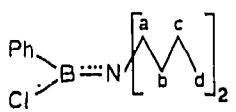
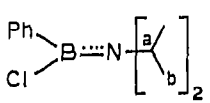
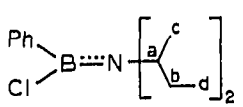
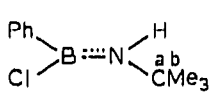
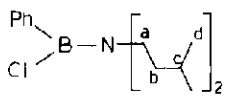
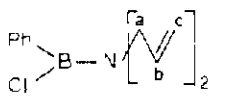
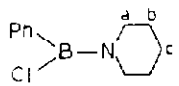
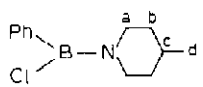
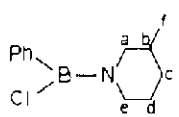
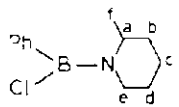
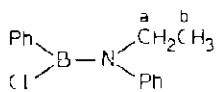


Fig. 8. The ^{13}C NMR spectrum of $PhBN(s\text{-}Bu)_2Cl$.

TABLE 4

^{13}C NMR DATA FOR CHLORODIALKYLAMINOPHENYLBORANES AT 23°C

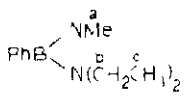
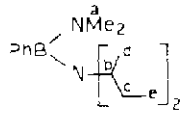
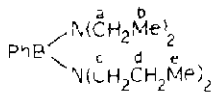
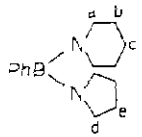
Compound	C(1) [a]	*o*	*p*	*m*	a	b	c	d	e	f
	137.2	132.7	129.0	127.5	40.6 40.0					
	0	0	0	0	15.0					
	138.0	132.0	128.6	127.5	43.6 42.7	15.3 14.8				
	0	0	0	0	21	18				
	138.3	132.0	128.5	127.3	51.0 50.2	22.9 22.4	11.3 11.0			
	0	0	0	0	20.	10	10			
	138.6	132.0	128.6	127.6	49.1 48.4	32.0 31.6	20.3 19.9	14.1 13.8		
	0	0	0	0	18	10	12	8		
	141.0	131.3	128.1	127.7	51.6 46.4	23.3 22.1				
	0	0	0	0	131	31				
	140.8	131.0	128.0	127.5	57.8 53.1 [b]	30.0 28.4	20.4 20 [b]	12.2 [b] 11.5		
	0	0	0	0	117	40	10	20		
	136.0	132.4	130.3	127.8	51.1	31.5				
	0	0	0	0	0	0				

	137 7	132 0	128 6	127 5	47 8 47 2	39 1 38,6	26,3 26 0	22 7 22 4		
	0	0	0	0	15	12	9	6		
	N A [c]	132 5	129 4	127 8	51 5 51 5	135 4 134 6	116 9			
	0	0	0	0	10	20	0			
	137 8	132 5	128 7	127 5	49 8 48 9	28 0 27 3	24 9			
	0	0	0	0	21	18	0			
	137 5	132 5	128 7	127 5	49 1 48 3	36 3 35 7	31 3	22 0		
	0	0	0	0	21	16	0	0		
	137 8	132 5	128 7	127 5	56 3 55,5	33 1 32,4	33 4 33,2	27 2 26 7	49 3 48 4	19,1 18 9
	0	0	0	0	22	19	3	15	21	3
	138 2	132 4 131 9	128 6	127 5	50 1 48 9	31 7 31 1	18 9	27 8 27 4	42 7 41 4	17 8 17 1
	0	12	0	0	31	15	0	9	34	18
	150 0	N A [c]	N A	N A	49 5 45 3	15 7 14 4				
	0	0	0	0	107	31				

[a] Cl signals obtained on neat samples [b] Signal further split because of chirality [c] Not available because of overlap

TABLE 5

^{13}C NMR DATA FOR UNSYMMETRICAL BIS(DIALKYLAMINO)PHENYLBORANES

Compound	C(1)	o	p	m	a	b	c	d	e
	142.3	133.6 133.1	127.1	127.1	41.1 overlap	42.0	15.7		
	0	12	0	0			0		
	144.8	133.5 133.3	126.8	126.8	54.0 53.3	41.1	31.8	22.3	12.4
	0	4	0	0	18	0	0	0	0
	142.5	133.2 132.6	127.2	127.2	49.1 48.8	22.0 21.6	41.5	15.3	11.4
	0	10	0	0	8	10	0	0	0
	142.1	132.1 131.4	127.5	127.5	49.3	28.5	25.6	49.3	26.5
	0	18	0	0	0	0	0	0	0

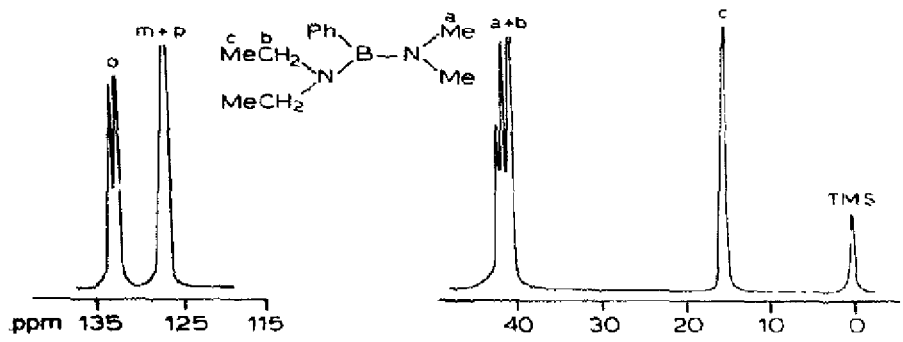


Fig. 9 The ^{13}C NMR spectrum of $PhB(NMe_2)NEt_2$

Experimental

The ^1H NMR spectra were recorded on a Perkin–Elmer R10 spectrometer and the ^{13}C NMR spectra were recorded on a JEOL PS100 FT spectrometer and line positions are relative to internal TMS. Two methods were used for the synthesis of chlorodialkylaminophenylboranes and an example of each method is reported in full.

Preparation of chlorodimethylaminophenylborane

Dichlorophenylborane (3.18 g, 0.02 mol) and bis(dimethylamino)phenylborane (3.52 g, 0.02 mol) were mixed together and set aside for 3 h. The mixture was then distilled under reduced pressure to give chlorodimethylaminophenylborane (6.3 g, 90%), b.p. 40°C/1 mmHg (lit. b.p. 51°C/2 mmHg [10–12].

Preparation of chloro(3-methylpiperidino)phenylborane

Dichlorophenylborane (15.9 g, 0.1 mol) was dissolved in benzene (250 ml) and cooled to +5°C. 3-Methylpiperidine (9.9 g, 0.1 mol), dissolved in benzene (50 ml), was added dropwise with stirring and the resulting mixture allowed to reach room temperature. Triethylamine (10.2 g, 0.1 mol), dissolved in benzene (50 ml), was added dropwise with stirring to the clear colourless solution. The resultant slurrey was refluxed for 3 h and then filtered to yield triethylammonium chloride (13.7 g, 0.1 mol). Removal of solvent from the filtrate gave a clear mobile liquid which, on vacuum distillation, afforded chloro(3-methylpiperidino)phenylborane (14.4 g, 65%), b.p. 75°C/0.1 mmHg. (Found: C, 63.91; H, 8.51; N, 6.21. $C_{12}H_{17}NBCl$ calcd.: C, 65.0; H, 7.67; N, 6.32%.)

Preparation of diethylamino(ethoxy)phenylborane

Sodium ethoxide (2.04 g, 0.03 mol) was added to 40/60 petroleum ether (60 ml). Chloro(diethylamino)phenylborane (5.87 g, 0.03 mol), dissolved in 40/60 petroleum ether (30 ml), was added slowly with stirring. The mixture was refluxed for 3 h and sodium chloride (1.76 g, 100%) was filtered off. The solvent was removed from the filtrate and the residue distilled under reduced

pressure to afford diethylamino(ethoxy)phenylborane (4.31 g, 70%), b.p. 60°C/0.1 mmHg. (Found: C, 69.7; H, 10.1; N, 6.8. $C_{12}H_{20}NBO$ calcd.: C, 70.2; H, 9.8; N, 6.8%).

Preparation of di-s-butylaminoethanethiophenylborane

Chlorodi-s-butylaminophenylborane (6.5 g, 0.025 mol) and ethanethiolead(II) (7.0 g, 0.021 mol) were refluxed in benzene for 3 h. After filtration and removal of the solvent under reduced pressure the residue on distillation afforded di-s-butylaminoethanethiophenylborane (3.57 g, 50%), b.p. 110°C/0.1 mmHg. (Found: C, 68.9; H, 10.1; N, 4.8. $C_{16}H_{28}NBS$ calcd.: C, 69.3; H, 10.1; N, 5.1%).

Preparation of di-s-butylaminodimethylaminophenylborane

Chlorodimethylaminophenylborane (1.67 g, 0.01 mol) was dissolved in benzene at room temperature and di-s-butylamine (1.30 g, 0.01 mol) was added slowly with stirring. Triethylamine (1.30 g, 0.013 mol) was added and the resultant mixture refluxed for 3 h. After filtration, to remove the triethylammonium chloride, and removal of solvent the residue on distillation afforded di-s-butylaminodimethylaminophenylborane (1.82 g, 70%) b.p. 95°C/0.2 mmHg. (Found: C, 73.2; H, 10.1; N, 10.7. $C_{16}H_{29}N_2B$ calcd.: C, 73.9; H, 11.2; N, 10.8%).

Interaction of phenylisocyanate and chlorodimethylaminophenylborane

Phenylisocyanate (3.4 g, 1 mol) was added to chlorodimethylaminophenylborane (4.8 g, 1 mol) in benzene. The mixture was refluxed for 1 h. On removal of the solvent the residue on recrystallisation afforded *N*-phenyl-*N*,*N'*-dimethylureidophenylchloroborane (7.3 g, 89%) m.p. 153—155°. (Found: C, 62.1; H, 6.2; N, 9.4. $C_{15}H_{16}N_2OClB$ calcd.: C, 62.8; H, 5.6; N, 9.8%). A sample of the ureidoborane was refluxed in benzene with n-butyl alcohol to give 1,1-dimethyl-3-phenyl urea m.p. 127°C (mixed m.p. 127—128°C).

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