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ORGANOBORON COMPOUNDS

XVI *. ALKYLAMINODIALKYLAMINOPHENYLBORANES

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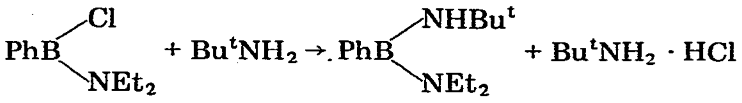
Summary

The synthesis and properties of a series of alkylaminodialkylaminophenylboranes, $PhB(NHR)NR'_2$, are reported. The ^{13}C NMR of these compounds indicate restricted rotation about the $>B{-}NR'_2$ bond.

We have, for a number of years, been interested in the nature of the $>B{-}N<$ bond in aminoboranes. Our present studies involve the determination and rationalisation of relative migratory aptitude (RMA) orders, for groups attached to boron, in the aminoboration of isocyanates and also the application of ^{13}C NMR in a study of the factors affecting $p_\pi{-}p_\pi$ bonding in aminoboranes. It appeared to us that valuable information concerning the factors influencing the aminoboration reaction could result from a study of the interaction of an alkylaminodialkylaminophenylborane and an organic isocyanate. As a class of compound the alkylaminodialkylaminophenylboranes have received little attention [2] and this present paper reports their synthesis and properties. The results of our RMA studies will be published shortly.

Three methods of synthesis were used for the preparation of alkylaminodialkylaminophenylboranes.

The first method involved the addition of an excess of a primary amine to a chlorodialkylaminophenylborane. However, this method is rather limited in so far as the required compound is only obtained when the amino group to be



$$PhB\begin{matrix}\diagup Cl\\ \diagdown NEt_2\end{matrix} + Bu^tNH_2 \rightarrow PhB\begin{matrix}\diagup NHBu^t\\ \diagdown NEt_2\end{matrix} + Bu^tNH_2\cdot HCl$$

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[*] For part XV see ref. 1.

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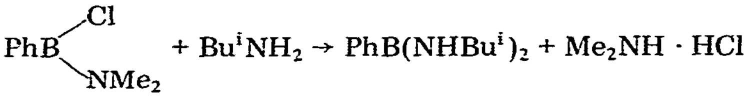
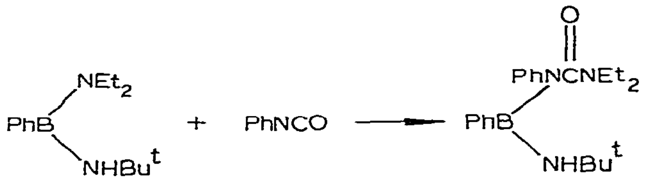
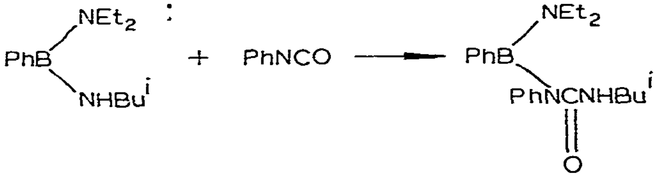
introduced is much more bulky than the amino group already present in the chlorodialkylaminophenyl borane. This can be illustrated by the following examples. It was observed that the product obtained from the interaction of an excess of n-, i- or s-butylamine and chlorodiethylaminophenylborane was the corresponding bisbutylaminophenylborane and analogous results were obtained using chlorodimethylaminophenylborane.



$$PhB(Cl)(NMe_2) + Bu^iNH_2 \rightarrow PhB(NHBu^i)_2 + Me_2NH \cdot HCl$$

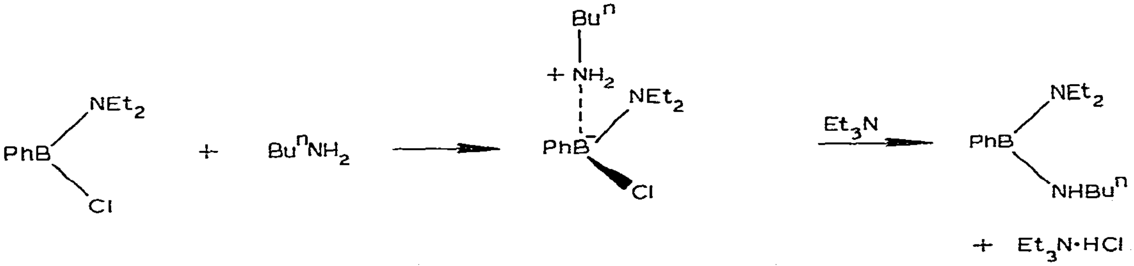
These observations correlate well with the results of competitive insertion reactions on these systems [3]. For example, when phenyl isomcyanate is refluxed in benzene with one mole of $PhB(NEt)_2NHBu^t$ the insertion occurs across the $>$B—NEt$_2$ bond. However, when $PhB(NEt)_2NHBu^i$ is similarly treated the insertion occurs across the less hindered $>$B—NHBu^i bond.





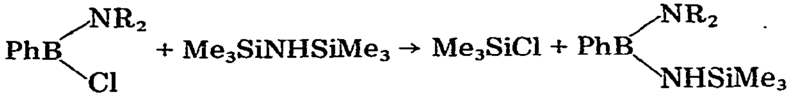
It would appear that adding an excess of a primary amine to a chlorodialkylaminophenylborane, in order to obtain the unsymmetrical alkylaminodialkylaminophenylborane, is only successful when the amino group to be introduced is more bulky than the amino group already present. If the amino group to be introduced is less bulky the symmetrical bisalkylaminophenylborane is obtained.

The second method used involves the addition of one mole of a primary amine to a cooled benzene solution of a chlorodialkylaminophenylborane followed by the addition of one mole of triethylamine.



This method was found to be a general method for the synthesis of alkylaminodialkylaminophenylboranes.

The third method, limited to the synthesis of dialkylaminotrimethylsilylaminophenylboranes involved the interactions of hexamethyldisilazane and a chlorodialkylaminophenylborane.



$$\mathrm{PhB}\begin{smallmatrix}\nearrow \mathrm{NR_2}\\ \searrow \mathrm{Cl}\end{smallmatrix} + \mathrm{Me_3SiNHSiMe_3} \rightarrow \mathrm{Me_3SiCl} + \mathrm{PhB}\begin{smallmatrix}\nearrow \mathrm{NR_2}\\ \searrow \mathrm{NHSiMe_3}\end{smallmatrix}$$

The analyses, yields and boiling points for the alkylaminodialkylaminophenylboranes are recorded in Table 1.

^1H NMR spectra

The proton NMR spectra of all ten compounds were recorded. However, no isomer shifts could be observed because of the complexity of the spectra, or in some cases, because of the absence of internal chemical shifts when the spectra were recorded at ambient temperature.

^{13}C NMR spectra

In contrast to the ^{1}H NMR spectra, the ^{13}C NMR spectra were much more informative. In the ^{13}C spectra, recorded at ambient temperature, split or broadened resonances were observed for the carbon atoms of the secondary amino groups. At lower temperatures these signals resolved into doublets, in contrast to the lines for the primary amino and phenyl groups which remained sharp singlets throughout. The ^{13}C spectra of all ten compounds, of the general

TABLE I

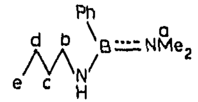
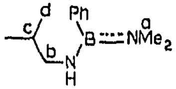
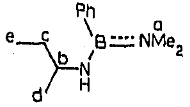
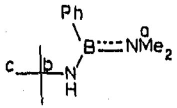
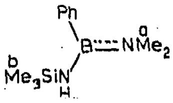
ALKYLAMINO(DIALKYLAMINO)PHENYLBORANES

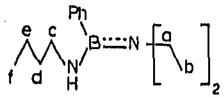
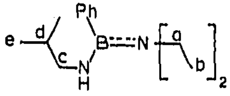
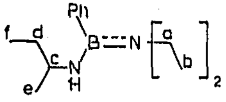
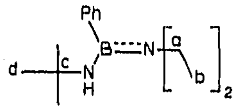
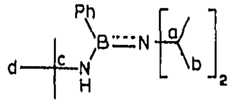
Compound	Yield (%)	B.P. (°C/mmHg)	Analysis Found (calcd.)			Ref.	Ref. B.P. (°C/mmHg)
			C	H	N		
$\mathrm{PhBNMe_2NHBu^n}$	70	85/0.3	71.2 (70.6)	10.3 (10.3)	13.3 (13.7)	—	—
$\mathrm{PhBNMe_2NHBu^i}$	70	86/0.6	70.9 (70.6)	9.9 (10.3)	13.8 (13.7)	—	—
$\mathrm{PhBNMe_2NHBu^s}$	75	64/0.2	71.6 (70.6)	10.9 (10.3)	13.4 (13.7)	—	—
$\mathrm{PhBNMe_2NHBu^t}$	75	72/0.6	71.8 (70.6)	11.2 (10.3)	13.4 (13.7)	4	64/0.3
$\mathrm{PhBNMe_2NHSiMe_3}$ [a]	50	72/0.3	—	—	—	5	82/3
$\mathrm{PhBNEt_2NHBu^n}$	70	84/0.1	72.5 (72.4)	11.9 (10.8)	12.1 (12.1)	—	—
$\mathrm{PhBNEt_2NHBu^i}$	70	86/0.1	72.5 (72.4)	10.7 (10.8)	11.8 (12.1)	—	—
$\mathrm{PhBNEt_2NHBu^s}$	70	85/0.1	71.7 (72.4)	11.2 (10.8)	11.1 (12.1)	—	—
$\mathrm{PhBNEt_2NHBu^t}$	70	85/0.1	71.9 (72.4)	11.0 (10.8)	11.5 (12.1)	4	60/0.2
$\mathrm{PhBN(Pr^i)_2NHBu^t}$	70	100/0.7	74.7 (73.9)	12.0 (10.8)	10.7 (11.2)	4	70/0.05

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

TABLE II

^{13}C NMR/DATA OF ALKYLAMINO(DIALKYLAMINO)PHENYLBORANES [a]

Compound	Temp. (°C)	C(1)	*O*	*p*	*m*	a	b	c	d	e	f
	−60	139.4 139.4 0	132.4 132.4 0	126.9 126.9 0	127.3 127.3 0	40.0 36.5 89	43.1 43.1 0	36.5 36.5 0	19.8 19.8 0	14.2 14.2 0	
	−12	139.9 139.9 0	131.8 131.8 0	126.3 126.3 0	126.9 126.9 0	39.4 34.9 89	50.7 50.7 0	31.4 31.4 0	19.3 19.3 0		
	−12	140.4 140.4 0	131.5 131.5 0	126.3 126.3 0	126.9 126.9 0	39.4 35.8 92	48.8 48.8 0	32.9 33.9 0	24.8 24.8 0	10.3 10.3 0	
	−64	142.0 142.0 0	131.8 131.8 0	126.1 126.1 0	126.7 126.7 0	39.7 36.7 83	48.8 48.8 0	33.4 33.4 0			
	−48	141.4 141.4 0	132.0 132.0 0	127.0 127.0 0	127.0 127.0 0	39.6 35.9 92	1.8 1.8 0				

		140.9	131.4	127.0	127.0	42.6	15.4	42.6	36.4	19.4	13.6
	−15	140.9	131.4	127.0	127.0	39.7	15.4	42.6	36.4	19.4	13.6
		0	0	0	0	73	0	0	0	0	0
		140.8	131.9	126.6	127.2	42.8	16.3	50.7	31.8	19.9	
	−60	140.8	131.9	126.6	127.2	39.6	15.2	50.7	31.8	19.9	
		0	0	0	0	82	28	0	0	0	
		141.1	131.3	126.2	127.0	43.0	15.4	48.9	33.0	25	10.4
	−15	141.1	131.3	126.2	127.0	39.7	15.4	48.3	33.0	25	10.4
		0	0	0	0	82	0	0	0	0	0
		143.2	132.0	126.1	126.8	42.5	16.0	48.7	33.4		
	−64	143.2	132.0	120.1	126.8	39.4	15.0	48.7	33.4		
		0	0	0	0	76	25	0	0		
		144.0	131.8	126.1	126.9	48.9	23.9	49.5	33.6		
	−64	144.0	131.8	126.1	126.9	42.2	21.7	49.5	33.6		
		0	0	0	0	168	55	0	00		

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[a] The chemical shift (in ppm) of a given signal arising from a particular carbon atom in one rotomer is given first followed by the chemical shift of the same nucleus in the other rotomer and the isomer shift, $\Delta\nu$, in Hz.

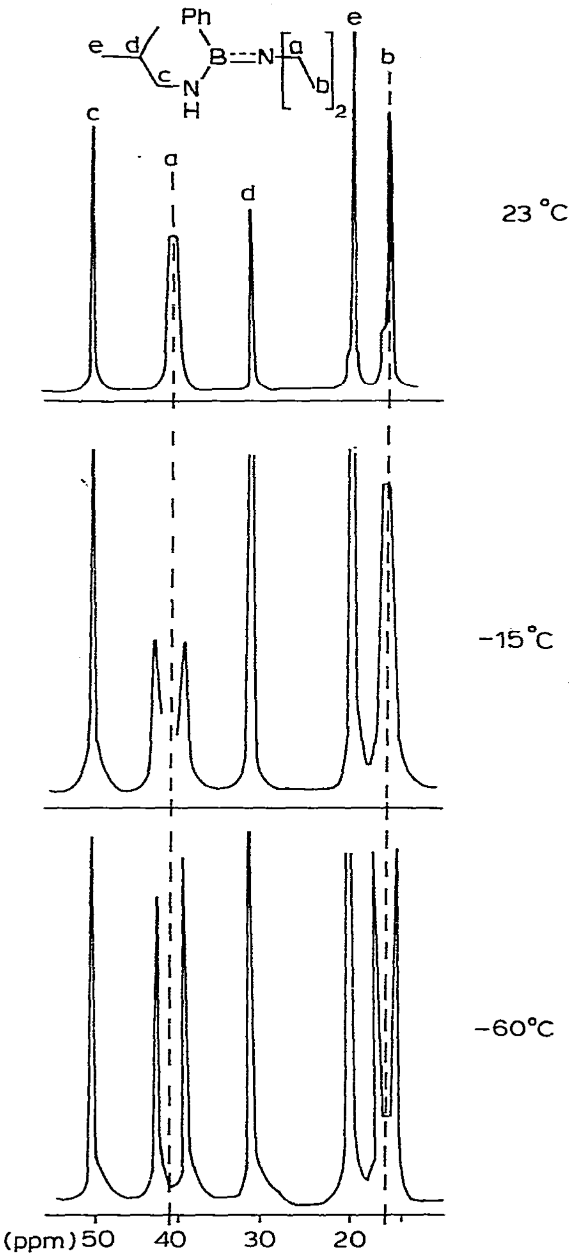

Fig. 1. The ^{13}C NMR spectra of PhB(NEt$_2$)NHBu^i.

type PhB(NRH)NR$'_2$, were therefore indicative of restricted rotation about the $>$B—NR$'_2$ bond, while the other two bonds were freely rotating at temperatures as low as —64°C. The ^{13}C NMR spectra of PhB(NEt)$_2$NHBu^i illustrates this behaviour as well as being typical of the series (Fig. 1). Restricted rotation about the $>$B—NEt$_2$ bond is indicated by the non-equivalence of the methylene and methyl carbon atoms of the diethylamino group. The ambient temperature spectrum shows these carbon atoms as broad peaks which resolved into doublets at —15° C and are at their maximum separation at —60° C. However, the lines corresponding to the carbon atoms in the isobutylamino group remain sharp throughout the temperature range. The same general results were obtained for the other three compounds in the series $PhBNEt_2(NHR)$ ($R = Bu^n$, Bu^s, Bu^t) and also for the series $PhBNMe_2(NHR)$ ($R = Bu^n$, Bu^i, Bu^s, Bu^t). In the latter series the dimethylamino group appears as a broad singlet at room temperature which resolves into a doublet at —12° C. The compounds $PhBNMe_2(NHSiMe_3)$ and $PhBNPr_2{}^iNHBu^t$ exhibit the same behaviour and it is of interest to note that in the latter compound the non-equivalence is large (~170 Hz for the methine carbon atom of the diisopropyl group). The ^{13}C NMR spectra are recorded in Table 2.

It is therefore concluded that in alkylaminodialkylaminophenylboranes there is restricted rotation about the $>B—NR'_2$ bond but not the $>B—NHR$ bond. This suggests that $p_\pi—p_\pi$ bonding involving a secondary amino group is considerably greater than for a primary amino group.

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; line positions are relative to internal TMS. Three methods were used for the synthesis of alkylaminodialkylaminophenylboranes and an example of each method is reported in full. Table 1 lists the boiling points and analytical data for each compound prepared. Method 3 is restricted to the synthesis of trimethylsilylamino(dialkylamino)phenylboranes while the choice between methods 1 and 2 is made on the basis of the amino group to be introduced.

Method 1: Preparation of t-butylamino(dimethylamino)phenylborane

t-Butylamine (7.3 g, 0.1 mol) was dissolved in 40/60 petroleum ether and cooled in an ice bath. Chloro(dimethylamino)phenylborane (5.01 g, 0.03 mol), dissolved in 40/60 petroleum ether was added dropwise with stirring. The mixture was refluxed for 3 hours and then filtered to yield t-butylammonium chloride (3.29 g, 0.03 mol). The solvent was removed from the filtrate to give a clear, mobile liquid which, on vacuum distillation, afforded t-butylamino(dimethylamino)phenylborane (4.9 g, 75%), b.p. 72° C/0.6 mmHg. (Found: C, 71.8; H, 11.2; N, 13.4. $C_{12}H_{21}N_2B$ calcd.: C, 70.6; H, 10.3; N, 13.7%).

Method 2: Preparation of n-butylamino(dimethylamino)phenylborane

Chloro(dimethylamino)phenylborane (5.01 g, 0.03 mol) was dissolved in benzene and cooled in an ice bath. n-Butylamine (2.19 g, 0.03 mol), dissolved in benzene, was added dropwise with stirring. The stirred mixture was allowed slowly to attain room temperature and a colourless clear solution of the 1 : 1 complex resulted. This complex was decomposed by the addition of triethylamine (3.03 g, 0.03 mol), dissolved in benzene, slowly with stirring. The resulting mixture was refluxed for 3 hours and then filtered to give triethylammonium chloride (4.13 g, 0.03 mol). The solvent was removed from the filtrate to give triethylammonium chloride (4.13 g, 0.03 mol). The solvent was removed from the filtrate to give a clear, mobile liquid which, on vacuum distillation, afforded n-butylamino(dimethylamino)phenylborane (4.28 g, 70%), b.p. 85° C/ 0.3 mmHg. (Found: C, 71.2; H, 10.3; N, 13.3. $C_{12}H_{21}N_1B$ calcd.: C, 70.6; H, 10.3; N, 13.7%).

Method 3: Preparation of dimethylamino(trimethylsilylamino)phenylborane
Bis(trimethylsilyl)amine (6.44 g, 0.04 mol) was dissolved in benzene and chloro(dimethylamino)phenylborane (6.68 g, 0.04 mol) was added, and the mixture refluxed for 2 hours. The solvent was removed and the resulting mobile liquid distilled under reduced pressure to yield dimethylamino(trimethylsilylamino)phenylborane (4.4 g, 50%), b.p. 72° C/0.3 mmHg. The precise mass of the molecular ion was determined. (Found: 220.1567551. $C_{11}H_{21}N_2SiB$ calcd.: 220.1567002. Error 0.25 ppm).

Acknowledgements

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