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ORGANOBORON COMPOUNDS

XX.* ALKYLAMINO- AND DIALKYLAMINO-PIPERIDINOPHENYL-BORANES

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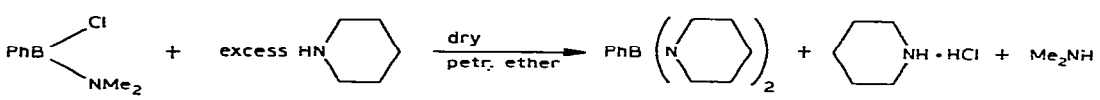
Summary

The synthesis and properties of a series of alkylamino- and dialkylamino-piperidinoboranes are reported and their ^{1}H and ^{13}C NMR spectra are discussed.

Over the last few years we have been involved in a study of the nature of the >B—N< bond and this has involved us in the synthesis of a considerable number of new aminoboranes. In this present paper we report the synthesis and properties of some alkylamino- and dialkylamino-piperidinophenylboranes. The compounds reported in this paper are novel and are further examples of unsymmetrical bis(amino)phenylboranes. The synthesis of bis(piperidino)phenylborane has been reported [2]. The synthesis of required compound is readily achieved provided it is appreciated that the least hindered bisaminophenylborane is obtained when an excess of an amine is added to a chloroaminophenylborane. The following examples illustrate the above generalisation.

It was observed that the interaction of a chlorodialkylaminophenylborane with an excess of piperidine resulted in the formation of bis(piperidino)phenylborane indicating that it is more stable than the unsymmetrical dialkylaminopiperidinophenyl borane.



In contrast the interaction of chloropiperidinophenylborane and an excess of

* For part XIX see Ref. 1.

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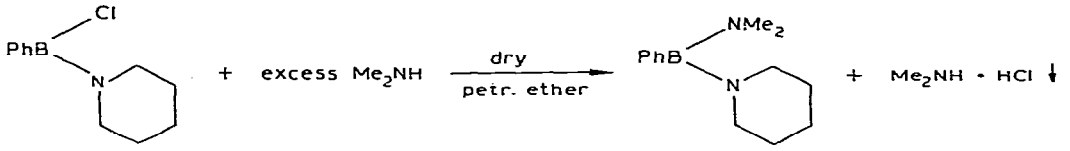
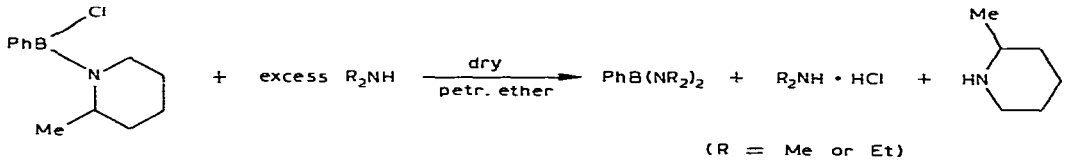
a secondary amine resulted in the formation of the required product.

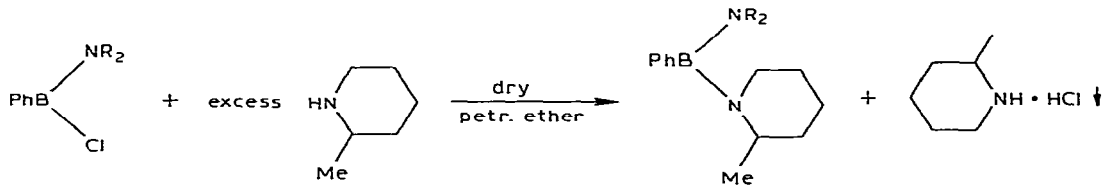


Similarly the interaction of chloro(2-methylpiperidino)phenylborane and an excess of a secondary amine resulted in the formation of the corresponding bis(dialkylamino)phenylborane.

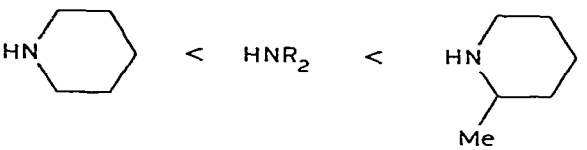


(R = Me or Et)

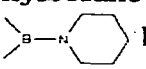
However the dialkylamino(2-methylpiperidino)phenylboranes were obtained via the interaction of a chlorodialkylaminophenylborane with an excess of 2-methylipiperidine.

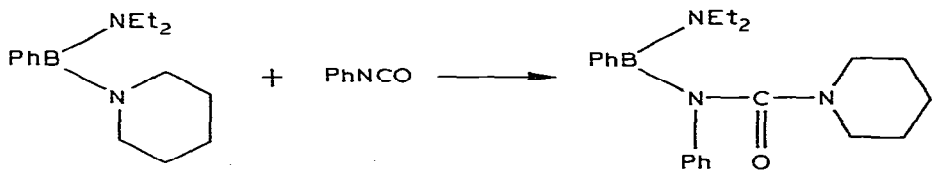


The above observations indicate that an order increasing steric hindrance of the amines is:



(R = Me or Et)

The results from aminoboration reactions of phenylisocyanate support the above order [4]. It is interesting to note that the interaction of phenylisocyanate and diethylaminopiperidinophenylborane results in the insertion reaction taking place with the less hindered  bond.



In contrast it is found that the interaction of phenylisocyanate and diethyl-

amino-2-methylpiperidinophenylborane results in the insertion reaction involving the $\geq B—NEt_2$ bond.

Alkylaminopiperidinophenylboranes were obtained from the reaction between a primary amine and a chloropiperidinophenylborane in the presence of triethylamine.

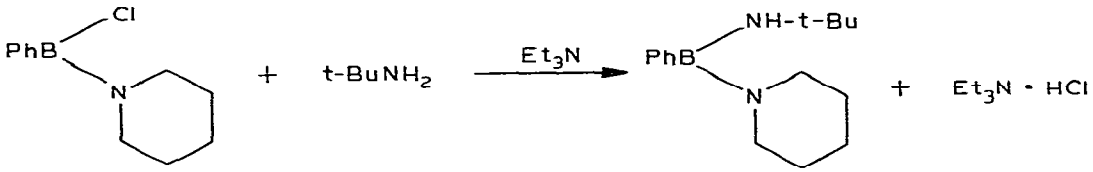


Table 2 lists the boiling points and analytical data for each compound prepared.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the alkylamino- and dialkylamino piperidinophenylboranes indicate restricted rotation about the $\geq BNHR$ or $\geq BNR_2$ bond. The spectra of dimethylaminopiperidinophenylborane (Fig. 1) and t-butylaminopiperidinophenylborane (Fig. 2) illustrate the point. In the case of the former compound and also dimethylamino-2-methylpiperidinophenylborane the dimethylamino group appears as a 1/1 doublet (with an isomer shift of about 15 Hz in each case) indicating restricted rotation about the $\geq B—NMe_2$ bond. In the case of the latter compound and t-butylamino-2-methylpiperidinophenylborane the t-butylamino group appears as a 1/1 doublet (with an isomer shift of 17 Hz). The observation of a symmetrical doublet suggests that the restricted rotation about the $\geq BNHBu^t$ bond arises from $p_\pi—p_\pi$ bonding and not steric hindrance. If the barrier to rotation was mainly a steric one then one rotamer would be expected to be more stable than the other resulting in an unsymmetrically doublet in the spectrum which is not observed.

(Continued on p. 148)

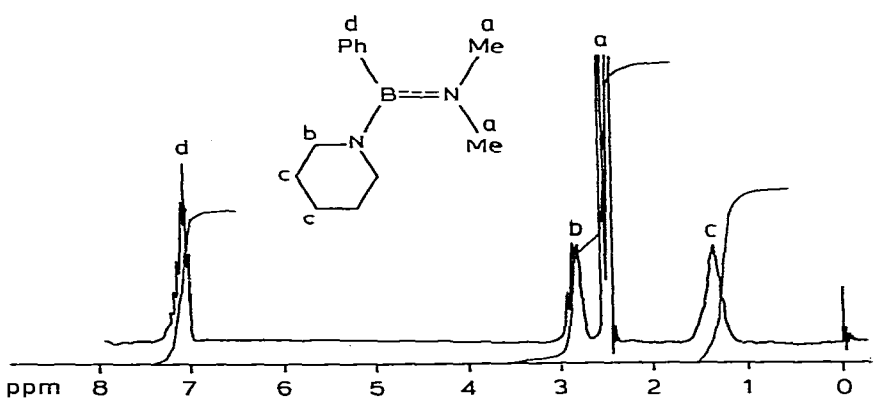
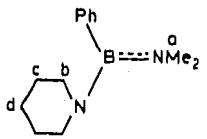
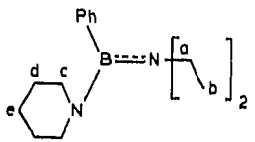
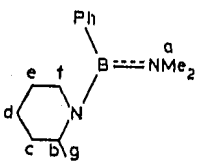
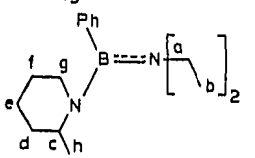
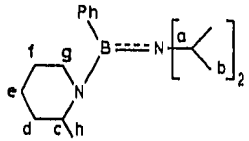
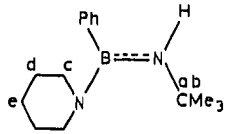
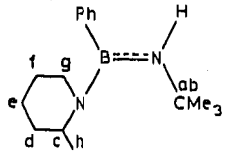
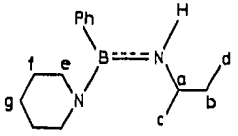


Fig. 1. ^{1}H NMR spectrum of $PhBNMe_2N$.

TABLE 1

^{13}C NMR DATA OF ALKYLAMINO- AND DIALKYLAMINO-PIPERIDINOPHENYLBORANES

Compound	C(1)	*o*	*p*	*m*	a	b	c	d	e	f	g	h
	141.6	133.5	127.3	127.3	41.1	49.3	28.3	25.6				
	0	0	0	0	0	0	0	0				
	142.0	133.0	127.3	127.3	42.3 41.7	15.7 15.4	49.3	28.3	25.5			
	0	0	0	0	15	6	0	0	0			
	142.2	133.0	127.3	127.3	42.5 42.2	48.2	31.9	19.7	28.6	41.0	18.0	
	0	0	0	0	8	0	0	0	0	0		
	142.9	132.6	126.9	127.3	42.2 41.7	18.1 17.7	48.3	31.8	19.5	28.5	42.2	15.5
	0	0	0	0	12	9	0	0	0	0	0	0

	145.0	133.2	126.7	126.7	48.1	25.5	46.8	31.8	19.5	28.6	42.2	17.6
	0	0	0	0	46.8 30	24.8 18	0	0	0	0	0	0
	142.4	132.3	126.9	126.3	49.1	33.6	47.1	27.8	25.7			
	0	0	0	0	0	0	0	0	0			
	142.7	132.3	127.0	126.4	48.9	33.7	46.8	31.7	19.9	27.8	39.6	17.2
	0	0	0	0	0	33.1 15	0	0	0	0	0	0
	141.0	132.1	127.4	126.7	49.3	33.4	25.2	10.7	47.4	28.0	25.8	
	0	0	0	0	0	0	0	0	0	0	0	

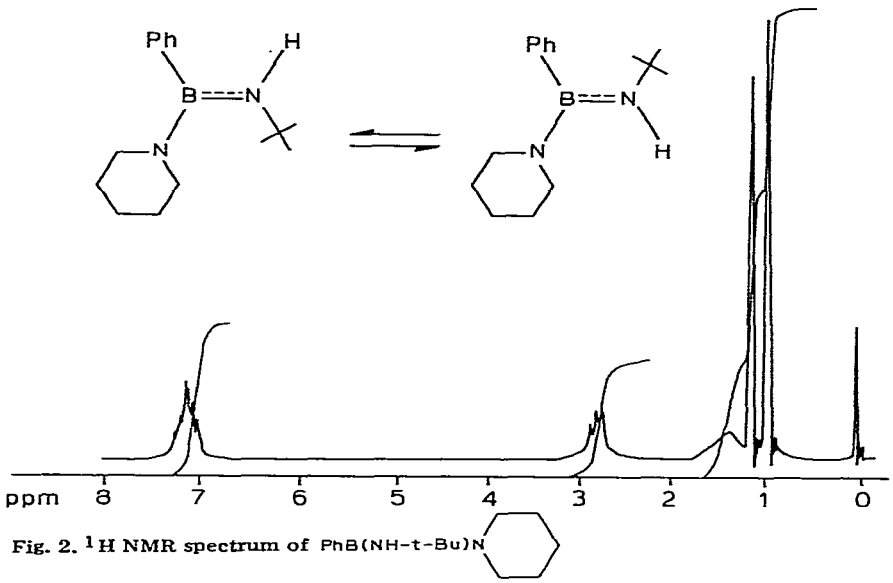


Fig. 2. ^{1}H NMR spectrum of PhB(NH-t-Bu)N

^{13}C NMR Spectra

The assignments for the ^{13}C NMR spectra recorded at ambient temperature are recorded in Table 1. Only in the case of t-butylamino-2-methylpiperidinophenylborane were we able to obtain evidence indicating restricted rotation about the $\geq$BNHR bond. In contrast the spectra of all the dialkylamino derivatives indicate that restricted rotation in this class of compound is exclusively about the $\geq B-NR_2$ bond. At room temperature the ^{13}C NMR spectrum of diethylaminopiperidinophenylborane (Fig. 3) contains well resolved doublets for the methylene and methyl carbon atoms of the diethylamino group and

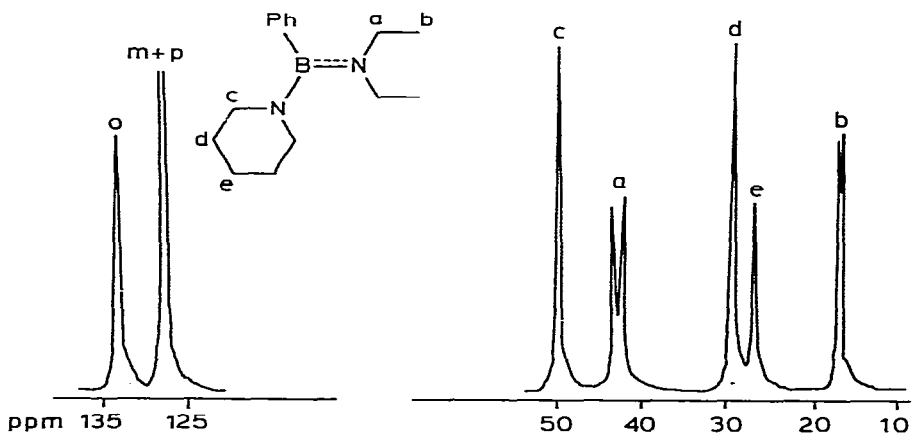
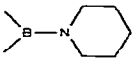


Fig. 3. ^{13}C NMR spectrum of diethylamino(piperidino)phenylborane.

singlets for the carbon atoms of the piperidino group. Perhaps the piperidino group is twisted out of the plane since we were unable to observe any evidence for p_π—p_π-bonding involving the  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 PS 100 FT spectrometer; line positions are relative to internal TMS.

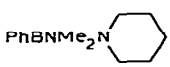
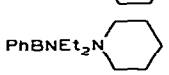
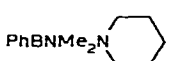
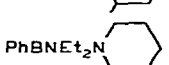
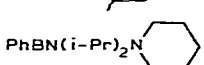
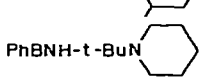
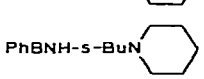
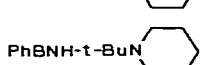
Two methods were used for the synthesis of alkylamino- and dialkylamino-piperidinophenylboranes and an example of each is reported in full. Table 2 lists the boiling points and analytical data for each compound prepared.

Preparation of diethylamino-2-methylpiperidinophenylborane

Chlorodiethylaminophenylborane (3.2 g, 0.016 mol) and 2-methylpiperidine (2.8 g, 0.033 mol) were refluxed in benzene for 3 h. After filtration to remove 2-methylpiperidine hydrochloride and removal of solvent from the filtrate the residue on distillation afforded diethylamino-2-methylpiperidinophenylborane (2.4 g, 60%) b.p. 100°C/0.02 mmHg, (Found: C, 74.4; H, 11.4; N, 10.8%. $C_{16}H_{27}H_2B$ calcd.: C, 74.4; H, 10.5; N, 10.9%).

TABLE 2

ALKYLAMINO- AND DIALKYLAMINO-PIPERIDINOPHENYLBORANES

Compound	Yield (%)	B.P. (°C/mmHg)	Analysis (Found (calcd.) (%))		
			C	H	N
	70	110/0.5	71.7 (72.2)	9.7 (9.7)	12.2 (13.0)
	70	110/0.3	74.2 (73.8)	10.6 (10.3)	11.0 (11.5)
	70	100/0.2	73.2 (73.0)	10.4 (10.0)	11.3 (12.2)
	60	100/0.2	74.4 (74.4)	11.4 (10.5)	10.8 (10.9)
	65	120/0.1	75.9 (75.5)	11.2 (10.8)	9.6 (9.8)
	65	95/0.1	73.9 (73.8)	10.4 (10.2)	11.5 (11.5)
	70	105/0.6	73.4 (73.8)	10.7 (10.2)	11.2 (11.5)
	70	105/0.2	73.5 (74.4)	11.5 (10.5)	11.3 (10.9)

Preparation of S-butylaminopiperidinophenylborane

Chloropiperidinophenylborane (8.30 g, 0.04 mol), s-butylamine (2.92 g, 0.04 mol) and triethylamine (4.05 g, 0.04 mol) were refluxed in benzene for 6 h. After filtration to remove triethylamine hydrochloride and removal of solvent from the filtrate the residue afforded on distillation s-butylaminopiperidinophenylborane (7.01 g, 70%) b.p. 105°C/0.6 mmHg, (Found: C, 73.4; H, 10.7; N, 11.2. $C_{15}H_{25}N_2B$ calcd.: C, 73.8; H, 10.2; N, 11.5%).

Acknowledgement

We thank Dr. D. Smith for recording the NMR Spectra.

References

1 R.H. Cragg and R.J. Miller, J. Organometal. Chem., 235 (1982) 135.
2 B.M. Mikhailov and V.A. Dorokhov, J. Gen. Chem. U.S.S.R., 31 (1961) 3504.
3 M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, Metal and Metalloid Amides, Ellis Horwood Ltd., 1980.
4 R.H. Cragg and T.J. Miller, J. Chem. Soc. Dalton. Submitted for publication.