Journal of Organometallic Chemistry, 243 (1983) 387–392
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOBORON COMPOUNDS

XXI *. DIALKYLAMINOETHANETHIOPHENYLBORANES

R. HARRY CRAGG * and TIM J. MILLER

The Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent (Great Britain)

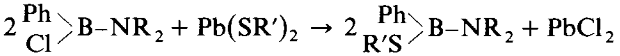
(Received September 13th, 1982)

Summary

The synthesis and properties of a series of dialkylaminoethanethiophenylboranes, $PhB(SEt)NR_2$, are reported. The ^{13}C NMR spectra of these compounds indicate restricted rotation about the $\rangle B{-}NR_2$ bond.

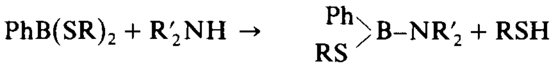
Over the last few years we have been evaluating the use of ^{13}C NMR spectroscopy with a view to obtaining a greater understanding of the factors affecting the nature of bonding in organoboranes [1]. This present paper reports the preparation and properties of some dialkylaminoethanethiophenylboranes. In addition the ^1H and ^{13}C NMR spectra of the compounds are discussed.

Two methods were used for the synthesis of dialkylaminoethanethiophenylboranes. High yields of the required compound were achieved from the interaction of a chlorodialkylaminophenylborane and lead ethanethiolate. Lead thiolates are valuable reagents for the synthesis of thioboranes [2]. They are easier to handle than the volatile mercaptans. In addition the reaction involving lead thiolates can be readily monitored and the lead chloride produced is easily separated by filtration from the reaction mixture.



$$2\,{}^{Ph}_{Cl}\rangle B{-}NR_2 + Pb(SR')_2 \rightarrow 2\,{}^{Ph}_{R'S}\rangle B{-}NR_2 + PbCl_2$$

An alternative method of synthesis involved the interaction of bis(ethanethio)phenylborane and a secondary amine.



$$PhB(SR)_2 + R'_2NH \rightarrow {}^{Ph}_{RS}\rangle B{-}NR'_2 + RSH$$

The dialkylaminoethanethiophenylboranes are thermally stable and were purified

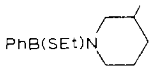
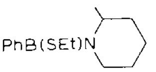
---

[*] For part XX see Ref. 1.

0022-328X/83/0000–0000/$03.00

TABLE 1

DIALKYLAMINOETHANETHIOPHENYLBORANES

Compound	Yield (%)	B.P. (°C/mmHg)	Analysis (Found (Calcd.) (%))		
			C	H	N
PhB(SEt)NMe$_2$	70	68/0.1	62.1	7.8	7.4
			(62.2)	(8.3)	(7.3)
PhB(SEt)NPr$^i_2$	60	88/0.1	67.0	8.6	5.7
			(67.5)	(9.6)	(5.6)
PhB(SEt)NBu$^s_2$	50	110/0.1	68.9	10.1	4.8
			(69.3)	(10.1)	(5.1)
	82	105/0.1	69.0	9.0	6.4
			(68.0)	(8.9)	(5.7)
	80	105/0.1	68.8	8.9	6.2)
			(68.0)	(8.9)	(5.7)

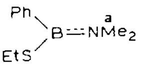
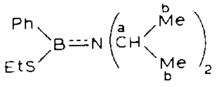
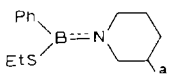
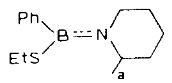
by distillation under reduced pressure. The analytical data and boiling points of the compounds prepared are given in Table 1.

^{1}H NMR spectra

We have previously demonstrated that p_π–p_π bonding between boron and sulphur is much less pronounced than p_π–p_π bonding between boron and oxygen [3]. It is therefore to be expected that the p_π–p_π bonding between boron and nitrogen would

TABLE 2

^{1}H NMR ISOMER SHIFTS FOR DIALKYLAMINOETHANETHIOPHENYLBORANES

Compound	Isomer shifts (Hz)	
	a	b
	20	
	0	40
	10	
	10	

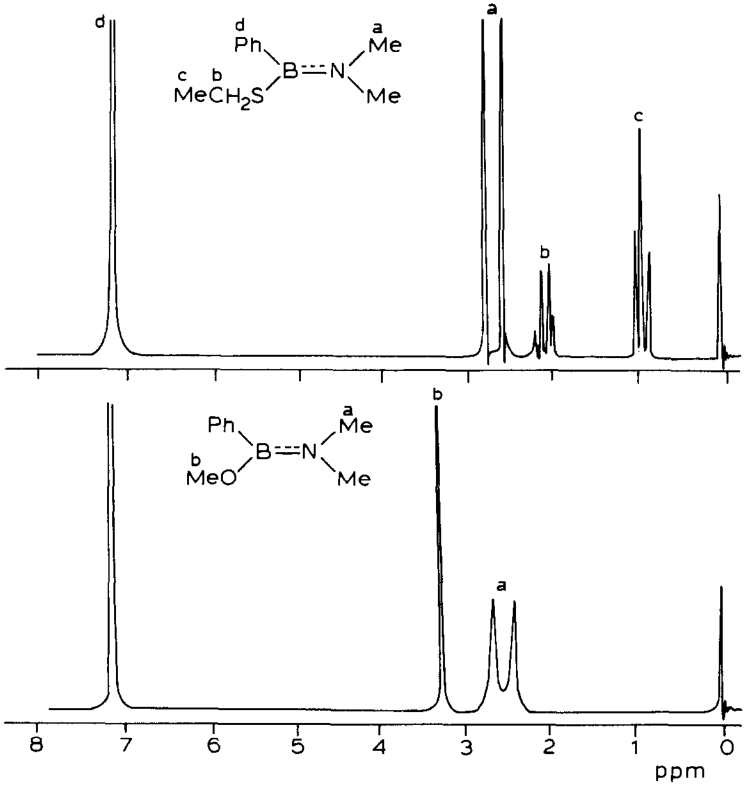


Fig. 1. A comparison of the ^{1}H NMRspectra of $PhBNMe_2OMe$ and $PhBNMe_2SEt$.

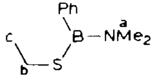
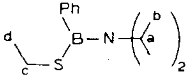
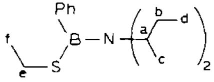
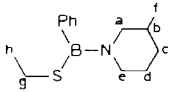
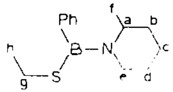
be greater in alkylthiodialkylaminophenylboranes than alkoxydialkylaminophenylboranes. A study of the ^{1}H NMR spectra of both types of organoborane supports this generalisation. Signals arising from non-equivalence, due to restricted rotation, are broad and close to coalescence in the case of the alkoxy compound whilst the alkylthio compounds show the non-equivalence as well resolved doublets. This is illustrated by comparing the room temperature (23°C) ^{1}H NMR spectra of dimethylaminoethanethiophenylborane with dimethylamino(methoxy)phenylborane (Fig. 1). In both cases the methyl protons of the dimethylamino group appear as doublets due to restricted rotation about the boron–nitrogen bond. However, the doublet observed in the thioborane is sharp and well resolved but in the case of the alkoxyborane the doublet shows considerable broadening and is close to coalescence. This observation indicates a more rapid rotation about the boron–nitrogen bond in the alkoxyborane. Table 2 summarises the ^{1}H NMR shifts for the alkylthiodialkylaminophenylboranes.

^{13}C NMR spectra

By comparison with the ^{1}H NMR spectra the ^{13}C NMR spectra are much more informative. Isomer shifts are more readily obtained from these spectra than the corresponding ^{1}H NMR spectra. The spectrum of ethanethio(3-methylpiperidino)phenylborane (Fig. 2) illustrates the importance of ^{13}C NMR spectroscopy as a

TABLE 3

^{13}C NMR DATA FOR DIALKYLAMINOETHANETHIOPHENYLBORANES

Compound	C(1)	*o*	*m*	*p*	a	b	c	d	e	f	g	h
	139.2 0	131.2 0	127.8 0	127.8 0	41.3 39.4 48.0	23.7 0	17.7 0					
	141.4 0	130.7 0	127.5 0	126.8 0	50.6 47.1 88.0	22.7 22.4 6.0	24.0 0	17.4 0				
	141.5 0	130.8 0	127.5 0	126.8 0	57.3 53.6 88.5	29.5 0	21.2 19.9 20.0	12.3 11.8 9.2	24.1 0	17.4 0		
	139.4 0	131.1 0	127.7 0	127.3 0	56.9 55.6 33.6	32.9 32.4 12.2	33.6 0	27.4 26.6 21.4	49.9 48.4 33.6	19.3 19.1 6.1	23.4 0	17.6 0
	139.9 0	131.0 130.7 9.2	127.8 0	127.3 0	50.6 49.4 27.5	31.8 31.2 18.3	19.4 0	28.0 27.5 15.3	43.3 41.9 33.6	17.6 0	23.4 0	17.1 0

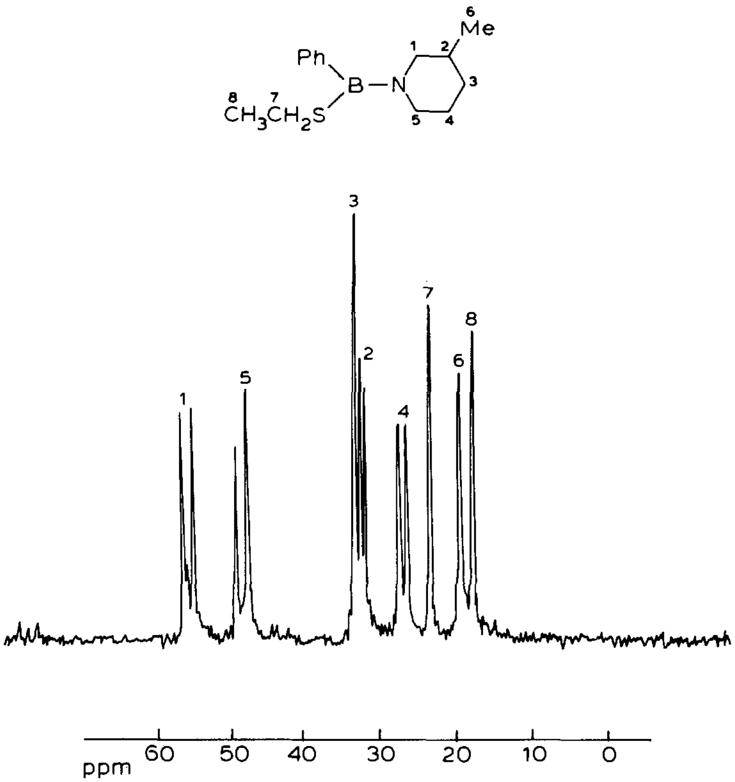
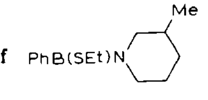


Fig. 2. ^{13}C NMR spectra of  .

technique for studying restricted rotation in organoboranes. In the aliphatic region of the spectrum five of the six carbon atoms of the 3-methylpiperidino group are observed as well defined doublets corresponding to the *cis* and *trans* rotomers. The ^{13}C NMR assignments for the alkylthiodialkylaminophenylboranes are given in

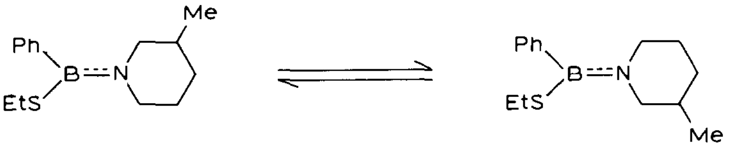


Table 3. The chemical shift (in ppm) of a signal arising from a particular carbon in one rotomer, (δr_1), is given first followed by the chemical shift of the same nucleus in the other rotomer, (δr_2), and the isomer shift in Hz. The C(1) resonances were obtained by recording the spectrum of the compound in the absence of a solvent.

One interesting feature in the spectrum of ethanethio(2-methylpiperidino)phenylborane is the observed splitting of the *ortho* carbon signal. Evidently the methyl group in the 2 position of the piperidino ring, which is demonstrated by models to be directed at the other boron substituents, is responsible for the non-equivalence of the *ortho* carbon atoms.

The ^{13}C NMR spectra demonstrate restricted rotation about the boron nitrogen bond in alkylthiodialkylaminophenylboranes.

Experimental

The ^{1}H NMR spectra were recorded on a Perkin–Elmer R10 spectrometer and the ^{13}C NMR spectra were recorded on a JEOL-PS-100FT spectrometer; line positions are relative to internal TMS. Two general methods were used for the synthesis of dialkylaminoethanethiophenylboranes and an example of each method is reported in full. Bis(ethanethio)phenylborane [4] and chlorodialkylaminophenylboranes [5] were obtained by previously published methods. The usual precautions were taken as is normal for air sensitive starting materials and products.

Preparation of diisopropylaminoethanethiophenylborane

Lead ethanethiolate (7.24 g, 0.022 mol) was added to petroleum ether, b.p. 40–60°C, (50 cc). Chlorodiisopropylaminophenylborane (8.92 g, 0.04 mol), dissolved in petroleum ether, (25 cc), was added slowly with stirring. The mixture was refluxed for 3 h and filtered to remove the lead chloride. After removal of the solvent from the filtrate, under reduced pressure, the residue afforded on distillation diisopropylaminoethanethiophenylborane (5.98 g, 60%) b.p. 88°C/0.1 mmHg. (Found: C, 67.0; H, 8.6; N, 5.7. $C_{14}H_{24}NSB$ calcd.: C, 67.5; H, 9.6; N, 5.6%).

Preparation of ethanethio(3-methylpiperidino)phenylborane

Bis(ethanethio)phenylborane (4.2 g, 0.02 mol) was cooled to −78°C and dry 3-methylpiperidine (1.98 g, 0.02 mol) was added slowly with stirring. The mixture was set aside to attain room temperature and then gently refluxed for 3 h. After removal of the volatile ethane thiol the residue on distillation afforded ethanethio(3-methylpiperidino)phenylborane (4.0 g, 82%), b.p. 105°C/0.1 mmHg. (Found: C, 69.0; H, 9.0; N, 6.4. $C_{14}H_{22}$ NSB calcd.: C, 68.0; H, 8.9; N, 5.7%).

Acknowledgement

We thank the S.R.C. for a grant to T.J.M. and Dr. D. Smith for recording the NMR spectra.

References

1 R.H. Cragg and T.J. Miller, J. Organometal. Chem., 235 (1982) 143.
2 R.H. Cragg, J.P.N. Husband and A.F. Weston, J. Inorg. Nucl. Chem., 35 (1973) 3685.
3 R.H. Cragg, J.P.N. Husband and P.R. Mitchell, Org. Mag. Res., 4 (1972) 469.
4 R.H. Cragg, M.F. Lappert and B.P. Tilley, J. Chem. Soc., A, (1967) 947.
5 R.H. Cragg and T.J. Miller, J. Organometal. Chem., 232 (1982) 201.