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Preliminary communication

PHENYLBORANES. DIRECT OBSERVATION OF ^{13}C NUCLEAR RESONANCES OF CARBON ATOMS BONDED DIRECTLY TO BORON

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Summary

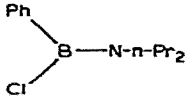
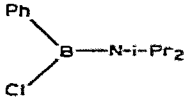
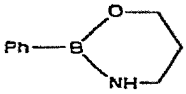
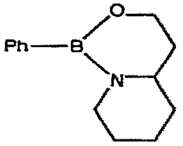
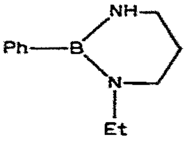
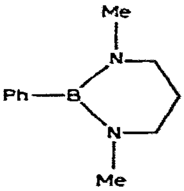
Neat samples of a wide variety of phenylboranes at room temperature exhibit well resolved resonances for carbon atoms bonded directly to boron, in contrast to their solutions where such resonances are either extremely broad or entirely undetectable.

Several workers have reported difficulty [1—4] in observing ^{13}C NMR signals due to carbons bonded directly to boron, unless the effect of the boron quadrupole moment is removed, as for example in the tetraphenylborate anion [5], where the electric field gradient at boron is zero. In many cases the resonances are severely broadened [1—3], even to the point of being undetectable in some [4], due to partial decoupling of the boron-11 (I 3/2) carbon-13 interaction.

We report here some results, obtained in the course of a ^{13}C NMR study of restricted rotation about B—N bonds [6], which show that chemical shifts of carbon atoms bonded directly to boron may conveniently be obtained by making measurements on neat samples. Niedenzu has recently reported [3] that recording ^{13}C NMR spectra at low temperatures (ca. —40°C) facilitates detection of directly bonded carbons in some phenylboranes. We reasoned, however, that the increased molecular correlation time leading to boron-decoupling achieved in this way might more conveniently and quickly be achieved by running liquid samples neat. Gratifyingly, samples which showed no detectable aromatic C-1 resonances in solution at room temperature had these signals well resolved in the spectra of neat samples run at room temperature. A typical result is shown in Fig. 1, and others are summarised in Table 1. A comparison of shifts obtained from neat samples with those obtained from solutions revealed no evidence for molecular association (dimerisation etc.) in the former, so we may conclude that the observed phenomena arise solely from increased sample viscosity. The C-1 shifts, obtained without the need for time-consuming low temperature measurements, may therefore be relied on for the purposes of structure determination in organoborane derivatives. The assignments of the *ortho*- and *para*-carbons in I—VI are in conflict with analogous ones reported [3] by Niedenzu et al., but ours are more reasonable from the point of view of accepted substituent effects. They were confirmed by off-resonance decoupled and selectively decoupled ^{13}C-{^{1}H}and by undecoupled ^{13}C spectral measurements.

TABLE 1

^{13}C NMR SHIFT DATA

Compound		Aromatic carbons^{a,b}			
		C-1	*ortho*	*meta*	*para*
I		139.2 (—)^c	132.9 132.0	128.4 127.6	129.4 128.5
II		141.8	132.3	128.6	129.2
III		136.8 (—)^c	133.4 (132.1)	128.5 (127.5)	130.5 (129.5)
IV		138.3 (—)^c	134.7 (133.2)	128.3 (127.3)	129.5 (128.4)
V		141.6 (—)^c	133.1 (132.1)	128.4 (127.4)	128.4 (127.4)
VI		141.1^d	133.1	128.3	127.7

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[a] Only aromatic carbons are shown: the resonances due to the aliphatic carbons were in agreement with the proposed structures, but complicated in some cases as the result of restricted rotation about the B—N bond. [b] The shifts of neat samples (($(CD_3)_2SO$/TMS capillary lock/reference) are given. [c] Figures in parenthesis are for ca. 30% $CDCl_3$ solutions, referenced to internal TMS. [d] Slightly broad at room temperature.

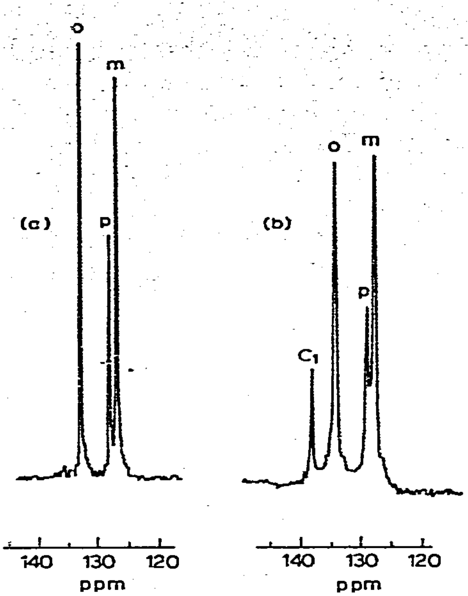

Fig. 1. $^{13}C-\{^1H\}$FT NMR spectrum (aromatic region) of compound IV; (a) in $CDCl_3$ solution at room temperature; (b) neat at room temperature. The pulse angle was ca. 22°, repetition rate 2 s.

References

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