Novel Organoborane Compound Type from the Reaction of Diphenylbromoborane with Di-isopropylcarbamoyl-lithium

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Summary Addition of diphenylbromoborane to di-isopropylcarbamoyl-lithium at low temperature followed by warming to ambient, and passage through silica gives 5-(di-isopropyliminio)-2,2,4,4-tetraphenyl-2,4-diborata-1-oxa-3-oxoniacyclopentane (**2**).

DURING attempts to obtain potentially 'superelectrophilic' compounds for study, we found[1] that the only report of the preparation of an acylborane was in fact incorrect. We decided to investigate reaction (A) as a possible approach to compound (**1**), and developed a new synthesis of di-isopropylcarbamoyl-lithium free from di-isopropylamine in order to do so.[2] We have not obtained (**1**) from this reaction, but instead we have identified another highly interesting new compound type.

$$\mathrm{R_2BBr + LiCONPr^i_2 \rightarrow \underset{(\mathbf{1})}{R_2BCONPr^i_2} + LiBr} \qquad \text{(A)}$$

Addition of diphenylbromoborane to a solution of di-isopropylcarbamoyl-lithium[2,3] at −78 °C or below in tetrahydrofuran (THF) alone[3] or in THF–ether–hexane,[2] followed by warming to room temperature and removal of solvent, gave a viscous air-sensitive oil with an intense carbonyl absorption at *ca.* 1650 cm^{-1}, whose properties suggested a more complex structure than that indicated for (**1**). However, when an ether solution of the carbonyl compound was washed with water, dried (MgSO$_4$), and evaporated, and the resultant solid chromatographed on silica, a solid (**2**) (> 80% overall yield), which could be recrystallized from ether–hexane, was obtained.

Compound (**2**) shows a fairly intense absorption at 1580 cm^{-1} in its i.r. spectrum, a major ion at *m/e* 458 in its mass spectrum, substantially only two peaks in its field desorption mass spectrum‡ [at *m/e* 475 (molecular ion $M^{\cdot+}$ and 398 ($M^{\cdot+}$ − Ph·)], and the following signals in its ^{1}H n.m.r. spectrum (CDCl$_3$); τ 2·78 (20H, overlapping signals, but showing separation into two groups in the ratio *ca.* 2:3); 5·84 (1H, exchangeable); 6·06 (1H, septet); 6·50 (1H, septet); 8·42 (6H, doublet); and 9·30 (6H, d). The ^{13}C n.m.r. spectrum shows the phenyl groups to be separated into two categories, and both the *ipso* carbon atoms give very small and broad signals, suggesting that all phenyl groups are attached to boron. This is confirmed upon oxidation of (**2**) with alkaline hydrogen peroxide, which yields at least 3·6 mol of phenol per mol of (**2**) according to g.l.c. estimation. The ^{11}B n.m.r. spectrum (CDCl$_3$) shows a single, very broad (1500 Hz) signal centred around −9·34 p.p.m. (*i.e.*, 9·34 p.p.m. upfield from BF$_3$–Et$_2$O)§ which has a flattish top suggestive of two overlapping peaks, but which could not be resolved into individual boron signals even on cooling. This suggests that both boron atoms might be tetrahedrally co-ordinated. All this information is consistent with a hydroxide adduct of ion (**3**), and preliminary results of an *X*-ray crystal structure determination show that the hydroxide bridges both boron atoms, as indicated in structure (**2**). Microanalysis of (**2**) is entirely consistent with the elemental composition $C_{31}H_{35}B_2NO_2$.

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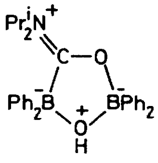
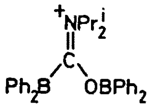
§ Using the new convention for ^{11}B n.m.r. chemical shift signs adopted at the IMEBORON III meeting, Ettal, 1975.



(2)



(3)

Compound (**2**) is the first example of this new class of compounds. Furthermore, it forms complexes with some simple amides, an intriguing property which we are investigating further.

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[2] K. Smith and K. Swaminathan, *J.C.S. Chem. Comm.*, 1976, 387; A. S. Fletcher, K. Smith, and K. Swaminathan, *J.C.S. Perkin I*, 1977, 1881.

[3] R. R. Fraser and P. R. Hubert, *Canad. J. Chem.*, 1974, **52**, 185.