Reinvestigation of the Preparation of 'Borylketones' (Acyldialkylboranes)

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Summary The report that benzoyldibutylborane, Bu_2BCOPh, has been prepared is wrong; the product is actually a mixture of benzyloxydibutylborane and benzyl benzoate.

Compounds of the type $R^1{}_2BCOR^2$ are of interest to us as potential 'superelectrophiles'.† Such compounds have been postulated as intermediates in the carbonylation of organoboranes,[1] but have not been isolated. Apparently they are highly reactive and rapidly rearrange. On the other hand, Schmid and Nöth claim to have isolated (**1**) by route (A),[2] but no chemical reactions to support the assigned structure were reported.

$$\mathrm{Bu_2BCl} \xrightarrow{\text{Na-K}} \mathrm{Bu_2BK} \xrightarrow{\text{PhCOCl}} \underset{(\mathbf{1})}{\mathrm{Bu_2BCOPh}} \qquad \text{(A)}$$

We have repeated (in duplicate) the work of Schmid and Nöth and have obtained a product with the reported characteristics (Table).

The product showed none of the properties expected for a compound of structure (**1**). For example, oxidation–hydrolysis with H_2O_2 and NaOH gave n-butanol (**2**) and benzyl alcohol (**3**) (mol. ratio *ca.* 1·5:1) as the major products, whilst hydrolysis with aqueous NaOH gave (**3**) in similar yield, but the quantity of (**2**) was considerably less than on oxidation. These results suggested that benzyloxydibutylborane, Bu_2BOCH_2Ph (**4**), could be a major component of the product, and this was confirmed by comparison of the i.r., ^1H n.m.r., and ^{11}B n.m.r. spectra, and g.c. with authentic (**4**).‡

Table. Properties of the product obtained by route (A).

	According to ref. 2	This report
B.p.	110 °C at 1 mmHg	102 °C at 0·7 mmHg
ν_{max}	1725 cm^{-1}	1725 cm^{-1}
^{11}B n.m.r. signal (relative to $BF_3.OEt_2$)	−53 p.p.m.	−52·5 p.p.m.[a]

[a] A second signal was observed at −31·5 p.p.m. which is probably due to an autoxidation product derived from (**4**).

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† We believe, based on circumstantial evidence, that compounds with adjacent atoms possessing vacant orbitals, or with resonance contributions from such structures, may show greatly enhanced electrophilic properties.

‡ This was prepared by a method analogous to that reported for methyl borinates (H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, 1972, **94**, 2112).

The minor component, which possessed the carbonyl group, was isolated by chromatography (on silica) of the material obtained upon hydrolysis of the product with water. It was identical by i.r. and ^{1}H n.m.r. spectra, g.c., and mass spectrum with authentic benzyl benzoate (**5**). The presence of (**5**) in the product prior to hydrolysis was confirmed by ^{1}H n.m.r. spectroscopy and g.c. Thus, the material which was previously assigned structure (**1**)[2] is, in fact, a mixture consisting of benzyloxydibutylborane and benzyl benzoate (mol. ratio *ca.* 4:1 by ^{1}H n.m.r. spectroscopy).

We have shown that (**5**) is produced by reaction of authentic (**4**) with PhCOCl. However, the production of (**4**) is inconsistent with the structure Bu_2BK for the reagent obtained by reaction of Bu_2BCl with Na–K alloy (route A). Our results support an earlier conclusion[3] that this reagent contains B–H and not B–K bonds. Its application in organoborane synthesis[4] remains unexplored.

The report that an acylborane, Bu_2BCOPh, is a stable, isolable compound may now be discounted. There is as yet no evidence which conflicts with our prediction that such a compound should be highly reactive and probably unstable at normal temperatures.

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[3] R. Köster and G. Benedikt, *Angew. Chem. Internat. Edn.*, 1963, **2**, 219.

[4] K. Smith, *Chem. Soc. Rev.*, 1974, **3**, 443.