Reaction of Dibutylchloroborane with Sodium–Potassium Alloy followed by Benzoyl Chloride; A Reinvestigation and Discussion [1]

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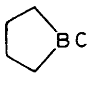
The title reaction does not give the previously claimed benzoyldibutylborane. Instead, reduction of benzoyl chloride occurs, leading to benzyloxydibutylborane, some of which reacts further with benzoyl chloride to give benzyl benzoate. The characteristics reported for ' benzoyldibutylborane ' are matched by a mixture of these two compounds. The work also raises doubts about the nature of the reagent previously designated as ' Bu_2BM '.

IN 1952 Auten and Kraus [2] prepared a reagent by the action of sodium–potassium alloy on dibutylchloroborane in diethyl ether [reaction (1)]. The exact nature of the reagent (*i.e.* the solution after removal of ether-insoluble material) was unknown (boron : alkali-metal ratio *ca.* 5 : 3), but the presence of nucleophilic BBu_2 units was said to be demonstrated by its reaction with iodomethane [reaction (2)], so the designation ' Bu_2BM ' was adopted. Parsons and his co-workers [3] carried out a similar reaction with CF_3I in triethylamine [reaction (3)]. However, Köster and Benedikt [4] could obtain no evidence for the presence of boron–metal bonds in the products of reactions of dialkylchloroboranes with alkali metals. Instead, they identified metal-free compounds, such as (2) from (1). Pasto and Wojtkowski [5] obtained only token yields of the appropriate trialkylboranes when they reinvestigated reactions such as (2), obtaining instead products indicative of one-electron-transfer reactions. However, neither could they support the work of Köster and Benedikt,[4] because hydrolysis of their reagent with D_2O, followed by oxidation, gave undeuteriated butanol.[5] Finally, Schmid and Nöth [6] employed ' Bu_2BM ' in the synthesis of

$$BBu_2Cl \xrightarrow{\text{Na-K}} MCl + BBu_2^{\bullet} \xrightarrow{\text{Na-K}} M(BBu_2) \quad (1)$$

$$M(BBu_2) + MeI \longrightarrow BMeBu_2 + MI \quad (2)$$

$$M(BBu_2) + CF_3I \xrightarrow{NEt_3} B(CF_3)Bu_2 + MI \quad (3)$$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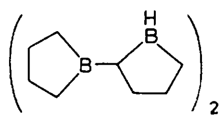
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[1] Preliminary communication, K. Smith and K. Swaminathan, *J.C.S. Chem. Comm.*, 1975, 719.

[2] R. W. Auten and C. A. Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 3398.

[3] T. D. Parsons, J. M. Self, and L. H. Schaad, *J. Amer. Chem. Soc.*, 1967, **89**, 3446; T. D. Parsons, E. D. Baker, A. B. Burg, and C. L. Juvinall, *ibid.*, 1961, **83**, 250.

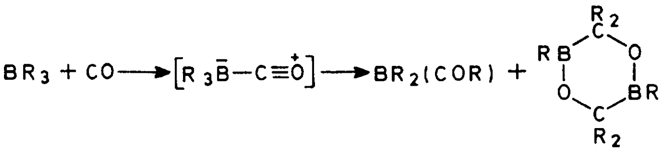
[4] R. Köster and G. Benedikt, *Angew. Chem. Internat. Edn.*, 1963, **2**, 219; *ibid.*, 1964, **3**, 515; R. Köster, G. Benedikt, and H. W. Schrötter, *ibid.*, p. 514.

[5] D. J. Pasto and P. W. Wojtkowski, *J. Organometallic Chem.*, 1972, **34**, 251.

acyldialkylboranes [*e.g.* reaction (4)], which appeared to confirm the original claims of Auten and Kraus[2] concerning the presence of nucleophilic BBu_2 units in the reagent.

$$M(BBu_2) + PhCOCl \longrightarrow \underset{(3)}{BBu_2(COPh)} + MCl \quad (4)$$

We have become interested in the properties of acyldialkylboranes, but we were surprised at the apparent stability of (3). After all, acyldialkylboranes are postulated as intermediates in the carbonylation of organoboranes (Scheme),[7] but in these reactions the



(4)

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first isolable intermediates are 1,4-dioxa-2,5-diboracyclohexanes (4).[8] In an attempt to clear up the anomaly concerning the stability of (3), and to gain some insight into the nature of the reagent designated ' Bu_2BM ', we have repeated the work of Schmid and Nöth.[6]

RESULTS AND DISCUSSION

Preparation of ' Bu_2BM '.—On addition of dibutylchloroborane to vigorously stirred sodium–potassium alloy in diethyl ether the solution became purple and a purple deposit formed. The supernatant still contained halide, and on hydrolysis was not alkaline. This was the case even after stirring for 6 h at room temperature. However, after 9 h the solution had become pale brown, and on hydrolysis produced only a faint turbidity with acidified Ag[NO_3]. Estimation of the alkali liberated on hydrolysis indicated the presence of *ca.* 20% of the theoretical alkali-metal content, assuming the hydrolysis shown in reaction (5). On prolonged stirring the solution became darker and the alkali-metal content increased (40% after 2 d; 50%, 5 d) to a maximum of 60%, achieved after *ca.* 10 d. Repeated experiments gave very similar results.

$$M(BBu_2) + 2H_2O \longrightarrow BBu_2(OH) + H_2 + M[OH] \quad (5)$$

These results compare closely with the original report of Auten and Kraus,[2] and may account for some of the anomalies concerning the reactions of ' Bu_2BM '. Some groups have employed reaction times much shorter than 10 d for preparation of the reagent, and have not reported any estimation of the alkali-metal content. They may have been dealing with a different reagent, possibly corresponding more closely to the first stage of the reduction of the chloroborane [reaction (1)] than to the second. For our subsequent studies, we employed the clear supernatant diethyl ether solution after a 10-day reaction period. Such solutions showed no tendency to precipitate further material during several days standing at room temperature.

Reaction of ' Bu_2BM ' *with* PhCOCl.—Addition of benzoyl chloride to the reagent solution resulted in a colour change from brown to pale yellow, and the precipitation of metal halide, much as reported by Schmid and Nöth.[6] Removal of the metal halide and evaporation of diethyl ether left a viscous liquid which was fractionally distilled.

The forerun (b.p. ⩽52 °C at 0.7 mmHg),* containing PhCOCl and tributylborane, was followed by a fraction (b.p. 102 °C at 0.7 mmHg) which exhibited the properties previously reported for (3) (Table). The boron-containing residue was not further investigated.

Properties of the product from reaction (4)

Property	According to ref. 6	This work
B.p., θ_c/°C (p/mmHg)	110(1)	102 (0.7)
$\bar{\nu}_{max.}$/cm^{-1}	1 725	1 725
^{11}B N.m.r. (p.p.m. relative to $OEt_2{\cdot}BF_3$)	−53	−52.5 and −31.5 *

* We can account for the appearance of this extra signal (see text).

Characterisation of the Fraction having b.p. 102 °C *at* 0.7 mmHg.—The ^{1}H n.m.r. of the product showed signals at τ 1.97 (doublet of doublets, approximate integral 1.5 units), *ca.* 2.74 (m, 30), 4.69 (s, 1), 5.04 (s, 9), 5.07 (s, 1), 6.16 (t, 1), *ca.* 8.67 (m, 70), and *ca.* 9.09 (m, 54). After the product had stood in contact with air, the signals at τ 5.07 and 6.16 increased in intensity, whereas that at τ 5.04 decreased, which suggested that the signals at τ 5.07 and 6.16 were due to an impurity caused by autoxidation of a genuine reaction product.

Oxidation–hydrolysis of the product with alkaline hydrogen peroxide[9,10] gave a mixture of two major neutral components (g.c.). One was butan-1-ol, and the other was identified by its ^{1}H n.m.r. spectrum (τ 2.74, imperfect singlet, 5 H; 5.44, s, 2 H; 7.37, br, 1 H) as benzyl alcohol (confirmed by full comparison with an authentic sample). The molar ratio of butan-1-ol : benzyl alcohol was *ca.* 1.5 : 1.

A number of possible precursors could give rise to alcohols of the type RCH_2OH under these conditions, but only alkoxyboron compounds would still give alcohols on simple hydrolysis with aqueous K[OH]. Treatment of the product in this way led to the formation of benzyl alcohol in almost the same yield as on oxidation–hydrolysis, but there was only a very low yield of butanol. These results suggested that benzyloxydibutylborane, $BBu^n_2(OCH_2Ph)$ (5), might be a major component of the product. This was confirmed by comparison of

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[6] G. Schmid and H. Nöth, *Chem. Ber.*, 1968, **101**, 2502.

[7] H. C. Brown, *Accounts Chem. Res.*, 1969, **2**, 65 and refs. therein.

[8] M. E. D. Hillman, *J. Amer. Chem. Soc.*, 1962, **84**, 4715.

[9] H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962.

[10] J. R. Johnson and M. G. van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 121.

the ^1H n.m.r. and ^{11}B n.m.r. spectra and g.c. trace of an authentic sample of (5) with those of the reaction product. The signals at τ 5.07 and 6.16 (^1H), and at -31.5 p.p.m. (^{11}B), in the n.m.r. spectra of the product, were clearly shown to be the result of some autoxidation of (5) during handling, and not due to another reaction product.

The carbonyl-group absorption in the i.r. spectrum had disappeared during the alkaline hydrolysis described above. However, hydrolysis with water [to destroy (5)] did not affect the carbonyl absorption, and the hydrolysate could be separated by chromatography on silica. The separated carbonyl compound ($\nu_{max.}$ at 1 725 cm^{-1}) was identified by its ^1H n.m.r. spectrum (τ 1.94, dd, 2 H; *ca.* 2.60, m, 8 H; 4.66, s, 2 H) as benzyl benzoate (6) [confirmed by full comparison with authentic (6)]. That (6) was a genuine component of the product, and not produced during the hydrolysis or separation, was confirmed by the ^1H n.m.r. spectra and g.c. (1-m column of 4% PEGA [polyethylene glycol adipate] on Chromosorb G at 175 °C) of the product and its mixture with authentic (6).

Thus, the product obtained by Schmid and Nöth [6] was not benzoyldibutylborane, but a mixture of benzyloxydibutylborane and benzyl benzoate. The analyses reported for $BBu_2(COPh)$ [6] were not entirely satisfactory. However, in our hands, microanalytical data were variable, whilst classical wet analysis for boron gave consistently high results, even for pure authentic (5). Furthermore, the composition of the product mixture may vary with different experimental conditions, and analyses, therefore, appear to be of no value.

Reaction of (5) *with* PhCOCl.—It seemed likely that the production of (6) was the result of a reaction between (5) and benzoyl chloride [reaction (6)]. To test this possibility, authentic (5) and PhCOCl were co-distilled. The fraction boiling at 90—91 °C (0.2 mmHg) had properties comparable with those of the product from reaction (4), including a carbonyl-group absorption ($\nu_{max.}$ at 1 725 cm^{-1}). The presence of (6) was confirmed by g.c. Reaction (6) is thus shown to be the likely source of benzyl benzoate in the product from reaction (4).

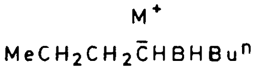
$$BBu_2(OCH_2Ph) + PhCOCl \longrightarrow BBu_2Cl + PhCO_2CH_2Ph \quad (6)$$

The Nature of ' Bu_2BM '.—The formation of (5) from PhCOCl requires a chemical reduction. Electron transfer followed by hydrogen abstraction appears unlikely because of the nature of the reduction products, which seem to be more consistent with a hydride reducing agent. However, if ' Bu_2BM ' has the properties of a hydride reducing agent, the validity of much of the earlier work with this reagent must be questioned.

The only previous report of the occurrence of B–H bonds in products from reactions of dialkylchloroboranes and alkali metals came from Koster and Benedikt,[4] but Pasto and Wojtkowski [5] could not confirm their results. In any event, the products of Köster and Benedikt did not contain alkali metal, whereas our reagent undoubtedly does. However, if an anion such as (7) were ever formed, there would be good reason to expect its ' rearrangement ' to a boron-stabilised anion [11] of type (8), which would doubtless oligomerise [*e.g.* to a trimer, (9)]. Our working hypothesis was that our reagent, although certainly in admixture with tributylborane and other compounds, consisted largely of such oligomers of (8). We have attempted to obtain evidence to support or refute this possibility.

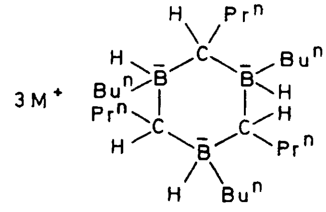
$Bu_2B^-M^+$

(7)



$MeCH_2CH_2\overset{M^+}{\bar{C}}HBHBu^n$

(8)



(9)

The i.r. spectrum of our reagent, either as a solution in diethyl ether or as a film after evaporation of solvent, showed a very broad flat-based band centred at *ca.* 2 000 cm^{-1}, which disappeared on exposure of the sample to air. The position of the band compares well with trialkylhydroborates in ether solvents, *e.g.* $K[BBu^s_3H]$ in tetrahydrofuran (thf),[12] 2 010 cm^{-1}; $Na[BPr^n_3H]$ in diglyme,[13] 1 975 cm^{-1}}.

Hydrolysis of pure (9) with D_2O–Na[OD], and subsequent oxidation with alkaline hydrogen peroxide, would be expected to give butanol and α-monodeuteriobutanol in a 1 : 1 ratio, but the reagent is known to contain only *ca.* 60% of the metal content required for pure (9), much of the rest of the material consisting of tributylborane. Thus, for the reagent as prepared, deuteriation–oxidation should produce butanol containing *ca.* 30% of α-monodeuteriobutanol. When this sequence of reactions was applied to the reagent, deuteriobutanol was clearly present, but problems of isolation in a pure form prevented its accurate estimation. Therefore, the corresponding hexyl reagent was prepared from bromodihexylborane [14] and excess of Na–K alloy. Treatment as described for the butyl analogue yielded hexan-1-ol which, after purification, indeed contained the expected *ca.* 30% monodeuterio-product (by ^1H n.m.r. and mass spectrometry). This result is

[11] G. Zweifel, R. P. Fisher, and A. Horng, *Synthesis*, 1973, 37; D. S. Matteson and L. A. Hagelee, *J. Organometallic Chem.*, 1975, **93**, 21; R. Kow and M. W. Rathke, *J. Amer. Chem. Soc.*, 1973, **95**, 2715 and refs. therein.

[12] C. A. Brown, *J. Org. Chem.*, 1974, **39**, 3913.

[13] P. Binger, G. Benedikt, G. W. Rotermnud, and R. Köster, *Annalen*, 1968, **717**, 21.

[14] A. Pelter, K. Rowe, D. N. Sharrocks, and K. Smith, *J.C.S. Chem. Comm.*, 1975, 531.

contrary to the results obtained by Pasto and Wojtkowski,[5] who were, however, using a ' 12-hour ' rather than a ' 10-day ' reagent.

These results, whilst not establishing the structure of the reagent, do show beyond doubt that it is not $M(BR_2)$, and are at least consistent with an oligomeric borohydride such as (9). That such a reagent should reduce PhCOCl to a benzyloxyboron compound would seem entirely reasonable.

EXPERIMENTAL

Sodium–potassium alloy [2] and dibutylchloroborane [15] were prepared according to published procedures. Diethyl ether was distilled from $Li[AlH_4]$ under nitrogen. All the operations involving organoboranes (except oxidation) were carried out under nitrogen using syringe techniques.[16] The compounds PhCOCl and $PhCH_2OH$ were distilled.

Spectra were recorded in HA100 (^1H and ^{11}B n.m.r.), Perkin-Elmer 257 (i.r.), and MS9 (mass) spectrometers.

Reaction of BBu_2Cl *with* Na–K *Alloy.*—Alloy prepared from Na (0.87 g, 37.9 mmol) and K (2.83 g, 73 mmol) was stirred magnetically, at room temperature, under diethyl ether (75 cm^3) in a flask (250 cm^3) fitted with a septum-capped stopcock. Dibutylchloroborane (3.5 g, 22 mmol) in diethyl ether (75 cm^3) was added over a period of 30 min, and stirring was then continued. Periodically the metal content of the solution was determined by addition of an aliquot portion (1 cm^3 of the clear supernatant, after the precipitate had been allowed to settle) to water (10 cm^3), and titration against 0.004 mol dm^{-3} HCl to a phenolphthalein end-point. After 10 d (metal content, 60% of theoretical and not increasing; solution, dark brown) stirring was stopped and the precipitate was allowed to settle. The clear supernatant was withdrawn by syringe.

Reaction of the Reagent with PhCOCl.—To the stirred reagent (120 cm^3 of a solution 0.096 mol dm^{-3} in alkali metal, 11.5 mmol) in a flask (250 cm^3) fitted with a septum-capped stopcock, was added, over 15 min, PhCOCl (1.62 g, 11.5 mmol) in diethyl ether (10 cm^3). Stirring was maintained for a further 1 h. The precipitate was allowed to settle and the clear supernatant was transferred to a separate flask and evaporated under reduced pressure. The viscous residue was fractionally distilled at 0.7 mmHg, giving a forerun boiling below 52 °C and the product (1.3 g) boiling at 102 °C.

Oxidation of the Product.—To the stirred product (0.35 g) in thf (5 cm^3) was added Na[OH] (5 cm^3 of 5 mol dm^{-3}) and H_2O_2 (3 cm^3 of 50%), the temperature being maintained below 30 °C. After 12 h of stirring the aqueous layer was saturated with NaCl and the organic layer was subjected to g.c. (1-m column of 4% PEGA on Chromosorb G, temperature programmed from 50 to 190 °C at 12° min^{-1}). Two major peaks were identified as butan-1-ol and benzyl alcohol. Addition of benzene (0.11 g) enabled estimation of the alcohols; molar ratio butanol : benzyl alcohol *ca.* 1.5 : 1.

Alkaline Hydrolysis of the Product.—The product (0.10 g) in thf (2 cm^3) was added to Na[OH] (5 cm^3 of 1 mol dm^{-3}) and stirred for 4 h. Work-up and g.c. as for the oxidation products showed $PhCH_2OH$, but little butanol.

Hydrolysis of the Product with Water.—Water (1 cm^3) was added to the product (0.10 g) and the mixture was stirred for 15 min. The mixture was extracted into diethyl ether, and the ether extract was chromatographed on a column of dry silica (20 g). The compound possessing a carbonyl group (0.018 g), eluted with CH_2Cl_2, was subsequently shown to be benzyl benzoate.

Preparation of Benzyloxydibutylborane.—The procedure was adapted from a method for dialkyl(methoxy)boranes.[17] Dibutylchloroborane (1.41 g, 8.8 mmol) was stirred magnetically in a flask fitted with a serum-capped stopcock. A needle was inserted through the septum, and connected to a paraffin-oil bubbler, whilst benzyl alcohol (0.95 g, 8.8 mmol) was added slowly. Hydrogen chloride was allowed to escape as it formed, and finally removed at the pump. Distillation under reduced pressure gave benzyloxydibutylborane, b.p. 85—88 °C at 0.07 mmHg (lit.,[18] 115—116 °C at 11 mmHg). ^1H N.m.r.; τ 2.72, imperfect singlet, 5 H; 5.04, s, 2 H; *ca.* 8.66, m, 8 H; *ca.* 9.10, m, 10 H. Boron-11 n.m.r. signal at −53 p.p.m. relative to $OEt_2{\cdot}BF_3$. After exposure to air, additional signals were observed at τ 5.07 and 6.16 (^1H) and at −31.5 p.p.m. (^{11}B) in the n.m.r. spectra.

Deuteriation–Oxidation of Alkali-metal–Boron Reagents.—To the stirred reagent (60 cm^3 of a solution 0.096 mol dm^{-3} in alkali metal, 5.8 mmol) was added D_2O (2 cm^3). After 15 min, K[OD] (half a pellet of K[OH] in 3 cm^3 of D_2O) was added, and after a further 45 min Na[OH] (5 cm^3 of 5 mol dm^{-3}) and H_2O_2 (3 cm^3 of 50%) were also added, stirring then being maintained for 12 h at room temperature. The aqueous layer was saturated with NaCl and the ether layer was removed, stirred with dilute HCl (5 cm^3 of 0.01 mol dm^{-3} saturated with NaCl, process duplicated), washed with saturated NaCl, dried ($Mg[SO_4]$), and evaporated under reduced pressure. Gas chromatography confirmed the presence of butan-1-ol as the only major component, but the recovery was very low. Cold-finger distillation gave a material which still contained impurities, as evidenced by the mass spectrum. The whole series of reactions was repeated on a reagent prepared from bromodi-n-hexylborane (2.75 g, 10.5 mmol) and alloy (0.42 g of Na, 1.44 g of K). Hexanol was more readily recovered and was distilled to give a pure sample, the mass spectrum of which clearly indicated the presence of monodeuteriohexan-1-ol. Integration of the α- and β-CH_2 group signals in the ^1H n.m.r. spectrum [expanded by addition of tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III)] showed that the deuteriated hexanol corresponded to *ca.* 30% of the total (integration of the α-CH_2 group was 15% less than the β-CH_2 group).

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[6/623 *Received*, 1*st April*, 1976]

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