Reaction of Higher Dialkyl(methylthio)boranes with Bromine: A New Synthesis of Dialkylbromoboranes [1]

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Higher dialkyl(methylthio)boranes, readily prepared *in situ* from the corresponding trialkylboranes, react rapidly at low temperature with bromine to give dialkylbromoboranes and dimethyl disulphide. Removal of the latter under reduced pressure gives a pure product in excellent yield.

As a result of the growing importance of organoboranes as synthetic reagents [2,3] there is a need for new and better routes to 'mixed' organoboranes,[4] and therefore for syntheses of potential intermediates. Halogenoboranes are of special significance in this context because of their central role in the interconversion of functional groups attached to boron (Scheme 1),[5] as well as being themselves of importance in organic synthesis.[6,7]

There are a number of methods reported for the preparation [8] of organochloroboranes, BR_nCl_{3-n} ($n = 1$ or 2), although all have some disadvantages. Thus, hydroborations of alkenes with chloroborane [9] or dichloroborane [10] are limited in scope, whilst redistribution [11,12] of BR_3 with BCl_3, dealkylation [13] of BR_3 with HCl, and

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

[2] G. M. L. Cragg, 'Organoboranes in Organic Synthesis,' Marcel Dekker, New York, 1973.

[3] H. C. Brown, 'Organic Synthesis *via* Boranes,' Wiley–Interscience, New York, 1975.

[4] For a recent review of organoborane syntheses see K. Smith, *Chem. Soc. Rev.*, 1974, **3**, 443.

[5] A. N. Nesmeyanov and R. A. Sokolik, 'Methods of Elemento-Organic Chemistry,' North Holland, Amsterdam, 1967, vol. 1, ch. 10.

[6] H. C. Brown, M. M. Midland, and A. B. Levy, *J. Amer. Chem. Soc.*, 1973, **95**, 2394.

[7] J. Hooz, J. N. Bridson, J. G. Calzada, H. C. Brown, M. M. Midland, and A. B. Levy, *J. Org. Chem.*, 1973, **38**, 2574.

[8] For a review of earlier syntheses of organohalogenoboranes see K. Niedenzu, *Organometallic Chem. Rev.*, 1966, **1**, 305.

[9] H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, 1973, **95**, 2396.

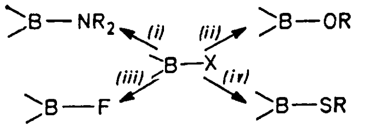
[10] H. C. Brown and N. Ravindran, (*a*) *J. Amer. Chem. Soc.*, 1972, **94**, 2112; (*b*) *J. Org. Chem.*, 1973, **38**, 182; (*c*) *ibid.*, p. 1617.

[11] H. C. Brown and A. B. Levy, *J. Organometallic Chem.*, 1972, **44**, 233.

[12] R. Köster and M. A. Grassberger, *Annalen*, 1968, **719**, 169.

[13] R. B. Booth and C. A. Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1415.

Friedel–Crafts reactions[14] for production of $BRCl_2$ (R = aryl) require elevated temperatures; reactions of BCl_3 with organotin reagents[15,16] are of use only when the appropriate organotin compounds are themselves readily available.



SCHEME 1 (*i*) NR_2H; (*ii*) ROH; (*iii*) SbF_3; (*iv*) RSH, $M(SR)_n$, or (for X = I) RSSR

In contrast to the chloro-compounds, the corresponding bromo- and iodo-compounds have been little studied. Dealkylation of tributylborane with anhydrous HBr is known to be incomplete after 75 min at 60 °C.[17] There is an unique redox reaction between aryl iodides and BI_3 which is useful for the synthesis of aryldi-iodoboranes.[18]

Dialkyl(alkylthio)boranes are particularly attractive intermediates for the preparation of borane derivatives as they are easily prepared from the readily available[4] trialkylboranes in essentially quantitative yields [reaction (1)],[19] the side product is not troublesome, and the dialkyl(alkylthio)boranes can be utilised directly. We now report their successful conversion into dialkylbromoboranes by reaction with bromine [reaction (2)].[1] It is interesting to note that this redox reaction occurs in the opposite sense to that in the iodoborane series [reaction (3)],[20] an illustration of the high oxidising power of bromine relative to iodine.

$$BR^1_3 + R^2SH \xrightarrow{\text{trace of air}} BR^1_2(SR^2) + R^1H \quad (1)$$

$$\underset{(1)}{2BR^1_2(SR^2)} + Br_2 \longrightarrow \underset{(2)}{2BR^1_2Br} + \underset{(3)}{R^2SSR^2} \quad (2)$$

$$2BR^1_2I + R^2SSR^2 \longrightarrow 2BR^1_2B(SR^2) + I_2 \quad (3)$$

RESULTS AND DISCUSSION

Initial studies showed that addition of bromine to dialkyl(alkylthio)boranes (1; $R^2 = Bu^n$ or n-hexyl) or dialkyl(phenylthio)boranes (I; $R^2 = Ph$) gave the corresponding dialkylbromoboranes (2) and dialkyl disulphides (3). We employed the methylthio-derivatives (I; $R^2 = Me$) for our further studies because the by-product, dimethyl disulphide (3; $R^2 = Me$), is easily removed at the pump.*

Reaction of neat methylthio(di-n-hexyl)borane (I; $R^1 = n\text{-}C_6H_{13}$, $R^2 = Me$) with the stoicheiometric quantity of Br_2 at 0 °C was markedly exothermic and gave bromodi-n-hexylborane (2; $R^1 = n\text{-}C_6H_{13}$) in 70% isolated yield. When the initial addition was made at low temperature† in the dark, followed by warming to room temperature, the yield of bromodi-n-hexylborane was essentially quantitative. However, excess of bromine, the presence of substantial quantities of tetrahydrofuran (thf), or exposure to light caused some reduction in the yield. The reaction occurred satisfactorily in solvents such as pentane or diethyl ether. The reduced yield obtained in thf may be the result of some cleavage of this solvent by the bromoborane; thf is also unsuitable for preparation of dialkylchloroboranes from monochloroborane.[10] The effect of light may be to encourage bromination at the α-carbon atoms, leading to some dealkylation.[21]

The procedure involving absence of solvent was applied to the synthesis of a number of representative dialkylbromoboranes (Table). For this study, where the bromoborane was the ultimate goal, all the products were distilled. However, the products were substantially pure prior to distillation, and may be employed directly if required for subsequent steps, thus avoiding at any stage the need for elevated temperatures or for isolation of sensitive compounds.

Production of $BBrR^1_2$ from $BR^1_2(SMe)$

R^1	Yield (%) [a]
Bu^n	89
n-Pentyl	97
n-Hexyl	98
n-Octyl	96
Cyclopentyl	82
Cyclohexyl	86
trans-2-Methylcyclopentyl [b]	78

[a] Yield of distilled product, prepared on a 25 mmol scale. Microanalyses were not practicable on these highly sensitive compounds, but they were fully characterised by bromine analyses, g.c. estimation of the alcohols formed on oxidation, and conversion into the corresponding methoxy- or hydroxy-boron compounds. [b] In our preliminary communication,[1] this entry was wrongly cited as 2-methylcyclohexyl.

It may be seen from the Table that whereas the reaction is essentially quantitative for bromodi-n-alkylboranes, somewhat lower yields (*ca.* 80%) of bromodi-s-alkylboranes are obtained. It is likely that this reduction in yield is the result of competitive α bromination, which is known to be faster for tri-s-alkylboranes.[21] Nevertheless, this reaction provides the first convenient and general route to dialkylbromoboranes, and yields of *ca.* 80% are usually acceptable.

In order to make the synthesis of dialkylbromoboranes even more attractive, the full sequence of steps starting from readily available alkenes (Scheme 2) was carried out in one vessel without isolation of any intermediates. This procedure was satisfactory, resulting in an overall yield of 89% (based on hex-1-ene) in the case of bromodi-n-hexylborane.

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* For the general case the methylthio-derivatives were always used. For dimethyl- and diethyl-bromoboranes the phenylthio-derivatives are useful.

† Normally −63 °C, but in one case −40 °C was satisfactory.

[14] E. L. Muetterties and F. N. Tebbe, *Inorg. Chem.*, 1968, **7**, 2663; R. A. Bowie and O. C. Musgrave, *J. Chem. Soc.* (*C*), 1970, 485.

[15] K. Niedenzu, J. W. Dawson, and P. Fritz, *Inorg. Synth.*, 1967, **10**, 126.

[16] J. Hooz and J. G. Calzada, *Org. Prep. Proc. Internat.*, 1972, **4**, 219.

[17] J. R. Johnson, H. R. Snyder, and M. G. van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 115.

[18] W. Siebert, F. R. Rittig, and M. Schmidt, *J. Organometallic Chem.*, 1970, **25**, 305.

[19] B. M. Mikhailov, V. A. Vaver, and Yu. N. Bubnov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **126**, 575; B. M. Mikhailov and Yu. N. Bubnov, *Zhur. obshchei Khim.*, 1961, **31**, 160.

[20] W. Siebert, F. R. Rittig, and M. Schmidt, *J. Organometallic Chem.*, 1970, **22**, 511.

[21] H. C. Brown and N. R. DeLue, *J. Amer. Chem. Soc.*, 1974, **96**, 311.

Bromodi-n-pentylborane was treated with pyridine to give a solid derivative (4), containing all of the elements of the original bromoborane [reaction (4)].[17] Compound (4) is air-stable, and its microanalytical data and spectral properties are consistent with its formulation.

$$\begin{tikzcd}
\mathrm{3RCH{=}CH_2 + BH_3} \arrow[r] & \mathrm{B(CH_2CH_2R)_3} \arrow[d, "(i)"'] \\
\mathrm{BBr(CH_2CH_2R)_2 + MeSSMe} & \mathrm{B(CH_2CH_2R)_2(SMe)} \arrow[l, "(ii)"'] \\
 & \mathrm{+\ RCH_2Me}
\end{tikzcd}$$

SCHEME 2 (*i*) MeSH (slight excess), trace of air; (*ii*)Br_2

$$\mathrm{BBr(n\text{-}C_5H_{11})_2 + 2py \longrightarrow \underset{(4)}{[B(n\text{-}C_5H_{11})_2(py)_2]Br}} \qquad (4)$$

The procedures reported here make dialkylbromoboranes readily available for the first time. The chemistry of these species, and in particular their potential as intermediates for the synthesis of ' mixed' organoboranes, is under investigation. We have already converted some into ' mixed ' organoboranes by reduction with sodium hydride in the presence of alkenes [reaction (5)],[22] and have converted the products into the corresponding tertiary alcohols [reaction (6)] [23] in high yields and without appreciable redistribution. These further reactions will be reported in detail separately.

$$\mathrm{BBrR^1_2 + R^2CH{=}CH_2 \xrightarrow{NaH} BR^1_2(CH_2CH_2R^2) + NaBr} \qquad (5)$$

$$\mathrm{BR^1_2(CH_2CH_2R^2) \xrightarrow[(\mathit{iii})\ H_2O_2/OH^-]{(\mathit{i})\ Na[CN],\ (\mathit{ii})\ excess\ of\ (CF_3CO)_2O} R^1_2C(OH)CH_2CH_2R^2} \qquad (6)$$

EXPERIMENTAL

Tetrahydrofuran (thf) and diethyl ether were purified by distillation from CaH_2 under N_2. Methanethiol (B. D. H., 99.5%) was transferred directly from the cylinder to make up a standard solution in thf. Bromine (B.D.H., 99%) was used without further purification. Pyridine was distilled from previously heated BaO under N_2. Trialkylboranes were prepared according to published procedures.[3, 24] All the operations were made under N_2 using syringe techniques.[3]

N.m.r. spectra were recorded on a Varian HA100 spectrometer and mass spectra on an A.E.I. MS9 instrument.

Preparations.—Methylthiodi-n-hexylborane. The method of Mikhailov *et al.*,[19] somewhat modified, was employed. Tri-n-hexylborane was prepared [24] from hex-1-ene (18.7 cm^3, 12.6 g, 150 mmol) and diborane (42.0 cm^3 of a thf solution, 1.19 mol dm^{-3} in ' BH_3', 50 mmol of ' BH_3') in a two-necked flask (100 cm^3), one neck of which was fitted with a septum-capped stopcock and the other connected *via* a three-way tap to a vacuum pump or N_2 cylinder. The mixture was stirred magnetically whilst MeSH (7.3 cm^3 of a solution in thf, 8.2 mol dm^{-3}, 60 mmol) was added at room temperature, then air (1 cm^3) was injected to initiate a mildly exothermic reaction. More air (1 cm^3) was injected after 2 h, and stirring was maintained for 12 h. All the volatile components were removed at the pump and the apparatus was then set up for short-path distillation. The product was fractionally distilled under reduced pressure to yield methylthiodi-n-hexylborane, 10.96 g (96%), b.p. 90—92 °C at 0.5 mmHg (lit.,[25] 99—103 °C at 2 mmHg),* τ ($CDCl_3$) 7.85 (3 H, s), *ca.* 8.70 (20 H, m), 9.11 (6 H, sextet). The mass spectrum (direct insertion) inevitably showed many peaks due to hydrolysed product $[B(n\text{-}C_6H_{13})_2]_2O$, in addition to peaks due to the thioborane; there was a strong characteristic peak at *m/e* 143 ($C_6H_{13}B{=}\overset{+}{S}Me$); n_D^{20} = 1.467 (lit.,[25] 1.469).

Other dialkyl(methylthio)boranes. The following dialkyl(methylthio)boranes, $BR_2(SMe)$, were prepared as described for methylthiodi-n-hexylborane: methylthiodi-n-butylborane, 89%, b.p. 43—44 °C at 1.1 mmHg (lit.,[20] 27 °C at 1 mmHg), *m/e* 115 for the characteristic ion, $RB{=}\overset{+}{S}Me$; methylthiodi-n-pentylborane, 85%; b.p. 56 °C at 0.5 mmHg, *m/e* 129; methylthiodi-n-octylborane, 75%, b.p. 132 °C at 0.9 mmHg, *m/e* 171; dicyclopentyl(methylthio)borane, 95%, b.p. 82—84 °C at 1.3 mmHg, *m/e* 127; dicyclohexyl(methylthio)borane, 81%, b.p. 96 °C at 0.1 mmHg (lit.,[25] 109—110 °C at 1 mmHg), *m/e* 141, n_D^{20} = 1.518 (lit.,[25] 1.520), and bis(*trans*-2-methylcyclopentyl)(methylthio)borane, 95%, b.p. 116 °C at 1.5 mmHg, *m/e* 141.

Bromodi-n-hexylborane. Methylthiodi-n-hexylborane (5.70 g, 25 mmol) was placed in a two-necked flask (100 cm^3) fitted with a septum-capped stopcock and attached to a vacuum pump–nitrogen cylinder arrangement as described above. The flask was protected from light with aluminium foil and the thioborane was cooled to −63 °C and stirred magnetically whilst bromine (0.65 cm^3, 2.00 g, 12.5 mmol) was added dropwise over 3 min. Decolourisation was rapid up to the last drops added. The cooling bath was removed and the mixture was stirred for a further 15 min before the pressure was reduced to remove dimethyl disulphide. When removal was complete the apparatus was set up for short-path distillation under reduced pressure. Fractionation yielded bromodi-n-hexylborane (6.39 g, 98%), b.p. 78 °C at 0.8 mmHg, as a colourless liquid which fumed in air. Its mass spectrum (direct insertion) showed mainly peaks due to the hydrolysis product, $[B(n\text{-}C_6H_{13})_2]O$.

An aliquot portion of the product (1.113 g, 4.26 mmol) was dissolved in thf (10 cm^3) and aqueous ethanol (50%, 10 cm^3) was added. A vigorous reaction resulted and the hydrolysate was titrated aginst 0.1 mol dm^{-3} Na[OH] to a Methyl Red end-point; titre 42.7 cm^3. A second aliquot portion (1.057 g, 4.05 mmol) was oxidised with alkaline hydrogen peroxide by the standard method.[24] To the product mixture was added pentane (10 cm^3) and hexadecane (g.c. standard, 0.500 g), and the aqueous layer was saturated with NaCl. Relative integration of the hexadecane and hexanol peaks (hexanol was a *ca.* 19 : 1 mixture of hexan-1-ol and hexan-2-ol because the original trihexylborane was prepared by hydroboration of hex-1-ene [24]) in the gas chromatogram (1-m column of 15% Carbowax 20M on Chromosorb G at 100 °C) of the pentane layer indicated the presence of 0.823 g (8.07 mmol, 99.5%) of hexanol. The identity of the product was finally confirmed by conversion into the known methoxyboron compound (see below).

Other dialkylbromoboranes. The following dialkylbromoboranes were prepared as described for bromodi-n-hexylborane: bromodi-n-butylborane, 89%, b.p. 36—38 °C at 1.7

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[22] A. Pelter, K. Rowe, and K. Smith, *J.C.S. Chem. Comm.*, 1975, 532.

[23] A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, *J.C.S. Perkin I*, 1975, 138.

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

[25] B. M. Mikhailov, T. A. Shchegoleva, V. D. Sheludyakov, and A. N. Blokhina, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1963, 646.

mmHg (lit.,[12,26] 70 °C at 10 mmHg, 65.5 °C at 6.4 mmHg); bromodi-n-pentylborane, 97%, b.p. 58 °C at 0.9 mmHg (lit.,[26] 58—60 °C at 2.1 mmHg); bromodi-n-octylborane, 96%, b.p. 126—128 °C at 1.5 mmHg; bromodicyclopentylborane, 82%, b.p. 68—70 °C at 1.0 mmHg; bromodicyclohexylborane, 86%, b.p. 48—52 °C at 0.002 mmHg (lit.,[12] 41—48 °C at 0.001 mmHg; and bromobis(*trans*-2-methylcyclopentyl)-borane, 78%, b.p. 88 °C at 0.5 mmHg. All of these compounds gave bromine and alcohol analyses within 2 and 3% respectively of the theoretical values, and were converted into the corresponding methoxy- or hydroxy-boron compounds (see below).

Methoxydi-n-hexylborane. The method used was analogous to that of Brown and Ravindran.[10a] A foil-wrapped two-necked flask (50 cm^3) equipped for magnetic stirring had one neck connected *via* a drying tube and a three-way tap to a nitrogen or a vacuum pump and the second neck fitted with a serum-capped stopcock. Bromodi-n-hexylborane (1.74 g, 6.67 mmol) was introduced, cooled to 0 °C, and stirred during the addition of super-dry methanol[27] (0.27 cm^3, 0.22 g, 6.7 mmol). Hydrogen bromide was allowed to bubble off as it formed, and after 2 min at 0 °C all traces of HBr were removed at the pump. The apparatus was set up for distillation under reduced pressure and fractionated to give methoxydi-n-hexylborane (1.10 g, 78%), b.p. 64 °C at 0.7 mmHg, $n_D^{20} = 1.430$ (lit.,[28] b.p. 72—73 °C at 2 mmHg, n_D^{20} 1.429). Mass spectrum (direct insertion): base peak at *m/e* 127, corresponding to $C_6H_{13}B{=}\overset{+}{O}Me$. Gas chromatography (1-m column, 5% SE 30 on Chromosorb G, 100 °C) showed a single peak (the small amount of product with a secondary hexyl group due to the method of preparation of the original trihexylborane was not resolved under these conditions, but non-isomeric products such as hexyldimethoxyborane were shown to be absent). Hydrogen-1 n.m.r.: τ 6.42 (3 H, s, affected by addition of D_2O), *ca.* 8.8 (20 H, m), and 9.16 (6 H, t). Conventional microanalyses were difficult with these compounds which are sensitive to air; nevertheless, with care, reasonable results could be obtained, although a larger margin of error had to be allowed (Found: C, 73.8; H, 14.0. Calc. for $C_{13}H_{29}BO$: C, 73.6; H, 13.8%).

Other dialkyl(methoxy)boranes. The following dialkyl(methoxy)boranes were prepared as described for methoxydi-n-hexylborane: methoxydi-n-butylborane, b.p. 68—70 °C at 10 mmHg, $n_D^{20} = 1.414$ (lit.,[10a] b.p. 56—58 °C at 5.0 mmHg, n_D^{20} 1.414); methoxydi-n-pentylborane, b.p. 48—49 °C at 1.0 mmHg, $n_D^{20} = 1.423$ (lit.,[29] b.p. 101—104 °C at 20 mmHg, n_D^{20} 1.424); methoxydi-n-octylborane, b.p. 108—109 °C at 0.8 mmHg, $n_D^{20} = 1.4382$, base peak in mass spectrum at *m/e* 155.1607 ($[M - C_8H_{17}]^+$, calc. for $C_9H_{20}{}^{11}BO$: *m/e* 155.1607), single peak by g.c. (Found: C, 75.3; H, 13.9. Calc. for $C_{17}H_{37}BO$: C, 76.1; H, 13.9%); dicyclopentyl(methoxy)borane, b.p. 71—73 °C at 0.9 mmHg, $n_D^{20} = 1.470$ (lit.,[10a] b.p. 82—84 °C at 2 mmHg, n_D^{20} 1.470); and methoxybis(*trans*-2-methylcyclopentyl)borane, b.p. 96 °C at 1.0 mmHg, $n_D^{20} = 1.4837$, *m/e* 125.1138 ($[M - C_6H_{11}]^+$, calc. for $C_7H_{14}{}^{11}BO$: *m/e* 125.1138), single peak by g.c. (Found: C, 75.3; H, 12.1. Calc. for $C_{13}H_{25}BO$: C, 75.0; H, 12.1%).

Dicyclohexylhydroxyborane. Dicyclohexylhydroxyborane was prepared from bromodicyclohexylborane by a method analogous to that used in the preparation of methoxydi-n-hexylborane, but using water instead of methanol. The product was a solid, m.p. 54 °C (aqueous methanol) (lit.,[30,31] 52,55 °C).

Pyridine–bromodi-n-pentylborane (2/1) adduct. Dry pyridine (2 cm^3, 7.76 mmol) in pentane (5 cm^3) was cooled to 0° C in a flask (50 cm^3) fitted with a magnetic stirrer bar and a septum-capped stopcock. Bromodi-n-pentylborane (1 cm^3, *ca.* 5 mmol) was added dropwise over 5 min, resulting in evolution of heat and the formation of a dense white precipitate. The mixture was stirred for 30 min, and the precipitate was collected by filtration, washed with pentane (3 × 25 cm^3), and dried at the pump. The solid seemed to undergo structural changes above 80 °C, but melted only at 167 °C. The mass spectrum showed major ions at *m/e* 153 $[BC_{10}H_{22}]^+$, 80 and 82 ($H^{79}Br$ and $H^{81}Br$), and 79 ($C_5H_5N^+$) (Found: C, 61.5; H, 8.2; N, 7.15. Calc. for $C_{20}H_{32}BBrN_2$: C, 61.5; H, 8.2; N, 7.15%). Hydrogen-1 n.m.r.: τ 1.34 (4 H, d, with fine structure), 1.68 (2 H, t), 2.86 (4 H, approximate t), and 8.6—8.4 (22 H, complex).

Bromodi-n-hexylborane directly from tri-n-hexylborane. Tri-n-hexylborane (50 mmol) was prepared and treated with methanethiol (55 mmol) as described above. After 20 h, solvent and the excess of methanethiol were removed at the pump, and the residue was cooled to −63 °C and protected from light with aluminium foil. Bromine (1.3 cm^3, 4.0 g, 25 mmol) was added dropwise and the mixture was stirred for 10 min at −63 °C, after which a pale red colour still persisted. The cooling bath was withdrawn and volatiles (Br_2, MeSSMe) were removed at the pump as the mixture warmed. Distillation under reduced pressure gave bromodi-n-hexylborane (11.6 g, 89%), b.p. 76—78 °C at 0.8 mmHg. Bromine and alcohol analyses (see above) were satisfactory, although a small quantity of methyl n-hexyl sulphone was shown (g.c.) to contaminate the alcohols produced on oxidation, indicating the presence of a small amount of a sulphur-containing impurity in the bromoborane.

Bromodi-n-hexylborane in pentane. Methylthiodi-n-hexylborane (2.73 g, 11.9 mmol) in pentane (10 cm^3) was cooled to −63 °C in a flask (25 cm^3) equipped as described for the reaction without solvent. Bromine (0.96 g, 6 mmol) was added dropwise over 3 min and the solution was then allowed to warm to room temperature. All the volatiles, including solvent, were removed at the pump and the residue was fractionally distilled to give bromodi-n-hexylborane (2.79 g, 93%) the purity of which was comparable with that achieved in the absence of a solvent.

Bromodi-n-octylborane in diethyl ether. Methylthiodi-n-octylborane (1.51 g, 5.24 mmol) in diethyl ether (5 cm^3) was cooled to −63 °C and treated with bromine (0.42 g, 2.62 mmol) as described for the preparation of bromodi-n-hexylborane in pentane. Bromodi-n-octylborane (1.37 g, 83%) was obtained, the purity of which was comparable with that achieved in the absence of solvent.

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[26] P. A. McCusker and J. H. Bright, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2261.

[27] H. Lund and J. Bjerrum, *Chem. Ber.*, 1931, **64**, 210.

[28] B. M. Mikhailov and L. S. Vasil'ev, *Zhur. obshchei Khim.*, 1965, **35**, 925.

[29] H. C. Brown and A. Tsukamoto, *J. Amer. Chem. Soc.*, 1960, **82**, 746.

[30] H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, 1971, **93**, 2802.

[31] H. Hartmann and K. H. Birr, *Z. anorg. Chem.*, 1959, **299**, 174.