Reactions of Dialkylbromoboranes with Alkali Metal Hydrides in the Presence of Alkenes. Synthesis of ' Mixed ' Trialkylboranes ($R^A{}_2R^BB$) in Solution

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Dialkylbromoboranes react steadily with hydroxide-free sodium hydride in diglyme, in the presence of alkenes, to give nearly quantitative yields of partly mixed trialkylboranes. The reaction proceeds too slowly to allow prior clean preparation of dialkylboranes, so reaction in the presence of alkenes possessing hydride-sensitive functional groups is not possible, although terminal alkynes can be hydroborated *in situ* by a modified experimental procedure. Potassium hydride reacts much more rapidly with dialkylbromoboranes, the reactions being complete within minutes at 20 °C, but the yields are lower. Addition of dibenzo-18-crown-6 leads to an increase in yield but the results are still inferior to those obtained using sodium hydride. Reaction of dialkylbromoboranes with lithium hydride is very sluggish.

THE growing importance of organoboranes as synthetic intermediates [1] creates a need for general procedures for the production of mixed organoboranes of the types $R^A{}_2R^BB$ and $R^AR^BR^CB$. Only a very limited range of such compounds is available from sequential hydroboration of alkenes.[2] In most cases hydroboration proceeds beyond the intermediate boranes R^ABH_2 or $R^A{}_2BH$ even when only the calculated quantity of alkene is added.

One approach to $R^A{}_nBH_{3-n}$ involves reduction of species of types R^ABX_2 and $R^A{}_2BX$ (*e.g.* X = halide, OMe, SMe).[3,4,5] However, most functional groups cannot tolerate the powerful reducing agents used in these reactions. Also, the by-products include soluble, basic lithium or aluminium species. In principle, the reaction of an alkali metal hydride with a halogenoborane [equation (1)] could be advantageous in that alkali metal hydrides do not reduce many functional groups. Furthermore, the alkali metal halide by-product should be sparingly soluble in the solvent used and in any case would be unlikely to have much influence on subsequent reactions.

$$R^A{}_2BX + MH \xrightarrow{\text{alkene B}} R^A{}_2BR^B + MX \qquad (1)$$
$$X = Cl, Br, \quad M = Li, Na, K$$

Previous studies [6] of the reactions of halogenoboron compounds with alkali metal hydrides have been concerned mainly with the simple trihalogenoboranes. Reduction does occur, but the reactions have not been developed into useful synthetic procedures. We now report detailed investigations of the reaction indicated in equation (1).[7] In view of their ready availability from trialkylboranes by a convenient preparation developed in our laboratory,[8] dialkylbromoboranes ($R^A{}_2BBr$) were chosen as substrates.

RESULTS AND DISCUSSION

The reaction between di-n-pentylbromoborane, sodium hydride, and an excess of oct-1-ene in diglyme was monitored by oxidation of aliquot portions and estimation of the octan-1-ol and pentan-1-ol so formed by quantitative gas chromatography. This revealed a steady increase in the yield of octan-1-ol with time, the reaction being complete after 6—7 h. Similar observations were made for other dialkylbromoborane–alkene combinations on reaction with sodium hydride. In tetrahydrofuran the reactions were slower, being complete only after 24 h. Table 1 shows the results of a series of reactions carried out in diglyme, as above.

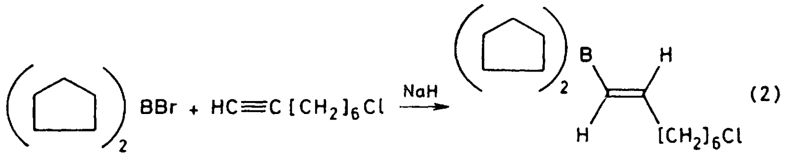
TABLE 1

Yield for the incorporation of alkene B, following equation (1) [a] (MH = NaH)

R^A of $R^A{}_2BBr$	Alkene B	Alcohol B [c,d]	Yield (%) [b]
n-Pentyl	Oct-1-ene	Octanol	99
n-Pentyl	Hex-1-ene	Hexanol	96
n-Pentyl	Cyclohexene	Cyclohexanol	97
n-Pentyl	Cyclopentene	Cyclopentanol	93
n-Pentyl	Norbornene	Norbornan-2-ol	88
n-Pentyl	$CH_2=CH[CH_2]_6Cl$	$HO[CH_2]_8Cl$	81
Cyclopentyl	Oct-1-ene	Octanol	98
Cyclopentyl	Hex-1-ene	Hexanol	95
Cyclopentyl	Cyclohexene	Cyclohexanol	98

[a] $R^A{}_2Br$ added at −63 °C, and reaction then stirred at 23 °C for 7 h. [b] By g.l.c. [c] The yields of alcohol A (from $R^A{}_2BR^B$) were >98% in each case and are not given in this or later Tables. [d] Alcohols A and B are defined from the oxidation of $R^A{}_2BR^B$ to $2R^AOH$ and R^BOH.

By a slight modification of the procedure it was also possible to convert dicyclopentylbromoborane into (8-chloro-oct-1-enyl)dicyclopentylborane by reaction with 8-chloro-oct-1-yne and sodium hydride (equation 2). The alkyne was added continuously to the reaction



(2)

mixture over 6 h. Hydroboration of the alkyne was confirmed by hydrolysis of the resulting borane to give 8-chloro-oct-1-ene (91% yield).

The studies described above were conducted using sodium hydride containing a very small amount of base other than hydride (see Experimental section). Use of sodium hydride containing substantial quantities of other base produced inferior results, the reaction rate being considerably lessened.

It was thought that the greater solubility of lithium hydride, when compared with sodium hydride, might result in a faster reaction, thus reducing the likelihood of redistribution of alkyl groups during preparation of R_2^ABH in the absence of alkene. In practice, however, lithium hydride reacted much more slowly than sodium hydride despite its complete solubility in the reaction medium. The reaction proceeded to the extent of only 13% after 17 h at the ambient temperature.

On the other hand, the intrinsically more reactive potassium hydride did indeed react rapidly with di-n-hexylbromoborane, but yields of alcohol B obtained by oxidation were variable and seldom better than 60% (Table 2). All combinations of modes of addition of hydride, alkene, and dialkylbromoborane were tried, as well as changes of temperature. A rapid but incomplete reaction occurred in all cases. Change of solvent to tetrahydrofuran resulted in a very poor yield of alcohol. A possible explanation for the observed results is that potassium bromide, rapidly formed during the reaction, coats the yet unchanged potassium hydride, thus preventing complete reaction. If this were so, addition of 10 mol per cent of dibenzo-18-crown-6 to solubilise the potassium salts might be expected to cause an increase in the yield of hydroboration product. Indeed, when this was done, the yields improved to 70—90%, and the reactions were complete well within 1 h at room temperature. Secondary alkenes required longer reaction times, but this was because of the slower rate of hydroboration and not the rate of production of dialkylborane. The results for some reactions are summarised in Table 3.

TABLE 2

Yields for the incorporation of alkene B, following equation (1) (MH = KH)

R^A of R^A_2BBr	Alkene B	T/°C	t/min	Yield (%) [a] of octanol
n-Hexyl	Oct-1-ene	−60 → room temp.	5	59
n-Hexyl	Oct-1-ene	−60 → room temp.	15	59
n-Hexyl	Oct-1-ene	−60 → room temp.	30	45
n-Hexyl	Oct-1-ene	0	60	55
n-Hexyl	Oct-1-ene	no cooling [b]	60	54
n-Hexyl	Oct-1-ene	60	60	1.5
n-Pentyl	Oct-1-ene	−60 → room temp.	10	64
n-Pentyl	Oct-1-ene	−60 → room temp.	10	73
n-Pentyl	Oct-1-ene	−60 → room	90	67
n-Pentyl	Oct-1-ene	no cooling [b]	60	63
n-Pentyl	Oct-1-ene	60	60	<1
n-Pentyl	Oct-1-ene	no cooling [b]	60	<1 [c]
n-Pentyl	Oct-1-ene	no cooling [b]	60	14 [d]
n-Hexyl	Oct-1-ene	−60 → room temp.	60	traces [e]

[a] Estimated by g.l.c. [b] The reaction was mildly exothermic, the temperature rising to *ca.* 40 °C. [c] Order of addition of reagents was dialkylbromoborane, potassium hydride, alkene. [d] Order of addition of reagents was alkene, dialkyl bromoborane, potassium hydride. [e] Tetrahydrofuran as solvent.

TABLE 3

Yields of alcohols formed by hydroboration–oxidation of alkenes with the system R^A_2BBr–KH–dibenzo-18-crown-6–diglyme

R^A of R^A_2BBr	Alkene B	t/min	Product	Yield (%) [a]
n-Hexyl	Oct-1-ene	10	Octanol	88
n-Hexyl	Oct-1-ene	60	Octanol	87
n-Hexyl	Cyclopentene	15	Cyclopentanol	48
n-Hexyl	Cyclopentene	60	Cyclopentanol	83
Cyclopentyl	Oct-1-ene	15	Octanol	92
Cyclopentyl	Oct-1-ene	15	Octanol	83 [b]
n-Pentyl	Hex-1-ene	15	Hexanol	77
n-Pentyl	Cyclopentene	15	Cyclopentanol	70

[a] Estimated by g.l.c. [b] Order of addition of reagents was potassium hydride, dialkylbromoborane, alkene.

Attempts to form dialkylboranes free from reducing agent or metal salts, by reaction of dialkylbromoboranes with potassium hydride followed by filtration, or by passage of dialkylbromoboranes through a column of potassium hydride, failed, as shown by negligible yields of octanol formed *via* hydroboration–oxidation of oct-1-ene by the products of such reactions.

The foregoing results indicate that hydroboration of alkenes by dialkylborane species produced from dialkylbromoboranes and sodium hydride or potassium hydride can occur in high yield, but the possibility remains that redistribution, leading to a mixture of trialkylboranes ($R^A_3B + R^A_2BR^B + R^ABR^B_2 + R^B_3B$) might occur. As a means of determining the degree of redistribution, a number of the trialkylboranes prepared were converted directly, without isolation, into the corresponding tertiary alcohols by the cyanoborate process [equation (3)]. In other reactions it has been shown [9] that the tertiary alcohol produced corresponds to the

$$R^AR^BR^CB \xrightarrow{i,\ ii,\ iii,} R^AR^BR^CCOH \qquad (3)$$

Reagents: *i*, KCN; *ii*, $(CF_3CO)_2O$; *iii*, basic H_2O_2

starting trialkylborane, *i.e.* that redistribution does not occur to any significant extent during the cyanoborate process.

In the cases examined, redistribution was found to be higher than 10% only when a secondary alkene was hydroborated using a dialkylborane generated from reaction of a dialkylbromoborane with potassium hydride. This must have been due to a rapid formation of the hydroborating species and relatively slow hydroboration of the alkene. This would allow maximum lifetime for compounds with free B–H bonds, which catalyse the redistribution process. Using the much slower reaction with sodium hydride, redistribution was never found to exceed 7% and was typically *ca.* 2% (Table 4). The yield of tertiary alcohol formed in the process involving sodium hydride was higher than that

TABLE 4

Extent of redistribution during formation of $R^A{}_2BR^B$ estimated by the three-migration cyanoborate reaction

Tertiary alcohol	Reagent	Yield (%)	Proportion of redistribution products
n-Hexyl(n-pentyl)$_2$COH	NaH	86 [a]	6
Cyclopentyl(n-pentyl)$_2$COH	NaH	83 [a]	<2
(Cyclohex)$_2$(cyclopentyl)COH	NaH	81 [a]	7
n-Octyl(n-hexyl)$_2$COH	KH	49 [b]	10
n-Octyl(cyclopentyl)$_2$COH	KH	30 [b]	<5
n-Hexyl(n-pentyl)$_2$COH	KH	37 [b]	6
Cyclopentyl(n-hexyl)$_2$COH	KH	47 [b]	Completely redistributed

[a] By isolation; yield includes any alkene formed from the tertiary alcohol during work-up. [b] This does not include alkene formed on work-up.

using potassium hydride because of the lower efficiency of production of the trialkylborane in the latter reaction.

In conclusion, the reagent of choice for the reduction of dialkylbromoboranes appears to be sodium hydride, which gives high yields of product and little redistribution of alkyl groups, provided a good sample of hydride is used. The only advantage to be gained in using potassium hydride is the speed of reaction. However, the inability to introduce secondary alkyl groups without scrambling is a serious disadvantage when potassium hydride is used.

EXPERIMENTAL

All reagents were prepared and purified by previously reported procedures.[10] Metal hydrides were estimated by hydrogen evolution and the base other than hydride was estimated by difference after titration of a sample with standard acid. All reactions were carried out in static atmospheres of dry nitrogen.

Typical Reduction of a Dialkylbromoborane by Sodium Hydride.—To a cooled [−63 °C (bath temp.)] stirred mixture of sodium hydride (*ca.* 0.16 g, *ca.* 5.5 mmol of 78.6% suspension; very low in base other than NaH), diglyme (5 ml), and oct-1-ene (1.25 ml, 8 mmol) was added di-n-hexylbromoborane (1.30 g, *ca.* 5 mmol) dropwise. The mixture was allowed to warm to room temperature and was stirred for 7 h. The excess of oct-1-ene was removed under reduced pressure and the excess of sodium hydride was destroyed with n-butanol. G.l.c. estimation of the alcohols produced by alkaline oxidation [10] showed a 99% yield of octan-1-ol.

Typical Potassium Hydride Reduction of a Dialkylbromoborane.—To a stirred mixture of potassium hydride (0.94 g, 5.55 mmol), diglyme (5 ml), and oct-1-ene (0.90 ml, 6 mmol) was added di-n-pentylbromoborane (1.00 ml, 4.50 mmol), in a dropwise fashion. An exothermic reaction (temperature rising to *ca.* 40 °C) resulted. After 1 h the excess of alkene was removed *in vacuo* and the excess of hydride was destroyed with n-butanol. Oxidation with alkaline hydrogen peroxide gave a 63% yield (g.l.c.) of octan-1-ol.

Typical Crown-ether-promoted Potassium Hydride Reduction.—To a stirred mixture of dibenzo-18-crown-6 (0.078 g), potassium hydride (0.80 g, 3.90 mmol), diglyme (4 ml), and oct-1-ene (1.30 ml, 8.0 mmol), cooled in a water bath, was added dicyclopentylbromoborane (0.84 g, 3.61 mmol) dropwise. After 15 min the experiment was worked up as usual to give a 92% yield of octan-1-ol.

Typical Triple-migration Cyanoborate Experiment.—To a stirred cooled (water-bath) mixture of dibenzo-18-crown-6 (0.111 g), potassium hydride dispersion (1.07 g, 5.23 mmol), diglyme (5 ml), and oct-1-ene (1.30 ml, 8.0 mmol) was added di-n-hexylbromoborane (1.39 ml, 5.23 mmol) dropwise. After 20 min a side-arm, pre-charged with potassium cyanide (0.343 g, 5.20 mmol), was rotated so as to introduce the solid, and the mixture was stirred for a further 1 h, after which time the cyanide had dissolved. The mixture was cooled (ice-bath) and trifluoroacetic anhydride (4.3 ml, 31.2 mmol) was added. After complete addition, the reaction mixture was heated under reflux for 6 h. The excess of trifluoroacetic anhydride was removed under reduced pressure. Butan-2-ol (1 ml) was added, and the mixture was oxidised as usual. Work-up, followed by chromatography over alumina (activity III, elution with light petroleum followed by dichloromethane), gave the tertiary alcohol [0.80 g, 49%; containing 10% (by g.l.c. on PEGA) of this as redistribution products] in the dichloromethane fraction. Distillation gave pure 7-hexylpentadecan-7-ol,[11] b.p. 115—118 °C at 0.005 mmHg; $\nu_{max.}$ (film) 3 440 cm^{-1}; τ ($CDCl_3$) 8.75 (35 H, broad, 17 CH_2 and OH), 9.13 (9 H, t, 3 CH_3) (on addition of D_2O the shoulder at τ 8.73 disappeared and the integral for the signal at τ 8.75 decreased to 34 H); *m/e* 294 $(M - H_2O)^{\cdot+}$ (0.8%), 227 $(M - C_6H_{13})^+$ (99%), and 199 $(M - C_8H_{17})^+$ (100%) (Found: C, 81.0; H, 14.1. Calc. for $C_{21}H_{44}O$: C, 80.7; H, 14.2%).

The following were prepared using sodium hydride: 6-pentyldodecan-6-ol, n_D^{20} 1.450 7, $\nu_{max.}$ (film) 3 440 cm^{-1} [Found: *m/e* 185.190 5 and 171.174 9. Calc. for $C_{12}H_{25}O$ $(M - C_5H_{11})^+$: *m/e* 185.190 530. Calc. for $C_{11}H_{23}O$ $(M - C_6H_{13})^+$: *m/e* 171.174 88]; 6-cyclopentylundecan-6-ol [Found: *m/e* 171.174 9 and 169.159 2. Calc. for $C_{11}H_{23}O$ $(M - C_5H_9)^+$: *m/e* 171.174 88. Calc. for $C_{11}H_{21}O$ $(M - C_5H_{11})^+$: *m/e* 169.159 23]; and cyclohexyldicyclopentylmethanol; g.l.c. of the crude product showed 7% of redistribution product; purification on alumina gave only dehydration product: n_D^{20} 1.510 5, $\nu_{max.}$ (film) 1 670 cm^{-1} [Found: C, 87.95; H, 12.05%; *m/e* 232.219 1 and 163.148 7. Calc. for $C_{17}H_{28}$: C, 87.92; H, 12.08%; *m/e* 232.219 09. Calc. for $C_{12}H_{19}$ $(M - C_5H_9)$: *m/e* 163.148 67.

The following were prepared using potassium hydride in the absence of crown ether: 6-pentyldodecan-6-ol, $\nu_{max.}$ (film) 3 425 cm^{-1}; τ ($CDCl_3$) 8.74 (26 H, broad, 13 CH_2), 8.82 (1 H, s, exchangeable, OH), 9.13 (9 H, t, 3 CH_3); *m/e* 238 $(M - H_2O)^{\cdot+}$ (5%), 185 $(M - C_5H_{11})^+$ (100%), and 171 $(M - C_6H_{13})^+$ (64%) [Found: *m/e* 238.266 0, 185.190 5, and 171.174 9. $C_{17}H_{34}$ $(M - H_2O)^{\cdot+}$ requires *m/e*, 238.266 04. $C_{12}H_{25}O$ requires *m/e*, 185.190 53. $C_{11}H_{23}O$ requires *m/e*, 171.174 88]; and 1,1-*dicyclopentylnonan*-1-*ol*, $\nu_{max.}$ (film) 3 490 cm^{-1}; τ ($CDCl_3$) 8.06 (2 H, m, 2 CH), 8.48 (16 H, broad, 8 CH_2), 8.76 (14 H, broad, 7 CH_2), 8.81 (1 H, s, OH), 9.13 (3 H, t, CH_3) [Found: *m/e*, 262.266 0, 211.205 7, and 167.143 6. $C_{19}H_{34}$ $(M - H_2O)^{\cdot+}$ requires *m/e*, 262.266 04. $C_{14}H_{27}O$ requires *m/e*, 211.206 18. $C_{11}H_{19}O$ requires *m/e*, 167.143 58].

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