Synthesis of Secondary or Tertiary Alcohols by Reactions of Trialkylboranes with Acyl Carbanion Equivalents[1]

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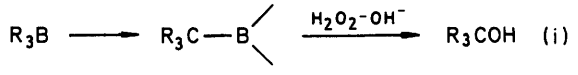
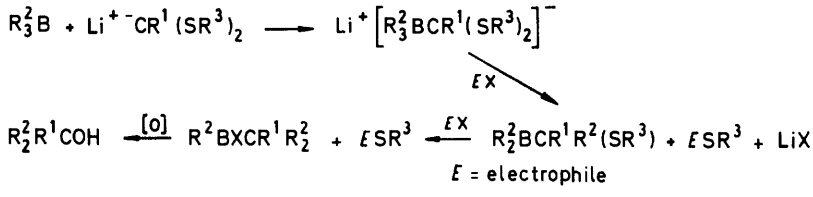
Reactions of trialkylboranes (R^2_3B) with 1-lithio-1,1-bis(phenylthio)alkanes [$R^1(PhS)_2C^-Li^+$; R^1 = H or Pr^n], followed by reaction with mercury(II) chloride and oxidative work-up, give high yields of secondary (R^1 = H) or tertiary (R^1 = Pr^n) alcohols ($R^1R^2_2COH$).

TRIALKYLBORANES have a unique potential as reagents for use in synthesis.[2] A particularly useful operation is their conversion into the corresponding tertiary alcohols [reaction (i)], as in reactions of trialkylcyanoborates with electrophiles,[3] and of trialkylboranes with carbon monoxide[4] or the anion derived from dichloromethoxymethane.[5]



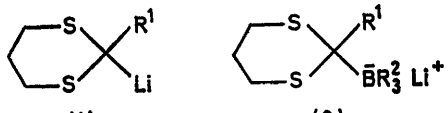
Utilisation of this reaction for making 'mixed' trialkylmethanols requires the preparation of 'mixed' trialkylboranes, for which few general methods are available.[6,7] Hence, we have looked for an approach to trialkylmethanols in which two alkyl groups are drawn from an organoborane and the third from an acyl carbanion equivalent. We chose[1] to work with sulphur-stabilised thioacetal anions[8] as the acyl carbanion equivalents (Scheme 1). A similar result has been achieved by using the reactions of dialkylchloroboranes with 1-iminoalkyl-lithium derivatives.[9]



SCHEME 1 E = electrophile

RESULTS AND DISCUSSION

Initial Studies of the Reaction of Organoboranes with 2-Lithio-1,3-dithian.—The reaction of 2-lithio-1,3-dithian



(1) (2)

(1; R^1 = H) with an equimolar quantity of tri-n-butylborane gave a complex of type (2; R^1 = H, R^2 = Bu^n), nonan-5-ol, but the yields were not encouraging. Furthermore, tricyclopentylborane gave only low yields of dicyclopentylmethanol under the same conditions. Although the yields could be improved (*e.g.* to 74% from trioctylborane and 32% from tricyclopentylborane) by employing a 100% excess of the lithiodithian (1; R^1 = H) with 4 mol. equiv. of mercury(II) chloride, this is still not a useful general synthetic method. Furthermore, from (1; R^1 = Pr^n) negligible yields of the corresponding tertiary alcohols ($R^1R^2_2COH$) were obtained.

Initial Studies on Reactions of 1-Lithio-1,1-bis(phenylthio)alkanes with Organoboranes.—We next turned to the as evidenced[1c] by an i.r. absorption at 2 720 cm^{-1} and a broad ^1H n.m.r. signal centred at τ *ca.* 10.1, characteristic of CH_2 attached to negatively charged boron.[10] However, the complex did not undergo the spontaneous alkyl migration reaction (characteristic of many other α-hetero-substituted organoboron compounds), even at 50 °C, as shown by the almost quantitative recovery of butan-1-ol and the failure to detect any pentanal or nonan-5-ol upon oxidation.

In an attempt to induce migrations, the reactions of a variety of electrophiles with the complex (2; R^1 = H, R^2 = Bu^n) were studied. The results (Table 1) indicated that it is possible to induce migrations, giving

[1] Preliminary communications, (*a*) R. J. Hughes, A. Pelter, and K. Smith, *J.C.S. Chem. Comm.*, 1974, 863; (*b*) R. J. Hughes, A. Pelter, K. Smith, E. Negishi, and T. Yoshida, *Tetrahedron Letters*, 1976, 87; (*c*) E. Negishi and T. Yoshida, A.C.S. Meeting, Chicago, August 1973.

[2] G. M. L. Cragg, 'Organoboranes in Organic Synthesis,' Dekker, New York, 1973; H. C. Brown, 'Boranes in Organic Chemistry,' Cornell University Press, Ithaca, 1972.

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

[4] H. C. Brown, *Accounts Chem. Res.*, 1969, **2**, 65; E. Negishi and H. C. Brown, *Synthesis*, 1972, 197, and references cited therein.

[5] H. C. Brown and B. A. Carlson, *J. Org. Chem.*, 1973, **38**, 2422; H. C. Brown, J.-J. Katz, and B. A. Carlson, *ibid.*, p. 3968.

[6] For a discussion of the problems associated with the synthesis of 'mixed' organoboranes, see K. Smith, *Chem. Soc. Rev.*, 1974, **3**, 443.

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

[8] For a review of nucleophilic acylating agents, see D. Seebach and M. Kolb, *Chem. and Ind.*, 1974, 687.

[9] Y. Yamamoto, K. Kondo, and I. Moritani, *J. Org. Chem.*, 1975, **40**, 3644.

[10] R. Damico, *J. Org. Chem.*, 1964, **29**, 1971.

reactions of 1-lithio-1,1-bis(phenylthio)alkanes (3; R^1 = H or Pr^n) in the hope that with phenylthio leaving groups migration in the intermediate borates (4) would

TABLE 1

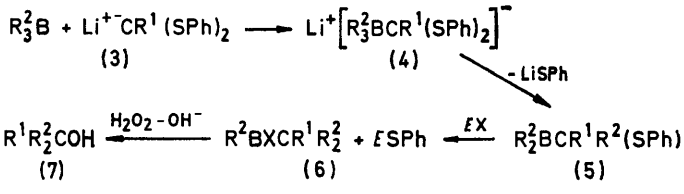
Production of nonan-5-ol by reaction of the complexes (2; R^1 = H, R^2 = Bu^n) with electrophiles

Electrophile	No. of mol. equiv.	Yield of Bu^n_2CHOH (%) [a]
FSO_3Me	1	0
FSO_3Me	2	8
FSO_3Me	4	62
MeI	4	15
$CuCl_2$–CuO	2	3
$HgCl_2$	4	50

[a] All reactions carried out in tetrahydrofuran; electrophile added at −78 °C and the mixture allowed to come to room temperature over 3 h before oxidation. Yield estimated by g.l.c. after addition of an internal standard.

be greatly improved (Scheme 2). During our work a communication appeared which showed that the rearrangement (4) ⟶ (5) was spontaneous,[11] so we concentrated upon attempting to achieve a high-yield conversion of (5) into (6), which upon oxidation would yield secondary or tertiary alcohols (7; R^1 = H or Pr^n).

The utility of various electrophiles for induction of this rearrangement was investigated by studying reactions, under standard conditions, of 4 mol. equiv. of



SCHEME 2

each with compound (5; R^1 = Pr^n, R^2 = n-octyl), prepared according to the conditions described by Mukaiyama[11] (Table 2). Mercury(II) chloride and

TABLE 2

Effect of electrophiles for induction of the rearrangement of (5; R^1 = Pr^n, R^2 = n-octyl) ⟶ (6)

Electrophile	Yield of (7; R^1 = Pr^n, R^2 = n-octyl) (%) [a]
MeI	18
FSO_3Me	78
Me_2SO_4	18
CuI	46
$HgCl_2$	96

[a] All reactions carried out in tetrahydrofuran. Electrophile added at −78 °C; mixture stirred 30 min at −78 °C and warmed to room temperature over 1 h before oxidation. Yield estimated by g.l.c.

methyl fluorosulphate gave acceptable yields of (7) after oxidation, although the latter electrophile also caused some polymerisation of the solvent (tetrahydrofuran), making isolation of the product more difficult. Diethyl ether and bis-(2-methoxyethyl) ether were tested as alternative solvents for the alkylation reaction, but reaction was much slower in these solvents. Thus, in bis-(2-methoxyethyl) ether, 18 h at room temperature was necessary to achieve a yield of 84%. Hence, mercury(II) chloride appeared to be the most convenient electrophile to induce the rearrangement of (5) ⟶ (6).

Variation of the amount of mercury(II) chloride used for the rearrangement (5; R^1 = Pr^n, R^2 = n-octyl) ⟶ (6) showed that the large excess used in the initial experiments was not necessary, and that reaction was essentially complete (86%) even when 1 mol. equiv. was employed. For further studies 1.5 mol. equiv. was used.

It was also shown that the period at room temperature prior to oxidation was unnecessary for completion of the rearrangement. The yield of (7; R^1 = Pr^n, R^2 = n-octyl) was essentially the same (93%) when oxidation was effected as soon as the mixture had reached 0 °C as when the mixture was left for 1 h at room temperature prior to oxidation. For subsequent experiments, therefore, oxidation was effected as soon as the mixture had warmed to 0 °C.

Synthesis of Tertiary Alcohols.—The optimum conditions established in the preliminary experiments were applied (Table 3) in reactions of representative sym-

TABLE 3

Synthesis of tertiary alcohols by reaction of trialkylboranes with the dithioacetals (3; R^1 = Pr^n)

R^2 of R^2_3B	Yield of $R^2_2Pr^nCOH$ (%) [a]
n-Octyl	90 [b]
n-Hexyl	96 [b]
Cyclohexyl	98
Cyclopentyl	85

[a] Yield of isolated product after chromatographic purification based on alkene used to form the trialkylborane, on the assumption that 3 mol of alkene (*i.e.* one of trialkylborane) gave 1 mol of product (see Scheme 2); reactions performed on 1 mmol scale. [b] Product contains *ca.* 10% of the isomer in which one of the n-alkyl groups is replaced by an s-alkyl group, present because hydroboration is not entirely regiospecific (H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962).

metrical trialkylboranes with the dithioacetals (3; R^1 = Pr^n). The reaction proved versatile for the synthesis of tertiary alcohols, accommodating both primary and secondary alkyl groups in the organoborane. Since the organoboranes were prepared by hydroboration, which is not a completely regiospecific reaction for simple alk-1-enes, the product necessarily contained small quantities of isomeric impurities. This, however, could be overcome by use of an alternative synthesis of the organoborane. One of the alkyl groups of the organoborane is necessarily wasted during the reaction (Scheme 2).

1,1,2-Trimethylpropyldi-n-octylborane (di-n-octylthexylborane) gave 9-propylheptadecan-9-ol in 80% yield under the same conditions, with no detectable yield of the product of migration of the tertiary alkyl group. This suggested that use of dialkylthexylboranes might

[11] S. Yamamoto, M. Shiono, and T. Mukaiyama, *Chem. Letters*, 1973, 961.

permit a general synthesis of partially mixed trialkylmethanols without loss of potentially valuable alkyl residues, or even permit syntheses of totally mixed trialkylmethanols. Dialkylthexylboranes have indeed been used to advantage in this way in the cyanoborate [12] and other [13] reactions. However, attempts to carry out the present reaction with cyclopentyl-n-octylthexylborane and dicyclopentylthexylborane resulted in only low yields of the tertiary alcohols, even after extended reaction periods. It seems that such highly hindered organoboranes do not readily form the intermediate complexes (4) because of steric inhibition, a supposition which is supported by the observation that another relatively hindered organoborane, tris-*exo*-2-norbornylborane, gives little tertiary alcohol under our standard conditions. We are now seeking ways of circumventing this difficulty. Meanwhile, the reaction is a useful synthesis of partially mixed trialkylmethanols where steric hindrance is not a major problem.

We have carried out one reaction on a larger (20 mmol) scale, obtaining 7-propyltridecan-7-ol from tri-n-hexylborane in 87% yield, without modification of the reaction conditions.

Synthesis of Secondary Alcohols.—Application of the standard conditions developed for tertiary alcohol synthesis to the reaction of tri-n-hexylborane with bis(phenylthio)methyl-lithium (3; $R^1 = H$) resulted in the production of tridecan-7-ol in only 15% yield. However, use of 3 mol. equiv. of mercury(II) chloride, instead of the 1.5 mol. equiv. used for tertiary alcohols, resulted in an improvement of the yield to 85%. These conditions were then applied successfully to the reactions of compounds (3; $R^1 = H$) with tricyclopentyl- and tricyclohexyl-boranes (Table 4). Furthermore, with

TABLE 4

Synthesis of secondary alcohols by reaction of trialkylboranes R^2_3B with dithioacetals (3; $R^1 = H$)

R^2 of R^2_3B	Yield of R^2_2CHOH (%) [a]
n-Hexyl	85 [b]
Cyclopentyl	88
Cyclohexyl	88
exo-2-Norbornyl	75

[a,b] As footnotes to Table 3.

additional slight modifications of the reaction conditions (see Experimental section), even hindered organoboranes such as tris-*exo*-2-norbornylborane (Table 4) and dicyclopentylthexylborane, which had given difficulties in the tertiary alcohol reaction, could be used satisfactorily for secondary alcohol preparation.

Dicyclopentylthexylborane gave dicyclopentylmethanol (80%) with no indication of the product of migration of the tertiary group, which suggested that there might be a clear order of migratory aptitudes, primary > secondary > tertiary, as in the cyanoborate reaction.[14] However, application of the reaction to di-n-octylthexylborane and cyclopentyl-n-octylthexylborane gave mixtures of all possible secondary alcohols, indicating that the migration step in these cases, if not entirely random, was certainly not highly selective. The migratory selectivities observed by us in the reactions of dicyclopentylthexylborane with (3; $R^1 = H$) and di-n-octylthexylborane with (3; $R^1 = Pr^n$), and observed by Corey [15] in the reaction of a 9-alkyl-9-borabicyclo[3.3.1]nonane with (3; $R^1 = Me$), cannot, therefore, be considered as general. Work is in hand to discover the factors which influence these migratory aptitudes.

In order to establish that there were no major problems associated with scaling up of the secondary alcohol synthesis, we have prepared dicyclopentylmethanol from tricyclopentylborane on a 20 mmol scale. Under the standard conditions, the yield of distilled product was 66%.

EXPERIMENTAL

Ether solvents were distilled from CaH_2 or $LiAlH_4$ under nitrogen prior to use. 1,3-Dithian (Aldrich) was used directly. 1,1-Bis(phenylthio)butane was prepared from butanol and benzenethiol,[16] and 2-propyl-1,3-dithian was prepared by the analogous reaction of butanal with propane-1,3-dithiol. Bis(phenylthio)methane was synthesised from di-iodomethane and sodium benzenethiolate.[17] Butyllithium (Ventron) was estimated by double titration [18] prior to use. Mercury(II) chloride (B.D.H.) was used without further purification. Organoboranes were prepared according to published procedures,[12,19] from alkenes which were distilled from $LiAlH_4$ prior to use. Diborane was kept as a boron trifluoride-free solution in tetrahydrofuran [12] and was standardised prior to use. G.l.c. was performed with a Perkin-Elmer F11 instrument. Mass spectra were obtained with an A.E.I. MS9 spectrometer, ^1H n.m.r. spectra with a Varian HA100 spectrometer, and i.r. spectra with a Perkin-Elmer 257 instrument.

The standard reaction vessel was a 100 ml three-necked flask equipped with stirrer. One neck was connected *via* a three-way tap to a vacuum pump or to a cylinder of oxygen-free nitrogen (with pressure release bubbler). The second was fitted with a pressure-equalised dropping funnel, the top of which was sealed with a tap capped by a silicone rubber septum which was used for the introduction of reagents or for sampling. The third neck was stoppered when only liquid reagents were to be added, or fitted [12] with a side-arm bent to an angle of *ca.* 100° for reactions in which it was necessary to introduce a solid at a late stage. Large-scale (20 mmol) experiments were carried out in similar apparatus, but with a 500 ml flask.

All manipulations prior to oxidation were carried out in dry glassware (oven-dried and assembled hot), under nitrogen (three repetitions of a cycle involving evacuation

[12] A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, *J.C.S. Perkin I*, 1975, 129.
[13] E. Negishi and H. C. Brown, *Synthesis*, 1974, 77.
[14] A. Pelter, M. G. Hutchings, and K. Smith, *J.C.S. Perkin I*, 1975, 145.
[15] E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *J. Org. Chem.*, 1976, **41**, 260.
[16] E. Benzing, U.S.P. 3,118,002/1964 (*Chem. Abs.*, 1964, **60**, 11899d); *cf.* W. Autenrieth and K. Wolff, *Ber.*, 1899, **32**, 1375.
[17] E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4098.
[18] H. Gilman and J. W. Morton, *Org. Reactions*, 1954, **8**, 286.
[19] H. C. Brown, 'Organic Synthesis *via* Boranes,' Wiley-Interscience, New York, 1975.

and refilling with nitrogen before the start of any reaction). Dry syringes (ref. 19; appendix) were used to transfer liquids.

Reaction of Tri-n-butylborane with 2-Lithio-1,3-dithian and Mercury(II) Chloride; Initial Study.—The flask was charged with 1,3-dithian (1.20 g, 10 mmol), the side arm with mercury(II) chloride (10.84 g, 40 mmol), and the apparatus was filled with nitrogen. Tetrahydrofuran (THF) (10 ml) was placed in the flask, and the mixture cooled to −30 °C and stirred during addition of n-butyl-lithium (4.8 ml of 2.27M-solution in hexane; 11 mmol). The mixture was stirred at −30 °C for 1.5 h to complete formation of the anion.[8] Meanwhile, to the dropping funnel was added borane–THF (9.8 ml of a solution 1.02M in 'BH_3'; 10 mmol) and, with swirling, but-1-ene (2M-solution in THF; 15.0 ml; 30 mmol), the temperature being controlled by surrounding the funnel with cotton wool soaked in acetone. The mixture was left at room temperature for *ca.* 1 h and then, with the temperature of the flask maintained at −30 °C, it was added to the solution of the anion. The mixture was stirred for 1 h at −30 °C, then cooled to −78 °C for addition of the mercury chloride. After stirring at −78 °C for 30 min, the mixture was allowed to warm to room temperature and stirred for a further 3 h. It was then exposed to the atmosphere and oxidised by cautious addition, at 0 °C, of 3N-sodium hydroxide (4.0 ml; 20% excess) and, at room temperature, 30% hydrogen peroxide (4.0 ml; 20% excess). The mixture was stirred overnight at room temperature, heated to 40—50 °C for 30 min to complete the oxidation, and then cooled. The organic products were extracted into pentane (aqueous layer saturated with NaCl) and analysed by g.l.c. (4% PEGA on Chromosorb G; 1 m column; temperature programme from 50 to 190 °C), with tridecane as an added standard. This showed the presence of 0.72 g (5.0 mmol, 50%) of nonan-5-ol.

Other Initial Experiments with 1,3-Dithian.—Reactions were carried out as above, with methyl fluorosulphate [(i) 10 mmol, (ii) 20 mmol, (iii) 40 mmol], iodomethane (40 mmol), or a mixture of copper(II) chloride–copper(II) oxide (20 mmol of each) as electrophiles. The yields of nonan-5-ol are in Table 1.

Heptadecan-9-ol by Reaction of Tri-n-octylborane with Two Equivalents of 2-Lithio-1,3-dithian.—The reaction was performed as in the initial experiments, but with oct-1-ene (3.36 g, 30 mmol) replacing but-1-ene, except that 20 mmol of 1,3-dithian (2.40 g) and 22 mmol of n-butyl-lithium (9.6 ml of 2.27M-solution) were used for preparation of the anion, and larger excesses of sodium hydroxide (100%) and hydrogen peroxide (100%) were employed for oxidation. After extraction of the product into pentane, the extract was dried and evaporated. The crude product was transferred to the top of a column of dry silica (60—120 mesh; B.D.H.; *ca.* 100 g) with the aid of a little pentane, and eluted first with pentane, then with dichloromethane, this latter eluant carrying the heptadecan-9-ol (1.89 g, 74%).

An identical experiment with tricyclopentylborane (10 mmol) gave dicyclopentylmethanol (0.54 g, 32%). The characterisation of these compounds is reported below.

Reactions with 1-Lithio-1,1-bis(phenylthio)butane; Preliminary Investigations.—To the flask was added 1,1-bis-(phenylthio)butane (2.74 g, 10 mmol), and the whole apparatus was filled with nitrogen. THF (10 ml) was added to the flask, which was cooled to −30 °C before addition of n-butyl-lithium (4.8 ml of 2.27M-solution; 11 mmol). The mixture was stirred at −30 °C for 1.5 h to complete formation of the anion.[11] Tri-n-octylborane (10 mmol) was prepared in the dropping funnel, as above, from oct-1-ene (4.8 ml, 30 mmol), BH_3–THF (8.3 ml of 1.20M-solution in THF), and THF (15 ml). The organoborane was added to the anion, still at −30 °C, and the funnel was washed with THF (5 ml), bringing the total volume of solution to *ca.* 50 ml. The mixture was stirred for 1 h at −30 °C and allowed to come to room temperature over a further 1 h.[11]

The mixture was divided (syringe) into five 10 ml portions; each was transferred to a 50 ml round-bottomed flask fitted with a septum-capped stopcock, which had previously been charged with an electrophile (8 mmol) and cooled to −78 °C. Each mixture was stirred for 30 min at −78 °C and allowed to warm to room temperature over 1 h. The stopcock and septum were removed and the mixture was oxidised as above. Biphenyl was added as internal standard, the aqueous layer was saturated with NaCl and the organic layer was examined by g.l.c. The results are in Table 2.

The reactions used to determine the effects of various quantities of mercury(II) chloride and various reaction conditions were performed in the same way.

Synthesis of 9-Propylheptadecan-9-ol (1 mmol scale).—The reaction was carried out as for the preliminary experiments, with mercury(II) chloride (0.407 g, 1.5 mmol); 1,1-bis(phenylthio)butane (0.274 g, 1 mmol) and n-butyl-lithium (0.55 ml of a 2.0M-solution; 1.1 mmol) in THF (10 ml); oct-1-ene (0.48 ml, 0.34 g, 3 mmol) and BH_3–THF (0.97 ml of 1.03M-solution; 1 mmol); and THF (5 ml) for washing to ensure quantitative transfer of the organoborane to the reaction flask. After addition of mercury(II) chloride at −78 °C, the mixture was allowed to warm to 0 °C, the dropping funnel attachment removed, and 5N-sodium hydroxide (5 ml) and hydrogen peroxide (3 ml of 50%) added. The mixture was stirred vigorously, allowed to reach room temperature, and maintained at that temperature overnight. The product was extracted into pentane (*ca.* 100 ml), washed with N-sodium hydroxide (*ca.* 20 ml) and water (4 × 20 ml), dried ($MgSO_4$), and evaporated. The crude product was transferred to the top of a column of dry silica (*ca.* 50 g; B.D.H.; 60—120 mesh) with the aid of a little pentane, and the column was developed first with pentane (*ca.* 100 ml) and then with dichloromethane (*ca.* 250 ml), which eluted the *9-propylheptadecan-9-ol* (0.27 g, 90%). Distillation (cold-finger) gave a product, b.p. 84—90 °C (bath temp.) at 0.05 mmHg; $n_D^{25.5}$ 1.477 (Found: C, 80.2; H, 13.6%; $M^+ - C_3H_7$, 255.2688; $M^+ - C_8H_{17}$, 185.1905. $C_{20}H_{42}O$ requires C, 80.5; H, 14.2%; $M - C_3H_7$, 255.2688; $M - C_8H_{17}$, 185.1905).

Other Tertiary Alcohols (1 mmol scale).—The following tertiary alcohols were prepared in the same manner: *7-propyltridecan-7-ol* (0.23 g, 96%) [from hexene (0.375 ml, 3 mmol)], b.p. 99—116 °C (bath temp.) at 1 mmHg; n_D^{20} 1.468 (Found: C, 79.5; H, 14.7%; $M^+ - C_3H_7$, 199.2068; $M^+ - C_6H_{13}$, 157.1592. $C_{16}H_{34}O$ requires C, 79.3; H, 14.15%; $M - C_3H_7$, 199.2067; $M - C_6H_{13}$, 157.1592); *1,1-dicyclohexylbutan-1-ol* (0.23 g, 98%) [from cyclohexene (0.31 ml, 3 mmol)], m.p. 69 °C (Found: C, 80.3; H, 12.4%; $M^+ - C_3H_7$, 195.1749; $M^+ - C_6H_{11}$, 155.1436. $C_{16}H_{30}O$ requires C, 80.6; H, 12.7%; $M - C_3H_7$, 195.1749; $M - C_6H_{11}$, 155.1436); *1,1-dicyclopentylbutan-1-ol* (0.18 g, 85%) [from cyclopentene (0.26 ml, 3 mmol)], m.p. 27 °C (Found:

C, 79.8; H, 12.1%; $M^+ - C_3H_7$, 167.1436; $M^+ - C_5H_9$, 141.1279. $C_{14}H_{26}O$ requires C, 79.9; H, 12.45%; $M - C_3H_7$, 167.1436; $M - C_5H_9$, 141.1279). 9-Propylheptadecan-9-ol (0.24 g, 80%) was also prepared from di-n-octylthexylborane [12,19] by an analogous procedure from 2,3-dimethylbut-2-ene (0.12 ml, 1 mmol) and octene (0.32 ml, 2 mmol).

7-Propyltridecan-7-ol (20 *mmol scale*).—The procedure was an exact scale-up of the 1 mmol reaction in terms of temperatures and times. For convenience rather less solvent was used, and a 500 ml flask was therefore sufficient. The quantities employed were: for the preparation of 1-lithio-1,1-bis(phenylthio)butane THF (60 ml), $Pr^nCH(SPh)_2$ (5 ml, 20 mmol), Bu^nLi (10 ml of 2.0M; 20 mmol); for the preparation of the organoborane THF (50 ml), BH_3–THF (20 ml of 1.0M; 20 mmol), hex-1-ene (7.56 ml, 60 mmol); $HgCl_2$ (8.5 g, 32 mmol). After the reaction was complete the dropping funnel was removed and 3N-sodium hydroxide (25 ml, large excess) was added, in portions over 30 min, the temperature being kept below *ca.* 30 °C by cooling in ice–water when necessary. An orange precipitate formed at this stage necessitated a stirrer of large torque. While efficient stirring was maintained, hydrogen peroxide (20 ml of 30%; large excess) was added dropwise over 1.5 h, at such a rate that the reaction proceeded at a manageable rate without cooling. When addition was complete the mixture was stirred overnight at room temperature. The organic products were extracted into light petroleum (*ca.* 200 ml; b.p. 40—60 °C); the extract was washed thoroughly with water (4 × 50 ml), dried ($MgSO_4$), filtered through cotton wool, and evaporated (5.4 g). The residue was divided into two equal parts. One was fractionally distilled under reduced pressure, giving a product (2.10 g, 87%), b.p. 102—115 °C at 1 mmHg, g.l.c. of which showed the presence of small quantities of impurities (4% PEGA on Chromosorb W; 50—190 °C at 12 °C min^{-1}). The other half was passed through a column of dry alumina (Woelm, activity 2; *ca.* 150 g), eluted (yield 2.29 g, 95%) with dichloromethane, and then fractionally distilled, giving a product (1.21 g, 50%) which was pure by g.l.c. except for a little (*ca.* 0.1 g) of the isomeric 5-methyl-6-propyldodecan-6-ol, the product of a non-regiospecific hydroboration step. Physical properties of this sample were as above.

Tridecan-7-ol (1 *mmol scale*).—The apparatus was charged with mercury(II) chloride (0.82 g, 3 mmol) in the side arm and bis(phenylthio)methane (0.232 g, 1 mmol) in the flask before filling with nitrogen. Preparation of bis(phenylthio)methyl-lithium was carried out as for 1-lithio-1,1-bis(phenylthio)butane (1 mmol scale), and conditions for the reaction of the anion with the organoborane (prepared as previously) were also identical. Oxidation and work-up as described for 9-propylheptadecan-9-ol (1 mmol scale) gave tridecan-7-ol (0.17 g, 85%), eluted from the column in 5% diethyl ether–dichloromethane. Distillation (cold finger) gave a solid, m.p. 41 °C (lit.,[20] 41—42 °C).

Other Secondary Alcohols (1 *mmol scale*).—Dicyclopentylmethanol (0.15 g, 88%), m.p. 45 °C (lit.,[21] 46 °C), and dicyclohexylmethanol (0.17 g, 88%), m.p. 64 °C (lit.,[22] 64—65 °C), were prepared as described for tridecan-7-ol, but from tricyclopentylborane (1 mmol) and tricyclohexylborane (1 mmol), respectively. The organoboranes were prepared as previously described.

Dicyclopentylmethanol (0.135 g, 80%) was also prepared from dicyclopentylthexylborane (1 mmol; prepared as previously described [12,19]), the conditions of reaction being only slightly different from those described above. Thus, the mixture was maintained at room temperature for 1 h extra before cooling for addition of mercury(II) chloride, and for 30 min at room temperature before oxidation.

Bis-exo-2-*norbornylmethanol* (0.165 g, 75%) was prepared from tris-*exo*-2-norbornylborane (1 mmol) [from norbornene (1.05 ml of 2.9M-solution in THF); prepared as for tri-n-octylborane], but 2 equiv. of the anion were utilised in this case. The conditions were as for dicyclopentylmethanol from dicyclopentylthexylborane. The product was a solid, m.p. 80 °C (Found: C, 81.7; H, 11.3%; $M^+ - C_7H_{11}$, 125.0966. $C_{15}H_{24}O$ requires C, 81.8; H, 11.0%; $M - C_7H_{11}$, 125.0966).

Dicyclopentylmethanol (20 *mmol scale*).—The temperatures and times were identical with those for the 1 mmol scale reaction. A 500 ml flask was employed, with the following quantities of reagents: in the reaction flask THF (60 ml), $CH_2(SPh)_2$ (4.6 g, 20 mmol), Bu^nLi (10 ml of 2.0M); in the side arm $HgCl_2$ (16.2 g, 60 mmol); in the funnel THF (50 ml), BH_3–THF (12.6 ml of 1.58M; 20 mmol), cyclopentene (5.3 ml, 4.08 g, 60 mmol). After reaction, oxidation was effected as for the 20 mmol scale preparation of 7-propyltridecan-7-ol.

The product was extracted as described above, and distilled under reduced pressure to give dicyclopentylmethanol (2.24 g, 66%), m.p. 45 °C (lit.,[21] 46 °C).

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