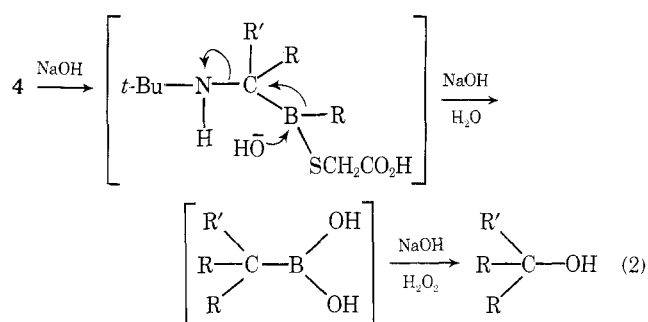


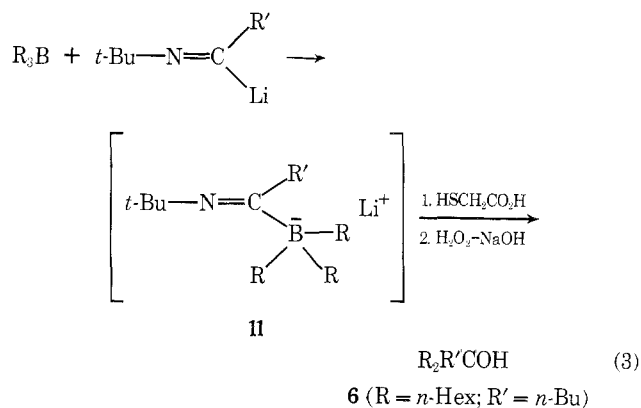


It was anticipated that the migration of an alkyl group (R) from boron to carbon in the initial intermediate (3) was induced by thioglycolic acid, leading to the intermediate borane (4). This was supported by the fact that the oxidation of 4 produced the alcohol (ROH) and *tert*-butylamine along with 5 and also by the previous results on the related reactions.<sup>12</sup> If so, partially mixed trialkylcarbinols may be obtained by achieving the migration of the second alkyl group (R) from boron to carbon in the intermediate (4). Accordingly, we examined the reaction of dihexylchloroborane with lithium aldimine derived from *n*-butyllithium. The yield of the product, 7-*n*-butyl-7-tridecanol (6), depended upon the reaction conditions as shown in Table I. Heating 4 at 80° in diglyme containing aqueous NaOH permitted the desired migration to produce the trialkylcarbinylborane derivatives. The alkaline hydrogen peroxide oxidation gave the partially mixed carbinols in good yields (eq 2).<sup>13</sup> The results are summarized in Table II.



There appears to be no difficulty in introducing primary and secondary alkyl groups. The present procedure offers the following advantages over the previous methods:<sup>5,6</sup> (1) the accommodation of the alkyl group such as isopropyl or methyl, which cannot be introduced via the hydroboration method,<sup>5</sup> (2) utilization of all three alkyl groups without loss of an alkyl group of the boranes.<sup>6,14</sup>

In contrast to the dialkylchloroboranes, the reaction of tri-*n*-hexylborane with the lithium aldimine prepared from *n*-butyllithium, followed by treatment with thioglycolic acid, produced, upon alkaline hydrogen peroxide oxidation, 6 in 87% yield (eq 3). The reaction could not be stopped at



the stage of ketone formation (eq 1), suggesting that the migration in the borate complex (11) proceeds quite rapidly. It seems that this result is a reflection of difference between 4 and 12 which is presumably derived from 11. We

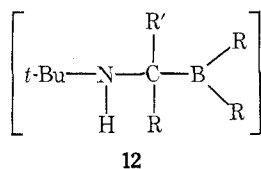


Table I  
Yield of 7-*n*-Butyl-7-tridecanol (6)<sup>a</sup>

Conditions	5-Undecanone (5), %	6, %
HSCH <sub>2</sub> CO <sub>2</sub> H, THF, reflux, 6 hr	44	
(CF <sub>3</sub> CO) <sub>2</sub> O, THF, reflux, 6 hr	16	47
HSCH <sub>2</sub> CO <sub>2</sub> H, 6 M NaOH, THF, reflux, 6 hr	Trace	73
HSCH <sub>2</sub> CO <sub>2</sub> H, 6 M NaOH, diglyme, reflux, 8 hr		87

<sup>a</sup> By GLC analysis. The yields were determined by the use of correction factors.

Table II  
Partially Mixed Trialkylcarbinols via the Reaction of 1 with 2

Dialkylchloroborane	Alkyl lithium	Product	Yield, <sup>a</sup> % (by isoln)
<i>n</i> -Hexyl	<i>n</i> -Butyl	7- <i>n</i> -Butyl-7-tridecanol (6)	87
<i>n</i> -Hexyl	Isopropyl	7-Isopropyl-7-tridecanol (7)	(75)
<i>n</i> -Hexyl	Methyl	7-Methyl-7-tridecanol (8)	(45) <sup>b</sup>
Cyclopentyl	Isopropyl	1,1-Dicyclopentyl-2-methyl-1-propanol (9)	77
<i>n</i> -Butyl	4- <i>n</i> -Pentenyl	5- <i>n</i> -Butyl-9-decen-5-ol (10)	(46) <sup>b</sup>

<sup>a</sup> The yields are based on GLC analysis, and are not necessarily optimum. <sup>b</sup> The low yield must be due to the unfavorable equilibrium of the lithium aldimine.<sup>9</sup>

speculate that the trialkylborane derivative (12) undergoes the further rearrangement more easily than the dialkylborane derivative (4).<sup>15</sup> In fact, simple alkaline hydrogen peroxide oxidation of 11 produced 6 (19% yield) along with 5-undecanone (67% yield). Consequently, if the mildness is required, the reaction with trialkylboranes is recommended. However, the disadvantage is that the reaction uses but two of the three alkyl groups on boron. In order to overcome this difficulty and to prepare totally mixed trialkylcarbinols, the reaction of thexyldialkylboranes (thexyl-BR<sub>2</sub> and thexy-BRR') with lithium aldimines was also attempted. However, such an approach is so far unsuccessful.

## Experimental Section

NMR spectra were recorded on a Jeol JNM-MH-60 instrument; chemical shifts ( $\delta$ ) are expressed in parts per million relative to Me<sub>4</sub>Si. IR spectra were recorded on a Hitachi 215 spectrophotometer. GLC analyses were performed on a Yanaco GCG-550T instrument, using a 2 m 10% SE-30 column. Elemental analyses were performed by Mr. Y. Harada at our Department. All temperatures were uncorrected.

**Reagents.** Reagent-grade solvents were purified by standard techniques and kept over a drying agent. B<sub>2</sub>H<sub>6</sub>-THF, BH<sub>2</sub>Cl-OEt<sub>2</sub>, tri-*n*-hexylborane, and dialkylchloroboranes were prepared according to the known procedures.<sup>16</sup> Butyllithium in hexane was a commercial product. Methyl lithium in ether and isopropyl lithium in pentane were prepared by standard procedures.<sup>17</sup> 4-*n*-Pentenyl lithium was prepared from 5-bromo-1-pentene and lithium dispersion in ether at -30 to -20°. The titration was performed by Gilman's<sup>19</sup> or Eastham's<sup>20</sup> method.

**General Procedure.** In a 200-ml flask maintained under N<sub>2</sub> and fitted with a septum inlet, magnetic stirrer, and reflux condenser were placed *tert*-butylisocyanide (3.6 ml, 30 mmol) and dry ether (60 ml). The solution was cooled to 0° and a solution of alkyl lithium (30 mmol) was added dropwise. The mixture was stirred for 30 min at 0°, and then cooled to -78° with a dry ice-acetone bath. Dialkylchloroborane (30 mmol) was added, and the resultant

Table III  
 Physical Data for Alcohols<sup>a</sup>

Compd	Bp, °C (mm)	<i>n</i> <sup>20</sup> <sub>D</sub>	NMR data, δ (CCl <sub>4</sub> , 60 MHz) <sup>b</sup>	Ir, cm <sup>-1</sup> (neat)
6	108–110 (1) 163–165 (10) <sup>c</sup>	1.4495 1.4489 <sup>c</sup>	0.90 (t, 9 H), 1.21 (br s, 26 H)	3400, 1140
7	94–95 (0.2)	1.4517	0.83 (d, 6 H), 0.88 (t, 6 H) 1.26 (br s, 20 H), 1.66–2.00 (m, 1 H)	3495, 1140
8	87–88 (1) 160–162 (15) <sup>d</sup>	1.4450	0.89 (t, 6 H), 1.07 (s, 3 H) 1.29 (br s, 20 H)	3385, 1140
9	76–78 (0.3)	1.4967	0.93 (d, 6 H), 1.55 (br s, 16 H) 1.63–2.28 (m, 3 H)	3535, 1175
10	90–93 (1)	1.4557	0.95 (t, 6 H), 1.37 (br s, 16 H) 1.85–2.15 (m, 2 H), 4.79 (m, 1 H) 4.99–5.08 (m, 1 H), 5.34–6.15 (m, 1 H)	3400, 1639, 1130 988, 905

<sup>a</sup> The alcohols gave satisfactory elemental analyses the results of which have been provided to the Editor. <sup>b</sup> The absorption corresponding to OH is not listed; br s = broad s. <sup>c</sup> A. D. Petrov and M. V. Vittikh, *Bull. Acad. Sci. URSS, Cl. Sci. Chim.*, 238 (1944). <sup>d</sup> M. Asano and T. Yamakawa, *J. Pharm. Soc. Jpn.*, 70, 474 (1950).

mixture was kept at -78° for 30 min. Thioglycolic acid (4.2 ml, 60 mmol) was then added, and the reaction mixture was allowed to come to room temperature over 1 hr. The solvent was removed at reduced pressure and replaced with diglyme (60 ml) and 6 M aqueous NaOH (15 ml). The resultant mixture was refluxed for 8 hr (the temperature in the flask was at 80°). Oxidation was accomplished by the addition of 6 M aqueous NaOH (20 ml)–30% H<sub>2</sub>O<sub>2</sub> (40 ml). Petroleum ether (60 ml) was added, and the organic phase was separated, washed with water (60 ml), and dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. The solvents were removed and the product was obtained by distillation under reduced pressure. GLC yields were determined by the use of correction factors with appropriate hydrocarbons as an internal standard. All new products exhibited expected spectral characteristics and provided satisfactory elemental analyses (Table III).

**Reaction of Dihexylchloroborane with Lithium Aldimine Derived from *n*-Butyllithium under Various Conditions.** Essentially the same procedure as above was employed (10-mmol scale). Thioglycolic acid or trifluoroacetic anhydride was added at -78° after the addition of dihexylchloroborane, and the reaction was allowed to come to room temperature over 1 hr. The solvent was replaced with THF. The resultant mixture was refluxed for 6 hr, or refluxed after the addition of 6 M NaOH. The mixture was oxidized and analyzed with GLC (Table I).

**Reaction of Trihexylborane with Lithium Aldimine Derived from *n*-Butyllithium.** The lithium aldimine (3 mmol) was prepared by the same procedure as above. To the solution was added trihexylborane (0.85 g, 3.2 mmol) at 0°, and the resultant mixture was stirred for 5 hr at room temperature. Thioglycolic acid (0.85 g, 9.2 mmol) was then added at 0°, and the mixture was stirred for 2 hr at room temperature. Oxidation was accomplished by the same method as above. GLC analysis revealed the formation of 6 in 87% yield, which was determined by the use of correction factors.

**Registry No.**—6, 56846-92-5; 7, 56846-93-6; 8, 19016-75-2; 9, 56846-94-7; 10, 56846-95-8; chlorodihexylborane, 18379-62-9; chlorodicyclopentylborane, 36140-18-8; chlorodibutylborane, 1730-69-

4; butyllithium, 109-72-8; isopropyllithium, 1888-75-1; methyllithium, 917-54-4; 4-*n*-pentenyllithium, 54313-25-6.

### References and Notes

- (1) For a preliminary communication, see Y. Yamamoto, K. Kondo, and I. Moritani, *Tetrahedron Lett.*, 2689 (1975).
- (2) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 2737 (1967).
- (3) A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, 1048 (1971); 186 (1973); A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, *J. Chem. Soc., Perkin Trans. 1*, 138 (1975).
- (4) H. C. Brown and B. A. Carlson, *J. Org. Chem.*, **38**, 2422 (1973); with HCClF<sub>2</sub> and related methanes, H. C. Brown, B. A. Carlson, and R. H. Prager, *J. Am. Chem. Soc.*, **93**, 2070 (1971).
- (5) H. C. Brown, E. Negishi, and S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 6648 (1970); H. C. Brown and S. K. Gupta, *ibid.*, **93**, 1818, 4062 (1971).
- (6) R. J. Hughes, A. Pelter, and K. Smith, *J. Chem. Soc., Chem. Commun.*, 863 (1974).
- (7) H. C. Brown, J.-J. Katz, and B. A. Carlson, *J. Org. Chem.*, **38**, 3968 (1973).
- (8) G. Zweifel and R. P. Fisher, *Synthesis*, 339 (1974).
- (9) G. E. Niznik, W. H. Morrison, III, and H. M. Walborsky, *J. Org. Chem.*, **39**, 600 (1974); H. M. Walborsky, W. H. Morrison, III, and G. E. Niznik, *J. Am. Chem. Soc.*, **92**, 6675 (1970).
- (10) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **94**, 2112 (1972).
- (11) Y. Yamamoto, K. Kondo, and I. Moritani, *Tetrahedron Lett.*, 793 (1974).
- (12) J. Casanova, Jr., in "Isonitrile Chemistry", I. Ugi, Ed., Academic Press, New York, N.Y., 1971, p 109; the previous results indicate that the boranes similar to 3 undergo dimerization. However, in the present case, the low temperature used probably suppresses such dimerization.
- (13) Although the intermediates in eq 2 are not isolated, the scheme is most consistent with the result.
- (14) Utilization of the xlyldioctylborane overcomes this difficulty.<sup>6</sup> However, the xlylboranes containing bulky alkyl groups are relatively labile.
- (15) If this speculation is correct, α-aminoalkyldialkylborane (12), a new class of organoboranes, may be preparable via this route. Such an attempt is now under way.
- (16) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, N.Y., 1975.
- (17) MeLi: "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 859. *t*-PrLi: H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).
- (18) E. J. Corey and R. D. Balanson, *J. Am. Chem. Soc.*, **96**, 6516 (1974).
- (19) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).
- (20) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).