Hydroboration. XXXVIII. Structural Study of the Hydroboration of Olefins with Thexylmonoalkylboranes. A Convenient Route to Thexyldialkylboranes, "Mixed" Dialkylboranes, and "Mixed" Trialkylboranes

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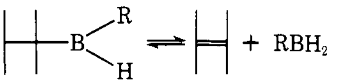
Abstract: A representative series of thexylmonoalkylboranes reacts cleanly with an equimolar amount of unhindered olefins, such as 1-pentene, to form the corresponding totally "mixed" thexyldialkylboranes in excellent yields (≥85%). The reaction is not complicated by disproportionation. As the steric requirements of olefins increase, the dehydroboration of tetramethylethylene (TME) becomes increasingly significant. With either less reactive disubstituted internal olefins, such as cyclohexene, or trisubstituted olefins, such as 2-methyl-2-butene, the dehydroboration of TME predominates so that the major products become the corresponding "mixed" dialkylboranes, a class of compounds which have been difficult to synthesize by other methods. The reaction of these "mixed" dialkylboranes with less hindered olefins provides a facile entry into certain totally "mixed" trialkylboranes, RR′R″B, which have hitherto been almost inaccessible. A dual reaction path mechanism which involves the straightforward hydroboration of the thexylmonoalkylboranes with olefins to form the thexyldialkylboranes, on one hand, and the dehydroboration of TME from the thexylmonoalkylboranes to form the monoalkylboranes followed by their reaction with olefins to produce "mixed" di- and/or trialkylboranes, on the other, is consistent with all of the results thus far obtained. Based on this mechanistic scheme, an improved procedure for the preparation of thexyldialkylboranes has been developed. It involves maintaining the reaction temperature at −20 to −25° until completion of the reaction in the presence of an appropriate amount of TME (0 to 100 mmol %). In this manner, certain highly hindered thexyldialkylboranes, such as thexylcyclohexyl(2-methyl-1-pentyl)borane and thexylcyclohexylcyclopentylborane, can be obtained in excellent yields (≥80%).

Thexylborane[2] (2,3-dimethyl-2-butylborane) derivatives have proved to be highly useful in applying organoborane chemistry to organic synthesis.[3] In the previous paper in this issue,[4] we clarified the course of the reaction of a representative series of olefins with thexylborane in the molar ratio of 1:1 and established procedures for the preparation of a wide range of thexylmonoalkylboranes. In that study, the importance of a competitive dehydroboration of tetramethylethylene (TME) from the thexylmonoalkylboranes (eq 1) was established. It was observed that the rate of dehydroboration of TME, which complicates the hydroboration of relatively hindered olefins with thexylborane, was quite dependent on the reaction temperature. By lowering the temperature to approximately −25°, it proved possible to obtain reasonably pure thexylmonoalkylboranes in high yields.[4]



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Earlier, we had observed that the dehydroboration of TME could be a serious side reaction in the reaction of thexylborane with 2 equiv of olefins.[5] However, no attempts were made at that time to overcome this difficulty. Thus, it was not possible to utilize the standard hydroboration procedures to synthesize in satisfactory yields thexyldialkylboranes of large steric requirements, derivatives such as thexyldinorbornylborane.[6] In view of the synthetic significance demonstrated for certain totally "mixed" thexyldialkylboranes,[3] it appeared highly desirable for us to achieve a practical synthesis for a wide range of such organoboranes in satisfactory purity and yield. Our recent success in obtaining either thexylmonoalkylboranes[4] or monoalkylboranes (as triethylaminates)[7] by controlling the equilibrium reaction of eq 1 prompted us to apply similar principles to control the subsequent reaction of the thexylmonoalkylboranes with representative olefins.

Consequently, the objectives of the present study were: (1) to clarify the exact course and products of the reaction of a representative series of olefins with thexylmonoalkylboranes of various steric requirements; (2) to establish reaction conditions suitable for the preparation of a wide variety of totally "mixed" thexyldialkylboranes in high yields; and (3) to define the reaction conditions which promote the dehydroboration of TME, thereby permitting the synthesis of otherwise difficultly obtainable "mixed" dialkylboranes and totally "mixed" trialkylboranes without the thexyl group.

Results and Discussion

Reaction of Thexylmonoalkylboranes with Olefins in the Molar Ratio of 1:1. As a representative series of thexylmonoalkylboranes of varying steric requirements, we selected those produced in the reaction of thexylborane with 2-methyl-1-pentene, cyclopentene, cyclohexene, 2-methyl-2-butene, and 1-methylcyclopentene. Each of these thexylmonoalkylboranes was prepared as described in the previous paper in this issue[4] by the reaction of an appropriate olefin (olefin A) with an equimolar quantity of thexylborane at −25°.

After stirring for 1 hr at −25°, the thexylmonoalkylborane was then treated at −25° with an equimolar quantity of a second olefin (olefin B) selected from a representative list consisting of 1-pentene, 2-methyl-1-pentene, cyclopentene, cyclohexene, 2-methyl-2-butene, and 1-methylcyclopentene. The reaction temperature was then allowed to rise to ca. 25°. The course of the reaction in each case was followed by analysis for residual hydride. At the completion of reaction, the amounts of residual hydride and residual olefins were determined. An aliquot of the reaction mixture was then oxidized with alkaline hydrogen peroxide and analyzed by GLC for alcohols. When necessary, another aliquot was methanolyzed, and the methanolysis product was examined by GLC and ^{1}H NMR as described in the previous paper in this issue.[4]

(**a**) **Terminal Olefins.** Terminal olefins, such as 1-pentene and 2-methyl-1-pentene, react readily with various thexyl-

Table I. Reaction of Thexylmonoalkylboranes with 1-Pentene and 2-Methyl-1-pentene in the Molar Ratio of 1:1[a]

Alkyl group (R_A) of thexylmonoalkylborane	Olefin	Residual hydride,[b] mmol	TME,[c] mmol	Alcohol,[d] mmol		
				⊢OH	R_AOH	R_BOH
2-Methyl-1-pentyl	1-Pentene	Trace	Trace	9.3	9.8	10.0
Cyclopentyl	1-Pentene	0.2	0.2	9.2	9.8	9.8
Cyclohexyl	1-Pentene	0.6	0.8	8.9	9.9	9.9
2-Methylcyclopentyl	1-Pentene	0.6	0.5	8.5	8.7	10.0
Cyclopentyl	2-Methyl-1-pentene	1.7	2.0	8.0	9.8	10.0
Cyclohexyl	2-Methyl-1-pentene	1.2	1.8	8.3	9.7	9.9

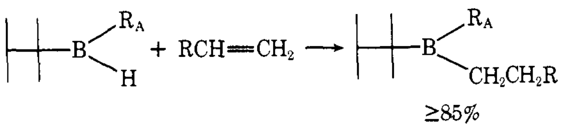
[a] To thexylmonoalkylborane (10 mmol) in THF was added an olefin (10 mmol) at −25°. The total volume was adjusted to 20 ml with THF The temperature was gradually raised to ca. 25°. [b] By hydrolysis with a 5:5:1 mixture of water, glycerine, and THF. [c] By GLC on a Carbowax 20M or adiponitrile column. [d] By GLC after oxidation on a Carbowax 20M column. The numbers include the amount (up to ca. 1%) of isomeric alcohols.

Table II. Reaction of Thexylmonoalkylboranes with Internal Olefins in the Molar Ratio of 1:1[a] (10 mmol Scale)

Alkyl group (R_A) of thexylmonoalkylboranes	Olefin	Residual hydride,[b] mmol	TME,[c] mmol	Alcohol,[d] mmol		
				⊢OH	R_AOH	R_BOH
2-Methyl-1-pentyl	Cyclopentene	0.6	1.4	8.4	9.8	9.8
Cyclohexyl	Cyclopentene	6.6	6.6	3.3	9.7	9.9
2-Methylcyclopentyl	Cyclopentene	4.3	5.8	4.0	9.1	9.8
2-Methyl-1-pentyl	Cyclohexene	5.2	7.0	2.7	9.8	9.8
Cyclopentyl	Cyclohexene	8.1	8.8	1.0	9.9	9.8
2-Methyl-1-pentyl	2-Methyl-2-butene	6.4	6.5	3.3	9.8	9.7
Cyclopentyl	2-Methyl-2-butene	6.2	7.2	3.4	9.7	9.6
Cyclohexyl	2-Methyl-2-butene	9.1	9.0	0.8	9.1	9.5
2-Methyl-1-pentyl	1-Methylcyclopentene	4.5	5.6	4.1	9.8	9.2
Cyclopentyl	1-Methylcyclopentene	7.5	8.1	1.7	9.8	9.3
Cyclohexyl	1-Methylcyclopentene	9.1	9.7		9.5	9.3

[a–d] See the corresponding footnotes of Table I.

monoalkylboranes. The reaction in each case was complete within 1 hr after the temperature had reached ca. 25°. The experimental results are summarized in Table I. As is clear from Table I, the amounts of residual hydride and TME are less than 1.0 mmol (10%) when 1-pentene is used as an olefin B. The formation of the thexylmonoalkylboranes themselves is accompanied by some dehydroboration of TME.[4] Comparison of the amounts of TME with those reported in Table II of the preceding paper in this issue[4] establishes that the reaction of the thexylmonoalkylboranes with an unhindered terminal olefin, such as 1-pentene, proceeds without appreciable further dehydroboration of TME. Oxidation of each product with alkaline hydrogen peroxide produced thexyl alcohol (2,3-dimethylbutanol, 2-/1- = 99/1), pentanol (1-/2- = 99/1), and the third alcohol (R_AOH) in nearly quantitative yields (>90%). From these results, we conclude that the reaction in each case produced the thexylalkyl-1-pentylboranes in yields of ≥85%[8] (eq 2). Since



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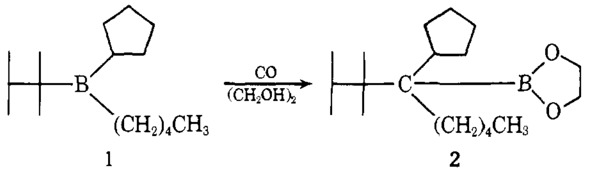
each mole of the monoalkylborane can hydroborate up to 2 mol of an olefin B, an estimated minimum amount of a thexyldialkylborane is (100 − 2TME)%.

That the reaction is not accompanied by any kind of disproportionation or redistribution was established in one case by the carbonylation of the hydroboration product. Thus, the carbonylation of thexylcyclopentyl-*n*-pentylborane (**1**) in the presence of ethylene glycol provided the corresponding boronate **2** in 92% yield[9] based on thexylborane or olefin used. Only one minor product (5%) was present, identified as **3**. The very broad objectives of the present study did not permit us to establish the exact structures of the products in each reaction. Nevertheless, it seems safe to conclude that, except for the minor dehydroboration of TME, the reaction of various thexylmonoalkylboranes with monosubstituted terminal olefins, such as 1-pentene, involves a straightforward hydroboration and is not complicated by any disproportionation.



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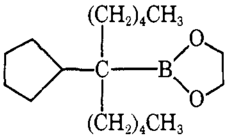

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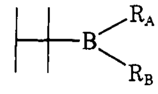
With disubstituted terminal olefins, such as 2-methyl-1-pentene, the extent of the dehydroboration of TME is greater (Table I). Fortunately, as discussed later in this paper, we have developed means for considerably improving the results realized with these olefins.

(b) Internal Olefins. In the reaction of thexylmonoalkylboranes with more reactive internal olefins, such as cyclopentene, the dehydroboration of TME is an even more serious side reaction than in the reaction with relatively unhindered disubstituted terminal olefins, such as 2-methyl-1-pentene. The experimental results with cyclopentene and related internal olefins are summarized in Table II. If it is assumed that here also disproportionation is not involved, then three products are possible in each case, i.e., the thexyldialkylborane (**4**), the "mixed" dialkylborane (**5**) and the "mixed" trialkylborane (**6**), in addition to the initial reactant, thexylmonoalkylborane (**7**) and its dehydroboration product, the monoalkylborane (**8**).[11] The essential absence of **8** in each case was readily established by ^1H NMR examination of the product mixture after methanolysis.[4] Unfortunately, the data obtained for cyclopentene, summarized in Table II, do not permit a meaningful evaluation of the amount of each of the other possible products. Nonetheless, it is clear from these data that, except for thexylcyclo-

Table III. Synthesis of Mixed Dialkylboranes and Mixed Trialkylboranes[a] (10 mmol Scale)

Olefin A	Olefin B	Yield of R_AR_BBH,[a] mmol	Olefin C	Yield of $R_AR_BR_CB$,[b] mmol
Cyclohexene	2-Methyl-2-butene	8.0	1-Pentene	5.9
			2-Methyl-1-pentene	5.6
			Cyclopentene	4.9
Cyclohexene	1-Methylcyclopentene	6.0	1-Pentene	6.0
			2-Methyl-1-pentene	6.6
			Cyclopentene	6.0
1-Methylcyclopentene	2-Methyl-2-butene	7.0	1-Pentene	5.1
			2-Methyl-1-pentene	4.8
			Cyclopentene	4.9

[a] By isolation as the dialkylmethoxyborane; the compounds give satisfactory ir, ^{1}H NMR, and elemental analyses data. [b] By GLC analysis on a SE-30 column after carbonylation in the presence of ethylene glycol using dodecane as internal standard.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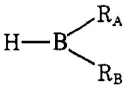
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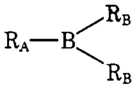
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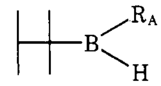
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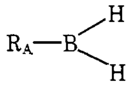
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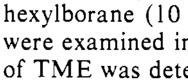
pentyl(2-methyl-1-pentyl)borane, no one product was formed in a yield of greater than 80%. In view of the complex nature of these product mixtures, no further attempts were made to determine the precise amount of each product. Instead, we undertook to improve the procedure and to circumvent these difficulties.

As the steric requirements of the olefin B increase and/or as its reactivity decreases, the amount of "mixed" dialkylborane (**5**) increases at the expense of the other possible products. The results obtained with cyclohexene, 2-methyl-2-butene, and 1-methylcyclopentene are summarized in Table II. Here again, it is not possible to determine the amount of each product based on these data, but it is possible to conclude that essentially no monoalkylborane was present in each case. The amount of thexyl alcohol or TME should correspond to the combined amount of **4** and **7**. Similarly, the amount of residual hydride should correspond to the combined amount of **5** and **7**. It is assumed that these organoborane species do not undergo any disproportionation. (In fact, we have no evidence for significant disproportionation of any of these derivatives under the mild conditions of these experiments.) In order to test the validity of these assumptions, the products derived from thexylcyclohexylborane (10 mmol) and 2-methyl-2-butene (10 mmol) were examined in detail. As shown in Table II, the amount of TME was determined to be 9 mmol (90%). Consequently, the combined amount of thexylcyclohexylborane (**9**) and thexylcyclohexyl(2-methyl-2-butyl)borane (**10**) is estimated to be 1 mmol. The determination of residual hydride indicated the presence of 9.1 mequiv of B-H bond. ^{1}H NMR examination[4] of an aliquot after methanolysis and evaporation of methanol and THF for dimethylcyclohexylboronate indicated the virtual absence of cyclohexylborane in the initial product. Thus, the combined amount of **9** and cyclohexyl(2-methyl-2-butyl)borane (**11**) is estimated to be 9.1 mmol. These results permit us to estimate the amount of **11** to be 8.1-9.1 mmol (81-91%). An aliquot (5 mmol) of the reaction mixture was treated with an equimolar amount of 1-pentene (25°, 1 hr) and carbonylated in the presence of ethylene glycol. GLC examination of the carbonylation product revealed the presence of 2.95 mmol (59%) of **12**, the peak area of which accounted for 90% of the total peak area. These results support the conclusion that **11** was formed in high yield as a reasonably pure product. Furthermore, the results indicate that the reaction of **11** with 1-pentene produced a totally "mixed" trialkylborane, siamylcyclohexyl-*n*-pentylborane (**13**), in high yield as a reasonably pure substance.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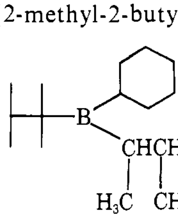
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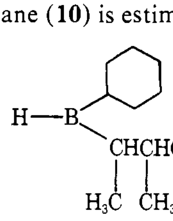
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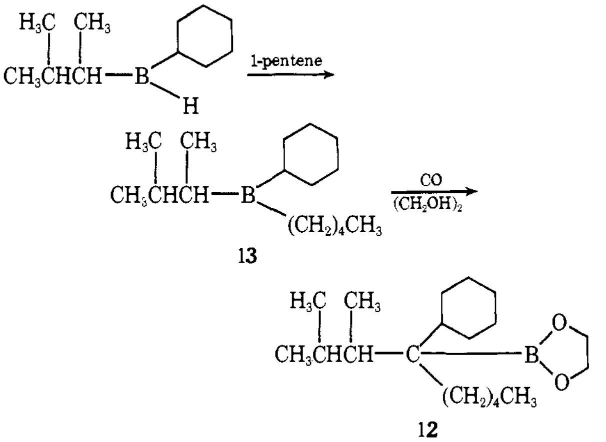

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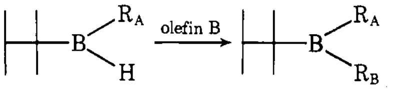
These results are highly significant in that they indicate the applicability of the reaction of thexylmonoalkylboranes with olefins to the synthesis of certain "mixed" dialkylboranes (**5**) and totally "mixed" trialkylboranes. Table III summarizes the estimated yields of some of such "mixed" organoboranes.

Mechanistic Pathway. Based on the results presented in the foregoing section, it is clear that the reaction of the thexylmonoalkylboranes with unhindered olefins, such as 1-pentene, involves nearly exclusively the straightforward hydroboration as shown by eq 5. One possible interpretation of the results is based on the assumption that the thexyldialkylboranes, formed according to eq 5, can dehydroborate TME to form the corresponding "mixed" dialkylboranes (**5**). These can now compete with **7** for the olefin B to form "mixed" trialkylboranes (**6**) (Scheme I).



7 **4**

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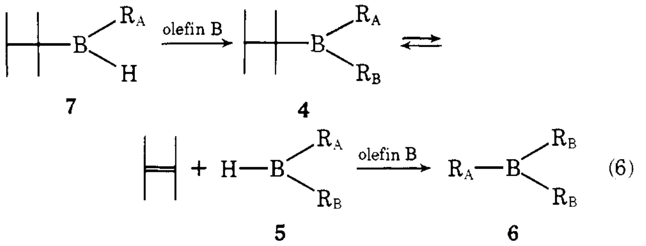
It may be noted that this scheme provides an attractive single mechanistic path for all of the results observed with various olefins of different steric requirements. However, another plausible mechanistic pathway exists, and it must also be considered. As mentioned earlier, we recently established that the thexylmonoalkylboranes exhibit a tendency to dehydroborate TME to form the corresponding monoalk-

Table IV. Reaction of Thexylmonoalkylboranes with Olefins in the Molar Ratio of 1:2[a]

Alkyl group (R_A) of thexylmonoalkylborane	Olefin B	Alcohol,[b] mmol $\vdash$OH	 R_AOH	 R_BOH
Cyclopentyl	1-Hexene	9.9	10.0	10.0
Cyclopentyl	2-Methyl-1-butene	8.2	9.9	11.0
Cyclopentyl	2,4,4-Trimethyl-1-pentene	2.0	10.0	17.9
Cyclohexyl	2-Methyl-1-butene	6.3	10.1	13.4
exo-Norbornyl	2-Methyl-1-butene	1.2	10.0	17.9

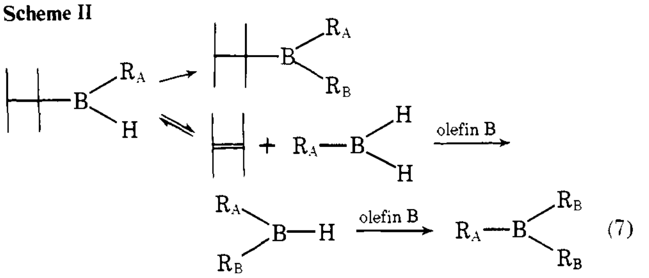
[a] Thexylmonoalkylboranes (10 mmol) were reacted with 24 mmol (20% excess) of olefins for 3 hr at 20–25°. [b] By GLC examination, after oxidation, on a Carbowax 20M column.

Scheme I



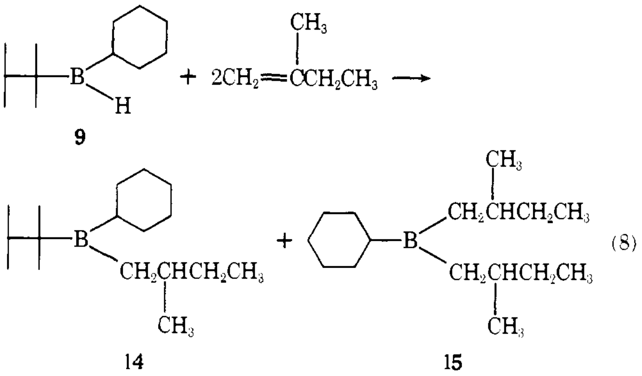
ylboranes.[4] In the presence of an olefin which is more reactive than TME, the monoalkylboranes thus formed would be converted to the corresponding di- and trialkylboranes. This scheme requires parallel reactions (Scheme II) in order to account for all of the observed products.

Scheme II

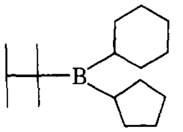


In the course of our experiments designed to select the preferred mechanistic pathway, we realized that the study could be greatly simplified by treating the thexylmonoalkylboranes with 2 equiv of olefins (olefin B). Under these conditions, there is a sufficient quantity of the olefin B to react with all of the B-H bonds. Even in the event of complete dehydroboration of TME, there are only two possible products, the thexyldialkylborane (**4**) and the "mixed" trialkylborane of the $R_AB(R_B)_2$ type, provided the reaction of the "mixed" dialkylborane (**5**) with the olefin B can proceed to completion. Accordingly, we studied several reactions of thexylmonoalkylboranes with ca. 2 equiv of olefins. The experimental results are summarized in Table IV.

The results of the reaction of thexylcyclohexylborane (10 mmol) with 2-methyl-1-butene (24 mmol) are particularly instructive. As shown in Table IV, the reaction proceeded to produce, after oxidation, thexyl alcohol (6.3 mmol), cyclohexanol (10.1 mmol), and 2-methyl-1-butanol (13.4 mmol). The results indicate the formation of 6.3 mmol of thexylcyclohexyl(2-methyl-1-butyl)borane (**14**) and 3.7 mmol of cyclohexylbis(2-methyl-1-butyl)borane (**15**). Quite significantly, addition of a large excess (10×) of 2-methyl-1-butene at 25° to the product mixture did not cause any noticeable change in the product ratio. The product mixture proved to be quite stable also to the action of alcohols, such as methanol, and trialkylamines, such as pyridine, trimethylamine, and triethylamine. All of these results suggest that, in contrast to the thexylmonoalkylboranes, the thexyldialkylboranes (**4**) are relatively stable with respect to dehydroboration. Clearly, these results favor the dual path mechanism (Scheme II) and, in fact, all of the results we have obtained thus far can be accounted for in terms of this dual path mechanism. The production of triethylamine-monoalkylboranes[4] by treatment of thexylmonoalkylboranes with excess triethylamine is also consistent with this mechanistic scheme. It is probable that it is the formation of dimers in the thexylmonoalkylboranes that favors the dehydroboration process.



An Improved Procedure for the Preparation of Thexyldialkylboranes. Having established the mechanistic pathway, we decided to return to the problem of synthesizing thexyldialkylboranes (**4**). If the mechanism formulated above were correct, it is clearly necessary to suppress the dehydroboration of TME from the thexylmonoalkylborane in order to obtain **4** in high yields. We chose the reaction of thexylcyclohexylborane with cyclopentene as a model system and examined the effect of reaction temperature and the amount of TME added to suppress the dehydroboration. The experimental results are summarized in Table V. Following several unsuccessful attempts, we found that the extent of dehydroboration of TME could be lowered from 51% observed under the initially selected conditions to a mere 10% by adding 100 mol % of TME and maintaining the reaction temperature at −20 to ca. −25° until essentially all of the cyclopentene had reacted (∼24 hr). We estimate the yield of thexylcyclohexylcyclopentylborane (**16**) to be 80–90%. The structure of **16** was confirmed by its oxidation products, by its conversion to thexylcyclohexylcyclopentylcarbinol via the DCME reaction[12] and by its conver-



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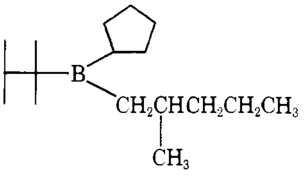

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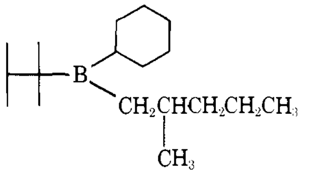

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Table V. Reaction of Thexylcyclohexylborane with Cyclopentene in the Molar Ratio of 1:1 (10 mmol Scale)

Temp, °C	TME added mmol	Residual hydride,[b] mmol	Thexyl alcohol,[c] mmol
a	0	3.8	4.9
a	5	3.6	
a	10	3.7	
a	20	3.6	
−20 to −25	0	2.9	5.9
−20 to −25	10	1.2	9.0

[a] At −25°, then raised to 25°. [b] See the corresponding footnote of Table I. [c] See footnote *d* of Table I.

Table VI. Reaction of Thexylmonoalkylboranes with 2-Methyl-1-pentene in the Molar Ratio of 1:1 (10 mmol Scale)

Alkyl group of thexylmonoalkyl-borane	Reaction conditions[a]	Residual hydride,[b] mmol	Thexyl alcohol,[c] mmol
Cyclopentyl	I	1.7	8.0
Cyclopentyl	II	0.4	9.6
Cyclohexyl	I	1.2	8.3
Cyclohexyl	II	Trace	10.0

[a] I = the same conditions as described in footnote *a* of Table I; II = at −20 to −25° in the presence of 50 mol % of TME. [b] See footnote *b* of Table I. [c] See footnote *d* of Table I.

sion to cyclohexyl cyclopentyl ketone via the cyanidation reaction.[6]

Also improved substantially were the results of the reaction of thexylmonoalkylboranes with disubstituted terminal olefins. As summarized in Table VI, the estimated yields of **17** and **18** were raised to 92-96 and ca. 100%, respectively, by maintaining the reaction temperature at −20 to −25° in the presence of 50 mol % of TME.

Finally, a word of caution is in order. As we have established above, the reaction of thexylmonoalkylboranes with olefins involves two competitive reaction paths. The partitioning of the two depends greatly on the steric requirements and reactivity of the olefins (olefin B) and to much less extent on the steric requirements of the alkyl group (R_A) of the thexylmonoalkylboranes (Table II). Thus, it is important to hydroborate the more bulky and/or less reactive of the two olefins first, followed by the hydroboration of the less bulky and/or more reactive olefin. Consider the preparation of **16** and **18**. As discussed above, these thexyldialkylboranes can be synthesized in high yields via thexylcyclohexylborane. Much less satisfactory results will be obtained if the order of hydroboration is reversed. This point may clearly be seen by comparing the corresponding data in Table II.

Experimental Section

All organoboranes were handled under dry nitrogen. ^1H NMR and ir spectra were recorded with a Varian T-60 and a Perkin-Elmer 700, respectively. GLC analyses were carried out on a Varian 1200. Boiling points are uncorrected.

Materials. The preparations of borane[13] and thexylborane[14] in THF were carried out as reported previously. Commercially available olefins, straight-chain hydrocarbons (used as internal standards), methanol, and trialkylamines were kept under nitrogen and used without further purification after checking the refractive indices. THF was distilled from lithium aluminum hydride and kept under nitrogen.

Preparation of Thexylmonoalkylboranes.[4] The following procedure for the preparation of thexylcyclopentylborane is representative. In a 50-ml flask, equipped with a septum inlet and a condenser connected to a mercury bubbler, was placed 4.92 ml (10 mmol) of a 2.03 *M* solution of thexylborane in THF. To this was added at −25° [a commercially available (Neslab, Inc.) low-temperature bath was used] 5.08 ml of a THF solution containing 10 mmol of cyclopentene and 5 mmol of *n*-decane (1 *M* in thexylborane and olefin). After stirring for 1 hr at −25°, the solution was used for further reactions.

Reaction of Thexylmonoalkylboranes with Olefins in the Molar Ratio of 1:1. The following procedure is representative. To 10 mmol of the thexylmonoalkylborane prepared as described above was added 10 mmol of an olefin (olefin B) at −25°. The total volume was adjusted to 20 ml with THF. The mixture was warmed up to room temperature. Periodically, a 1-ml aliquot was hydrolyzed with 5:5:1 mixture of water, glycerol, and THF and the amount of hydrogen recorded. Another aliquot was methanolyzed (with 100% excess methanol) and analyzed for TME and residual olefin on a 6-ft Carbowax 20M (or an adiponitrile) column, using *n*-decane as internal standard. At the completion of the reaction (indicated by the absence of the olefin B), the amount of hydrogen evolved and the amount of TME dehydroborated were recorded. Another 1-ml aliquot was oxidized with alkaline hydrogen peroxide and analyzed for alcohols by GLC (Carbowax 20M).[15] Analysis of monoalkylboranes was performed by methanolysis of another aliquot, followed by removal of volatile materials under diminished pressure [1 hr, 25° (15 mm)],[4] and examination by ^1H NMR using benzene as internal standard. The results are summarized in Tables I and II.

Reaction of Thexylmonoalkylboranes with Olefins in the Molar Ratio of 1:2. The following procedure is representative. To 10 mmol of thexylcyclohexylborane prepared as described above was added 24 mmol of 2-methyl-1-butene at −25°, and the reaction mixture was allowed to stir for 3 hr at 20-25°. After this period of time, addition of methanol to an aliquot did not cause any gas evolution, revealing the absence of active hydride species. After oxidation with alkaline hydrogen peroxide, alcohols were analyzed by GLC (Carbowax 20M).[15] The results are summarized in Table IV. Addition of a large excess of 2-methyl-1-butene (100 mmol, 10 times excess), stirring for 3 hr at 20-25°, followed by oxidation, yielded the corresponding alcohols in a ratio similar to the one found when only 24 mmol of 2-methyl-1-butene was used. This shows that no further dehydroboration took place. Treatment of the reaction mixture (10 mmol) with 20 mmol of methanol (100% excess) failed to give any gas evolution after 48 hr at room temperature. Similarly, when 20 mmol of a tertiary amine (trimethylamine, triethylamine, or pyridine) was added to the hydroboration mixture (10 mmol), no dehydroboration of TME took place, as shown by alcohol analysis, after oxidation with alkaline hydrogen peroxide.

Preparation of "Mixed" Dialkylboranes and Their Reaction with Olefins to Form "Mixed" Trialkylboranes. The following procedure for the preparation of (2-methyl-2-butyl)cyclohexylborane and (2-methyl-2-butyl)cyclohexylpentylborane is representative. To 10 mmol of thexylcyclohexylborane prepared as described previously was added 10 mmol (1.06 ml) of 2-methyl-2-butene. After stirring for 1 hr at −25° and then for 3 hr at 25°, GLC analysis of an aliquot after methanolysis showed complete disappearance of 2-methyl-2-butene and a 90% yield of 2,3-dimethyl-2-butene (TME). Methanolysis of the mixture with 20 mmol of methanol yielded 230 ml of hydrogen (90.5%). Distillation under reduced pressure gave 1.57 g (80% yield) of methyl (2-methyl-2-butyl)cyclohexylborinate: bp 58-59° (0.7 mm); n^{20}_D 1.4525; ^1H NMR (CCl_4, Me_4Si) δ 0.76-1.1 (m, 9 H), 1.1-2.0 (m, 13 H), and 3.7 (s, 3 H) ppm; ir (neat) 1460 (s).

Anal. Calcd for $C_{12}H_{25}BO$: C, 73.48; H, 12.85; B, 5.51. Found: C, 73.42; H, 13.08; B, 5.59. Five millimoles of the reaction mixture prepared separately was treated with an equimolar amount of 1-pentene (5 mmol, 0.55 ml). The reaction was exothermic at room temperature.

After addition of 5 mmol of dodecane (used as internal standard) and 15 mmol (0.9 ml) of ethylene glycol, the reaction mixture was carbonylated as described previously.[10] GLC examination of the mixture on a 2-ft SE-30 column revealed the presence of the expected product **12** in 59% yield (2.95 mmol). The reaction mixture was washed with water (2 × 10 ml) and extracted with pentane (3 × 10 ml); the combined organic phases were dried over magnesium sulfate; the solvents were removed on a Rotovac, and the residue was prepared by GLC: n^{20}_D 1.4825; ^1H NMR (CCl_4, Me_4Si): δ 0.6-1.1 (m, 12 H), 1.1-2.1 (m, 21 H), and 4.06 (s, 4 H) ppm; ir (neat) 1460 (m), 1390 (s), 1210 (s).

Anal. Calcd for $C_{19}H_{37}BO_2$: C, 74.01; H, 12.10; B, 3.51. Found: C, 74.30; H, 11.97; B, 3.75.

The experimental results are summarized in Table III.

Preparation and Carbonylation of "Mixed" Thexyldialkylboranes. The following procedure for preparation of thexylcyclopentylpentylborane is representative. To 10.0 mmol of thexylcyclopentylborane prepared as described above was added, at −25°, 10 mmol (1.1 ml) of 1-pentene. The solution was brought to room temperature and stirred for 3 hr to complete the hydroboration reaction (hydrolysis of an aliquot did not cause any gas evolution). Ethylene glycol (1.8 ml, 30 mmol) was added, and the resulting mixture was carbonylated.[10] The ethylene trialkylcarbinylboronate (92% yield by GLC) was isolated by GLC: ^{1}H NMR (CCl_4, Me_4Si) δ 0.76-1.1 (m, 15 H), 1.1-2.3 (m, 18 H), and 4.03 (s, 4 H) ppm.

Reaction of Thexylcyclohexylborane with Cyclopentene in the Molar Ratio of 1:1 under Various Conditions. To 10 mmol of thexylcyclohexylborane prepared as described previously were added, at −25°, 10 mmol (0.88 ml) of cyclopentene, 5 mmol of *n*-decane, and 0, 5, 10, or 20 mmol of TME. The temperature was raised to 25° and the reaction followed by GLC analysis of cyclopentene (Carbowax 20M). When the reaction was complete, an aliquot was hydrolyzed and the amount of hydrogen evolved recorded. Another aliquot was oxidized, and the amount of thexyl alcohol was determined. The same experiment was repeated except that the temperature was maintained at −20 to −25° until the reaction was complete (24 hr). The experimental results are summarized in Table V.

We encountered unusual difficulties in oxidizing thexylcyclohexylcyclopentylborane and developed a new procedure applicable to hindered derivatives. Five millimoles of **16** were prepared as described above. All volatile materials were removed under reduced pressure [1 hr, 25° (15 mm)]. To the residue was added under nitrogen 30 mmol (1.2 g, sixfold excess) of sodium hydroxide (pellets) followed by 5 ml of 95% ethanol. The mixture was heated to 40-50° to dissolve the base. Oxidation was achieved by adding, at 40°, 5 ml of 30% hydrogen peroxide (*very slowly*). The solution was heated an additional hour at 50-60°. The aqueous layer was saturated with sodium chloride and the organic layer analyzed by GLC using decane as internal standard (CW-20M). There was obtained thexyl alcohol (96%), cyclopentanol (98%), and cyclohexanol (93%).

An Improved Procedure for the Preparation of Thexyldialkylboranes. The following procedure for the preparation of thexylcyclohexyl(2-methyl-1-pentyl)borane is representative. To 10 mmol of thexylcyclohexylborane prepared as described previously were added, at −25°, 5 mmol of TME and 10 mmol (1.24 ml) of 2-methyl-1-pentene in this order. The reaction mixture was stirred for 4 hr at this temperature. Hydrolysis of an aliquot did not cause any gas evolution indicating the absence of active hydride species. After oxidation, the mixture was analyzed for alcohols (Carbowax 20M). The yield of thexyl alcohol was quantitative. The results are summarized in Table VI.

Cyanidation of Thexylcyclohexylcyclopentylborane. As compared with the published procedure,[6] the title borane was found to react very slowly with sodium cyanide in THF. Systematic study of the reaction, using 10, 20, and 100% excess cyanide revealed that a maximum yield of 84% of cyclohexyl cyclopentyl ketone could be obtained after 3 days at room temperature using 100% excess sodium cyanide. At THF reflux temperature, this time could be reduced to 24 hr. The following procedure is therefore representative. To 5 mmol of **16** (10 ml of 0.5 *M* solution in THF) prepared as previously described was added 0.49 g of sodium cyanide (100% excess, as a *dried fine powder*) under nitrogen. After 24 hr of reflux, the mixture was cooled to −78°, and 0.85 ml of trifluoroacetic anhydride was added. The mixture was then warmed up and stirred 20 min at 25°. Nine milliliters of 3 *M* sodium hydroxide and 9.0 ml of 30% hydrogen peroxide were then *simultaneously* added to the mixture (if the base is added first, up to 15% of a side product, identified as a trifluoroacetamide, can be formed). After 1 hr at 50-55°, the aqueous phase is saturated with sodium chloride, and the organic layer was analyzed by GLC (SE-30) (using decane as internal standard). It was found that cyclohexyl cyclopentyl ketone was formed in 81% yield.

References and Notes

(1) (a) Graduate assistant on a research grant, GM 10937, supported by the National Institutes of Health; (b) Postdoctoral Research Associate on a research grant, DA 31-134 ARO(D) 453, supported by the U.S. Army Research Office (Durham).

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(8) We have established that, in the reaction of thexylborane with olefins in the ratio of 1:1, the amount of TME corresponds to that of a monoalkylborane formed by the dehydroboration of TME.[4]

(9) In a preliminary communication,[10] we reported a yield of 71%. This result was obtained by using **1** prepared at 0°. Clearly, the present procedure provides a much more satisfactory result.

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(11) In the present study, we have not observed any indication of the dehydroboration of olefins other than TME.

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