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ORGANOBORANES FOR SYNTHESIS. 1. PROTONOLYSIS OF TRIALKYLBORANES. A CONVENIENT NON-CATALYTIC CONVERSION OF ALKENES INTO SATURATED COMPOUNDS *via* HYDROBORATION-PROTONOLYSIS[1,2]

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Abstract - The protonolysis of trialkylboranes with carboxylic acids proceeds very rapidly for the first group, somewhat slower for the second, but requires elevated temperatures for removal of the third. A close examination of the protonolysis of representative symmetrical, as well as mixed trialkylboranes, reveals that the steric requirements of the alkyl groups attached to boron play an important role in the rate. Secondary alkyl groups protonolyze less readily than primary alkyl groups. More hindered alkyl groups are still more resistant. Since the hydroboration-protonolysis sequence involves relatively mild conditions, this procedure can be applied for hydrogenating olefinic derivatives containing labile groups, such as active sulfur, halogen and nitrogen functionalities. The stereochemistry of protonolysis has been established *via* deuteroboration of norbornene and deuterolysis of the product. It is evident that protonolysis proceeds with retention of configuration at the migrating carbon. Partially alkylated boranes can be used for hydroboration-protonolysis with improved regioselectivity. Subsequent protonolysis of the resulting mixed trialkylboranes provides the desired alkanes in good yields. Products sensitive to the action of hot acetic acid offer difficulties. For example, when this procedure was applied to the preparation of l-menthene from *d*-limonene, the product was racemic.

The ready conversion of unsaturated derivatives into organoboranes through the hydroboration reaction makes these compounds available as intermediates for synthesis.[3] Although trialkylboranes are relatively stable toward hydrolysis by water,[4] acetic acid removes one alkyl group rapidly.[5] Recently we have reported the effect of solvent, temperature and added reagents on the protonolysis of triethylborane with acetic acid.[6] In a continuation of our study of the utility of this reaction for synthetic purposes, we undertook to examine in detail the protonolysis of different types of organoboranes as a feasible route for the conversion of olefinic derivatives into the corresponding saturated compounds and to establish the stereochemistry of this reaction so that the structure of the product could be predicted. In light of our previous observation[6] that the removal of the third alkyl group requires drastic conditions, it appeared interesting to study the selective protonolysis of mixed trialkylboranes derived from common partially alkylated borane derivatives and the desired alkene. Protonolysis under mild conditions would provide the corresponding alkanes in high yields, leaving behind the blocking groups on boron.

RESULTS AND DISCUSSION

Trialkylboranes are inert toward water or strong mineral acids with the exception of anhydrous HF (eq 1).[7a]

$$R_3B + 3\ HF \xrightarrow{\text{room temperature}} 3\ RH + BF_3 \qquad (1)$$

$$R = CH_3,\ C_2H_5,\ i\text{-}C_3H_7$$

For example, hydrogen bromide reacts slowly and incompletely (eq 2).[7b]

$$R_3B + HBr \xrightarrow{55\text{-}60^\circ C} RH + R_2BBr \quad (2)$$

$R = n\text{-}C_4H_9$

However, acetic acid reacts very rapidly at room temperature to produce one mole of alkane and the reaction then proceeds more slowly to produce a second mole (eq 3).[2]

$$(n\text{-}C_6H_{13})_3B + 2\ CH_3CO_2H \longrightarrow 2\ n\text{-}C_6H_{14} + n\text{-}C_6H_{13}B(O_2CCH_3)_2 \quad (3)$$

Subsequent oxidation of the product with alkaline hydrogen peroxide provides one mole of 1-hexanol.

Our preliminary studies on the reaction of triethylborane with a variety of reagents revealed that carboxylic acids are particularly effective for the protonation of this organoborane.[6] During the present study, tri-*n*-hexylborane was treated with various acids and the results show that in this case also protonolysis is especially facile with carboxylic acids (Table 1). The high reactivity of alkylboranes with carboxylic acids is somewhat unexpected, although not unreasonable. This reactivity may be ascribed to an initial coordination of the electron-rich carbonyl oxygen of the acid with electron-deficient boron, placing the acidic proton in a proper geometry (Figure 1). This mechanism[8] was later confirmed by Dessy and coworkers[9] through kinetic data. Following the protonolysis of the first alkyl group (eq 4), the resulting dialkylboron acetate reacts with a second molecule of the acid. However, the coordination with boron is weaker, partly because of the steric hindrance of the first acid moiety and more likely because of the decreased Lewis acidity on boron *via* internal coordination.[10]

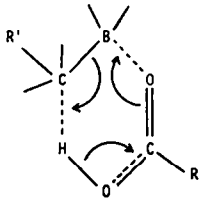


Figure 1. Coordination mechanism for the protonolysis of organoboranes

Table 1. Reaction of tri-*n*-hexylborane with various acids[a]

Acid (mmol)	Temp. °C	Time, h	Hexane, % Yield
acetic (1.66)	120	2	60
acetic (0.83) + acetic anhydride (0.53)	128	23	84
propionic (1.35)	143	13	80
isobutyric (1.14)	156	6	81
butyric (1.08)	172	5	80
glycolic[b] (0.73)	114	24	55
methanesulfonic (0.70)	175	4	41
hydrochloric[c] (0.54)	65	24	36
phosphoric (0.94)	85	24	12

[a] Tri-*n*-hexylborane (66.6 mmol), free from any solvent, was treated with 100 mL of acid. [b] 70% solution in water. [c] Hydrogen chloride in methanol.

$$R_3B + CH_3CO_2H \xrightarrow[5\ min]{25^\circ C} RH + R_2BO_2CCH_3 \quad (4)$$

Consequently, the removal of the second alkyl group is much slower (eq 5).

$$R_2BO_2CCH_3 + CH_3CO_2H \xrightarrow[8\ h]{25^\circ C} RH + RB(O_2CCH_3)_2 \quad (5)$$

In the reaction of a third molecule of acid with alkylboron diacetate, the carbonyl coordination is very weak. Thus, higher temperatures are required for the cleavage of the third B–C bond (eq 6).

$$RB(O_2CCH_3)_2 + CH_3CO_2H \longrightarrow RH + B(O_2CCH_3)_3 \longrightarrow 1/2(CH_3CO)_2O + 1/2(CH_3CO_2)_2BOB(O_2CCH_3)_2 \quad (6)$$

When the organoborane was heated under reflux with higher boiling carboxylic acids, such as propionic, butyric, or isobutyric acid, the protonolysis of the third alkyl group could be readily achieved (Table 1). Since it is convenient to prepare an organoborane in diglyme, protonolysis in this solvent was studied. A mixture of propionic acid and diglyme provides a convenient reflux temperature, ∿ 140°C. Consequently, representative boranes were protonolyzed under these conditions. A mixture of caprylic acid and triglyme permits the protonolysis to be carried out at 210°C.

Protonolysis of Representative Organoboranes. The protonolysis of tri-*n*-hexylborane with propionic acid in diglyme afforded a 91% yield of hexane in 2 h. Under similar conditions, the organoborane from 2-hexene (tri-2- and -3-hexylborane) provided only 50% of hexane. A more hindered alkyl group, the one derived from 2,4,4-trimethyl-2-pentene, formed only 5% of the corresponding alkane under these conditions (Table 2). This difficulty can be easily circumvented by first isomerizing the organoborane to place the boron atom on the primary position prior to carrying out the protonolysis operation. Protonolysis with caprylic acid in triglyme permitted higher reaction temperature (210 °C) at which primary organoboranes reacted in 1 h or less (Table 2). Even under these conditions,

organoboranes containing secondary alkyl groups required isomerization before protonolysis for a quantitative yield of the desired alkane in a reasonable time.

It is evident that the steric hindrance of the alkyl group plays an important role in protonolysis. A more detailed study of the relative rates of protonolysis confirms this observation.

Since the alkenes containing active sulfur, chlorine and nitrogen substituents readily undergo hydroboration,[3,11] the hydroboration-protonolysis sequence opens up the possibility of hydrogenating such olefinic derivatives often sensitive to hydrogenation catalysts.

Table 2. Protonolysis of representative organoboranes

Alkene	Yield of Alkane, %: Propionic Acid in Diglyme[a]	Caprylic Acid in Triglyme[b]
1-hexene	91	90
1-octene	95	90
2-hexene	50	
cyclohexene	76	84
2,4,4-trimethyl-1-pentene	82	
styrene	88	84
2-heptene	51	79
2,4,4-trimethyl-2-pentene	5[d]	
2-heptene[c]	85	90
2,4,4-trimethyl-2-pentene[c]	77	85

[a]Reaction temperature, 140°C; time, 2 h. [b]Reaction temperature, 210°C; time, 1 h. [c]Isomerized before protonolysis. [d]Determined by GC.

Relative Rates of Protonolysis. In the course of this study, it was observed that for primary alkylboranes, the first alkyl group was protonolyzed instantaneously, the second more slowly, and that relatively harsh conditions were required for the protonolysis of the third. The protonolysis of secondary alkylboranes was noticeably slow. These observations suggested the desirability of a more quantitative study of the influence of structure upon the rate of protonolysis to permit a decision on the appropriate reaction conditions to achieve a given protonolysis. Accordingly, a detailed study of the effect of structure on the rate of protonolysis with acetic acid was undertaken.

Since the protonolysis of organoboranes in diglyme results in a heterogeneous reaction mixture, tetrahydrofuran was chosen as the solvent. Organoborane derived from 100 mmol of the alkene under study and 33 mmol of BH_3·THF contained in 50 mL of solution was treated with 50 mL of a 10 *M* solution of acetic acid in THF (500 mmol) at 30°C. The amount of alkane produced was measured by GC analysis using an internal standard. The initial concentration of the organoborane was 0.33 *M* and that of acetic acid was 5.0 *M*. The reaction, being first-order each in borane and acid, becomes *pseudo* first-order.

Since the data from protonolysis were so varied, both with respect to the rate of reaction and to the extent of alkane product (0, 1 or 2 groups), a very arbitrary method of obtaining relative reactivities was established. The yield of alkane was plotted as a function of time for all of the organoboranes, the time required for 50% formation of *n*-pentane from tri-*n*-pentylborane (standard for comparison) was determined graphically to be 7 h and this rate was set equal to 1.000. The extent of protonolysis of other organoboranes in 7 h was determined for comparison with the standard, tri-*n*-pentylborane (Table 3).

The sensitivity of protonolysis to steric factors is indicated by a large decrease in the rate caused by a β-methyl substitution. Thus, the trialkylborane from 2-methyl-1-butene reacted five times slower than tri-*n*-pentylborane. When the methyl group was moved to the γ-position, decreasing the steric hindrance to the attack of acetic acid, the rate of reaction increased markedly. Thus, tris(3-methyl-1-butyl)borane protonolyzed at a rate comparable to that of tri-*n*-pentylborane. Increase in the length of the carbon chain caused only a slight decrease in the rate of protonolysis.

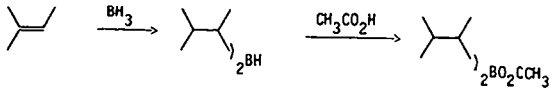
Table 3. Relative rates of protonolysis of organoboranes with acetic acid at 30 ± 1°C[a]

Alkene	Alkane Yield After 7 h, %	Rel. React.
1-pentene	50	1.000
1-hexene	46.3	0.927
2-methyl-1-butene	11	0.22
3-methyl-1-butene	44.5	0.89
3,3-dimethyl-1-butene	36	0.76
2-methyl-2-butene	0.4	0.008
styrene	50[b]	2.34
α-methylstyrene	32.5	0.65
trans-β-methylstyrene	3.2	0.064
cis-2-pentene	2.6	0.052
cyclopentene	46	0.92
cyclohexene	31.5	0.63
norbornene	27	0.54

[a]The reaction mixture was 0.33 *M* in the borane and 5.0 *M* in acetic acid. [b]In 3 h.

The protonolysis of secondary alkyl groups was extremely slow. The organoborane derived from 2-pentene, which contains 2- and 3-pentyl groups, produced only 4.9% of pentane in 24 h (Table 3). Further substitution, as in the case of bis(3-methyl-2-butyl)borane, decreased the rate by a

factor of 125. In the case of 2,3-dimethyl-2-butylborane, no alkane was produced, even at 200°C. There is another factor which complicates the protonolysis in these two cases. Neither of these alkenes forms trialkylboranes. When the acid is added, the corresponding boron acetates are formed (eqs 7 and 8). The acetate groups further decrease the rate of protonolysis.



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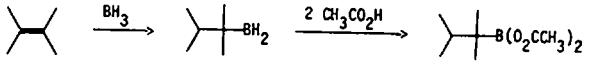

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The organoborane from styrene (20% of boron on benzylic position and 80% on β-carbon)[12] underwent protonolysis 2.34 times faster than tri-*n*-pentylborane. Initially the rate enhancement appeared to be due in part to the rapid cleavage of the benzylic carbon-boron bond. But the values for β-methyl styrene reveal that this hypothesis is false. The organoborane derived from β-methyl styrene (containing 85% boron on benzylic carbon and 15% on β-carbon)[12] protonolyzes at a rate slightly faster than would be expected for the protonolysis of a secondary alkylborane. Therefore, the electron-withdrawing character of the phenyl group must be accelerating the protonolysis reaction. The organoborane from α-methyl styrene reacted three times faster than the corresponding aliphatic compound.

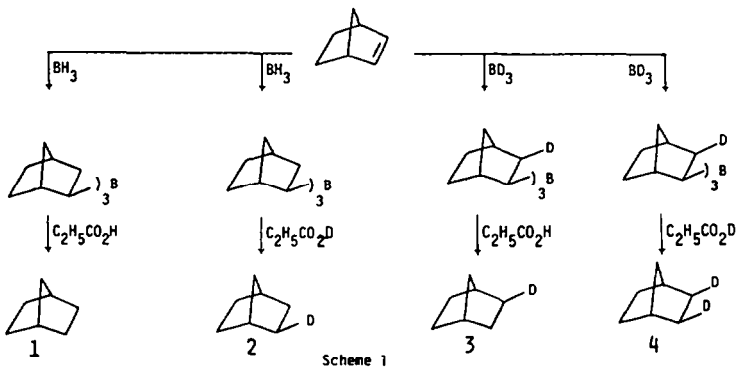
Tricyclopentylborane undergoes protonolysis much faster than tri-2- or -3-pentylborane. Although tricyclohexylborane was insoluble in THF initially, it protonolyzed only 1.6 times slower than tri-*n*-pentylborane. Increasing the steric requirements by the introduction of a methylene bridge, as in the case of trinorbornylborane, decreased the rate.

It is evident from the relative rate studies that steric hindrance is the most important factor in the protonolysis of trialkylboranes. When the boron atom is attached to a highly branched alkyl group, protonolysis does not proceed, even under drastic conditions. These results are consistent with the coordination mechanism. A similar effect is noted if the steric requirement of the acid is increased. This has been established for the protonolysis of vinyldialkylboranes.[13]

Stereochemistry of Protonolysis. A knowledge of the stereochemistry of protonolysis, similar to that now available for the hydrogen peroxide oxidation of organoboranes,[14] would permit application of the protonolysis reaction for the stereospecific synthesis of alkanes and deuteroalkanes.

Tri-*exo*-norbornylborane reacted with propionic acid to protonolyze two alkyl groups, producing norbornane (1) in 46.5% yield. Oxidation of the residue with alkaline hydrogen peroxide converted the third group into *exo*-norbornanol in 21% yield.

A set of experiments involving hydroboration or deuteroboration of norbornene, followed by protonolysis or deuterolysis, provided the corresponding norbornanes (1-4, Scheme 1).



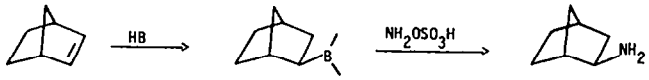
Scheme I

The structures of 1-4 were determined by ^1H NMR spectral studies. These results are consistent, both with the pure *cis* addition of hydrogen-boron bond from less hindered (*exo*) side,[14] and with the retention of configuration during protonolysis. A study of the hydroboration (deuteroboration)-

protonolysis (deuterolysis) in an acyclic system has yielded the same results. The reaction proceeds with the *syn* addition of H_2 (HD) to the alkene. Consequently, we can conclude that this is a general phenomenon.[15]

The protonolysis of vinylboranes, obtained *via* the hydroboration of acetylenes, proceeds with retention of configuration.[13,16] The stereochemistry of alkaline hydrogen peroxide oxidation has been demonstrated to proceed with retention of configuration in many systems.[14,17] In this reaction, trinorbornylborane behaves the same stereochemically as other cyclic and acyclic systems.[14]

Besides hydrogen peroxide oxidation, other organoborane transfer reactions, such as amination, which also proceeds *via* the initial complexation of the reagent with boron, followed by the migration of the alkyl group from boron to the heteroatom, are known to proceed with retention of stereochemistry (eqs 9-11).[18] From these analogies, one can safely conclude that protonolysis of organo-



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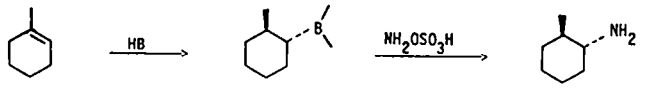

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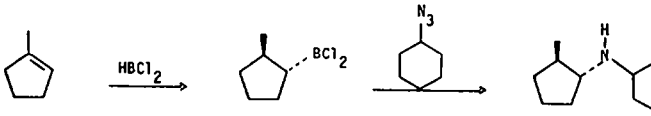


(11)

boranes proceeds with retention of configuration at the alkyl group.

Protonolysis of Mixed Organoboranes. Partially alkylated borane derivatives, such as bis(3-methyl-2-butyl)borane (Sia_2BH), dicyclohexylborane (Chx_2BH) and 2,3-dimethyl-2-butylborane ($ThxBH_2$), exhibit superior regioselectivity as well as functional group selectivity in hydroboration. Consequently, it appeared that selective hydroboration of dienes or functionally substituted alkenes would be possible using these reagents. A study of the protonolysis of resulting mixed organoboranes would enable one to apply the protonolysis technique for organic synthesis. Therefore, we examined the selective protonolysis of mixed organoboranes derived from these partially alkylated borane derivatives and representative alkenes.[19]

The results summarized in Table 4 indicate that dicyclohexylalkylboranes are protonolyzed even

Table 4. Protonolysis of mixed trialkylboranes[a] with acetic acid

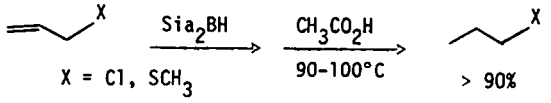
Hydroborating Agent	Alkene	Alkane (%) Produced in Time, h					Alkane From Reagent mmol (after 20 h)
		1	2	6	8	20	
Chx_2BH[b]	1-hexene	59	67	90	95	100	31
	2-hexene	9	13	27	31	50	24
	cyclopentene	47		77		84	31
	2,4,4-trimethyl-1-pentene		40		62	75	30
Sia_2BH[c]	1-octene	100					
	2-octene	35	57	94		100	15
	cyclopentene	46	66		100		trace
	2,4,4-trimethyl-1-pentene	52	79				trace
	allyl chloride[d]	53	56	66		90	0
	allyl methyl sulfide	61	72	84		92	
	d-limonene	42	75	91		97	
$ThxBH_2$[c]	1-hexene	61	75	84		96	
	2-hexene	28	35	52		65	
	cyclopentene	49	59	83		97	
	2,4,4-trimethyl-1-pentene	50	67	84		90	

[a]Reaction with 25 mmol of RR'_2B. [b]Protonolysis at room temperature (30°C) when Chx_2BH was used for hydroboration. [c]Protonolysis at 100°C. [d]Protonolysis at 90°C.

at room temperature at a reasonable rate. Unfortunately, protonolysis of the cyclohexyl groups occurs competitively so that a considerable amount of cyclohexane was also produced. It appears that Sia_2BH would be a more generally useful hydroborating agent for hydroboration-protonolysis

since the resulting mixed boranes can protonolyze more selectively. Despite the fact that these boranes require higher temperature (100°C) for protonolysis, the products were obtained in good yields, without noticeable protonolysis of the blocking groups.

The enhanced regioselectivity[20] and functional group tolerance[21] exhibited by Sia_2BH in hydroboration permits the use of this reagent for the selective hydrogenation of dienes and functionally substituted alkenes (Table 4). Accordingly, the hydrogenation of allyl chloride and allyl methyl sulfide was achieved *via* hydroboration with Sia_2BH, followed by protonolysis with acetic acid at 100°C (eq 12). Similarly, *d*-limonene was converted to 1-menthene in 62% yield (eq 13). However,



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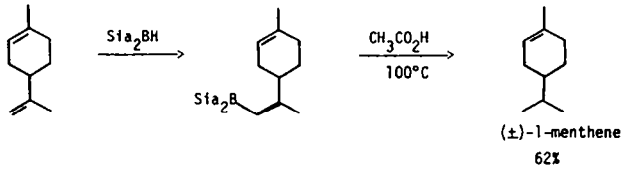
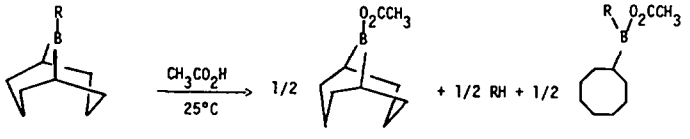


(13)

the menthene had been completely racemized. Even when hydroboration was carried out externally in order to avoid the presence of $BF_3 \cdot OEt_2$, which might have been responsible for racemization, 1-menthene with only 17% ee was isolated in 68% yield.

More recently, 9-borabicyclo[3.3.1]nonane (9-BBN) has shown to have several advantages over Sia_2BH. It has been successfully used in the selective monohydroboration of dienes[22] and in the hydroboration of alkenes carrying functional groups.[11c] Therefore, it appeared that selective protonolysis of *B*-alkyl-9-BBN derivatives would provide a convenient way of hydrogenating such alkenes. Unfortunately, the protonolysis of *B*-octyl-9-BBN with acetic acid at 25°C afforded only a 42% yield of *n*-octane (eq 14).[23] Evidently, even in the case of primary alkyl groups, there is competing



(14)

protonolysis of the cyclooctyl moiety.

CONCLUSIONS

The present study reveals that organoboranes react readily with carboxylic acids to liberate the corresponding alkanes. The first alkyl group of a trialkylborane is protonolyzed easily, followed by increased difficulty in the removal of second and third alkyl groups. Protonolysis of the third alkyl group requires elevated temperatures. The reactivity of an organoborane depends mainly on the steric requirements of the alkyl groups. Thus, primary alkyl groups undergo facile protonolysis under mild conditions, whereas the secondary, tertiary and hindered alkyl groups require harsher conditions. This property has been useful in the selective protonolysis of mixed organoboranes. The protonolysis reaction proceeds with retention of stereochemistry at the carbon center. The reaction conditions established during this study enable one to carry out a non-catalytic *cis* hydrogenation of alkenes from the less hindered side *via* hydroboration-protonolysis. Protonolysis by anhydrous hydrogen fluoride[7] is a promising development which deserves systematic exploration.

EXPERIMENTAL SECTION

Materials. Diglyme and triglyme (Ansul Chemical Co.) and tetrahydrofuran (Fisher) were distilled from lithium aluminum hydride. Boron trifluoride etherate was distilled under reduced pressure from calcium hydride. The hydrides were obtained from Metal Hydrides, Inc. Cyclopentene, cyclohexene, 1-hexene, 1-octene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2-hexene, 3-methyl-1-butene and 2,3-dimethyl-2-butene were obtained from Phillips Petroleum Co. and were utilized after checking their purities. Allyl chloride (Matheson, Coleman and Bell) and allyl methyl sulfide (Columbia Organic) were analyzed by GC prior to use. *d*-Limonene (K and K) was distilled

under reduced pressure. Styrene, α-methyl styrene and β-methyl styrene from Eastman Kodak were distilled from $LiAlH_4$ under reduced pressure. Acetic acid (Allied Chemical Co.) and propionic acid (Eastman Kodak) were purified by distillation from the corresponding anhydrides. All other acids were Eastman Kodak White Label and were used without further purification. Deuterium oxide (~ 99.5%) from Stuart Oxygen Company was used as obtained.

Methods. The techniques used in handling air-sensitive materials and the preparation and estimation of diborane are described elsewhere. The reaction products were analyzed by GC on a F and M-500 gas chromatograph using 6 ft x 1/4 in columns packed with 10% SE-30 or adiponitrile on Firebrick. The ^1H NMR spectra of norbornane and deuteronorbornanes were recorded on a 60 MHz Varian A-60 instrument.

Reaction of Tri-*n*-hexylborane With Acetic Acid. In a 200-mL three-necked round-bottom flask equipped with a thermometer, reflux condenser and diborane inlet tube were placed 16.8 g of 1-hexene (200 mmol) and 100 mL of THF. Diborane from 60 mL of 1 *M* sodium borohydride (60 mmol) and boron trifluoride (excess) in diglyme was bubbled into this solution during 1 h. When the hydroboration was complete, the flask was fitted to a Todd column and THF was distilled. The flask was cooled and 100 mL of acetic acid (1.65 mol) was added slowly. The heterogeneous mixture was heated under reflux (120°C), *n*-hexane was distilled off and collected in a calibrated receiver. There was 10.25 g of *n*-hexane (a yield of 60%) collected in 2 h. The reaction flask was cooled, excess acetic acid was neutralized with NaOH and 20 mL of 3 *N* NaOH (60 mmol) was added, followed by the addition of 14 mL of 30% hydrogen peroxide. After stirring the mixture for 2 h at 60°C, extracted with ether (2 x 20 mL), the organic layer was dried over anhydrous $MgSO_4$ and analyzed for 1-hexanol by GC using 1-octanol as an internal standard. There was 62 mmol of 1-hexanol. Other trialkylboranes were prepared and treated with acetic acid in a similar way.

Reaction of Tri-*n*-hexylborane With Carboxylic Acids. Tri-*n*-hexylborane, 66.6 mmol, was prepared as previously described and reacted with a 100-mL portion of the carboxylic acid to be tested. The heterogeneous mixture was fitted to a Todd column and the *n*-hexane distilled. Propionic acid (1.35 mol) liberated 14.1 g (164 mmol, 80% yield) of *n*-hexane after 3 h at 143°C. *n*-Butyric acid (1.08 mol) liberated 13.65 g (159 mmol, 79.5% yield) of *n*-hexane after 5 h at 172°C. Acetic acid (0.83 mol) mixed with 0.53 mol of acetic anhydride liberated 14.42 g (168 mmol, 84% yield) of *n*-hexane after 23 h at 128°C. Glycolic acid (70% solution in water) liberated 9.45 g (110 mmol, 55% yield) of *n*-hexane after 24 h at 114°C.

Protonolysis With Propionic Acid in Diglyme. The reaction of tri-*n*-hexylborane is representative. In a 200-mL three-necked flask equipped with a reflux condenser, 60-mL pressure-equalizing funnel, thermometer well and magnetic stirring bar were placed 16.8 g of 1-hexene (200 mmol) and sodium borohydride (55 mmol) in diglyme (55 mL). To a stirred mixture was added boron trifluoride etherate (75 mmol) in 25 mL of diglyme over a period of 1 h. The mixture was stirred for an additional hour at room temperature. The reflux condenser and the funnel were replaced by a distillation set, propionic acid (300 mmol) was added and heated to its boiling point for 2 h. The distillate containing ethyl ether and *n*-hexane was washed with bicarbonate solution, dried and distilled through a Todd micro column. There was obtained 15.6 g (91% yield) of *n*-hexane, bp 68-69°C. Similarly, 1-octene, 2,4,4-trimethyl-1-pentene, allyl methyl sulfide and styrene were converted to the corresponding alkanes (Table 2). When 2,4,4-trimethyl-2-pentene was reacted in this manner, the GC analysis of the ether solution showed only 5% of the desired alkane. The organoboranes from 2-hexene and 2,4,4-trimethyl-2-pentene were also isomerized by heating at 164°C for 3-4 h prior to the addition of propionic acid when good yields of the corresponding alkanes were obtained.

Protonolysis With Caprylic Acid in Triglyme. The hydroboration was carried out as described above, except that triglyme was used as a solvent in this case. Caprylic acid was used for the protonolysis.

Determination of Relative Rates of Protonolysis. To a dry 100-mL round-bottom flask equipped with a thermometer well, pressure-equalizing separatory funnel and a sidearm containing rubber septum was added 8.4 g (100 mmol) of 1-hexene, followed by 5.0 mL of cyclohexane (46.3 mmol, internal standard for GC analysis) and 11.5 mL of THF. The flask was cooled to 0°C and 16.8 mL of a 2 *M* solution of BH_3·THF was added dropwise through the funnel. The funnel was washed with 3 mL of THF to make the total volume 50 mL. The hydroboration was complete in 1 h at room temperature. Then 50 mL of a 10 *M* solution of acetic acid in THF (500 mmol) was added at 30 ± 1°C. The total volume was 100 mL with 5.0 *M* in acid and 0.33 *M* in borane. The formation of *n*-hexane with time was followed by GC (Adiponitrile column, 65°C). This procedure was followed for all alkenes. In the case of solid alkene, norbornene, 25 mL of 4 *M* solution of the alkene in THF was added.

Preparation of Deuterated Propionic Acid. The deuteropropionic acid was prepared by heating under reflux 5 g (250 mmol) of heavy water (D_2O) with 32.5 g (250 mmol) of propionic anhydride. The mixture was heated for 4 h until a constant boiling point was obtained, bp 140.5°/752 mm, $n^{20}D$ 1.3857. The product was cooled under nitrogen and stored for future use.

Preparation of Monodeuterated Norbornane by the Use of Deuterated Propionic Acid. The standard procedure was used, but this time, deuteropropionic acid was used instead of the normal propionic acid. There was obtained 1.8 g (18.5 mmol, 38% yield) of *d*-norbornane, mp 85.5-86.5°.

Preparation of Monodeuterated Norbornane by the Use of Deuterodiborane. The standard procedure was used, but this time 15 mmol of lithium aluminum deuteride was used as the hydride source. There was obtained 2.02 g (20.8 mmol, 41.7% yield) of norbornane, bp 104-105°/743 mm, mp 85-86°. The infrared spectra of both monodeuterated norbornanes were identical.

Preparation of *exo*-Dideuteronorbornane. The standard procedure was employed, but this time, both the deuterated acid and lithium aluminum deuteride were employed. There was obtained 2.05 g (20.9 mmol, 41.8% yield) of dideuteronorbornane, bp 104-105°/753 mm, mp 86-86.5°.

Spectral Analyses of Deuteronorbornanes. The ^1H NMR of simple norbornane (1) shows a doublet (partially separated from the *endo*- and bridgehead protons) due to four *exo*-protons. Monodeutero derivatives obtained by both methods (2, 3, Scheme 1) were identical and integrated for only three protons in the region expected for *exo*-protons. The dideuteronorbornane (4) showed only two *exo*-protons. The IR spectra of samples 2 and 3 were superimposable. Mass spectral analyses at low ionizing voltage revealed the following minimum isotopic purities: Sample 2, 95%; Sample 3, 82%; Sample 4, 82%.

Protonolysis of Alkyldisiamylboranes at 100°C. A standard procedure was adopted for all of the seven alkenes. In the usual apparatus, 20.6 mL of 1 *M* sodium borohydride (10% excess) in diglyme was mixed with 5.85 mL of 2-methyl-2-butene (55 mmol) and 2.5 mL of cyclohexane (23.15 mmol, internal standard). Then 7.5 mL of 3.65 *M* boron trifluoride diglymate was added and allowed to react at 0-5°C. Then 25 mmol of 1-octene was added to form *n*-octBSia$_2$. To the reaction mixture was added 40 mL of acetic acid and heated to 100°C. The formation of *n*-octane was followed by GC analysis. Similar procedures were employed for other alkenes. The protonolysis of *n*-HexBSia$_2$ at room temperature gave only 12% of *n*-hexane in 24 h.

Protonolysis of Alkyldicyclohexylborane. Dicyclohexylborane was prepared in the same way as described for Sia$_2$BH and treated with alkenes. Protonolysis was carried out by adding 40 mL of acetic acid and maintaining the reaction mixture at 30°C. The alkane produced was analyzed by GC.

Protonolysis of Thexyldialkylboranes. In the usual apparatus, 3.58 mL (30 mmol) of 2,3-dimethyl-2-butene was treated with 25 mmol of borane generated *in situ* from sodium borohydride and boron trifluoride diglymate. 1-Hexene (50 mmol) was hydroborated with this reagent. The resulting thexyldi-*n*-hexylborane was heated at 100°C with 40 mL of acetic acid and the production of *n*-hexane was followed by GC. A similar procedure was adopted for other alkenes.

Preparation of l-Menthene. In the usual apparatus, 150 mmol of disiamylborane in diglyme was prepared and 150 mmol of *d*-limonene hydroborated. Then 230 mL of acetic acid was added and heated to 100°C. When protonolysis was complete, the reaction mixture was cooled, diluted with 200 mL of water and extracted with ether (2 x 100 mL). The ether extract was washed with water (3 x 100 mL), bicarbonate (75 mL) and again with water (100 mL), and finally, dried over anhydrous $MgSO_4$. Ether was removed and 12.75 g (92 mmol) of l-menthene was obtained on distillation, bp 173-174°C/743 mm, $n^{20}D$ 1.4551; $[\alpha]^{20}D$ 0.02. The product is of > 98% chemical purity, but completely racemized. When borane, free from boron trifluoride, was bubbled through a diglyme solution containing 2-methyl-2-butene and the resulting Sia$_2$BH was used for the hydroboration of *d*-limonene, protonolysis afforded l-menthene with only 17% optical purity.

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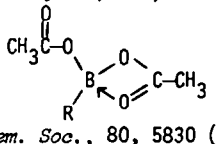

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