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ORGANOBORANES FOR SYNTHESIS. 10.[1] THE BASE-INDUCED REACTION OF BROMINE WITH ORGANOBORANES. A CONVENIENT PROCEDURE FOR THE CONVERSION OF ALKENES INTO ALKYL BROMIDES *VIA* HYDROBORATION[2,3]

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Abstract - The reaction of trialkylboranes with bromine is greatly accelerated by base. Bromination in the presence of sodium hydroxide provides alkyl bromide along with a large amount of the corresponding alcohol. The use of sodium methoxide as a base eliminates this undesirable side-reaction and provides an improved yield of alkyl bromide. Consequently, hydroboration, followed by bromination in the presence of sodium methoxide, provides a convenient new procedure for the conversion of alkenes into alkyl bromides. The organoboranes, obtained *via* hydroboration of terminal alkenes, react with the utilization of all three alkyl groups attached to boron, providing nearly quantitative yields of alkyl bromides. This procedure also accommodates common organic functional groups, as demonstrated by the preparation of methyl 11-bromoundecanoate and 11-bromoundecyl acetate from the corresponding functionally substituted alkenes. Under these conditions, secondary and bulky primary alkyl groups react more sluggishly. However, a procedure involving simultaneous addition of bromine and methanolic sodium methoxide provides improved results for such derivatives. Surprisingly, the base-induced bromination of tri-*exo*-norbornylborane results in an inversion of configuration at the reaction center to give predominantly *endo*-2-bromonorbornane. A mechanism is proposed to account for this remarkable inversion.

The facile hydroboration[5] of alkenes has provided a convenient synthesis of a wide variety of trialkylboranes. Oxidation of these organoboranes with alkaline hydrogen peroxide[6] gives the corresponding alcohols, providing a simple procedure for the *anti*-Markovnikov hydration of the double bond. A similar reaction of a trialkylborane with a halogen is expected to give the corresponding alkyl halide, providing a useful new procedure for the overall *anti*-Markovnikov hydrohalogenation of the double bond.

The first report of a halogenation reaction of a trialkylborane was in 1938 concerning the reaction of bromine with tri*n*-butylborane in the absence of a solvent to give 1-bromobutane and di-*n*-butylboron bromide.[7] However, less than one of the three alkyl groups on the trialkylborane was converted into an alkyl bromide and substantial amounts of hydrogen bromide and *n*-butane were also observed.[8] The reaction of iodine with organoboranes was found to proceed under quite vigorous conditions, requiring a temperature of 150°C to convert a single alkyl group into alkyl iodide.[9] Besides halogens, cupric halides have been reacted with trialkylboranes to provide the corresponding alkyl halides under relatively mild conditions (eq 1).[10]

$$R_3B + 2\,CuX_2 + H_2O \xrightarrow{THF} HX + Cu_2X_2 + R_2BOH + HX \quad (X = Br, Cl) \qquad (1)$$

An indirect method for the conversion of trialkylboranes into alkyl halides involving the mercuration of a trialkylborane, followed by bromodemercuration, has been developed (eq 2).[11]

$$1/3\,R_3B \xrightarrow[THF]{Hg(OAc)_2} RHgOAc \longrightarrow RHgX \xrightarrow[Pyr]{X_2} RX + HgX_2 \qquad (X = Br, I) \qquad (2)$$

This hydroboration-mercuration-halogenation sequence has been used to convert a large number of terminal alkenes into primary bromides and iodides.

The base-induced iodination of organoboranes converts two out of three alkyl groups of a trialkylborane into alkyl iodide in less than 5 min at 25°C (eq 3).[12]

$$R_3B + 2I_2 + 2NaOH \xrightarrow{THF} 2RI + 2NaI + RB(OH)_2 \qquad (3)$$

Consequently, the hydroboration-iodination procedure has made possible a simple and convenient method for the overall *anti*-Markovnikov hydroiodination of terminal alkenes. We now report details of a systematic study of the corresponding bromination reaction.

RESULTS AND DISCUSSION

The reaction of organoboranes with iodine is greatly facilitated by the addition of sodium hydroxide. Therefore, the present study was undertaken to determine the effect of sodium hydroxide or other bases on the reaction of trialkylboranes with bromine in THF.

Effect of Base on Bromination. The reaction of bromine with tri-*n*-hexylborane in THF was first examined to determine the extent of bromination in the absence of base. The yield of 1-bromohexane was invariably low (< 20%), even with a large excess of bromine, after 1 h at 0-5°C, followed by 1 h at 25°C. Thus, when 30 mmol of bromine was added to 10 mmol of tri-*n*-hexylborane in THF at 0-5°C, the product consisted of 5.9 mmol (19.7%) of 1-bromohexane, 0.4 mmol (1.3%) of 2-bromohexane, and 0.8 mol (2.6%) of *n*-hexane. When methanolic sodium hydroxide (30 mmol) was added to the above reaction mixture, a virtually instantaneous decolorization occurred, with the formation of 35% 1-bromohexane. Consequently, a detailed study of the bromination reaction was undertaken

Table 1. Reaction of tri-*n*-hexylborane with bromine under the influence of methanolic sodium hydroxide[a]

R_3B mmol	Br_2 mmol	NaOH mmol	Product Yields, %[b] 1-Bromohexane	1-Hexanol	1-Hexanol[c]
10	10	10	26	8	68
10	20	20	28	18	63
10	30	30	35	26	57
10	30	40	43	36	51
10	30	60	0[d]	40	
10	30	50	68[e]	32	

[a]Brominations were carried out at 20-25°C by adding methanolic sodium hydroxide to a THF solution of the organoborane and bromine. [b]By GC analysis based on the amount of starting 1-hexene; the secondary isomers were formed in only trace amounts. [c]After oxidation of the reaction mixture with alkaline hydrogen peroxide, these yields of 1-hexanol, plus those for 1-bromohexane, account for 94% hydroboration at the terminal carbon.[5] [d]Bromine was added to the base in methanol at 0°C, followed by the addition of the organoborane in THF at 0°C; analysis after warming to 20-25°C. [e]Procedure used in this case involved simultaneous dropwise addition of bromine and base to the borane at 0-5°C.

following the procedure which had been efficient for the base-induced iodination of trialkylboranes.[12] The results are summarized in Table 1.

The base-induced iodination reaction gave a maximum conversion of two of the three alkyl groups in a trialkylborane into the corresponding alkyl iodide (67%). However, the same procedure, when applied to bromination, has resulted in a much lower conversion of alkyl groups into an alkyl bromide (43%). Also, a major side-reaction occurs during sodium hydroxide-induced bromination, which results in the oxidation of tri-*n*-hexylborane to give 1-hexanol.

Trialkylboranes are readily oxidized by sodium hypochlorite.[13] As shown in Table 1, only 1-hexanol and a trace of 2-hexanol were formed when a THF solution of tri-*n*-hexylborane was added to a colorless solution of bromine in methanolic sodium hydroxide at 0°C.[14] Therefore, in the present study, 1-hexanol is formed *via* the oxidation of tri-*n*-hexylborane with sodium hypobromite by a reaction analogous to that proposed for the hypohalite oxidation of arylboronic acids.[15]

The procedure adopted for bromination was to add bromine to the organoborane in THF, followed by the dropwise addition of methanolic sodium hydroxide. By changing to a simultaneous dropwise addition of bromine and base to the organoborane in THF, the yield of primary bromide derived from a terminal alkene could be increased to around 68%. If enough sodium hydroxide was added to decolorize bromine completely, a quantitative recovery of all three alkyl groups was obtained (eq 4, Table 1). However, the loss of one alkyl group as alcohol could limit the synthetic applications of this procedure.

$$R_3B + 3Br_2 + 4NaOH \longrightarrow 2RBr + ROH + B(OH)_3 + 4NaBr \quad (4)$$

Various bases were then examined to see if the third alkyl group could also be converted into an alkyl bromide. The effect of various bases upon the bromination reaction of trialkylboranes is summarized in Table 2. When sodium methoxide in methanol was used as the base, an 85% yield of bromide was observed with only a trace amount of alcohol. Consequently, the undesirable oxidation proved to be easily circumvented by using this base,

Table 2. Reaction of tri-*n*-hexylborane with bromine in the presence of various bases[a]

Base	Product Yields[b]		
	1-Bromohexane		2-Bromohexane
	mmol	%[c]	mmol
H_2O	9.1	30.4	0.3
$NaOAc/H_2O$	11.	39.4	0.2
$NaOH/H_2O$	10.0	33.3[d]	0.4
$NaOH/CH_3OH$	20.8	69.4[d]	trace
$NaOCH_3/CH_3OH$	25.4	84.7[e]	0.7
$KOC(CH_3)_3/(CH_3)_3COH$	9.8	32.6	0.7
$KOC(CH_3)_3/THF$	10.4	34.7	0.2

[a]All reactions involve the simultaneous dropwise addition of bromine (30 mmol) and base (30 mmol) to a THF solution of tri-*n*-hexylborane (10 mmol) at 0-5°C. [b]By GC analysis. [c]Based on the maximum production of 30 mmol of bromohexane. [d]A large amount of 1-hexanol was present also. [e]Only a trace amount of 1-hexanol was observed.

presumably because the reaction of bromine with sodium methoxide does not result in the formation of sodium hypobromite.[16-19]

The stoichiometry of methoxide-induced bromination was given a careful examination. Results summarized in Table 3 indicate that it is necessary to use a large excess of bromine as well as base to obtain a 93% yield of 1-bromohexane.This is essentially a quantitative yield since the hydroboration of 1-hexene proceeds to place 94% of boron on the terminal carbon.[5]

Effect of Mode of Addition. The procedure described above where bromine is first added to organoborane, followed by the addition of methanolic sodium methoxide (Procedure A), gave excellent results with simple (eq 5) and functionally substituted terminal alkenes (eq 6).

Table 3. Reaction of tri-*n*-hexylborane with bromine in the presence of methanolic sodium methoxide[a]

R_3B mmol	Br_2 mmol	$NaOCH_3$ mmol	Yield of 1-Bromohexane %
10	10	10	32
10	20	20	61
10	30	30	72
10	40	40	82
10	40	50	93

[a]All brominations were carried out at 0°C by adding methanolic sodium methoxide to a THF solution of the organoborane and bromine. [b]By GC analysis based on the amount of starting 1-hexene. 1-Methoxyhexane was never observed in any detectable amount. However, 1-hexanol and 2-bromohexane were present in trace amounts.

$$RCH{=}CH_2 \xrightarrow{BH_3} (RCH_2CH_2)_3B \xrightarrow[NaOMe]{Br_2} RCH_2CH_2Br \quad (5)$$

$$X(CH_2)_nCH{=}CH_2 \xrightarrow{BH_3} \xrightarrow[NaOMe]{Br_2} X(CH_2)_{n+2}Br \quad (6)$$

Representative terminal alkenes were transformed into the corresponding bromides using this procedure (Table 4). However bulky terminal alkenes and internal alkenes provided lower yields of bromide when this procedure was applied. For example, hydroboration-bromination of cyclopentene gave only a 31% yield of bromocyclopentane. A systematic examination of various reaction parameters, such as temperature, stoichiometry and mode of addition, resulted in the development of a second procedure (Procedure B), which involves a simultaneous dropwise addition of bromine (30 mmol), and base (33 mmol) to a THF solution of the organoborane (10 mmol) at 20-25°C. This mode of addition appeared to be more generally applicable than Procedure A. Representative conversions were carried out, and in a number of cases, the alkyl bromides were isolated in reasonable yields (eqs 7 and 8).

A summary of results obtained for the hydroboration-bromination of various alkenes using both procedures is given in Table 4.

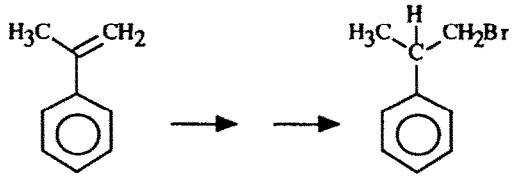
Bromination of Mixed Organoboranes. In the hydroboration-iodination reaction,[12] the third alkyl group of a trialkylborane failed to react. However, this difficulty was circumvented by using disiamylborane for the hydroboration of alkene. Since the primary alkyl groups react in preference to the bulky secondary alkyl (3-methyl-2-butyl, siamyl) groups, an essentially quantitative conversion of terminal alkenes into primary iodides was achieved.[5] However, in the present study, excellent results were possible through a simpler procedure involving treatment with bromine in THF, which discouraged the undertaking of a detailed investigation into the use of

disiamylborane for the hydroboration-bromination reaction. A limited study of representative mixed trialkylboranes uncovered some interesting phenomena, as shown in Table 5.

Table 4. Conversion of representative alkenes into bromides *via* hydroboration-bromination

Alkene	Procedure[a]	Product	Yield, %[b]
1-butene	A	1-bromobutane	91
1-hexene	A	1-bromohexane	93[c]
	B		85[c]
1-octene	A	1-bromooctane	94[c]
methyl 10-undecenoate	A	methyl 11-bromoundecanoate	92(85)[c]
11-chloro-1-undecene	A	1-bromo-11-chloroundecane	(75)[c]
10-undecenyl acetate	A	11-bromoundecyl acetate	(77)[c]
2-methyl-1-pentene	A	1-bromo-2-methylpentane	99
2,4,4-trimethyl-1-pentene	A	1-bromo-2,4,4-trimethyl-pentane	80
	B		80(70)
α-methylstyrene	A	1-bromo-2-phenylpropane	68
	B		74(63)
β-pinene	A	*cis*-myrtanyl bromide	55
	B		65(59)
cyclopentene	A	bromocyclopentane	31
	B		69
cyclohexene	B	bromocyclohexane	64
2-butene	B	2-bromobutane	74

[a]Procedure A, bromine (40 mmol) added to organoborane (10 mmol) in THF at 0°C, followed by dropwise addition of methanolic sodium methoxide (50 mmol) at 0°C. Procedure B, simultaneous addition of bromine (30 mmol) and methanolic sodium methoxide (33 mmol) to a THF solution of the organoborane (10 mmol) at 20-25°C. [b]By GC analysis (isolated yields in parentheses). The yields are based on the amount of starting alkene. [c] Small amounts of 2-bromoalkane (1-2%) are present also.



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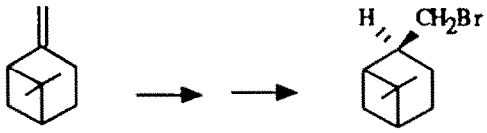
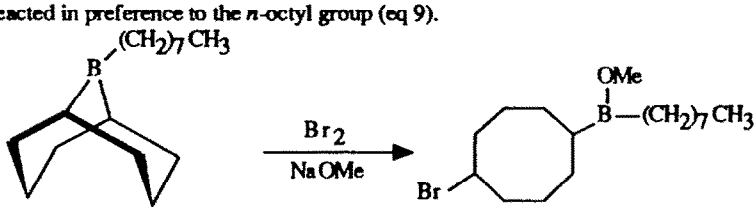


(8)

The reaction of *n*-hexyldisiamylborane with bromine (one molar equivalent) using Procedure A gave only a 17% yield of 1-bromohexane. Presumably, the large bulky siamyl groups inhibit the reaction of the organoborane with bromine to such an extent that side-reactions become competitive. In the reaction of *n*-octyldicyclohexylborane, a large amount of bromocyclohexane was formed, indicating that there is only a slight preference for the bromination of *n*-octyl group over the cyclohexyl group. In the bromination of *B*-*n*-octyl-9-borabicxyclo[3.3.1]nonane,[20] the *B*-cyclooctyl bond reacted in preference to the *n*-octyl group (eq 9).



(9)

Such high degree of selectivity for opening the boracycloalkane[21] ring bears great synthetic potential. With a second mole each of bromine and base, *n*-octyl group reacts with a slight preference. Finally, with a third mole of base and bromine, 1-bromooctane is formed in essentially quantitative yield.

Table 5. Reaction of *n*-octyldialkylboranes with bromine in the presence of sodium methoxide[a]

R_2BR'[b] R' = *n*-oct	Br_2 mmol	$NaOCH_3$ mmol	React. Temp. °C	Yield of 1-Bromooctane %
Sia_2BR'	10	11	25	17
	20	22	25	44
	30	33	25	54
	10	11	0	44
	20	22	0	84
Chx_2BR'	10	11	25	62(2.7)
	20	22	25	87(7.3)
	30	33	25	87(9.7)
	10	11	0	77(2.9)
	20	22	0	98(6.5)
B-R'-9-BBN	10	11	0	trace
	10	11	25	trace
	20	22	25	61
	30	33	25	97

[a]Hydroboration carrried out by adding 1-octene (10 mmol) to a THF solution of the dialkylborane (10 mmol). Bromination *via* simultaneous addition of bromine and methanolic sodium methoxide. [b]Sia_2BH, disiamylborane; Chx_2BH, dicyclohexylborane; 9-BBN, 9-borabicyclo[3.3.1]nonane. [c]By GC analysis based on the amount of starting 1-octene. The yields in parentheses are the amounts of bromocyclohexane (mmol) formed in the bromination of *n*-octyldicyclohexylborane.

Alkyl bromides are obtained in high yields when 9-BBN is used for the hydroboration of monosubstituted alkenes. With disubstituted alkenes, the yields are lower, comparable to those obtained by a much simpler procedure utilizing borane-THF. The results are summarized in Table 6.

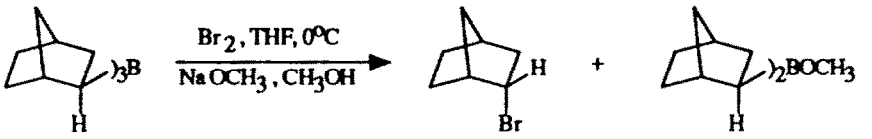
Table 6. Reaction of *B*-alkyl-9-borabicyclo[3.3.1]nonanes with bromine in the presence of methanolic sodium methoxide[a]

Alkene for *B*-Alkyl-9-BBN	Product	Yield, %[b]
1-hexene	1-bromohexane	95
1-octene	1-bromooctane	97
α-methylstyrene	1-bromo-2-phenylpropane	61
β-pinene	*cis*-myrtanyl bromide	40
cyclopentene	bromocyclopentane	60

[a]Brominations were carried out by the simultaneous addition of bromine (30 mmol) and methanolic sodium methoxide (33 mmol) to a THF solution of the organoborane (10 mmol) at 20-25°C. [b]By GC analysis based on the amount of starting alkene.

Stereochemistry of Base-Induced Bromination. For the proper application of any synthetic procedure, it is necessary to know the regio- and stereoselectivity of that reaction. The hydroboration-bromination sequence represents a regioselective *anti*-Markovnikov hydrobromination of alkenes, as already established in this study. Consequently, it was of interest to establish the stereochemistry of the bromination reaction.

The bromination of tri-*exo*-norbornylborane under mild conditions converted only one norbornyl group into bromide. Surprisingly, the 2-bromonorbornane obtained was predominantly endo, indicating that an inversion of configuration had occurred at the carbon atom undergoing reaction (eq 10).



(10)

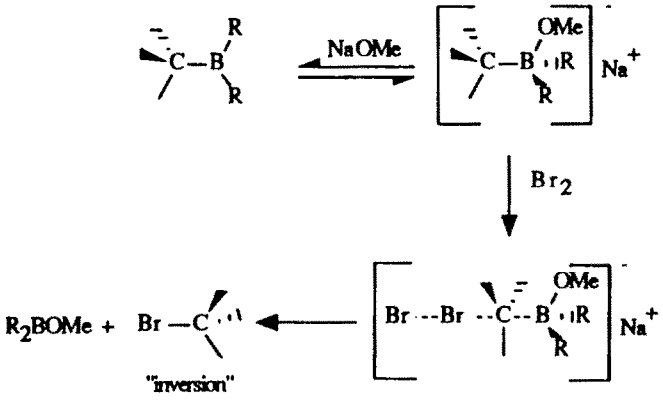
The procedure was repeated a number of times and the norbornyl bromide formed was always 75 ± 5% endo (by either GC or NMR analysis).

This result was quite unexpected since most reported electrophilic substitution reactions proceed with retention of configuration.[22] However, a few electrophilic substitution reactions have been reported to proceed with inversion of configuration. Thus, the reaction of bromine with *exo*- or *endo*-norbornyl lithium,[23] with menthyl lithium,[24] or with 4-*t*-butylcyclohexyl lithium[24] results in predominant, though not stereospecific, inversion.

This inversion of configuration for the base-induced bromination is even more unusual when compared to the highly consistent behavior of other reactions of organoboranes.[25] Essentially all of the non-free radical reactions of organoboranes, *e.g.*, protonolysis with carboxylic acids, oxidation with alkaline hydrogen peroxide, amination with hydroxylamine-*O*-sulfonic acid, carbonylation and ethoxycarbonylmethylation, are highly stereospecific reactions which occur with complete retention of configuration at the carbon atom undergoing the reaction.[26]

Mechanistic Considerations. The base used in the bromination reaction has pronounced effects upon both the rate and stereochemistry of the reaction. Thus, the reaction of bromine in the dark at 20°C with an equimolar quantity of tri-*n*-butyl- or tri-*s*-butylborane in THF in the absence of added base was quite slow, being only 30-40% complete after 8 h.[27] Similar reactions in the presence of base were virtually 100% complete as fast as the analysis could be made following the addition of methoxide. The bromination of tri-*exo*-norbornylborane in the absence of base under analogous conditions was also quite slow and the small amount of bromide formed was > 99% exo by GC analysis.

A mechanism which can account for this remarkable inversion is shown in Scheme I.



Scheme 1

The tremendous acceleration in rate upon the addition of base is presumably due to "ate" complex formation (1). This should increase the electron density on carbon and increase the ease of bond scission upon backside attack by bromine. Most electrophilic substitutions which result in retention of configuration are thought to involve four-center transition states.[22] In the "ate" complex, such a four-center transition state is not possible, so the reaction

takes a different mechanistic course, resulting in inversion.The fact that the bromine-chloride also reacts with trialkylboranes to yield alkylbromides supports the proposed mechanism.[28]

The small amount of *exo*-norbornyl bromide formed may arise from a competing mechanism proceeding through a free radical substitution[27] or through a typical electrophilic substitution of a small amount of tri-*exo*-norbornylborane in equilibrium with the "ate" complex. We are not yet able to define the precise path for the minor product.

Although the mechanistic implications of this study are interesting, the synthetic importance may be even greater because this base-induced bromination of tri-*exo*-norbornylborane provides a convenient means of preparing *endo*-2-bromonorborane[29] and, presumably, related bicyclic derivatives. The simultaneous addition procedure, followed by selective solvolysis of the more reactive exo form in 80% aqueous ethanol,[30] gave, after distillation, pure *endo*-2-bromonorborane (> 99% endo by GC and NMR analysis). More recently the reaction has been utilized to effectively incorporate radioactive bromine into pharmaceuticals.[31]

CONCLUSIONS

The sodium methoxide-induced bromination of trialkylboranes has been developed into a highly convenient method for the preparation of alkyl bromides. Thus, hydroboration-bromination provides a new and important procedure for the overall *anti*-Markovnikov addition of the elements of hydrogen bromide to a terminal alkene.

Two different procedures were developed for the base-induced bromination of trialkylboranes. Procedure A provided essentially quantitative conversions of monosubstituted alkenes into primary bromides. Unfortunately, the yield dropped with the secondary and the more hindered primary alkyl groups. Procedure B provided more satisfactory yields for these derivatives and appeared to be of more general applicability.

Examination of the stereochemistry of the product from the base-induced bromination of tri-*exo*-norbornylborane showed that the 2-bromonorbornane obtained was predominantly endo, indicating that an unusual inversion of configuration had occurred at the carbon atom undergoing reaction.

EXPERIMENTAL SECTION

Materials. The purification of solvents, preparation and standardization of borane-THF solution were carried out as described elsewhere.[5] Stock solutions of disiamylborane and 9-borabicyclo[3.3.1]nonane were also prepared and standardized as previously reported.[5] Analytical reagent grade bromine was used directly as obtained from Mallinckrodt Chemical Works. Baker reagent grade methanol was dried by distilling from magnesium methoxide. The sodium methoxide was prepared by the addition of sodium metal to the dried methanol and then stored under nitrogen. Except for the 10-undecenyl derivatives, the alkenes used in this study were obtained from various commercial sources. In general, the simple alkenes were distilled from lithium aluminum hydride and stored under nitrogen. Methyl 10-undecenoate was obtained by the methanesulfonic acid catalyzed esterification of 10-undecenoic acid. 11-Chloro-1-undecene was prepared from the alcohol by treatment with thionyl chloride. 10-Undecenyl acetate was prepared by treating the alcohol with acetic anhydride. The 10-undecenyl derivatives were purified by vacuum distillation and all were at least 99% pure by GC.

GC Analysis. A Hewlett-Packard Model 5750 temperature-programmed gas chromatograph equipped with appropriate columns was used for all of the analyses. The bromides were analyzed on a 6 ft x 1/4 in column of SE-30, 10% on Aeropak 30. The alcohols were analyzed on a 6 ft x 1/4 in column of Carbowax 20 M -0.5% Armeen 18 D, 19.5% on AW/DMCS Chromosorb W and the stereochemistry of 2-bromonorbornane was determined on a 20 ft x 1/4 in column of Zonyl E-7, 5% on AW/DMCS Chromosorb W. Identification of the alkyl bromides was carried out by comparison of the retention times with those of authentic samples. In cases where an authentic sample was not available, the bromide from a preparative scale reaction was isolated and characterized (physical constants, IR and NMR spectroscopy).

cis-Myrtanyl Bromide. Standard Procedure. The general procedure described here for the hydroboration-bromination of β-pinene is representative for the simultaneous addition of the bromine and sodium methoxide (Procedure B). A dry, 500-mL flask equipped with a septum inlet, thermometer well, two pressure-equalizing dropping funnels and a magnetic stirrer was flushed with nitrogen and maintained under a positive nitrogen pressure. The flask was charged

with 100 mL of dry THF, 47.2 mL (300 mmol) of dry β-pinene and cooled to 0-5°C with an ice water bath. Hydroboration was achieved by a dropwise addition of 39.0 mL of a 2.68 *M* solution of borane (325 mmol of hydride) in THF. After the addition of the hydride, the ice water bath was removed and the solution was stirred for 1 h at 25°C. Excess hydride was destroyed by the careful addition of 2 mL of methanol. Bromine (16 mL, 300 mmol) was placed in one addition funnel and 86 mL of a 3.84 *M* solution of sodium methoxide (330 mmol) in methanol was placed in the other addition funnel. Bromine and base were then added simultaneously at a rate such that the reaction mixture was always slightly yellow. The reaction flask was cooled intermitently with an ice water bath during the 30 min addition period in order to maintain a reaction temperature of 20-25°C. The reaction mixture was then treated with 20 mL of water and sufficient potassium carbonate to destroy excess bromine. The organic layer was separated from the aqueous layer, the aqueous layer was extracted with pentane (3 x 50 mL), the combined organic layer was extracted with water (2 x 50 mL) and once with 50 mL of saturated aqueous sodium chloride. After drying over anhydrous magnesium sulfate, the solvents were removed on a rotary evaporator under reduced pressure, leaving a slightly yellow oil. Vacuum distillation of this oil gave 38.5 g (59%) of *cis*-myrtanyl bromide; bp 94°C/14 mm; n^{20}D 1.5109. Anal. Calcd. for $C_{10}H_{17}Br$: C, 55.31; H, 7.89; Br, 36.80. Found: C, 55.54; H, 8.05; Br, 36.77.

11-Bromoundecyl Acetate. Standard Procedure. (Procedure A). The general procedure described here for the hydroboration-bromination of 10-undecenyl acetate was used for all cases involving the addition of bromine, followed by sodium methoxide (Procedure A). The hydroboration was carried out in a manner similar to that described for b-pinene using 32 g (150 mmol) of 10-undecenyl acetate, 19.5 mL of a 2.58-*M* solution of borane (150 mmol of hydride) in THF and 75 mL of THF. After adding 1 mL of methanol to destroy any excess hydride, the reaction flask was cooled to -10°C to 0°C with an ice-salt bath. Bromine (10 mL, 200 mmol) was added at such a rate that the reaction mixture was maintained below 0°C, followed by the dropwise addition of sodium methoxide in methanol (60 mL of a 4.16 *M* solution, 250 mmol) over a period of 30 min. Isolation and vacuum distillation of the above reaction product gave 33.9 g (77%) of 11-bromoundecyl acetate: bp 126-127°C/0.65 mm [lit.[32] bp 140-143°C/1.0 mm]; n^{20}D 1.4631 [lit.[32] n^{25}D 1.4620].

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REFERENCES AND NOTES

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16. The reaction of bromine with sodium methoxide presumably gives methyl hypobromite, which does not react under the conditions employed with trialkylboranes. In the absence of base, at -40°C, methyl hypobromite reacted with tri-*n*-heptylborane to give a 47% yield of 1-bromoheptane,[17] presumably *via* free radical reactions. However, in the present study, a free radical reaction is unlikely.[18]

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18. Free radical reactions of trialkylboranes only give a maximum utilization of two of the three groups, base-induced bromination utilizes all three groups.Also in radical reactions of trialkylborane, the secondary alkyl groups are more reactive than primary alkyl groups. Finally, the stereochemical results tend to rule out a free radical reaction.
19. For example, when bromine (30 mmol) was added to sodium methoxide (60 mmol) in methanol at 0°C, a clear solution and a white precipitate results. This slurry was then passed into a THF solution of tri-*n*-hexylborane (30 mmol) at 0°C *via* a stream of dry nitrogen. GC analysis of the resulting mixture indicated that neither 1-hexanol nor 1-bromohexane was formed in any detectable amount.
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