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Hydroboration. 56. Convenient and Regiospecific Route to Functionalized Organosilanes through the Hydroboration of Alkenylsilanes

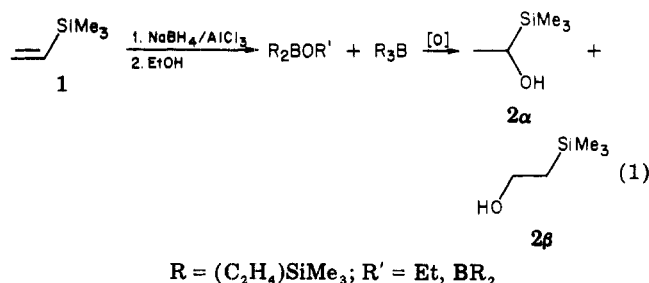John A. Soderquist[1] and Herbert C. Brown*

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A systematic and detailed study of the hydroboration of several representative alkenylsilanes is reported. By use of a 1:1 molar stoichiometry, the hydroboration of vinyltrimethylsilane (1) at 0 °C with BH_3·THF gives a mixture of dialkylborane products exclusively with a ca. 60:40 distribution of α- and β-silylethyl groups in these adducts. Redistribution of the reaction mixture at a somewhat higher temperature (50 °C) gives the corresponding monoalkylboranes. The redistribution process is regiospecific, leaving the original 60:40 ratio of α- and β-silylethyl groups in the dialkylboranes unchanged in the monoalkylboranes produced. With a 3:1 ratio of 1 to BH_3·THF, equimolar amounts of dialkyl- and trialkylborane products are formed in the hydroboration reaction. Under these conditions, the α to β ratio changes modestly to 50:50. The failure of the hydroboration to attain complete conversion to the trialkylborane stage is attributed largely to the low reactivity of *meso*-bis[1-(trimethylsilyl)-ethyl]borane produced in the reaction in the further hydroboration of 1. The change in the regioselectivity from 60:40 to 50:50 with a 3:1 stoichiometry is attributed to the higher β selectivity of dialkylboranes in the hydroboration of 1. Thus, the hydroboration of 1 with 9-borabicyclo[3.3.1]nonane (9-BBN) is regiospecific, giving exclusively the *B*-[β-(trimethylsilyl)ethyl]-9-borabicyclo[3.3.1]nonane (3) product. Redistribution of 3 with BH_3·THF gives essentially complete conversion to 9-BBN and pure bis[2-(trimethylsilyl)ethyl]borane. This compound hydroborates 1 rapidly at 0 °C, giving predominantly (ca. 85%) the β adduct, tris[2-(trimethylsilyl)ethyl]borane. Hydroboration of propen-2-yltrimethylsilane with BH_3·THF gives primarily (91%) β boron placement. However, use of 9-BBN eliminates the formation of the minor internal product and gives (2-Me_3Si-1-Pr)-9-BBN exclusively. Hydroboration of *cis*-1-propenyltrimethylsilane (17) with BH_3·THF proceeds to the dialkylborane stage, with no significant formation of the corresponding trialkylborane. The hydroboration is highly regioselective, giving the bis[1-(trimethylsilyl)-1-propyl]borane product in 95% regioisomeric purity. This borane is unusual in that it is monomeric in solution, as revealed by the IR and ^{11}B NMR data. Hydroboration of 17 with 9-BBN is much less selective than that with BH_3·THF, a rare occurrence, giving essentially equal amounts of regioisomeric adducts. Hydroboration of allyltrimethylsilane with either BH_3·THF or 9-BBN gives the (γ-silylpropyl)borane product exclusively. Hydroboration of 3-buten-1-yltrimethylsilane with BH_3·THF gives the (δ-silylbutyl)borane adduct in 94% isomeric purity. With 9-BBN, the hydroboration is regiospecific, giving the (δ-silylbutyl)borane adduct exclusively. Thus, through hydroboration, the syntheses of α, β, γ, and δ boron-functionalized organosilanes are achieved, making such compounds available for use as synthetic intermediates. The ^{13}C and ^{11}B spectra for all compounds are presented and discussed. Several new silylated organoboranes available from Grignard methods are also described together with several new silylated alcohols. This study has resolved some long-standing anomalies in the hydroboration of alkenylsilanes and has led to a full understanding of the phenomena involved.

The synthetic utility of the hydroboration reaction in organic chemistry is well-known.[2] Terminal alkenes such as 1-hexene or 3,3-dimethyl-1-butene undergo smooth reaction with diborane or borane complexes to place the boron atom 93–94% at the terminal position of the double bond, giving trialkylboranes of high isomeric purity. These derivatives can in turn undergo a variety of conversions characteristic of this class of compounds.

In 1958, Seyferth reported the hydroboration of vinyltrimethylsilane (1), which exhibited a number of unusual features. The hydroboration produced mixtures of both dialkyl- and trialkylboranes. On oxidation, these gave roughly equal amounts of the two isomeric trimethylsilylethanols (2, eq 1).[3]

$$R = (C_2H_4)SiMe_3; \ R' = Et, \ BR_2$$

This lack of regioselectivity exhibited by borane–tetrahydrofuran (BH_3·THF) in the hydroboration of 1 has since been confirmed by others.[4]

Recently we reported that dialkylboranes, such as disiamyl- and dicyclohexylborane, as well as 9-borabicyclo[3.3.1]nonane (9-BBN), exhibit very high regioselectivities in the hydroboration of 1, placing the boron atom at the terminal position of the double bond with isomeric distributions of ≥95% (eq 2).[4f]

This development encouraged us to examine in detail the hydroboration of 1, as well as several other representative alkenylsilanes, to understand better the nature of the products formed and to establish the utility of this reaction for the preparation of functionalized organosilanes.[5]
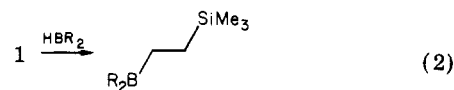
(1) Postdoctoral research associate on Grant CHE 76-20846 of the National Science Foundation.

(2) Brown, H. C.; Midland, M. M.; Levy, A. B.; Kramer, G. W. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(3) (a) Seyferth, D. *J. Inorg. Nucl. Chem.* **1958**, *7*, 152; (b) *J. Am. Chem. Soc.* **1959**, *81*, 1844.

(4) (a) Seyferth, D.; Yamazak, H.; Sato, Y. *Inorg. Chem.* **1963**, *2*, 734. (b) Kumada, M.; Imaki, N.; Yamamoto, K. *J. Organomet. Chem.* **1966**, *6*, 490. (c) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (d) Jones, P. R.; Myers, J. K. *J. Organomet. Chem.* **1972**, *34*, C9. (e) Lim, T. F. O.; Myers, J. K.; Rogers, G. T.; Jones, P. R. *Ibid.* **1977**, *135*, 249. (f) Soderquist, J. A.; Hassner, A. *Ibid.* **1978**, *156*, C12.

Table I. Distribution of Isomeric (Trimethylsilyl)ethanols (2) under Various Hydroboration Conditions

| entry	hydro-borating reagent[a]	1/BH$_3$ ratio	temp, °C (time, h)	2α/2β ratio	yield,[b] %
1	BH$_3$	0.5	0 (0.25)	60:40	98
2	BH$_3$	1	0 (1)	61:39	99
3	BH$_3$	2	0 (1)	57:43	98
4	BH$_3$	3	0 (1)	49:51	84
5	BH$_3$	3	25 (9)	49:51	86
6	BH$_3$	3	65 (9)	50:50	92
7	9-BBN[c]		25 (1)	0:100	100[d]

[a] All reactions were carried out in THF with a final borane molarity of 1.00 except for entries 3 and 4 where 0.94 M borane solutions were used. [b] Determined by GC using an internal standard. [c] A 1:1 molar ratio of 9-BBN to 1 was used for the hydroboration. [d] The cis-1,5-cyclo-octanediol coproduct was obtained quantitatively by GC analysis.

Results and Discussion

Vinyltrimethylsilane. Using BH$_3$·THF or 9-BBN[6] as a representative hydroborating reagent, we carried out the hydroboration of 1, under the conditions given in Table I. With excess hydride, the hydroboration of 1 proceeds cleanly to completion, giving, after oxidation, a mixture of 2α/2β of approximately 60:40 (eq 3). With the stoi-

$$1 \xrightarrow[0\,°C]{H_3B\cdot THF} CH_3CHSiMe_3 + CH_2CH_2SiMe_3 \qquad (3)$$

60%   40%
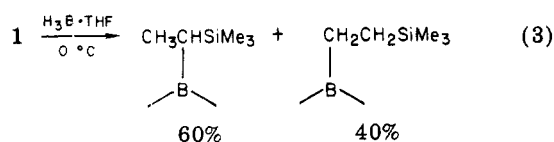
chiometric quantity of hydride, the reaction does not go to completion, containing both residual 1 and residual hydride. The usual oxidation of the product gives a 50:50 mixture of the two alcohol products. These findings agree well with those reported by Seyferth[3b] in that more 2β is produced by use of less hydride. On the other hand, the hydroboration with 9-BBN is regiospecific, giving the [β-(trimethylsilyl)ethyl]borane product 3 exclusively. Oxidation of 3 gives only the β-silylated alcohol 2β in quantitative yield (eq 4).

$$1 \xrightarrow{9\text{-BBN}} \text{3} \xrightarrow{[O]} 2\beta + \text{(diol)} \qquad (4)$$
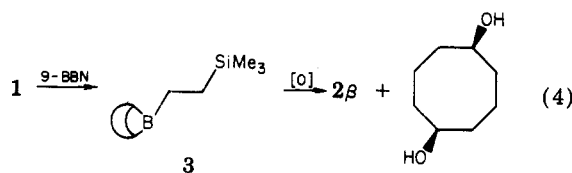
None of the conditions given in Table I led to the exclusive formation of the α product (2α). However, this compound was conveniently prepared for analysis and

identification purposes through the BH$_3$·THF reduction of acetyltrimethylsilane (4, eq 5).[4f]

$$4 \xrightarrow[2.\ H_2O]{1.\ BH_3\cdot THF} 2\alpha \qquad (5)$$
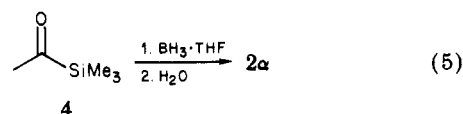
To obtain more information as to the nature of the borane adducts formed under the various reaction conditions (Table I), we examined the hydroboration mixtures spectroscopically, following methanolysis, using ^{11}B NMR. Owing to the different chemical shifts of the various alkylated borane products, the relative amounts of each could be determined from the peak areas for each derivative. These results are summarized in Table II.

In the case of the 1:1 stoichiometry (entry 1), the initial product formed was the dialkylborane, essentially exclusively. When the reaction mixture is maintained at a higher temperature, 50 °C, prior to methanolysis, redistribution of this product occurs to form major amounts of the monoalkylborane (entry 5). Oxidation of this mixture, following hydrolysis, gives the identical 61:39 distribution of alcohol products 2 obtained following the original hydroboration, indicating that the redistribution is regiospecific and does not involve any migration of the boron position. These findings account for earlier results in which monoalkylboranes were obtained from the hydroboration of 1 with excess BH$_3$·THF at elevated reaction temperatures.[4a]

The hydroboration mixtures were also examined spectroscopically by ^{11}B NMR prior to methanolysis to obtain information on the extent of association of the dialkylboranes present. With one known prior exception, all dialkylboranes form dimeric species in solution, dimerized through the usual boron–hydrogen bridge. These exhibit an absorbance in the 25–30-ppm region. One monomeric dialkylborane, dithexylborane, is known. It exhibits an absorbance only at 81 ppm.[7] With the 1:1 stoichiometry, the dialkyl product from 1 has a principal absorbance at 45 ppm as well as a shoulder to this peak at ca. 53 ppm. A small absorbance at 83 ppm is also observed. With the 2:1 stoichiometry, the 83-ppm peak is of equal intensity to that of the former. With the 3:1 stoichiometry, the 83-ppm peak constitutes the major absorbance with only a small peak observed at 53 ppm.

These observations suggest that an equilibrium mixture of both dimeric and monomeric dialkylboranes must be present in the reaction mixtures. Increasing the 1/BH$_3$ stoichiometry ratio results in an increase in the amount of trialkylborane relative to the dialkylborane in the product. The increase in trialkylborane must result from a preferential reaction of the more reactive dialkylborane species with 1. The remaining dialkylboranes, the less reactive derivatives, evidently tend to be largely monomeric in solution, absorbing in the 80–90-ppm region. Infrared analysis of the 3:1 mixture reveals the absence of any band in the 1500–1600-cm^{-1} region where a bridged dimer would be expected to absorb.[7]

Addition of dimeric 9-BBN (δ 28) to the 2:1 reaction mixture slowly brings about a new absorbance, observed as a shoulder at ca. 33 ppm. This result suggests that the 2:1 mixture equilibrates slowly to form mixed dimers under these conditions.

In principle, four isomeric dialkylborinate esters (5) could be formed from the hydroboration/methanolysis of 1 under the 1:1 stoichiometric conditions.

(5) For representative applications of the hydroboration reaction for the preparation of functionalized organosilanes, see ref 4a,c,e,f. See also: (a) Brook, A. G.; Pierce, J. B. *J. Am. Chem. Soc.* **1965**, *87*, 2566; (b) Brook, A. G.; Kucera, H. W.; MacRae, D. M. *Can. J. Chem.* **1970**, *48*, 818; (c) Weber, W. P.; Felix, R. A.; Willard, A. K.; Boettger, H. G. *J. Org. Chem.* **1971**, *36*, 4060; (d) Koch, T. H.; Soderquist, J. A.; Kinstle, T. H. *J. Am. Chem. Soc.* **1974**, *96*, 5576; (e) Pitt, C. G.; Friedman, A. E.; Rector, D.; Wani, M. C. *Tetrahedron* **1975**, *31*, 2369; (f) Barcza, S.; Hoffman, C. W. *Ibid.* **1975**, *31*, 2367; (g) Jesus, M. D.; Rosario, O.; Larson, G. L. *J. Organomet. Chem.* **1977**, *132*, 300; (h) Freppel, C.; Poirier, M. A.; Richer, J. C.; Maroni, Y.; Manuel, G. *Can. J. Chem.* **1974**, *52*, 4133; (i) Cudlin, J.; Schraml, J.; Chvalovski, V. *Collect. Czech. Chem. Commun.* **1964**, *29*, 1476; (j) Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, *543*; (k) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263; (l) Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2941; (m) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, C1; (n) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184.
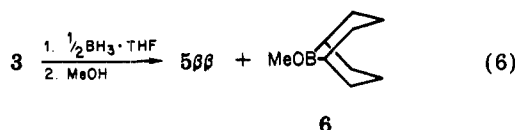
(6) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.

(7) Negishi, E.; Katz, J.-J.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 4025.

meso-5αα
dl-5αα   5αβ   5ββ
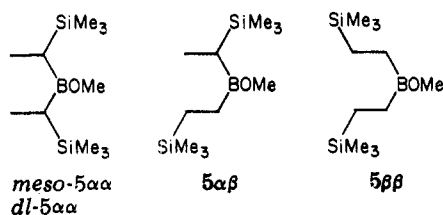
Since the ^{13}C NMR spectrum of this mixture was quite complex, we chose to prepare several of these compounds by alternative routes to determine their presence in this mixture.

Our finding that the redistribution of organoboranes containing these groups was regiospecific suggested that this process might allow the preparation of pure *5ββ*. A 2:1 mixture of **3** and BH$_3$·THF was heated for 2 h at 70 °C. ^{11}B NMR analysis of the reaction mixture revealed the complete disappearance of the starting materials, with the formation of a large peak at 28 ppm as expected for 9-BBN, together with a shoulder absorbance at 33 ppm. Methanolysis produced the dialkyl product (*5ββ*) and *B*-MeO-9-BBN (**6**) (eq 6).

$$3 \xrightarrow[\text{2. MeOH}]{\text{1. }\frac{1}{2}\text{BH}_3\cdot\text{THF}} 5\beta\beta + \text{MeOB} \qquad (6)$$

6

Oxidation of this mixture gives **2β** as the only silylated alcohol, confirming the regiospecificity of the redistribution process.

From the Grignard reagent derived from (1-chloroethyl)trimethylsilane and *B*-MeO-9-BBN, the α 9-BBN adduct is readily obtained. However, the exchange of **7** with BH$_3$·THF does not occur at any observable rate for this hindered derivative (eq 7). The instability of BH$_3$·THF precluded the application of higher temperatures.

$$(7)$$

7
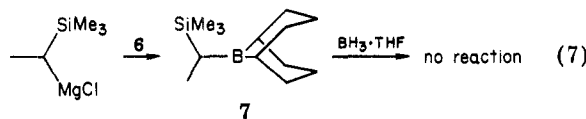
Reaction of this Grignard reagent with methyl borate provides the desired dialkylborinate ester, *5αα*, in good yield. Exchange of this compound with (−)-myrtanol gives the corresponding optically active compound **8** (eq 8).

5αα

$$(8)$$

8
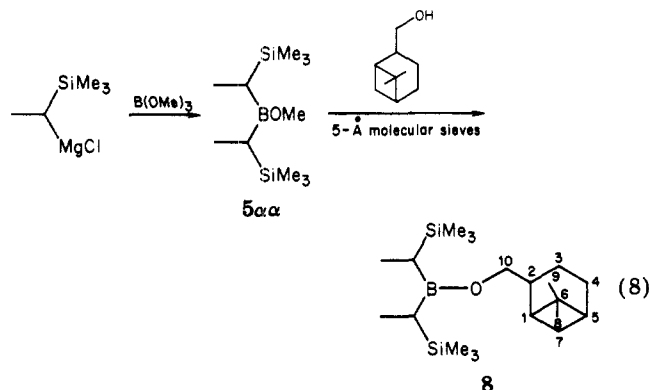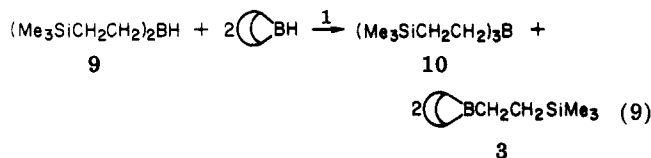
From the nonequivalence of the ^{13}C NMR signals for the alkoxy carbon (C-10) in **8** for the meso, *d*, and *l* isomers, it was possible to identify the meso and *dl* components of *5αα*. These were found to be in a 2:1 ratio.

With ^{13}C spectral data for three of the four possible isomeric dialkylboranes **5** in hand, the remaining signals in the hydroboration/methanolysis mixture could be assigned to the *5αβ* isomer. From the relative heights of the trimethylsilyl peaks, the relative amounts of *meso-5αα*,

dl-5αα, *5αβ*, and *5ββ* were 28:14:39:19. Synthetic mixtures of *5αα* and *5ββ* revealed that the relative peak heights provide a good basis for determining the amounts of each component in these mixtures. Furthermore, the α/β distribution calculated from this data agrees well with the 61:39 ratio actually obtained.

Owing to the considerable differences in their structures, the various dialkylboranes might be expected to exhibit markedly different reactivities toward further hydroboration of **1**. Consequently, we examined the ^{13}C NMR spectrum of the methanolyzed mixture obtained after 9 h of reaction at 25 °C with the 3:1 stoichiometry (cf. Table I, entry 5, and Table II, entry 4). The methoxy signal from the *meso-5αα* compound vs. an internal standard was nearly unchanged in intensity from the value with the 1:1 stoichiometry, indicating that *meso*-bis[1-(trimethylsilyl)ethyl]borane is relatively unreactive toward **1** under these conditions. Residual amounts of both *dl-5αα* and *5αβ* were also observed in the mixture. Signals due to the isomeric *5ββ* were not present in the reaction mixture.

In order to learn more about the reactivity of *5ββ*, we carried out the redistribution of **3** with BH$_3$·THF as above (cf. eq 6). Sufficient **1** was added to consume all of the hydride, and complete reaction occurred after 1 h at 25 °C (eq 9).

$$(\text{Me}_3\text{SiCH}_2\text{CH}_2)_2\text{BH} + 2 \bigcirc\text{BH} \xrightarrow{\mathbf{1}} (\text{Me}_3\text{SiCH}_2\text{CH}_2)_3\text{B} +$$

9   **10**

$$2 \bigcirc\text{BCH}_2\text{CH}_2\text{SiMe}_3 \qquad (9)$$

3

Oxidation of the above mixture gives **2α** and **2β** in a ca. 3:97 ratio, indicating that **9** hydroborates **1**, placing the boron atom predominantly (ca. 85%) β to the trimethylsilyl group.

With only 1 mol of **1** for the 3 mol of hydride present in the mixture, complete reaction occurs in 1 h at 0 °C, giving, after methanolysis, 0.5 mol each of **3**, *5ββ*, and **10** as well as 1.5 mol of **6**. From these data it is clear that **9** possesses sufficient reactivity to form **10** under these conditions. Examination of the ^{13}C spectrum of the 2:1 stoichiometric mixture described in Table II reveals that signals due to *5ββ* are absent, and new signals due to **10** are present. This suggests that the trialkylborane formed under these conditions was largely the result of the relatively high reactivity of **9** with primary alkyl groups as compared to that of the other isomeric dialkylboranes with one or more secondary alkyl groups present in the mixture.

It is interesting to note that 9-BBN undergoes only very slow hydroboration of **1** at 0 °C. In stoichiometric amounts, 9-BBN reacts with **1** at 35 °C, exhibiting smooth first-order kinetics in CDCl$_3$ solvent with a rate constant of $7.1 \pm 0.3 \times 10^{-4}$ s^{-1}. This result agrees well with earlier findings which suggest that dissociation of dimeric 9-BBN is rate limiting in the hydroboration of monosubstituted alkenes (eq 10).[8]

$$(9\text{-BBN})_2 \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} 2(9\text{-BBN}) \xrightarrow{\mathbf{1}} 3 \qquad (10)$$
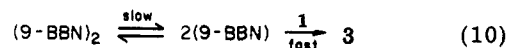
Taken together, these results suggest that the rapid formation of equal amounts of **3** and **10** at 0 °C from the hydroboration of **1** with the 9-BBN-**9** mixture may be the result of the formation of a mixed dimeric species in solution. Hydroboration of **1** with this species, either through

(8) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589.

(9) Sommer, L. H.; Gold, J.; Van Strien, S. T.; Whitmore, F. C. *J. Am. Chem. Soc.* **1947**, *69*, 1551.

Table II. Products[a] Formed from the Hydroboration/Methanolysis of 1 from $BH_3 \cdot THF$ under Various Conditions

entry	$1/BH_3$ ratio	temp, °C (time, h)	RB(OMe)$_2$[b]	R$_2$BOMe[b]	R$_3$B[b]
1	1	0 (0.25)		100	
2	2	0 (1)		75	25
3	3	0 (1)		50	50
4	3	25 (9)		33	67
5	1	50 (3)[b]	63[c]	37	

[a] For RB(OMe)$_2$, R$_2$BOMe, and R$_3$B, downfield chemical shifts (BF$_3 \cdot$OEt$_2$ at 0 ppm) of 31.6, 53.8, and 81 ppm, respectively, were obtained in THF solvent. [b] R = (C$_2$H$_4$)SiMe$_3$. The initial hydroboration was carried out as in entry 1. [c] Analysis of a methanolyzed and concentrated sample of this mixture gave signals for the α- and β-(trimethylsilyl)boronate esters in the ^{13}C NMR (see Table III) in a 58:42 ratio.

Table III. ^{13}C NMR Assignments for Organoboranes[a,b]

[a] Recorded in CDCl$_3$ solution as δ values with tetramethylsilane (δ 0.0) as the internal standard. Positive values indicate absorbances which are downfield from the standard. [b] For several of these compounds a broad absorbance was observed in the 20–30-ppm region, corresponding to carbons directly bound to boron. [c] Assignments for this minor component are to be considered tentative.

a direct reaction or through a prior dissociation into monomeric species, would account for the equal product distribution.

From our studies on the hydroboration of 1, it was clear that the trimethylsilyl group exerts very little directive influence on the regiochemistry for the addition of $BH_3 \cdot THF$ until the dialkyl stage is reached. These dialkylboranes either hydroborate 1 to give largely β boron placement or fail to undergo reaction. These results can
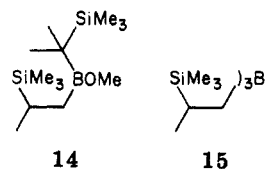
be accounted for by steric interactions between the substituted boron atom and the trimethylsilyl group which favor placement of the boron at the terminal position or which, in the case of severely hindered boranes, prevent hydroboration from occurring at all.

In order to evaluate the effect of trimethylsilyl substitution on the hydroboration of simple 1-alkenes, we prepared the various propenylsilanes,[10] and their behavior in the hydroboration reaction was investigated.

Propen-2-yltrimethylsilane. The hydroboration of propen-2-yltrimethylsilane (11) with $BH_3 \cdot THF$ was carried out at 0 °C in a 3:1 stoichiometric ratio. Oxidation of the mixture gives the internal (12) and terminal (13) alcohols in a 9:91 ratio and a total yield of 92% (eq 11).

(11)
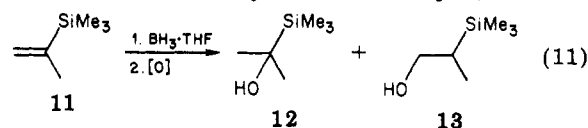
Spectroscopic analysis of the methanolyzed reaction mixture revealed that a 1:3 mixture of dialkyl- and trialkylborane products was present. From ^{1}H and ^{13}C data on the methanolyzed derivatives (14 and 15), it was possible to assign the mixed configuration to the dialkyl product (14) and the all terminal configuration to the trialkyl product (15). The small diminution of regiose-

lectivity in hydroboration of 11 with $BH_3 \cdot THF$, as compared to propene (i.e., 6:94), is consistent with the minor α-directing influence of the trimethylsilyl group. As expected, with 9-BBN as the hydroborating reagent, only the terminal product 16 is formed. On oxidation, this gives 13 exclusively (eq 12).


(12)
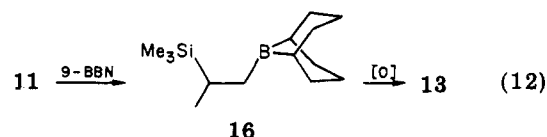
At 35 °C, smooth first-order kinetics are observed for this reaction, with a rate constant of 6.8 ± 0.1 × 10^{-4} s^{-1}, essentially the same as that for 1, suggesting that the dissociation of dimeric 9-BBN is rate limiting.

While this method provides a clean route to β-silyl-substituted organoboranes and β-silyl-substituted alcohols such as 13, the isomeric alcohol 12 was not available through a hydroboration route. However, this derivative

(10) Soderquist, J. A.; Thompson, K. L. *J. Organomet. Chem.* 1978, *159*, 237.

was conveniently prepared from the reaction of methyl-lithium with acetyltrimethylsilane (4, eq 13).

$$4 \xrightarrow[\text{2. H}_2\text{O}]{\text{1. LiMe}} 12 \qquad (13)$$
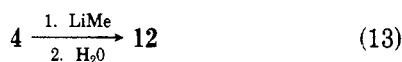
***cis*-Propen-1-yltrimethylsilane.** The hydroboration of *cis*-propen-1-yltrimethylsilane (17) with $BH_3\cdot THF$ was carried out at 0 °C in a 3:1 stoichiometric ratio. Oxidation of the mixture gave a yield of 65% of 1-(trimethylsilyl)-1- and -2-propanols in a ratio of 95:5 (eq 14).

$$ (14) $$
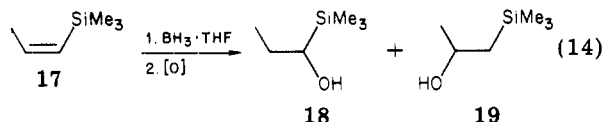
These alcohols were prepared for analysis and characterization purposes. The product **19** was available from reported procedures.[9] The novel isomeric product **18** is readily prepared by using the $BH_3\cdot THF$ reduction of propanoyltrimethylsilane with the conditions previously described for **2a**.

Analysis of the hydroboration product from **17** by ^{11}B NMR revealed that a single absorbance at 83 ppm was present. On methanolysis, 1 mol of hydrogen was evolved, and a single ^{11}B absorbance at 54 ppm was obtained. These facts indicated that hydroboration of **17** stopped cleanly at the dialkyl stage. ^{13}C data for the methanolyzed product revealed that the major constituent was an approximately 2:1 mixture of *meso-* and *dl*-bis[1-(trimethylsilyl)propyl]borinate esters (**21**, eq 15).

$$ (15) $$
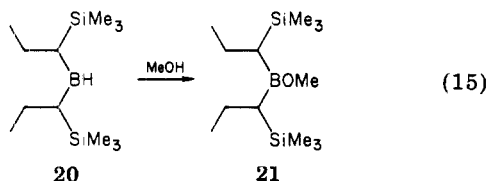
Hydroboration of **17** with a 2:1 stoichiometry produces the same product exclusively. With this stoichiometry, a reaction temperature of 50 °C allows the formation of **20** in a ratio of ca. 1:1 meso to *dl* without changing the regiochemistry (i.e., 95:5) of the hydroboration process significantly.

The structural similarity between **20** and the α,α-dialkylboranes derived from the hydroboration of **1** led us to investigate the properties of this derivative in more detail. The ^{11}B NMR signal at 83 ppm suggested that **20** was also monomeric in solution. Infrared analysis confirmed that the bridged dimeric absorbance in the 1500–1600-cm^{-1} region was absent for **20**, with the expected B–H stretching vibration at 2440 cm^{-1} being present.[7] The synthesis of monomeric dithexylborane required the presence of a large excess of 2,3-dimethyl-2-butene.[6] Consequently, **20** represents the only known monomeric dialkylborane which can be synthesized and is stable in the absence of excess alkene. This hindered dialkylborane (**20**) is extraordinarily inert toward further hydroboration. Thus, reaction of **20** with **1** at 25 °C for 12 h results in the formation of only 14% **2β**. Even in the case of a very reactive alkene, allyltrimethylsilane, hydroboration proceeds only to 70% completion under these conditions. These data support our previous conclusions as to the low reactivity of the α-silyl-substituted dialkylboranes produced as intermediates in the hydroboration of **1** with $BH_3\cdot THF$.

The hydroboration of **17** with 9-BBN proceeds somewhat slower than that of the previously discussed silylalkenes, approximately three-halves-order kinetics, with

a rate constant of $(3.0 \pm 0.1) \times 10^{-4}\ M^{-1/2}\ s^{-1}$. This behavior is also observed for the all-carbon analogue of **17**.[11] Oxidation of the reaction mixture gives a 56:44 mixture of **18** and **19** in quantitative yield. Spectroscopic analysis of the hydroboration mixture reveals that the corresponding two isomeric *B*-alkyl-9-BBN derivatives (**22** and **23**) are formed in the reaction (eq 16).

$$ (16) $$
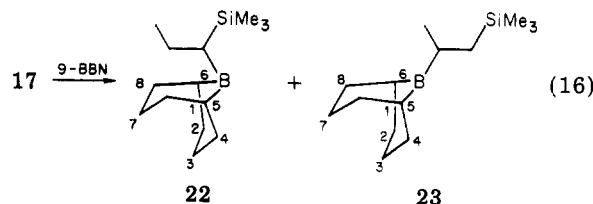
Owing to the presence of a chiral center in the alkyl group on each of these boranes, the ring methylene carbons at positions 2, 4, 6, and 8 might be expected to give rise to two sets of signals for each in the ^{13}C spectrum of the mixture.[12] Such nonequivalence of these methylene carbons is observed for **7** and **16**. In fact, only three signals were observed for this mixture in place of the four expected. However, the ^{13}C spectrum of *B*-2-Bu-9-BBN shows only a single absorbance for these carbons. Consequently, it appeared likely that the split absorbances are due to **22** and the single absorbance to **23**. To confirm this assignment, we added 1 molar equiv of pyridine per boron to the mixture. As a result, the ^{11}B spectrum shifted from a single peak at 88 ppm to two peaks centered at 79 and 1 ppm, respectively, in a 53:47 area ratio. From this, it was clear that one of the isomeric boranes underwent essentially complete complexation with pyridine, while the other was virtually unaffected. Complexation of this type had been observed for *B*-Et- and *B*-[2-(Me₃Si)Et]-9-BBN as well as for **3**. However, the ^{11}B spectrum of **7** shows only a shift to 53 ppm with the addition of 1 mol of pyridine, indicating incomplete complexation. From the change in the ^{13}C spectrum of the pyridine-containing mixture of **22** and **23** compared to the spectrum without added pyridine, it was clear that **22** gave split signals for the ring methylene carbons. Additionally, assignments for all of the carbons in both isomers could be made from the spectral comparison data (see Table III).

For **17**, $BH_3\cdot THF$ shows a very high regioselectivity, giving (α-silylalkyl)boranes of high isomeric purity (95%). This result is consistent with the β-directive effect of the methyl group and the minor α-directive influence of the trimethylsilyl group.

With 9-BBN, the amount of (β-silylalkyl)borane product **23** is comparable to the amount of the α isomer **22**. This is likely to result from steric interactions of 9-BBN with the large trimethylsilyl group which counterbalances the directive effect of the methyl group and results in essentially equivalent distribution at the two positions. Related findings have been observed for the analogous all-carbon system (vide infra).[13]

$BH_3\cdot THF$ 58%   42%
9-BBN   99.9%   0.1%
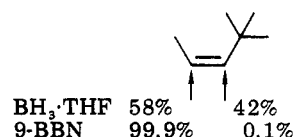
Allyltrimethylsilane. The hydroboration of allyltrimethylsilane (**24**) with $BH_3\cdot THF$ in a 3:1 stoichiometric ratio proceeds cleanly to the trialkyl stage at 0 °C in 1 h.

(11) Scouten, C. G. Ph.D. Thesis, Purdue University, 1975.

(12) For examples of this phenomena, see: Brown, H. C.; Soderquist, J. A. *J. Org. Chem.*, in press.

(13) Scouten, C. G.; Brown, H. C. *J. Org. Chem.* 1973, *38*, 4092.

Oxidation of the mixture provides isomerically pure 3-(trimethylsilyl)-1-propanol (**26**) in quantitative yield (eq 17).
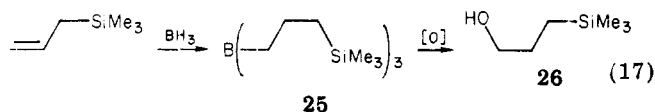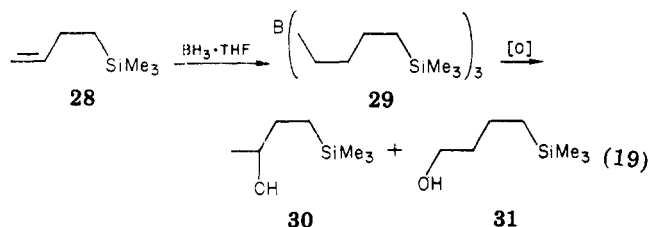

Spectroscopic analysis of the hydroboration mixture is clearly consistent with the formation of **25** as the sole reaction product. Concerned that very minor amounts of the isomeric alcohol **19** might be destroyed under the reaction conditions, we subjected this alcohol to the oxidation conditions. It proved to be stable. Therefore, our findings confirm earlier studies which indicated that the hydroboration of **24** is highly regiospecific.[4a,d]

With 9-BBN, the reaction shows first-order kinetics at 35 °C in $CDCl_3$, providing a rate constant of $(7.3 \pm 0.1) \times 10^{-4}$ s^{-1}, essentially identical with those found for 1 and 11. Oxidation of this adduct gives isomerically pure **26** quantitatively. Spectroscopic analysis of the adduct is wholly consistent with the formation of the (γ-silylpropyl)borane product **27** (eq 18).
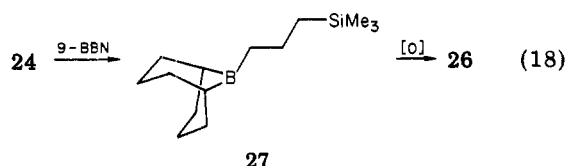
Thus, through hydroboration of allylsilanes, the (γ-silylalkyl)boranes are readily prepared in exceptional isomeric purity.

3-Buten-1-yltrimethylsilane. To determine the influence of a trimethylsilyl group in a more remote position from the double bond, we carried out the hydroboration of 3-buten-1-yltrimethylsilane (**28**)[10] with $BH_3 \cdot THF$ at 0 °C for 1 h in the theoretical 3:1 stoichiometric ratio. Oxidation of the mixture gave the internal[10] and terminal alcohols quantitatively in a 6:94 ratio (eq 19).

Spectroscopic analysis of the hydroboration mixture was consistent with the conclusion that the (δ-silylbutyl)borane **29** is the principal reaction product.

The behavior of **28** toward $BH_3 \cdot THF$ is identical with that exhibited by representative 1-alkenes, indicating that the silyl group in the δ position exerts little effect on the stoichiometry or regiochemistry of the hydroboration process.

With 9-BBN, hydroboration of **28** shows first-order kinetics at 35 °C in $CDCl_3$ solvent, giving a rate constant of $(7.1 \pm 0.3) \times 10^{-4}$ s^{-1}, virtually identical with that shown by the other monosubstituted alkenylsilanes as well as with that of **11**. Oxidation of this product gives isomerically pure **31** quantitatively, which together with spectroscopic
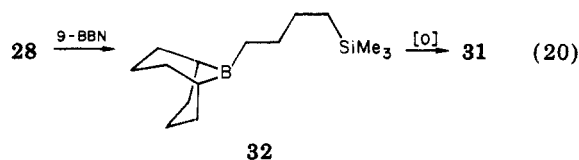
evidence, confirms the δ relationship of the silicon and boron atoms in the adduct **32** (eq 20; see Table III).

Conclusion

Through these studies on the hydroboration of alkenylsilanes, it is clear that this reaction provides a very efficient entry to α, β, γ, and δ boron-functionalized organosilanes of high isomeric purity for use in synthetic organic chemistry. The study has served to clarify a number of anomalies previously noted in the hydroboration of alkenylsilanes. A number of unusual directive effects of the trimethylsilyl substituent have been observed. Finally, this study has provided the first monomeric dialkylborane (**20**) to be synthesized without the need to provide excess alkene to repress dehydroboration.

Experimental Section

General Methods. The ^{13}C and ^{11}B NMR spectra were obtained by using a Varian FT-80A spectrometer. The ^1H NMR spectra were obtained by using a Varian T-60 spectrometer. Infrared analyses were performed by using solution cells equipped with syringe inlets[2] on a Perkin-Elmer Model 137 spectrophotometer. Mass spectra were recorded on a CEC 21-110 spectrometer. Elemental analyses were performed at the Microanalytical Laboratories of Purdue University. VPC analyses were carried out on a Hewlett-Packard 5750 dual-column thermal-conductivity gas chromatograph using 6 ft $\times$ $^1/_4$ in. columns packed with 10% SE-30 (organoboranes) and 20% Carbowax (alcohols) on DCDMS-treated Chromosorb W. Yields were determined by comparison of corrected response areas to those of internal hydrocarbon standards.[2]

Purification of solvents and stock $BH_3 \cdot THF$ solutions was carried out in the standard manner.[2,14] Alkenylsilanes were prepared as previously described.[10] Methoxyboranes were prepared and purified as reported.[14,15] 9-BBN was recrystallized from monoglyme prior to use (mp 152–154 °C).

All reactions were carried out under a nitrogen atmosphere with oven-dried glassware.

Hydroboration of Alkenylsilanes with $BH_3 \cdot THF$. The ^{13}C NMR data for trimethylsilyl-substituted alcohols are summarized in Table IV. See Table III for ^{13}C NMR data for the organoboranes. By use of 5–10 mmol of $BH_3 \cdot THF$ solution, the appropriate quantity of alkenylsilane was added dropwise to the stirred mixture, held at 0 °C by using an ice bath, with a syringe. After the addition was complete, the reaction mixtures were stirred for the appropriate time. In some cases the solution was allowed to reach a higher temperature after the addition for the times indicated in the tables.

For spectroscopic samples, the solutions were either analyzed directly or treated with methanol and concentrated under a stream of nitrogen.

The ^1H NMR spectra of these products were obtained in $CDCl_3$ solvent. The Me_3Si peaks (0.00–0.05 ppm) were in the expected area ratio to the remaining alkyl region (0.5–2.0 ppm). Methoxy protons were observed in the 3.5–3.8-ppm region for partially alkylated boranes, and these gave the expected area ratio to the remaining signals.

For yield analyses, an appropriate n-alkane standard was added to the reaction mixture prior to hydrolysis and/or oxidation.[2]

Oxidation of the organoboranes was accomplished by successive treatment with water, 3 N NaOH (1 equiv/mol of borane), and 30% H_2O_2 (1.1 equiv/B–C bond) dropwise to maintain a reaction temperature of 30–50 °C. The reaction mixtures were allowed to reflux for 1 h to assure complete oxidation and destroy residual peroxide. After cooling, the mixture was treated with K_2CO_3 to saturate the aqueous phase. The organic layer was withdrawn, dried over K_2CO_3, and analyzed.

B-[2-(Trimethylsilyl)ethyl]-9-borabicyclo[3.3.1]nonane (3). Vinyltrimethylsilane (20.0 g, 200 mmol) was added over 10 min with a syringe to a stirred slurry of 9-BBN crystals (24.4 g, 200 mmol) and THF (25.0 mL) in a distillation apparatus. After

(14) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.
(15) Holden, C. M.; Whittaker, D. *Org. Magn. Reson.* **1975**, *7*, 125.

Table IV. ^{13}C NMR Data for Trimethylsilyl-Substituted Alcohols^a

| compd | Me$_3$Si | assignments | | | |
		C-1	C-2	C-3	C-4
HOCH$_2$CH$_3$		57.2	17.6		
HOCH(SiMe$_3$)CH$_3$ (2α)	-4.4	61.4	19.3		
HOCH$_2$CH$_2$(SiMe$_3$) (2β)	-1.5	59.4	21.9		
HOCH$_2$CH$_2$CH$_3$		63.0	25.5	9.8	
HOCH(SiMe$_3$)CH$_2$CH$_3$ (18)	-3.9	67.7	26.6	11.4	
HOCH$_2$CH(SiMe$_3$)CH$_3$ (13)	-3.1	65.5	24.7	11.6	
HOCH$_2$CH$_2$CH$_2$(SiMe$_3$) (26)	-1.8	65.5	27.1	12.3	
CH$_3$CHOHCH$_3$		24.9	63.7	24.9	
CH$_3$C(SiMe$_3$)OHCH$_3$ (12)	-4.5	27.1	63.8	27.1	
(Me$_3$Si)CH$_2$CHOHCH$_3$ (19)	-0.8	29.0	66.1	26.7	
HOCH$_2$CH$_2$CH$_2$CH$_3$		61.9	34.6	18.8	13.6
HOCH$_2$CH$_2$CH$_2$CH$_2$(SiMe$_3$) (31)	-1.7	62.5	36.6	20.2	16.6
CH$_3$CHOHCH$_2$CH$_3$		22.5	68.9	31.2	9.7
CH$_3$CHOHCH$_2$CH$_2$(SiMe$_3$) (30)	-1.8	22.7	70.3	33.5	12.3

^{a} See footnote a in Table III. Parent alcohol spectra are given for reference.

dissolution of the 9-BBN, the mixture was allowed to stir for 1 h at 25 °C, concentrated in vacuo, and distilled to give 43 g (97%) of **3**: bp 80 °C (100 μm); ^{1}H NMR (CCl$_4$) δ 0.05 (s, 9 H), 0.52 (m, 2 H), 1.37 (m, 2 H), 1.80 (m, 14 H); mass spectrum, m/e (relative intensity) 222 (16), 207 (14), 85 (30), 73 (100), 59 (25).

Oxidation of **3** or the hydroboration mixture as described above gives a quantitative yield of **2β** as well as cis-1,5-cyclooctanediol (analyzed as the silyl ether).

Redistribution of 3 with BH$_3$·THF. After the addition of **3** (2 molar equiv) to BH$_3$·THF at 0 °C, the mixture was allowed to reflux for 2 h. This mixture was allowed to cool and was used in subsequent studies. Formation of the borinate esters was accomplished by the dropwise addition of methanol (100% excess) followed by concentration of the mixture under nitrogen.

B-[1-(Trimethylsilyl)ethyl]-9-borabicyclo[3.3.1]nonane (7). The Grignard reagent^9 from (1-chloroethyl)trimethylsilane (PCR) was prepared on a 50-mmol scale in THF (25 mL), and this solution was added dropwise to B-MeO-9-BBN (7.6 g, 50 mmol) in pentane (25 mL) at -78 °C. The mixture was allowed to reach at room temperature and centrifuged, and the supernatant liquid was drawn off. Fresh pentane (25 mL) was added to wash the solid, and this supernatant was combined with the first. The mixture was concentrated and distilled to give 7.2 g (65%) of **7**: bp 88-92 °C (1 torr); NMR (CCl$_4$) δ 0.00 (s, 9 H), 1-2 (m, 18 H); mass spectrum, m/e (relative intensity) 222 (10), 148 (11), 73 (100), 59 (24), 45 (12), 41 (16).

Oxidation of **7** as described gave only **2α** and cis-1,5-cyclooctanediol, both in essentially quantitative yield.

Attempted Redistribution of 7 with BH$_3$·THF. As for **3**, **7** was treated with BH$_3$·THF for 2 h at reflux temperature. Loss of BH$_3$·THF was apparent from the ^{11}B NMR spectrum of the resulting mixture. However, no 9-BBN dimer absorbance was observed. The lack of active hydride in the solution indicated the loss of diborane. Attempted room-temperature redistribution with excess neat borane–methyl sulfide was similarly unsuccessful, even after a 1-week reaction time.

Hydroboration of Alkenylsilanes with 9-BBN. For spectroscopic analysis, the hydroborations were conducted at 35 °C in CDCl$_3$ with equimolar quantities of 9-BBN (monomer) and alkenylsilane each of a 1.0 M concentration initially. The ^{1}H NMR spectra gave the expected area ratio for the Me$_3$Si (0.00-0.05 ppm) to alkyl (0.5-2.0 ppm) regions. Kinetic data were obtained by comparing the peak area in the ^{11}B spectrum of 9-BBN (δ 28) with that of the product (80-90 ppm). The products absorbed at 86.4 (**3**), 85.9 (**7**), 88.9 (**16**), 84.1 (**22** and **23**), 88.3 (**27**), and 87.7 (**32**) ppm.

For alcohol analysis, the reactions were carried out as above, using THF as solvent and the normal oxidation procedure.

***meso-* and *dl*-Methyl Bis[1-(trimethylsilyl)ethyl]borinates (5αα).** The Grignard reagent (50 mmol) described for **7** was prepared and added to methyl borate (2.6 g, 25 mmol) in pentane (25 mL). After a treatment similar to that for **7**, distillation gave 4.3 g (70%) of **5αα**: bp 59 °C (200 μm); NMR (CDCl$_3$) δ 0.03 (s, 9 H), 0.5-1.2 (m, 4 H), 3.60, 3.70 (s, 3 H total in a ca. 2:1 area ratio); mass spectrum, m/e (relative intensity) 244 (1), 229 (74), 143 (100), 73 (96).

Ligand Exchange of 5αα with (-)-Myrtanol. With CDCl$_3$ as solvent, **5αα** and (-)-myrtanol were stirred over molecular sieves (5 Å) for 12 h at 25 °C. On the basis of assignments given for cis-myrtanol,^{13} the borinate product **8** gave signals at 43.4, 43.3, 26.2, 19.1, 41.7, 38.6, 33.2, 28.1, and 23.4 ppm, respectively, for carbons at positions 1-9. Position 10 appeared as three signals in a 1:1:4 ratio at 71.0, 70.9, and 70.0 ppm, respectively. The *dl* portion exhibited methyl signals at 10.1 and -1.0 ppm while the meso compound showed these signals at 10.5 and -1.2 ppm for the 1-(trimethylsilyl)ethyl groups in **8**.

2-(Trimethylsilyl)-2-propanol (12). Acetyltrimethylsilane (2.40 g, 20.7 mmol) was added dropwise to a solution of methyllithium (17 mL, 1.49 M, 25 mmol) in ether at 0 °C over 20 min. After the addition was complete, saturated ammonium chloride (5 mL) was used to carefully quench the mixture. The organic layer was further washed with H$_2$O (5 mL) and dried over K$_2$CO$_3$. Distillation gave 2.0 g (73%) of **12**: bp 44 °C (33 torr); NMR (CCl$_4$) δ 0.07 (s, 9 H), 1.1 (s, 1 H), 1.20 (s, 6 H). Anal. Calcd for C$_6$H$_{16}$OSi: C, 54.52; H, 12.14. Found: C, 54.15; H, 12.23.

2-(Trimethylsilyl)-1-propanol (13). To a stirred mixture of 9-BBN (12.4 g, 102 mmol) in THF (84 mL) at 25 °C was added propen-2-yltrimethylsilane (11.4 g, 100 mmol). The mixture was allowed to stir for 1 h. Oxidation was carried out by the successive addition of H$_2$O (10 mL), 3 N NaOH (40 mL), and 30% H$_2$O$_2$ (40 mL) dropwise to maintain a controlled reaction (~50 °C). After the mixture was held an additional 1 h at reflux temperature, the aqueous phase was saturated with K$_2$CO$_3$. After separation, the organic layer was dried (K$_2$CO$_3$) and distilled to give 12.25 g (93%) of **13**: bp 76 °C (33 torr); NMR (CCl$_4$) δ 0.03 (s, 9 H), 1.0 (m, 4 H), 2.45 (s, 1 H), 3.6 (m, 2 H). Anal. Calcd for C$_6$H$_{16}$OSi: C, 54.52; H, 12.14. Found: C, 54.29; H, 11.98.

1-(Trimethylsilyl)-1-propanol (18). Propanoyltrimethylsilane^{16} (1.95 g, 15 mmol) was added dropwise to BH$_3$·THF (9.4 mL, 1.60 M; 15 mmol) at 0 °C. After careful hydrolysis (5 mL), ether (10 mL) was added, and after separation from the saturated (K$_2$CO$_3$) aqueous layer, the organic layer was dried (K$_2$CO$_3$) and distilled to give 1.44 g (73%) of **18**: bp 55 °C (28 torr); NMR (CCl$_4$) δ 0.07 (s, 9 H), 1.07 (m, 4 H), 1.57 (m, 1 H), 3.13 (dd, 1 H, J = 7.5, 5.5 Hz). Anal. Calcd for C$_6$H$_{16}$OSi: C, 54.52; H, 12.14. Found: C, 54.28; H, 12.14.

4-(Trimethylsilyl)-1-butanol (31). The preparation of **31** was carried out on a 30-mmol scale as for **13**. Distillation gives 2.6 g (60%) of **31**, bp 97 °C (35 torr) [lit.^{17,18} bp 40-41 °C (0.5 torr)].

(16) This compound was prepared from the oxidation of the dicyclohexylborane adduct^{10} of propynyltrimethylsilane in toluene with anhydrous trimethylamine *N*-oxide (3 equiv).^{18} In 1 h at 110 °C, the reaction was complete by ^{11}B NMR spectroscopy, and the product [bp 118-120 °C (745 torr)] was obtained after methanolysis and a distillative workup: NMR (CCl$_4$) δ 0.33 (s, 9 H), 1.07 (t, 2 H, J = 6.8 Hz), 2.68 (q, 2 H, J = 6.8 Hz); IR (THF) 1643 cm^{-1} (C=O).

(17) Steudel, W.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 6129.

(18) Köster, R.; Morita, Y. *Justus Liebigs Ann. Chem.* **1967**, *704*, 70.

8 (meso), 74128-17-9; 8 (dl), 74219-19-5; 9, 74128-18-0; 10, 17940-88-4; 11, 18163-07-0; 12, 40965-54-6; 13, 74128-19-1; 14, 74128-20-4; 15, 74128-21-5; 16, 72610-07-2; 17, 17680-01-2; 18, 74128-22-6; 19, 18182-10-0; 20 (meso), 74128-23-7; 20 (dl), 74143-39-8; 21 (meso), 74128-24-8; 21 (dl), 74128-25-9; 22, 74128-26-0; 23, 74128-27-1; 24, 762-72-1; 25, 18546-69-5; 26, 2917-47-7; 27, 74128-28-2; 28, 763-13-3;

29, 74128-29-3; 30, 18387-24-1; 31, 2917-40-0; 32, 74128-30-6; $Me_3SiCH(CH_3)B(OMe)_2$, 18603-92-4; $Me_3SiCH_2CH_2B(OMe)_2$, 18551-02-5; 9-BBN, 280-64-8; $BH_3\cdot THF$, 14044-65-6; cis-1,5-cyclooctanediol, 23418-82-8; (1-chloroethyl)trimethylsilane, 7787-87-3; $B(OMe)_3$, 121-43-7; (−)-myrtanol, 473-01-8; propanoyltrimethylsilane, 30608-90-3.

A Mild and Convenient Procedure for Conversion of Alkenes into Alkyl Iodides via Reaction of Iodine Monochloride with Organoboranes

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Alkenes are rapidly converted to alkyl iodides under mild conditions via a hydroboration–iodination sequence which utilizes iodine monochloride as the iodinating agent. The iodination proceeds with inversion of configuration. A series of functionally substituted iodides was synthesized via the new procedure.

The iodination of organoboranes in the presence of strong bases results in the regio- and stereospecific introduction of iodine in high yields.[1-3] The utility of the

$$R_3B \xrightarrow[\text{NaOCH}_3]{I_2} 3RI$$
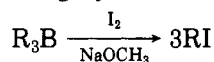
iodination reaction is due to the variety of functionally substituted organoboranes which are available via hydroboration.[1] The reaction is also important due to the variety of iodine containing radiopharmaceuticals which have been developed in recent years.[4-6]
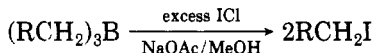
The iodination reaction does, however, have two potential problems. The first is the necessity of using a strong base which could either react with sensitive functional groups in complex molecules or initiate dehydrohalogenation reactions. The second is the fact that one-half of the iodine molecule is lost as iodide which is not economical when radionuclides of iodine are employed.

We report that alkenes are rapidly converted to alkyl iodides under mild conditions via a hydroboration–iodination sequence which utilizes iodine monochloride as the iodinating agent.

$$RCH{=}CH_2 \xrightarrow{BH_3} \xrightarrow{ICl} RCH_2CH_2I$$
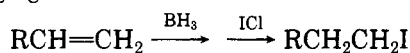
Results and Discussion

When trialkylboranes derived from the hydroboration of terminal alkenes are treated with iodine monochloride and methanolic sodium acetate, two of the three groups on boron react instantaneously.[7] In the case of trialkyl-

$$(RCH_2)_3B \xrightarrow[\text{NaOAc/MeOH}]{\text{excess ICl}} 2RCH_2I$$

Table I. Conversion of Trihexylborane n-Hexyl Iodide[a]

ratio of ICl/R₃B[a]	yield, %[c]		
	1:1 NaOAc/R₃B[b]	2:1 NaOAc/R₃B	3:1 NaOAc/R₃B
1	21	33	20[d]
2	34	58	65
3	30	59	66

[a] Reaction of trihexylborane (10 mmol) with ICl in THF (10 mL) at room temperature for 15 min. NaOAc added as 1.0 M solution in methanol. [b] Ratios refer to ratio of millimoles of reagents. [c] GLC yields. [d] In the presence of a large excess of sodium acetate, yields decrease.

Table II. Synthesis of Primary Iodides[a]

substrate	product	% yield (iso-lated)[b]
		88
		97
		75
		82
1-hexene	1-iodohexane	80[c]

[a] Reactions were run with 2 equiv of ICl and 3 equiv of NaOAc at room temperature for 45 min. [b] Percentage yield is based on ICl (which corresponds to two of the three alkyl groups on boron). [c] GLC analysis indicates 100% yield.

boranes derived from internal alkenes, one of the three alkyl groups on boron rapidly migrates. These results parallel those obtained when organoboranes are treated with iodine in the presence of sodium hydroxide.[8,9]

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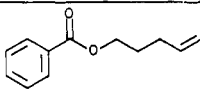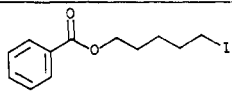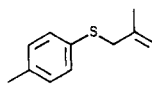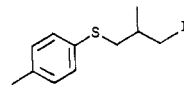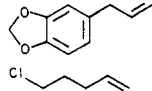(6) Lambrecht, R. M.; Mantesen, C.; Redvanly, C. S.; Wolf, A. P. J. Nucl. Med. 1972, 13, 266.
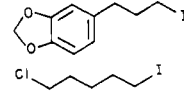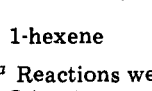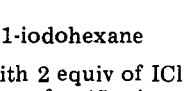
(7) It is interesting to note that the product is exclusively the 1-iodoalkane even though 6% of the hexyl groups are attached to boron at the nonterminal carbon. Obviously, primary alkyl groups migrate preferentially to secondary alkyl groups.