steam distilled. Pure (*Z*)-1-bromo-1-heptene came out as colorless liquid, 6.66 g (84%). GC analysis showed the isomeric purity to be 99% *Z*; IR (neat): ν 3000, 1635, 1470, 1300, 700 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.07 (m, 2 H), 2.17 (m, 2 H), 1.33 (m, 4 H), 0.87 (t, 3 H); ^{13}C NMR ($CDCl_3$/TMS) δ 134.46, 107.48, 31.31, 29.54, 27.87, 22.42, 13.75.

Registry No. HC≡CBu, 693-02-7; (*Z*)-BrCH=CHBu, 13154-12-6; (*E*)-BrCH=CHBu, 13154-13-7; HC≡CPr, 627-19-0; $HC{\equiv}C(CH_2)_4CH_3$, 628-71-7; $HC{\equiv}C(CH_2)_5CH_3$, 629-05-0; PhC≡CH, 536-74-3; EtC≡CEt, 928-49-4; (*Z*)-BrCH=CHPr, 31849-75-9; (*E*)-BrCH=CHPr, 31849-76-0; (*Z*)-BrCH=CH-$(CH_2)_4CH_3$, 39924-57-7; (*E*)-BrCH=CH$(CH_2)_4CH_3$, 53434-74-5; (*Z*)-BrCH=CH$(CH_2)_5CH_3$, 42843-49-2; (*E*)-BrCH=CH-$(CH_2)_5CH_3$, 51751-87-2; (*Z*)-PhCH=CHBr, 588-73-8; (*E*)-PhCH=CHBr, 588-72-7; (*Z*)-EtCH=C(Br)Et, 16645-01-5; (*E*)-EtCH=C(Br)Et, 42843-52-7; (*E*)-$CH_3(CH_2)_5CH$=CHB$(OH)_2$, 42599-16-6; (*E*)-PhCH=CHB$(OH)_2$, 6783-05-7; (*Z*)-ICH=CH-$(CH_2)_5CH_3$, 52356-93-1; (*Z*)-ICH=CHBu, 16538-47-9; (*Z*)-ICH=CH$(CH_2)_3$Cl, 95835-51-1; (*E*)-ICH=CHC$(CH_3)_3$, 61382-45-4; (*E*)-PhCH=CHI, 42599-24-6; (*E*)-BuCH=CHB$(OH)_2$, 42599-18-8; (*E*)-Cl$(CH_2)_3$CH=CHB$(OH)_2$, 37490-32-7; (*E*)-$(CH_3)_3$CCH=CHB$(OH)_2$, 86595-37-1; Cl$(CH_2)_3C{\equiv}CH$, 14267-92-6; (*Z*)-BrCH=CH$(CH_2)_3$Cl, 88357-37-3; (*E*)-$CH_3(CH_2)_4$CH=CHBBr_2·SMe_2, 123507-49-3; (*E*)-2-cyclohexyl-1-ethenylboronic acid, 37490-33-8; (*E*)-1-octenylboronic acid catechol ester, 73349-13-0; (*E*)-2-cyclohexyl-1-ethenylboronic acid catechol ester, 37490-23-6; (*E*)-2-phenyl-1-ethenylboronic acid catechol ester, 6783-04-6; (*E*)-3-hexenylboronic acid catechol ester, 94427-77-7; (*Z*)-1-bromo-2-cyclohexyl-1-ethene, 42843-50-5; (*E*)-1-bromo-2-cyclohexyl-1-ethene, 67478-59-5; (*E*)-1-hexenylboronic acid catechol ester, 37490-22-5; (*E*)-5-chloro-1-pentenylboronic acid catechol ester, 37490-27-0; (*E*)-3,3-dimethyl-1-butenylboronic acid catechol ester, 37490-25-8; (*E*)-2-cyclohexyl-1-iodo-1-ethene, 42599-23-5; (*Z*)-2-cyclohexyl-1-iodo-1-ethene, 67404-69-7; cyclohexylethyne, 931-48-6.

Supplementary Material Available: ^1H NMR spectrum of the compound [*Z*]-1-iodo-5-chloro-1-pentene (1 page). Ordering information is given on any current masthead page.

Vinylic Organoboranes. 14. A Stereospecific Synthesis of (*E*)-1-Halo-1-alkenes from 1-Alkynes[1,2]

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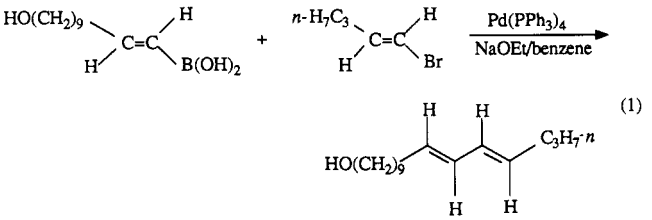
The reactions of (*E*)-1-alkenylboronic acids and their esters and (*E*)-1-alkenyldibromoborane–dimethyl sulfide complexes with iodine under various conditions were investigated. All of these compounds react with iodine in the presence of base, producing (*E*)-1-iodo-1-alkenes in excellent yields and in very high stereochemical purities. A stereospecific synthesis of (*E*)-1-bromo- and 1-chloro-1-alkenes is herein described, based on (*Z*)-1-alkenylboronic acids and esters. These reactions appear to be general. The above procedures provide convenient stereospecific syntheses of (*E*)-1-halo-1-alkenes. A plausible mechanism in each case has been discussed.

Introduction

Synthetic applications of alkenylboranes have been steadily increasing over the past decade.[4] One of the areas we focused our attention on was the synthesis of stereochemically pure (*E*)- and (*Z*)-1-halo-1-alkenes.[5-7] These vinyl halides are very useful intermediates in the synthesis of biologically important molecules, such as insect sex pheromones, containing 1,3-diene grouping. For example, bombykol ((10*E*,12*E*)-10,12-hexadecadien-1-ol) was synthesized by the palladium-catalyzed cross-coupling between alkenylborane and alkenyl halide (eq 1).[8] Similarly,



(1)

Bombykol [10*E*,12*E*]

by using the appropriate alkenylborane and alkenyl halide, the other three (10*Z*,12*Z*; 10*E*,12*Z*; 10*Z*,12*E*) isomers were synthesized.[8] Other sex pheromones with *E*,*Z* or *E*,*E* diene configuration have also been prepared.[9] We had earlier reported the synthesis of pure (*Z*)-1-halo-1-alkenes[1,7] from 1-halo-1-alkynes and (*E*)-1-alkenylboronic acids. In view of the growing synthetic importance of these vinyl halides, it was desirable to have available a convenient synthesis of their geometrical isomers, (*E*)-1-halo-1-alkenes. The

(1) For part 13 in this series, see: Brown, H. C.; Subrahmanyam, C.; Hamaoka, T.; Ravindran, N.; Bowman, D. H.; Misumi, S.; Unni, M. K.; Somayaji, V.; Bhat, N. G. *J. Org. Chem.*, preceding paper in this issue.

(2) For preliminary reports, see: (a) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786. (b) Brown, H. C.; Somayaji, V. *Synthesis* **1984**, 919.

(3) (a) Visiting Scholar on funds provided by the Fuji Photo Film Company Ltd., Tokyo, Japan. (b) Postdoctoral research associate on grants provided by G. D. Searle and Co., Chicago, IL, and the National Science Foundation (Grant No. 27742X). (c) Postdoctoral research associate on Grants CHE-79-18881 and 6449 from the National Science Foundation. (d) Postdoctoral research associate on Grant ARO DAAG 29-79-C-0027 from the United States Army Research Office. (e) Postdoctoral research associate on Grant CHE-8414171 from the National Science Foundation.

(4) (a) Brown, H. C.; Campbell, J. B., Jr. *Aldrichimica Acta* **1981**, *14*, 3–10. (b) Negishi, E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Chapter 45.8, Vol. 7, pp 303–322.

(5) Brown, H. C.; Bowman, D. H.; Misumi, S.; Unni, M. K. *J. Am. Chem. Soc.* **1967**, *89*, 4531.

(6) (a) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 6456. (b) Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. Vinylic Organoboranes. 12. *J. Org. Chem.*, first of four articles in this issue.

(7) (a) Kabalka, G. W.; Gooch, E. E.; Hsu, H. C. *Synth. Commun.* **1981**, *11*, 247. (b) Kalbalka, G. W.; Sastry, K. A. R.; Somayaji, V. *Heterocycles* **1982**, *18*, 157. (c) Kabalka, G. W.; Sastry, K. A. R.; Knapp, F. F.; Srivastava, P. C. *Synth. Commun.* **1983**, *13*, 1027.

(8) Miyaura, N.; Suginome, H.; Suzuki, A. *Tetrahedron Lett.* **1983**, *24*, 1527.

(9) Cassani, G.; Massardo, P.; Piccardi, P. *Tetrahedron Lett.* **1982**, *24*, 2513.

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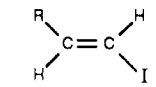
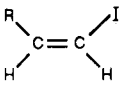
Table I. Synthesis of (*E*)-1-Iodo-1-alkenes

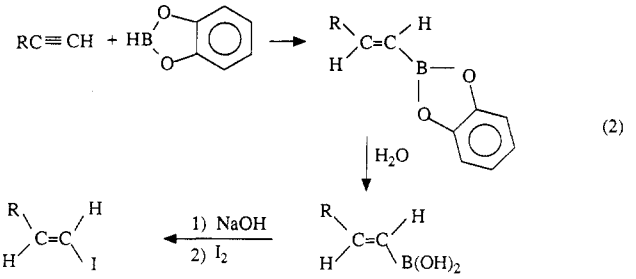
R	X_2	procedure[a]	% of 	% of 	yield,[b] %
n-C_6H_{13}	$(OH)_2$	A	>99		80 (100)
n-C_6H_{13}	Br_2·SMe_2	B	95	5	66
c-C_6H_{11}	$(OH)_2$	A	>99		83 (100)
$Cl(CH_2)_3$	Br_2·SMe_2	B	93	7	57 (74)
$Cl(CH_2)_3$	$(OH)_2$	A	98	2	78 (91)
c-C_6H_{11}	Br_2·SMe_2	B	>99		51 (74)
t-C_4H_9	$(OH)_2$	A	>99		85 (100)
C_6H_5	$(OH)_2$	A	>99		79 (93)

[a] Procedures A and B are as explained in the Experimental Section. [b] GC yields in parentheses using n-hexadecane as an internal standard.

present paper describes such an efficient method for the preparation of these compounds in high yields and in excellent stereochemical purities.

We recently reported the synthesis of alkyl bromides[10] and alkyl iodides[11] from trialkylboranes and the corresponding halogens under basic conditions. However, similar reactions with trialkenylboranes or dialkenylborinic acids resulted in the formation of dienes instead of alkenyl halides. This problem was overcome by utilizing alkenylboronic acids and their derivatives.

Iodination of (*E*)-1-Alkenylboronic Acids. Formation of (*E*)-1-Iodo-1-alkenes. Catecholborane hydroborates[12] 1-alkynes, giving the catechol esters of the corresponding (*E*)-1-alkenylboronic acids. Initial experiments indicated that catechol interfered with the base-induced reaction of iodine with the boronic acid. However, pure (*E*)-1-alkenylboronic acid could be prepared by a simple treatment with water. An ethereal solution of the boronic acid was treated with 3 equiv of sodium hydroxide, followed by 1 mol equiv of elemental iodine at 0 °C. After the reaction mixture stirred for 0.5 h and a workup, pure (*E*)-1-iodo-1-alkene was obtained in nearly quantitative yield (eq 2).



(2)

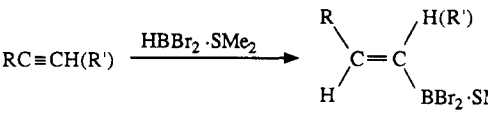
The general procedure outlined above worked very well for both simple and branched 1-alkynes (see Table I). In all cases the stereochemical purities were >98%, as determined by gas chromatographic analysis. The ^1H and ^{13}C spectral data of these (*E*)-1-iodo-1-alkenes are described in Table II.

Iodination of (*E*)-1-Alkenyldibromoborane–Dimethyl Sulfide Complexes. Formation of (*E*)-1-Iodo-1-alkenes. Development of the dibromoborane–dimethyl sulfide ($HBBr_2$·SMe_2) reagent[13] opened up yet another door to the chemistry of vinylboranes. This reagent cleanly monohydroborates[14] terminal and internal

Table II. ^1H and ^{13}C NMR Spectral Data of the (*E*)-1-Iodo-1-alkenes

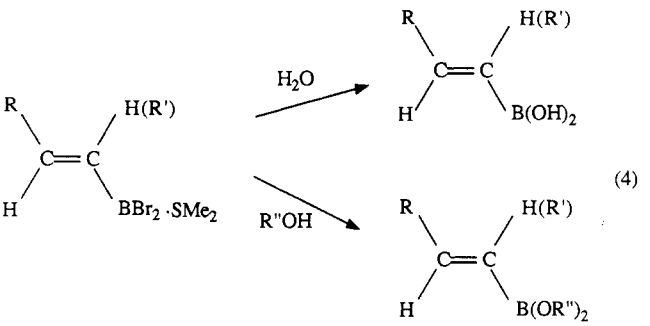
(*E*)-1-iodo-1-alkene	—CH_2–HC=CHI (3 2 1) 1 ^1H	1 ^{13}C	2 ^1H	2 ^{13}C	3 ^1H	3 ^{13}C
(*E*)-1-iodo-1-octene	5.9 (d)	74.4	6.5 (d/t)	146.7	2.1 (m)	36.1
(*E*)-5-chloro-1-iodo-1-pentene	5.9 (d)	77.3	6.43 (d/t)	144.9	2.42 (m)	44.5
(*E*)-2-cyclohexyl-1-iodo-2-ethene	5.84 (d)	74.1	6.45 (q)	151.8	2.4 (m)	44.8
(*E*)-3,3-dimethyl-1-iodo-1-butene	5.4 (d)	73.0	6.4 (d)	158.1		34.1

alkynes, giving the corresponding alkenyldibromoborane–dimethyl sulfide complexes (eq 3). We have recently



(3)

standardized the procedure for the conversion of these complexes into the corresponding alkenylboronic acids and esters[15] (eq 4).



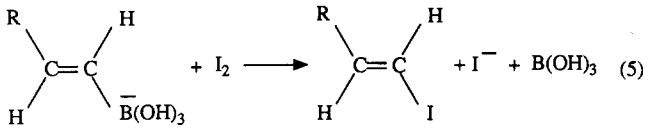
(4)

However, direct conversion of alkenyldibromoborane–dimethyl sulfide complexes into (*E*)-1-iodo-1-alkenes means a simple one-pot synthesis, avoiding the isolation of the intermediate boronic acids. Consequently, we reacted (*E*)-1-octenyldibromoborane–dimethyl sulfide with 1 equiv of iodine under the influence of 5 equiv of base. The usual workup of the reaction mixture gave (*E*)-1-iodo-1-octene in 66% (isolated) yield. This method was equally efficient for other simple and branched alkynes as well (see Table I and Experimental Section for details).

Mechanism. The formation of (*E*)-1-iodo-1-alkenes may be envisioned in various ways.

(i) By a direct displacement of the neutralized boronic acid moiety with iodine (eq 5). This is analogous to the

(10) Brown, H. C.; Lane, C. F. *Tetrahedron* **1988**, *44*, 2763.
(11) Brown, H. C.; Rathke, M. W.; Rogić, M. M.; De Lue, N. R. *Tetrahedron* **1988**, *44*, 2751.
(12) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370.
(13) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938.
(14) Brown, H. C.; Campbell, J. B., Jr. *J. Org. Chem.* **1980**, *45*, 389.
(15) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311.

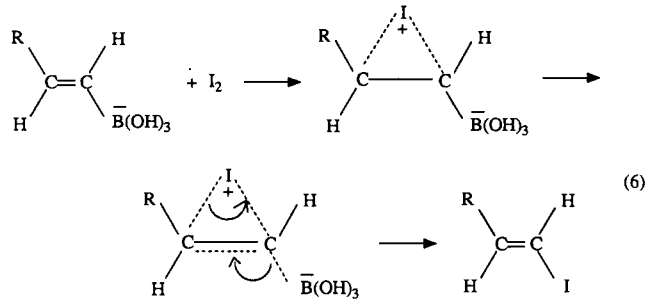


mechanism proposed for the formation of (*E*)-1-iodo-1-alkenes in the iodination of vinylsilanes.[16] However, the failure of phenylboronic acid and other alkylboronic acids to give the corresponding iodides under similar reaction conditions rules out this mechanism.

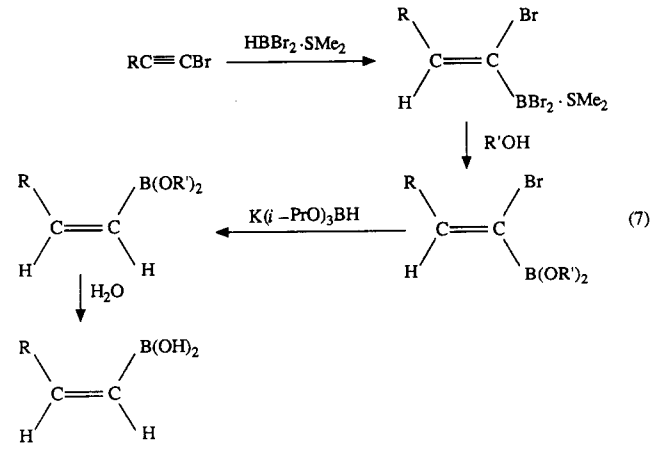
(ii) An anti-addition syn-elimination sequence could give *E* iodides. However, in the presence of a base and at low temperatures, this syn elimination is unlikely. Moreover, the time involved (usually 0.5 h) is insufficient for any significant addition of iodine. Further, the following experiment showed further support against this mechanism. Addition of 1.2 mmol of iodine to a vigorously stirred solution of 3.0 mmol of (*E*)-1-octenylboronic acid in ether and 9.0 mmol of sodium hydroxide resulted in an instantaneous disappearance of iodine (color). However, analysis of the ethereal layer showed the presence of 0.44, 1.02, and 1.21 mmol of octenyl iodide in 1, 5, and 15 min, respectively.

A similar reaction of 3.0 mmol of boronic acid with 1.2 mmol of iodine was performed without the base. After 10 min, the excess iodine was destroyed, and the product was treated with base. Formation of <2% of vinyl iodide ruled out any quick addition of iodine across the double bond.

The above results point to a mechanism involving the fast reaction of the neutralized vinyl boronic acid with iodine to form an intermediate, which is converted to the (*E*)-vinyl iodide relatively slowly (eq 6).



Bromination and Chlorination of (*Z*)-1-Alkenylboronic Acids and Esters. Formation of (*E*)-1-Bromo- and (*E*)-1-Chloro-1-alkenes. We recently reported the synthesis of pure (*Z*)-alkenylboronic esters from 1-bromo-1-alkynes[17] (eq 7). These (*Z*)-1-alkenylboronic



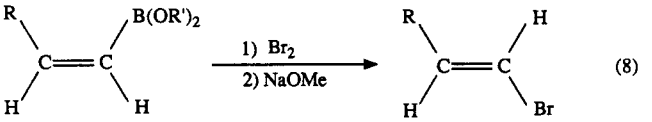
(16) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

Table III. Synthesis of (*E*)-1-Bromo-1-alkenes: RCH=CHBr[a]

R	bp,[a] °C/mmHg	n^{25}_D[b]	isolated yield,[c] %	isomeric purity, %	M⁺
n-C_4H_9	61-62/30[21]	1.4581[21]	80	99	162, 164
n-C_6H_{13}	59-60/6[22]	1.4620[22]	81	99	190, 192
c-C_6H_{11}	50-52/4[23]	1.5043[23]	80	98	188, 190
$(CH_3)_3C$	48-50/50[24]	1.4625[24]	79	100	162, 164
$Cl(CH_2)_3$[d]	66-68/6	1.4774	80	97	182, 184

[a] All of the structures were confirmed by IR,[25] ^1H NMR,[25] and mass spectral data. [b] The values agree with literature values. [c] Yields were based on the starting (*Z*)-1-alkenylboronate esters. [d] This compound appears to be new in the literature, and the ^1H NMR spectrum is given in the supplementary material (see the paragraph at the end of the paper).

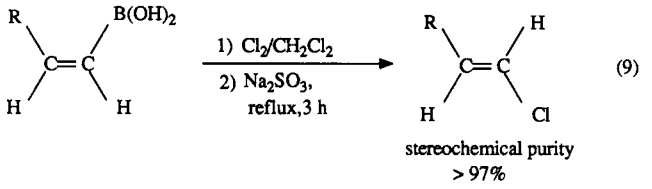
esters reacted with iodine in the presence of a base at 0 °C, giving the corresponding (*Z*)-1-iodo-1-alkenes.[1] On the other hand, addition of bromine at −25 °C to these esters, followed by treatment with sodium methoxide, resulted in the formation of the corresponding (*E*)-1-bromo-1-alkenes (eq 8). It is interesting to note that the actual



isolation of (*Z*)-1-alkenylboronic ester was unnecessary. The byproduct, triisopropoxyborane, did not interfere with the reaction and on workup went with the aqueous layer as the alcohol and boric acid.

A representative selection of (*E*)-1-bromo-1-alkenes was prepared, and the results are summarized in Table III.

Similarly, chlorination of (*Z*)-1-alkenylboronic acids afforded stereochemically pure (*E*)-1-chloro-1-alkenes (eq 9).



In a typical experiment, (*Z*)-1-octenylboronic acid[15] in methylene chloride was reacted with chlorine in the dark at 0 °C. After refluxing with sodium sulfite for 3 h, (*E*)-1-chloro-1-octene was obtained in 70% yield.

The corresponding stereoisomer, viz., (*Z*)-1-chloro-1-octene, was prepared[18] by using Kabalka's procedure. These isomers separated cleanly on a 10% SE-30 column (12 ft × $^1/_8$ in.).

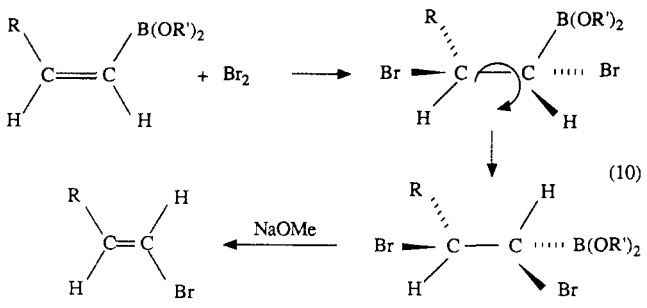
Mechanism. Our primary objective in this study was to explore the synthetic utility of (*Z*)-1-alkenylboronic esters. Consequently, it is not possible to arrive at a definitive conclusion about the mechanism of these reactions.

Formation of (*E*)-1-bromo-1-alkenes may be envisioned via an anti addition–anti elimination[19] sequence, as shown in eq 10.

Experimental Section

Materials. Manipulations of boron reagents were performed under an atmosphere of dry nitrogen using extensively the

(17) Brown, H. C.; Imai, T. *Organometallics* **1984**, *3*, 1392.
(18) Kunda, S. A.; Smith, T. L.; Hylarides, M. D.; Kabalka, G. W. *Tetrahedron Lett.* **1985**, *26*, 279.
(19) Matteson, D. S.; Liedtke, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 1526.



techniques outlined in Chapter 9 of ref 20. Alkynes used were from Chemical Samples Co. Catechol esters of alkenylboronic acids were synthesized via the hydroboration of alkynes with catecholborane.[12] The dibromoborane–dimethyl sulfide reagent was prepared from tribromoborane and borane–dimethyl sulfide according to the procedure developed in this laboratory.[13] The alkenyldibromoborane–dimethyl sulfide complexes were prepared according to published procedure.[14] (*E*)-1-Alkenylboronic acids were prepared by the hydrolysis of the corresponding catechol esters[12] or the dibromoborane–dimethyl sulfide complexes.[15] (*Z*)-1-Alkenylboronic esters were prepared according to a literature procedure.[17]

Methods. Gas chromatographic analyses were performed on either a Hewlett-Packard Model 5750 gas chromatograph equipped with a T.C. Detector or a H-P Model 5730A capillary GC equipped with a flame ionization detector. In either case, a H-P Model 3390A digital integrator was used. One of the following columns was used as was appropriate: Carbowax 20M (10%) on Chromosorb W (60–80 mesh) in 12 ft × 0.25-in.-o.d. steel column; SE-30 (10%) on Chromosorb W (60–80 mesh) in 12 ft × 0.25-in.-o.d. steel column; methylsilicone fluid in 12 m × 0.25 mm glass capillary column. In all cases, the *E* isomer had a higher retention time than the corresponding *Z* isomer.

^{1}H NMR spectra (δ, relative to Me_4Si) were recorded in a Varian T-60 spectrometer. ^{11}B NMR (δ, relative to $BF_3{\cdot}OEt_2$) and ^{13}C NMR (δ, relative to Me_4Si) were recorded on a Varian FT-80A spectrometer equipped with a broad-band probe and a H-P 3335A frequency synthesizer. The IR spectra were recorded on a Perkin-Elmer Model 137B spectrometer.

All compounds were characterized fully based on IR, ^{1}H NMR, ^{13}C NMR, and mass spectral analysis and also by their physical constants.

Synthesis of (*E*)-1-Iodo-1-alkenes. Procedure A. Preparation of (*E*)-1-iodo-1-octene is illustrative of the general procedure adopted for the synthesis of these compounds from vinylboronic acids. (*E*)-1-Octenylboronic acid (7.8 g, 50 mmol) was dissolved in ethyl ether (50 mL) in a 250-mL round-bottom flask, and a sodium hydroxide solution (50 mL, 3 N) was added. The mixture was cooled to 0 °C, and a solution of iodine (15.2 g, 60 mmol, 20% excess) in ethyl ether (100 mL) was added. After stirring the mixture for 0.5 h, the excess iodine was destroyed with saturated sodium thiosulfate solution. The ethereal layer was separated, and the aqueous layer was extracted with ether (2 × 25 mL). The combined ether extract was washed with water (2 × 50 mL) and brine (1 × 50 mL) and dried over anhydrous magnesium sulfate. The residue after solvent removal was distilled to give 9.6 g (80%) of (*E*)-1-iodo-1-octene, bp 58 °C/0.2 mmHg. The stereochemical purity of the product as determined by GC analysis was >99%.

Synthesis of (*E*)-1-Iodo-1-alkenes from Alkenyldibromoborane–Dimethyl Sulfide Complexes. Procedure B. The synthesis of (*E*)-1-iodo-2-cyclohexylethylene is representative. Cyclohexylethyne (5.4 g, 50 mL) in methylene chloride (25 mL) was placed on a 250-mL round-bottom flask covered with water at room temperature. Dibromoborane–dimethyl sulfide solution (50 mmol) was added slowly, and the mixture stirred overnight. After the mixture was cooled to 0 °C, solid iodine (12.7 g, 50 mmol) was added quickly to the reaction flask, followed by 25 mL of methylene chloride. Sodium hydroxide solution (50 mL, 5 N) was then added to the reaction mixture, and stirring was continued for 2 h at 0 °C and another 2 h at room temperature. Upon workup, (*E*)-1-iodo-2-cyclohexylethylene was obtained in 51% yield (steam distillation).

Synthesis of (*Z*)-1-Bromo-1-alkenylboronic Esters. These compounds were prepared by the hydroboration of 1-bromo-1-alkynes with dibromoborane–dimethyl sulfide complex, followed by the alcoholysis of the alkenyldibromoborane–dimethyl sulfide according to the procedure developed in this laboratory.[13] Preparation of dimethyl (*Z*)-1-bromo-1-octenylboronate is representative. 1-Bromo-1-octyne (100 mmol) was hydroborated with dibromoborane–dimethyl sulfide complex (100 mmol) in dichloromethane. The reaction was complete in ~8 h. Pentane (100 mL) was added, and the flask was immersed in an ice–salt bath. Methanol (400 mmol) was slowly introduced into the flask with rapid stirring. After the mixture was stirred at ~−5 °C for 15 min, the pentane layer was separated from the heavy methanol layer containing excess of hydrogen bromide. The latter was extracted with pentane (2 × 20 mL), and the combined pentane extract, upon solvent evaporation, followed by fractionation, gave pure dimethyl (*E*)-1-bromo-1-octenylboronate, bp 76–78 °C/0.2 mmHg, in 80% yield.

Preparation of (*E*)-1-Bromo-1-alkene. The synthesis of (*E*)-1-bromo-1-octene is representative. The reaction of diisopropyl (*Z*)-1-bromo-1-octenylboronate (25 mmol) with potassium triisopropoxyborohydride (25 mmol) was carried out as described.[17] Ether and most of the triisopropoxyborane were removed from the centrifugate under reduced pressure, and the residue was dissolved in dichloromethane (20 mL) and cooled to −25 °C. Bromine (25 mmol) in dichloromethane (10 mL) was added to it, and the reaction mixture was stirred for 1 h at −25 °C. Sodium methoxide in methanol (25 mmol) was then introduced into the flask, and stirring was continued for 1 h at −25 °C and an additional 0.5 h at room temperature. Pentane (25 mL) was added to the mixture and the product was worked up as usual. Fractionation gave pure (*E*)-1-bromo-1-octene, bp 59–60 °C/6 mmHg in 81% yield. The results are given in Table II.

Procedure for Preparing (*E*)-1-Chloro-1-octene. The (*Z*)-1-octenylboronic acid (13.30 mmol, 2.10 g) was added to methylene chloride (40 mL), cooled to 0 °C, and protected from light. The chlorine was passed through the reaction mixture until a slight yellow color persisted. The reaction mixture was stirred for 10 min at 0 °C and then for 20 min at 20 °C. The aqueous Na_2SO_3 solution (25 mL of a 10% solution) was added slowly to destroy excess chlorine. The reaction mixture was refluxed for 3 h. After cooling, the layers were separated, and the aqueous layer was extracted once again with CH_2Cl_2 (30 mL). The combined organic layer was washed with saturated NaCl solution and then dried over anhydrous $MgSO_2$. Removal of the solvent afforded the crude (*E*)-1-chloro-1-octene, which was purified by distillation; yield 70%, 1.40 g, bp 88–90 °C/40 mmHg, n^{20}_D 1.4385 [lit.[21a] bp 74 °C/15 mmHg, n^{26}_D 1.4404]. GC analysis showed >97% stereochemical purity. ^{1}H NMR ($CDCl_3$/TMS) δ 6.23–5.80 (m, 2 H), 2.26–1.83 (m, 2 H), 2.20–1.40 (m, 8 H), 1.00–0.80 (m, 3 H).

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Registry No. (*E*)-*n*-$C_6H_{13}CH{=}CHB(OH)_2$, 42599-16-6; (*E*)-c-$C_6H_{11}CH{=}CHB(OH)_2$, 37490-33-8; (*E*)-$Cl(CH_2)_3CH{=}CHB(OH)_2$, 37490-32-7; (*E*)-*t*-$C_4H_9CH{=}CHB(OH)_2$, 86595-37-1; (*E*)-$C_6H_5CH{=}CHB(OH)_2$, 6783-05-7; (*E*)-*n*-$C_6H_{13}CH{=}CHI$, 42599-17-7; (*E*)-c-$C_6H_{11}CH{=}CHI$, 42599-23-5; (*E*)-$Cl(CH_2)_3CH{=}CHI$, 78461-58-2; (*E*)-*t*-$C_4H_9CH{=}CHI$, 61382-45-4; (*E*)-$C_6H_5CH{=}CHI$, 42599-24-6; (*Z*)-*n*-$C_6H_{13}CH{=}CHI$, 52356-93-1; (*Z*)-$Cl(CH_2)_3CH{=}CHI$, 95835-51-1; *n*-$C_6H_{13}C{\equiv}CH$, 629-05-0; $Cl(CH_2)_3C{\equiv}CH$, 14267-92-6; C-$C_6H_{11}C{\equiv}CH$, 931-48-6; $HBBr_2{\cdot}SMe_2$, 55671-55-1; (*E*)-*n*-$C_4H_9CH{=}CHBr$, 13154-13-7;

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(*E*)-*n*-$C_6H_{13}CH$=CHBr, 51751-87-2; (*E*)-c-$C_6H_{11}CH$=CHBr, 67478-59-5; (*E*)-$(CH_3)_3CCH$=CHBr, 38203-90-6; (*E*)-Cl-$(CH_2)_3CH$=CHBr, 95835-52-2; (*Z*)-*n*-$C_6H_{13}CH$=CBrB$(OMe)_2$, 86595-49-5; *n*-$C_6H_{13}C$≡CBr, 38761-67-0; (*Z*)-*n*-$C_6H_{13}CH$=CBr-$(B(OPr\text{-}i)_2)$, 123594-50-3; (*Z*)-*n*-$C_6H_{13}CH$=CH$B(OH)_2$, 121021-30-5; (*E*)-*n*-$C_6H_{13}CH$=CHCl, 59871-24-8.

Supplementary Material Available: ^1H NMR spectrum of [*E*]-1-bromo-5-chloro-1-pentene (1 page). Ordering information is given on any current masthead page.

Vinylic Organoboranes. 15.[1] Mercuration of 2-Alkenyl-1,3,2-benzodioxaboroles and Boronic Acids. A Convenient Stereospecific Procedure for the Conversion of Alkynes into (*E*)-1-Halo-1-alkenes via Mercuric Salts

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Vinylboranes derived from terminal and internal alkynes via hydroboration with 1,3,2-benzodioxaborole undergo an instantaneous reaction with mercuric acetate at 0 °C to give the corresponding vinylmercuric acetates in exceptionally good yields. The reaction is stereospecific, proceeding with retention of configuration. The use of vinyl-1,3,2-benzodioxaboroles vastly improves our earlier procedure involving vinyldicyclohexylborane. A side reaction involving the migration of cyclohexyl group to the olefinic carbon lowers the yield of the vinylmercurial in the latter case. With the vinylbenzodioxaboroles, the reaction is exceptionally clean, leading to the desired product in near quantitative yield. Mercuration of various (*E*)-alkenylborane is also explored. Various (*E*)-1-alkenylboronic acids readily react with mercuric acetate to produce the corresponding (*E*)-1-alkenylmercurials, which are converted by bromine and iodine in pyridine into the corresponding (*E*)-1-bromo- and (*E*)-1-iodo-1-alkenes in >95% stereochemical purities. However, chlorination of these (*E*)-1-alkenylmercurials results in the formation of a mixture of stereoisomers.

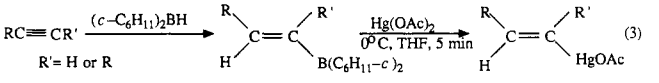
One of our major research programs since the facile synthesis of organoboranes using the hydroboration reaction[3] has been to demonstrate their versatility in organic synthesis. The conversion of organoboranes to organomercury compounds is an important attempt to fulfill that goal.

Mercury(II) salts have been shown to react with aryl-, alkyl-, and alkenylboronic acids,[4a-f] diarylborinic acids,[4g] and triaryl- and trialkylboranes[4h,i] to yield a variety of organomercurials. Consequent to the discovery of hydroboration, we studied the reaction of trialkylboranes with mercury(II) salts in great detail. We found that trialkylboranes derived from terminal alkenes reacted instantaneously with $Hg(OAc)_2$ to yield the corresponding alkylmercury acetate, which could be converted to the more stable alkylmercury halides (eq 1 and 2).[5] These

$$(RCH_2CH_2)_3B + 3Hg(OAc)_2 \xrightarrow[5\ min]{THF,\ 0\ °C} 3RCH_2CH_2HgOAc + B(OAc)_3 \quad (1)$$

$$RCH_2CH_2HgOAc \xrightarrow[H_2O]{NaX} RCH_2CH_2HgX \quad (2)$$

alkylmercury compounds are highly useful in organic synthesis.[6] Subsequently, we showed that trialkylboranes derived from internal alkenes react with $Hg(OAc)_2$ much slower than those with primary alkyl groups. However, we could accomplish the mercuration by using prolonged duration and higher temperature.[7] Our next objective was to study the mercuration of vinylboranes. Our finding that secondary alkyl–boron bonds are sluggish in their reactivity with $Hg(OAc)_2$ prompted us to study the reaction of vinyldicyclohexylboranes with mercuric acetate.[8] We were pleased to observe the remarkable ease with which the alkenyl–boron bond took part in the reaction (eq 3) and



(3)

the stereospecificity (retention of configuration), but were unhappy with a small amount of a side reaction involving the migration of the cyclohexyl moiety, leading to the cyclohexyl olefin 1 as a side product. To eliminate the side reaction, we studied the mercuration of 2-alkenyl-1,3,2-

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