(*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.

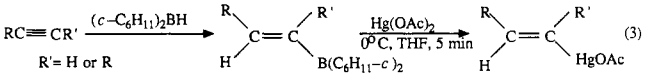
One of our major research programs since the facile synthesis of organoboranes using the hydroboration reaction[3] has been to demonstrate their versatility in organic synthesis. The conversion of organoboranes to organomercury compounds is an important attempt to fulfill that goal.

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-

(1) For part 14 in this series, see: Brown, H. C.; Hamaoka, T.; Ravindran, N.; Subrahmanyam, C.; Somayaji, V.; Bhat, N. G. *J. Org. Chem.*, preceding paper in this issue.

(2) (a) National Science Foundation Fellow, 1967–1971. (b) Postdoctoral research associate (1968–1971) on Grant GM-10937, supported by the National Institutes of Health. (c) Postdoctoral research associate on Grant CHE-79-18881 from the National Science Foundation. (d) Postdoctoral research associate on Grant CHE-8706102 from the National Science Foundation.

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(4) (a) Michaelis, A. *Ber.* **1894**, *27*, 244. (b) Torssell, K. *Acta Chem. Scand.* **1959**, *13*, 115. (c) Nesmeyanov, A. N.; Borisov, A. E.; Osipova, M. A. *Dolk. Akad. Nauk. SSSR* **1966**, *169*, 602. (d) Sazonova, V. A.; Kronrod, N. Ya. *Zh. Obshch. Khim.* **1956**, *26*, 1876. (e) Borisov, A. E. *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk* **1951**, 402. (f) Matteson, D. S.; Tripathy, P. B. *J. Organomet. Chem.* **1970**, *21*, 6. (g) Koenig, W.; Scharrnbeck, W. *J. Prakt. Chem.* **1930**, *128*, 153. (h) Wittig, G.; Keicher, G.; Ruechert, A.; Raff, P. *Justus Liebigs Ann. Chem.* **1949**, *563*, 110. (i) Honeycutt, J. B., Jr.; Riddle, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 3051.

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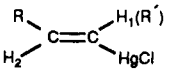
0022-3263/89/1954-6079$01.50/0

Table I. Mercuration of 2-Alkenyl-1,3,2-benzodioxaboroles

2-alkenyl-1,3,2-benzodioxaborole derived from	product	isolated yield, %	mp,[a] °C
1-pentyne	*trans*-1-pentenylmercuric chloride	98	130–130.5
5-chloro-1-pentyne	(*trans*-5-chloro-1-pentenyl)mercuric chloride	98	94.5–95.0
cyclohexylethyne	(*trans*-3-cyclohexylethenyl)mercuric chloride	99	134–135
3-hexyne	*cis*-3-hexenylmercuric chloride	98	47.5–48.0
4,4-dimethyl-2-pentyne	(*cis*-4,4-dimethyl-2-pentenyl)mercuric chloride	97	108–108.5

[a] Recrystallized from 95% ethanol.

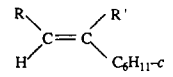
Table II. NMR Data of Vinylmercuric Chlorides



compound	δ_1	δ_2	$J_{H_1H_2}$, Hz	$J_{^{199}Hg-H_1}$, Hz	$J_{^{199}Hg-H_2}$, Hz
trans-1-pentenylmercuric chloride	≈5.8	≈5.8		296[a]	296[a]
(*trans*-5-chloro-1-pentenyl)mercuric chloride	≈5.9	≈5.9		303[a]	303[a]
(*trans*-cyclohexylethenyl)mercuric chloride	≈5.8	≈5.8		292[a]	292[a]
cis-3-hexenylmercuric chloride		5.43			308
(*cis*-4,4-dimethyl-2-pentenyl)mercuric chloride[b]		5.47			362

[a] It is clear from the multiplet pattern that these coupling constants are not truly identical. [b] $J_{^{199}Hg-CH_3}$ = 230 Hz, J_{H-CH_3} = 1.8 Hz.

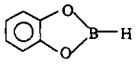
benxodioxaboroles since B–O bonds do not migrate.[9] We report our observations in detail in this paper.



1

Results and Discussion

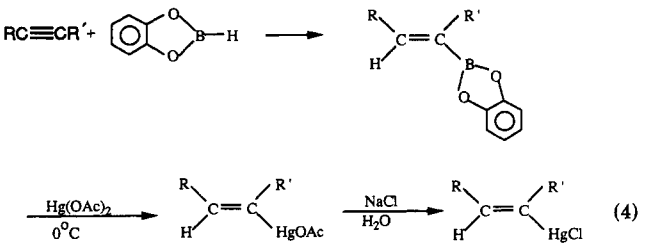
1,3,2-Benzodioxaborole (catecholborane, **2**) obtained from catechol and BH_3·THF[10] or BH_3·Me_2S[11] is a convenient hydroborating agent.[12] It hydroborates terminal



2

and internal alkynes at 70 °C to give the monohydroboration products cleanly.[13] With unsymmetrical alkynes, the reaction is fairly regiospecific (placing ≥90% of boron on the less hindered carbon). Since hydroboration is a cis addition reaction, the products are exclusively *trans*-2-alkenyl-1,3,2-benzodioxaboroles.

Mercuration of 2-Alkenyl-1,3,2-benzodioxaboroles. We subjected the 2-alkenyl-1,3,2-benzodioxaboroles obtained via the hydroboration of terminal and internal alkynes with 1,3,2-benzodioxaborole to mercuration using $Hg(OAc)_2$ in THF at 0 °C (eq 4). The reaction was ex-



(4)

tremely facile and was over in a few minutes. The resulting vinylmercuric acetates were converted into the corresponding chloride by treatment with aqueous NaCl. The data for the vinylmercuric chlorides are summarized in Table I.

As mentioned earlier, the side reaction observed with vinyldicyclohexylboranes does not occur here, and consequently the yields of the vinylmercurials are excellent.

Alkenylmercury compounds are usually prepared by the reaction of alkenylmagnesium or -lithium compounds with mercuric halides (eq 5).[14] Our procedure using 2-alkenyl-1,3,2-benzodioxaboroles offers a very good method of making vinylmercurials in good yields.

$$RCH{=}CHMgX + HgX_2 \rightarrow RCH{=}CHHgX$$

$$RCH{=}CHLi + HgX_2 \rightarrow RCH{=}CHHgX \quad (5)$$

Stereochemistry. The configuration of the vinylmercuric chlorides was determined by ^1H NMR spectroscopy. The alkenylmercuric chlorides derived from terminal alkynes all gave complicated NMR spectra in the vinyl hydrogen region from which proton–proton coupling constants could not readily be determined; ^{199}Hg–H coupling constants clearly showed these compounds to be trans. Thus, overlapping satellites due to both cis and geminal ^{199}Hg–H coupling were observed with coupling constants of $J_{^{199}Hg-H}$ = 292–303 Hz (Table II). Integration of the satellite areas gave 17–19% of the total vinyl hydrogen area (^{199}Hg has a relative abundance of 16.86%). These facts are consistent with a trans configuration.[15] The alkenylmercuric chlorides derived from internal alkynes also gave ^{199}Hg–H coupling constants consistent only with a *cis*-Hg–H configuration. Thus the NMR studies clearly show that the mercuration proceeds with a retention of the configuration present in the alkenylborane.

Since our publication of a preliminary communication on this reaction,[9] it has been applied to the synthesis of a prostaglandin analogue.[16] Numerous other examples on the use of vinylmercuric chlorides in organic synthesis are reported also.[6]

Mercuration of Various (*E*)-1-Octenylboranes. We chose (*E*)-1-octenylmercuric chloride as the model compound and examined its preparation from a variety of (*E*)-1-octenylboranes.[9]

In a typical experiment, the mercuration was carried out by adding solid mercuric acetate (1 equiv) to an ice-cold

(9) For a preliminary communication, see: Larock, R. C.; Gupta, S. K.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 4371.
(10) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 1816.
(11) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1482.
(12) Lane, C. F.; Kabalka, G. W. *Tetrahedron* **1976**, *32*, 981.
(13) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370.
(14) Makarova, L. G.; Nesmeyanov, A. N. *Methods of Elementoorganic Chemistry: The Organic Compounds of Mercury*; North Holland Publishing Co.: Amsterdam, 1967; Vol. 4.
(15) Vinylmercuric acetate exhibits the following ^{199}Hg–H coupling constants: J_{gem} = 291 Hz, J_{cis} = 331 Hz, and J_{trans} = 658 Hz: Wells, P. R.; Kitching, W.; Henzell, R. F. *Tetrahedron Lett.* **1964**, *18*, 1029.
(16) Pappo, R.; Collins, P. W. *Tetrahedron Lett.* **1972**, 2627.

solution of the appropriate (*E*)-1-octenylborane in THF or pyridine (1 M). The resultant homogeneous solution was stirred at 0 °C for an hour and then poured into a cold aqueous solution of sodium chloride. The solvent was then removed under aspirator vacuum, and the resultant solid was filtered. The crude product so obtained was purified by recrystallization using 95% ethanol. The results of the preparation of (*E*)-1-octenylmercuric chloride via mercuration of various (*E*)-1-octenylboranes are listed in the supplementary material (see the paragraph at the end of the paper).

Both THF and pyridine appear to be suitable solvents for the mercuration of (*E*)-1-octenylboronic acid. The product derived via mercuration of (*E*)-1-octenylboronic acid was found to be the most pure of the various (*E*)-1-octenylboranes employed in this study. Also, in this instance, a good yield of (*E*)-1-octenylmercuric chloride was realized. Even the crude product was found to be relatively pure, crystalline and easy to recrystallize.

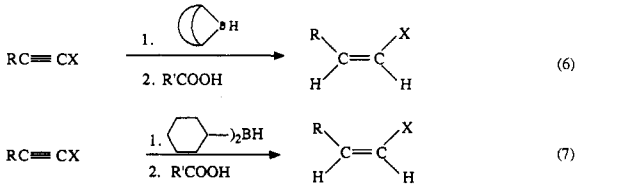
On the other hand, use of (*E*)-2-octenyl-1,3,2-benzodioxaborole either as crude material or as distilled pure material resulted in highly impure (*E*)-1-octenylmercuric chloride. In these instances, appreciable amounts of elemental mercury was observed during the mercuration step. Finally, the crude product derived via mercuration of methyl or propylene glycol esters of (*E*)-1-octenylboronic acid was gummy and considerable difficulty was encountered in isolating it as a crystalline product.

It is therefore apparent from the above discussion that the mercuration procedure employing (*E*)-1-octenylboronic acid is the most convenient for the preparation of pure (*E*)-1-octenylmercuric chloride.

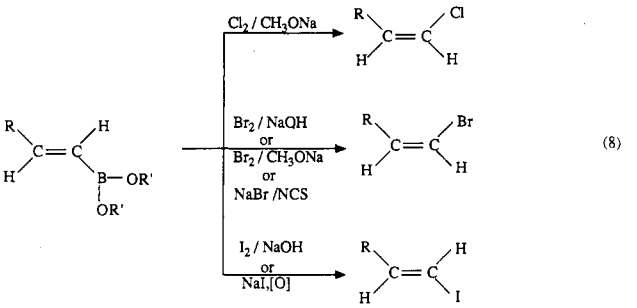
Sequential Mercuration–Halodemercuration of (*E*)-1-Alkenylboronic Acids. A Highly Stereoselective Synthesis of (*E*)-1-Halo-1-Alkenes. Over the past few years there has been a surge of interest in the development of novel synthetic routes for the preparation of alkenyl halides.[17] This was brought about by the fact that stereodefined alkenyl halides are useful synthetic intermediates for stereoselective syntheses of substituted alkenes and 1,3-dienes of the type occurring as part structures in a number of biologically important molecules such as insect pheromones. For example, bombykol ((10*Z*,12*E*)-10,12-hexadecadien-1-ol), the pheromone of the female silk moth, *Bombyx mori*, and its geometrical isomer have been synthesized by palladium-catalyzed cross coupling of 1-alkenylboronic acids with 1-alkenyl halides.[18]

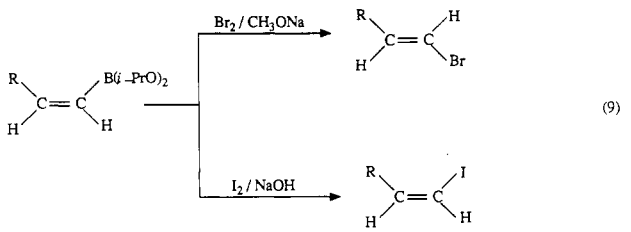
Various approaches are currently available for the preparation of 1-halo-1-alkenes via organoboranes. We[19] and Zweifel et. al.[20] have independently shown that hydroboration–protonolysis of 1-halo-1-alkynes provides the corresponding isomerically pure (*Z*)-vinyl halides (eq 6 and 7).

We have reported that (*Z*)- and (*E*)-alkenyl bromides can be prepared from the dibromo derivatives of alkenyldialkylboranes.[21] For example, solvolysis of the dibromides induces anti elimination of the bromine and dialkylboron moieties to afford the (*Z*)-alkenyl bromide. Alternatively, heating the dibromo intermediate results in syn elimination of the bromine and dialkylboron moieties to yield the (*E*)-alkenyl bromides.

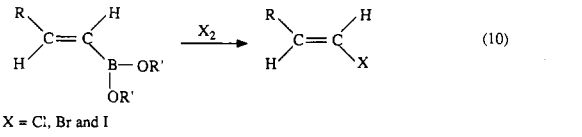


Various methodologies have been developed for the preparation of alkenyl halides via halogenation of (*E*)-1-alkenylboronic acids or esters (eq 8).[22] The methodology





of eq 8 has also been extended to (*Z*)-1-alkenylboronic esters (eq 9).[23] It should be noted that in the reactions of eq 8 the replacement of the boron moiety by chlorine or bromine proceeds with inversion of configuration, whereas the replacement by iodine proceeds with retention of configuration of the alkenylborane. To date, however, there has been no report of a general methodology wherein the boron moiety in (*E*)-1-alkenylboronic acids or esters is replaced by halogens with retention of configuration (eq 10).



We felt that transmetalation of (*E*)-1-alkenylboronic acids or esters with mercury(II) salts followed by halogenation might provide a general synthesis of (*E*)-1-halo-1-alkenes via organoboranes (eq 11). Halogenation of vinylmercurials has been well documented in the literature.[6,24] However, no single procedure of a general scope

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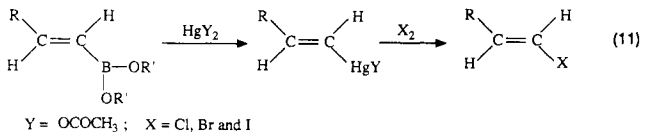


(11)

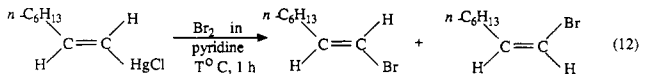
Y = $OCOCH_3$; X = Cl, Br and I

has been reported for the preparation of (*E*)-1-halo-1-alkenes from (*E*)-1-alkenylboronic acids or esters via the corresponding mercurials.

A research program was therefore initiated with the following objectives: (a) to develop a high yield procedure for the preparation of vinylmercurials from vinylboronic acids or esters; (b) to develop a stereospecific procedure for the halogenation of vinylmercurials; (c) to delineate the scope of the preparation of (*E*)-1-halo-1-alkenes via mercuration–halodemercuration of (*E*)-1-alkenylboronic acids or esters by a one-pot procedure.

Bromination of (*E*)-1-Octenylmercuric Chloride. Bromination of vinylmercuric halides provides a very simple route to vinyl bromides. The bromination of vinylmercurials is normally stereospecific in polar solvents and nonstereospecific in nonpolar solvents. Examples of bromination occurring with retention of stereochemistry include the bromination of (*Z*)- and (*E*)-stilbenylmercuric bromide in dioxane,[25] the bromination of (*Z*)- and (*E*)-β-styrylmercuric bromide in methanol or dimethyl sulfoxide,[26] and the bromination of (*Z*)- and (*E*)-2-butenylmercuric bromide in pyridine.[27] In contrast, the bromination of (*Z*)- and (*E*)-1-propenyl- and -2-butenylmercuric bromide in carbon disulfide occurs with predominant inversion of configuration at the double bond.[27] Examples of nonstereospecific bromination include the bromination of (*Z*)- and (*E*)-β-styrylmercuric bromide in carbon tetrachloride or benzene[26] and the bromination of (*E*)-5-iodo-1-pentenylmercuric bromide in benzene.[28]

To establish the best reaction conditions for the bromination of (*E*)-1-octenylmercuric chloride, we carried out the following systematic study. This study involved bromination at a particular temperature, the reaction mixtures were subjected to standard aqueous workup procedure and then analyzed by GC using a suitable internal standard (eq 12).



(12)

The yields and isomeric purities of 1-bromo-1-octene derived via bromination of (*E*)-1-octenylmercuric chloride under various reaction conditions are listed in Table III. In all instances a mixture of (*E*)- and (*Z*)-1-bromo-1-octenes, predominating in the *E* isomer, was formed in high yields. Our attempts to further improve the isomeric ratio in favor of the *E* isomer by changes in solvent or temperature of bromination resulted in no success. Therefore, we proceeded to examine the scope of preparing (*E*)-1-bromo-1-alkenes from (*E*)-1-alkenylboronic acids via a one-pot sequential mercuration–bromodemercuration procedure.

In view of the only moderate success realized in the bromination of (*E*)-1-alkenylmercuric chlorides and also

Table III. Yields and Isomeric Purities of 1-Bromo-1-octene Derived via Bromination of (*E*)-1-Octenylmercuric Chloride under Various Reaction Conditions

reaction conditions for bromination			
solvent	temp, °C	time, h	yield, % (*E*:*Z*)[c]
THF-pyridine[a]	rt	1	86 (87:13)
	0	1	85 (89:11)
	0–rt[d]		
	−30	1	90 (90:10)
	−30 to rt		
pyridine[b]	rt	1	88 (91:9)
	0	1	91 (91:9)
	0–rt		
	−30	1	80 (91:9)
	−30 to rt		

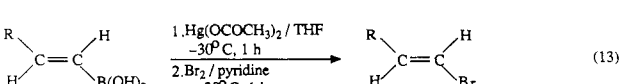
[a] To a solution of (*E*)-1-octenylmercuric chloride in THF (1 M) maintained at the appropriate temperature was added a solution of bromine in pyridine (1 M). [b] To a solution of (*E*)-1-octenylmercuric chloride in pyridine (1 M) maintained at the appropriate temperature was added a solution of bromine in pyridine (1 M). [c] Yields and isomeric purities were determined by GLC analysis. [d] Room temperature.

Table IV. Yields and Isomeric Purities of 1-Bromo-1-octene Derived via Mercuration–Bromodemercuration of [*E*]-1-Octenylboronic Acid under Various Reaction Conditions

reaction conditions for mercuration[a]		reaction conditions for bromination[a]		% yield
solvent	temp,[b] °C	solvent	temp, °C	[*E*:*Z*][c]
THF	0	pyridine	rt	81 (90:10)
	0–rt			
THF	0	pyridine	0	89 (95:5)
			0–rt	
THF	−30	pyridine	−30	84 (97:3)
			−30 to rt	
pyridine	0	pyridine	rt	90 (90:10)
	0–rt			
pyridine	0	pyridine	rt	90 (96:4)
			0–rt	
pyridine	−30	pyridine	−30	84 (97:3)
			−30 to rt	

[a] The time for all reactions was 1 h. [b] rt = room temperature. [c] Yields and isomeric purities were determined by GLC analysis.

since this approach still entails the prior preparation and isolation of (*E*)-1-alkenylmercuric chlorides, we sought a direct one-pot conversion of (*E*)-1-alkenylboronic acids into (*E*)-1-bromo-1-alkenes. Table IV lists the results of the various experiments that were carried out to optimize the yields and isomeric purities of 1-bromo-1-octene derived via mercuration–bromodemercuration of (*E*)-1-octenylboronic acid in a one-pot procedure. In all instances, the vinyl bromide product was formed in high yields. The change in solvent from "THF–pyridine" to "pyridine only" did not affect the isomeric purity of the vinyl bromide product appreciably. However, the temperature of bromination was found to have a profound influence on the isomeric purity of 1-bromo-1-octene. For example, lowering the temperature of bromination from room temperature to −30 °C changed the *E*:*Z* ratio of 1-bromo-1-octene from 90:10 to 97:3 in both THF–pyridine or pyridine solvents. Since the best result was observed at −30 °C (see Table IV), we settled on the procedure that employed THF for mercuration (eq 13). A representative selection of (*E*)-1-bromo-1-alkenes was prepared by this



(13)

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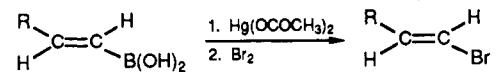
Table V. Preparation of (*E*)-1-Bromo-1-alkenes from (*E*)-1-Alkenylboronic Acids



1a–f 2a–f

R[a]	product[b]	isomeric yield,[c] %	purity,[d] %	MS, *m/e* (M^+)
n-C_4H_9	**2a**	70	97	162, 164
n-C_6H_{13}	**2b**	76	96	190, 192
c-C_6H_{11}	**2c**	73	98	188, 190
t-C_4H_9	**2d**	72	99	162, 164
$Cl(CH_2)_3$	**2e**	77	96	182, 184
C_6H_5	**2f**	74	96	182, 184

[a] In all instances, except **1c** and **1f**, a 1 M solution of the appropriate alkenylboronic acid in THF was employed for mercuration. In the cases of **1c** and **1f**, a 0.5 M solution in THF was used. [b] Boiling points and refractive indexes are described in the Experimental Section. [c] Yield of isolated product. [d] Isomeric purities were determined by gas chromatographic analysis.

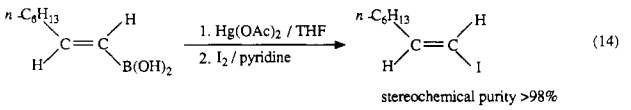
Table VI. Chlorination of (*E*)-1-Octenylmercuric Acetate[a]

solvent	temp, °C	time, h	isomeric ratio[b] *E*	*Z*
CH_2Cl_2	−30	1	53	47
THF + CH_2Cl_2 (1:1)	−30	2	48	52
THF + pyridine (1:1)	−30	2	48	52
pyridine	−30	2	40	60
THF + pyridine + CH_2Cl_2 (1:1:1)	−30	2	33	67

[a] All of the reactions were carried out on a 5-mmol scale and in all cases >70% yields of the chlorooctenes were realized. [b] Stereochemical ratio was determined by analyzing samples on a 10% SE-30 column (12 ft × $^1/_8$ in. programmed at 50–250 °C, 8 °C/min).

procedure in excellent purities (>95% isomeric purity, >98% chemical purity) as shown in Table V.

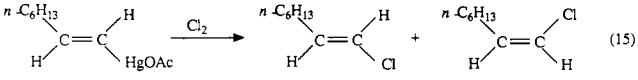
Iodination of (*E*)-1-octenylmercuric acetate at −30 °C produced (*E*)-1-iodo-1-octene in >98% stereochemical purity (eq 14).



(14)

stereochemical purity >98%

Since (*E*)-1-iodo-1-alkenes are readily prepared by direct iodination of (*E*)-1-alkenylboronic acids,[29] the proposed mercury route to these compounds does not offer any significant advantage. Consequently, the iodination reaction was not studied in detail. Unfortunately, the chlorination of (*E*)-1-octenylmercuric acetate did not give satisfactory results. It gave a mixture of stereoisomers (eq 15). The results are summarized in Table VI.



(15)

In conclusion, the present procedure represents the first general, one-pot stereoselective synthesis of (*E*)-1-bromo-1-alkenes from (*E*)-1-alkenylboronic acids. Because of the simplicity of the procedure, ready availability of the alkenylboronic acids, and high product yields, this procedure provides a new, facile, one-step route to (*E*)-1-bromo-1-alkenes. Similarly, (*E*)-1-iodo-1-alkenes could also be prepared in excellent stereochemical purities. However, since these compounds are readily prepared by direct iodination of (*E*)-1-alkenylboronic acids,[29] the present procedure does not offer any significant advantage. Unfortunately, the present methodology is not useful for preparing stereochemically pure (*E*)-1-chloro-1-alkenes. In such cases one has to adopt a procedure developed for preparing (*E*)-1-chloro-1-alkenes[1] based on (*Z*)-1-alkenylboronic acids.

Experimental Section

All manipulations of air- and moisture-sensitive compounds were carried out under a purified nitrogen atmosphere.[29] All glassware used was dried in an oven at 140 °C, assembled hot, and cooled with a stream of nitrogen. Tetrahydrofuran was freshly distilled under nitrogen from sodium and benzophenone prior to use. Pyridine (Fisher Scientific Co.) was used as received. Alkynes were commercial products from Chemical Samples Co. and used without purification. Catechol esters of alkenylboronic acids were synthesized via the hydroboration of alkynes with catecholborane.[9] The (*E*)-1-alkenylboronic acids were prepared by the hydrolysis of these esters and crystallized from hot water.[9] Mercuric acetate (Fisher Scientific Co.) was used directly as obtained.

All of the (*E*)-1-bromo-1-alkenes and (*E*)-1-iodo-1-alkenes have been fully characterized by ^1H NMR and IR spectra. The ^1H NMR spectra were recorded on a Varian T-60 instrument and the chemical shift values, all in $CDCl_3$, are given in parts per million (δ) relative to $(CH_3)_4Si$. IR spectra were recorded with a Perkin-Elmer 1420 ratio recording IR spectrophotometer. Gas chromatographic analysis was performed using a 10% SE-30 column (6 ft × $^1/_8$ in.) in a Hewlett-Packard Model 5730A instrument coupled with a H-P 3390A integrator or using a 50-m methylsilicone glass capillary column (0.25-mm i.d.) in a Hewlett-Packard Model 5890 instrument coupled with a H-P 3392A integrator, using either *n*-dodecane or *n*-hexadecane as internal standards.

Hydroboration of Acetylenes with 1,3,2-Benzodioxaborole. The procedure for the hydroboration of alkynes by 1,3,2-benzodioxaborole has been described previously.[9] A mixture of the alkyne and 1,3,2-benzodioxaborole was stirred at 70 °C until the reaction was complete: terminal alkynes generally require 2 h and internal alkynes about 4–6 h.

Mercuration of 2-Alkenyl-1,3,2-benzodioxaboroles. The following procedure is typical. Mercuric acetate (25 mmol) was added to a well-stirred solution of 2-(*trans*-2-cyclohexylethenyl)-1,3,2-benzodioxaborole (25 mmol, 5.7 g) in THF (25 mL) at 0 °C. The mixture was stirred several minutes until all of the mercuric acetate disappeared and then poured into 100 mL of ice water containing 25 mmol of NaCl. The THF was removed under vacuum, and the resulting white solid was filtered, washed very thoroughly with water, and dried overnight in a vacuum desiccator. There was obtained 8.57 g (99%) of (*trans*-cyclohexylethenyl)mercuric chloride, mp 134–135 °C (95% ethanol). The data on this and the other compounds are given in Table I.

General Procedure for the Preparation of (*E*)-1-Bromo-1-alkenes from (*E*)-1-Alkenylboronic Acids via Alkenylmercury Derivatives: (*E*)-1-Bromo-1-hexene. To a solution of (*E*)-1-hexenylboronic acid (1.28 g, 10 mmol) in THF (10 mL) cooled to −30 °C was added under nitrogen finely powdered mercuric acetate (3.1 g, 10 mmol). The resultant slurry was stirred for an hour at −30 °C and was then treated with a solution of bromine in pyridine (11 mL, 1 M, 11 mmol). The reaction mixture, which became green, was stirred for an hour at −30 °C, allowed to warm to room temperature, and then was slowly poured into a vigorously stirred ice-cold mixture of 6 N hydrochloric acid (20 mL) and *n*-pentane (20 mL). The layers were separated, and the aqueous phase was extracted with *n*-pentane (2 × 20 mL). The combined organic layers were washed successively with 6 N hydrochloric acid (20 mL) and saturated aqueous sodium thiosulfate solution (20 mL) and then dried over anhydrous magnesium sulfate. The solvents were removed by distillation at atmospheric pressure and the residue was distilled through a short-path column to give (*E*)-1-bromo-1-hexene in 70% (1.14 g) yield: bp 60–61 °C/50 mmHg, n^{26}_D 1.4600 [lit.[17d] bp 77 °C/65 mmHg, n^{26}_D 1.4582].

(29) For the special experimental techniques used in handling air- and moisture-sensitive materials, see: Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

GC analysis on a 50-m methylsilicone capillary column indicated this product to be 97% isomerically pure; ^{1}H NMR ($CDCl_3$/TMS) δ 5.8–6.4 (m, 2 H, CH=CH), 2.0–2.3 (m, 2 H, CH_2—C=C), 1.2–1.6 (m, 4 H, $(CH_2)_2$), 0.9 (deformed triplet, 3 H, CH_3); IR (neat) ν 3065 (C=C—H), 1618 (C=C), 944 cm^{-1} (*trans*-CH=CH); MS, *m/e*, (M^+) 162, 164.

(*E*)-1-Bromo-1-octene. Following the preceding procedure, (*E*)-1-octenyl-boronic acid was converted into (*E*)-1-bromo-1-octene in 76% yield: bp 74–75 °C/7 mmHg, n^{26}_D 1.4606 [lit.[30] bp 67 °C/5 mmHg, n^{26}_D 1.4617]. GC analysis on a 50-m methylsilicone capillary column showed this product to be 96% isomerically pure; ^{1}H NMR ($CDCl_3$/TMS) δ 5.8–6.4 (m, 2 H, CH=CH), 2.0–2.3 (m, 2 H, CH_2—C=C), 1.2–1.6 (m, 8 H, $(CH_2)_4$), 0.9 (deformed triplet, 3 H, CH_3); IR (neat) ν 3059 (C=C—H), 1618 (C=C), 937 cm^{-1} (*trans*-CH=CH); MS, *m/e* (M^+) 190, 192.

(*E*)-1-Bromo-2-cyclohexyl-1-ethene. According to the above-described general procedure, (*E*)-2-cyclohexyl-1-ethenylboronic acid was converted into (*E*)-1-bromo-2-cyclohexylethene in 73% yield: bp 72–73 °C/6 mmHg, n^{26}_D 1.5035 [lit.[23b] bp 50–52 °C/4 mmHg, n^{26}_D 1.5039]. GC analysis on a 50-m methylsilicone capillary column indicated this product to be 98% isomerically pure. ^{1}H NMR data agree with the literature[23a] values. IR (neat) ν 3072 (C=C—H), 1615 (C=C), 941 cm^{-1} (*trans*-CH=CH); MS, *m/e* (M^+) 188, 190.

(*E*)-1-Bromo-3,3-dimethyl-1-butene. Following the general procedure, (*E*)-1-bromo-3,3-dimethyl-1-butene was prepared from (*E*)-3,3-dimethyl-1-butenylboronic acid in 72% yield: bp 63–64 °C/90 mmHg, n^{26}_D 1.4620 [lit.[23b] bp 48 °C/50 mmHg, n^{26}_D 1.4621]. GC analysis on a 50-m methylsilicone capillary column showed the compound to be 99% isomerically pure. ^{1}H NMR data agree with the literature[23a] values. IR (neat) ν 3085 (C=C—H), 1611 (C=C), 944 cm^{-1} (*trans*-CH=CH); MS, *m/e* (M^+) 162, 164.

(*E*)-1-Bromo-5-chloro-1-pentene. According to the previously described general procedure, (*E*)-5-chloro-1-pentenylboronic acid was converted into (*E*)-1-bromo-5-chloro-1-pentene in 77% yield: bp 73–74 °C/9 mmHg, n^{26}_D 1.4950 [lit.[23b] bp 66–68 °C/6 mmHg, n^{26}_D 1.4770]. GC analysis on a 50-m methylsilicone capillary column showed the compound to be 96% isomerically pure; ^{1}H NMR ($CDCl_3$/TMS) δ 5.9–6.4 (m, 2 H, CH=CH), 3.5 (t, J = 6 Hz, 2 H, CH_2–Cl), 1.7–2.5 (m, 4 H, $(CH_2)_2$); IR (neat) ν 3065 (C=C—H), 1618 (C=C), 937 cm^{-1} (*trans*-CH=CH); MS, *m/e* (M^+) 182, 184.

(*E*)-1-Bromo-2-phenyl-1-ethene. Following the above-described general procedure, (*E*)-2-phenyl-1-ethenylboronic acid was converted into (*E*)-1-bromo-2-phenyl-ethene in 74% yield: bp 82–83 °C/3 mmHg, n^{26}_D 1.6040 [lit.[17d] bp 62–63 °C/2 mmHg, n^{26}_D 1.6031]. GC analysis on a 50-m methylsilicone capillary column revealed this compound to be 96% isomerically pure. ^{1}H NMR data agree with the literature[23a] values. IR (neat) ν 1604 (C=C, vinylic and aromatic), 1571 (C=C aromatic), 941 (trans-CH=CH), 732 and 691 cm^{-1} (monosubstituted phenyl ring); MS, *m/e* (M^+) 182, 184.

Preparation of (*E*)-1-Iodo-1-octene. To a solution of (*E*)-1-octenylboronic acid (10 mmol, 1.56 g) in THF (10 mL) cooled to −30 °C was added finely powdered mercuric acetate (10 mmol). The reaction mixture was stirred for 1 h at −30 °C and was then treated with a solution of iodine in pyridine (10 mL, 1 M). It was then stirred at −30 °C for 1 h and slowly allowed to warm to room temperature. It was then poured into a vigorously stirred ice-cold mixture of 6 N hydrochloric acid (20 mL) and *n*-pentane. The layers were separated, and the aqueous phase was extracted with *n*-pentane (2 × 20 mL). The combined organic layers were successively washed with 6 N hydrochloric acid (20 mL) and saturated aqueous sodium chloride solution and then dried over anhydrous magnesium sulfate. The solvent was removed and the distillation afforded pure (*E*)-1-iodo-1-octene in 76% (1.80 g) yield: bp 82–84 °C/3.80 mmHg, n^{24}_D 1.4952 [lit.[30] bp 85 °C/3 mmHg, n^{24}_D 1.5010]. GC analysis on a 5890A capillary GC (50-m methylsilicone column) indicated the compound to be >98% isomerically pure; ^{1}H NMR ($CDCl_3$/TMS) δ 0.93 (deformed t, 3 H), 1.10–1.50 (m, 8 H), 1.86–2.16 (m, 2 H), 5.76–6.73 (m, 2 H); MS, *m/e* (M^+) 238.

Typical Procedure for the Chlorination of (*E*)-1-Octenylmercuric Acetate. To a solution of (*E*)-1-octenylboronic acid (5 mmol, 0.789) in THF (5 mL) cooled to −30 °C was added finely powdered mercuric acetate (5 mmol). The reaction mixture was stirred at −30 °C for 1 h. In another flask containing 5 mL of pyridine chlorine gas was passed at −30 °C for 10 min. It was then added slowly through a double-ended needle to a flask protected from light, containing (*E*)-1-octenylmercuric acetate generated at −30 °C. It was then stirred at −30 °C for 2 h. The reaction mixture was brought to room temperature, and it was then poured into an ice-cold solution of 6 N hydrochloric acid (10 mL). It was then extracted with *n*-pentane (2 × 20 mL). The pentane extract was washed with 6 N hydrochloric acid (10 mL) followed by water (2 × 25 mL). It was then dried over anhydrous magnesium sulfate, and the GC analysis was performed on a 10% SE-30 column. The results are described in Table VI.

Acknowledgment. We are indebted to the National Science Foundation (Grants CHE-79-18881, CHE-8706102) and the National Institutes of Health (Grant GM 10937) for support of this work.

Registry No. **1a**, 42599-18-8; **1b**, 42599-16-6; **1c**, 37490-33-8; **1d**, 86595-37-1; **1e**, 37490-32-7; **1f**, 6783-05-7; **2**, 274-07-7; **2a**, 13154-13-7; **2b**, 51751-87-2; **2c**, 67478-59-5; **2d**, 38203-90-6; **2e**, 95835-52-2; **2f**, 588-72-7; (*E*)-*n*-C_6H_{13}CH=CHB(OMe)$_2$, 86595-39-3; (*E*)-*n*-C_6H_{13}CH=CHBO$(CH_2)_3$O, 86595-52-0; 1-pentyne, 627-19-0; 5-chloro-1-pentyne, 14267-92-6; cyclohexylethyne, 931-48-6; 3-hexyne, 928-49-4; 4,4-dimethyl-2-pentene, 999-78-0; 2-(*trans*-1-pentenyl)-1,3,2-benzodioxaborole, 37494-02-3; 2-(*trans*-5-chloro-1-pentenyl)-1,3,2-benzodioxaborole, 37490-27-0; 2-(*trans*-cyclohexylethenyl)-1,3,2-benzodioxaborole, 37490-23-6; 2-(*cis*-3-hexenyl)-1,3,2-benzodioxaborole, 37490-28-1; 2-(*cis*-4,4-dimethyl-2-pentenyl)-1,3,2-benzodioxaborole, 37490-30-5; *trans*-1-pentenylmercuric chloride, 36525-00-5; (*trans*-5-chloro-1-pentenyl)mercuric chloride, 38010-66-1; (*trans*-cyclohexylethenyl)-mercuric chloride, 36525-01-6; *cis*-3-hexenylmercuric chloride, 36525-04-9; (*cis*-4,4-dimethyl-2-pentenyl)mercuric chloride, 38010-69-4; (*E*)-1-iodo-1-octene, 42599-17-7; (*E*)-2-chloro-1-octene, 59871-24-8; (*Z*)-1-chloro-1-octene, 64531-23-3; (*Z*)-1-bromo-1-octene, 42843-49-2; (*E*)-1-octenyl-1,3,2-benzodioxaborole, 73349-13-0.

Supplementary Material Available: Preparation of (*E*)-1-octenylmercuric chloride via mercuration of various (*E*)-1-octenylboranes (2 pages). Ordering information is given on any current masthead page.

(30) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 430.