Vinylic Organoboranes. 13. A Convenient Stereospecific Synthesis of (Z)-1-Halo-1-alkenes from 1-Alkynes via (E)-1-Alkenylborane Derivatives with Halogens[1,2]

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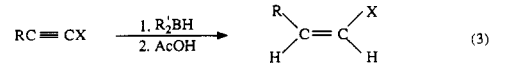
The reaction of (E)-1-alkenylborane derivatives with bromine under various conditions was investigated, and a simple stereospecific synthesis of (Z)-1-bromo-1-alkenes has been developed. Addition of bromine to (E)-1-alkenyldisiamylborane, derived from the reaction of 1-alkynes with bis(3-methyl-2-butyl)borane (Sia_2BH), gives either (Z)- or (E)-1-bromo-1-alkenes, depending upon the procedure used to eliminate the elements of disiamylboron bromide from the dibromide intermediate. Hydrolysis of dibromide yields the Z derivative, and thermal decomposition (in refluxing carbon tetrachloride) yields the E derivative. However, the yields and the isomeric purities are not completely satisfactory. (E)-Alkenylboronic acids, obtained via the hydroboration of 1-alkynes with catecholborane followed by hydrolysis, or the catechol esters of alkenylboronic acids add bromine readily at low temperatures to produce the intermediates which are converted by a base into (Z)-1-bromo-1-alkenes in 99% stereochemical purities and in almost quantitative yields. (E)-1-Alkenylboronic acids also add chlorine and with iodine (when in excess) to produce intermediates that upon treatment with a base provide (Z)-1-chloro- and (Z)-1-iodo-1-alkenes, respectively, in excellent stereochemical purities. In these reactions, the replacement of the boronic acid substituent by halogens proceeds with inversion of configuration. A simple procedure to prepare (Z)-1-iodo-1-alkenes via (Z)-1-alkenylboronic esters is also described. The reaction of (E)-1-alkenyldibromoborane–dimethyl sulfide complexes, readily prepared via the hydroboration of 1-alkynes with dibromoborane dimethyl sulfide ($BHBr_2{\cdot}SMe_2$), with bromine at low temperatures, followed by treatment with NaOH or water, produces (Z)-1-bromo-1-alkenes in >99% stereochemical purities and in quantitative yields, thus providing a convenient stereospecific synthesis of (Z)-1-bromo-1-alkenes from 1-alkynes. A plausible mechanism for these transformations has been discussed.

Hydroboration of alkenes and alkynes provides the corresponding organoboranes, which can be utilized for a variety of organic transformations.[4-6] Alkyl bromides[7] (eq 1) and alkyl iodides[8] (eq 2) are obtained by the action of

$$R_3B \xrightarrow[NaOMe]{Br_2} RBr \qquad (1)$$

$$R_3B \xrightarrow[NaOH]{I_2} RI \qquad (2)$$

organoboranes with bromine and iodine, respectively, under the influence of a base. In the preceding paper,[1] we reported a highly general and stereospecific synthesis of (Z)-1-halo-1-alkenes via hydroboration of 1-halo-1-alkynes with a dialkylborane followed by protonolysis (eq 3). We



(3)

X = Cl, Br and I

now report our investigations on the reaction of various (E)-alkenylborane derivatives with halogens under different conditions, thus providing a convenient synthesis of (Z)-1-halo-1-alkenes from 1-alkynes in >99% isomeric purity and in essentially quantitative yields.

Table I. Bromination and Solvolysis of 1-Hexenyldisiamylborane

1-hexenyldisiamylborane, mmol	bromination, medium	solvolysis medium	% yield of 1-Br-1-hexene[a] Z	E	total	Z:E ratio
40	none	EtOH	51	2	53	96:4
40	EtOH	EtOH	11	18	29	38:62
50	THF	water	17	tr	17	100:0
50	Et_2O	water	70	5	75	93:7
33	diglyme	EtOH	52	9	61	85:15
40	pentane	EtOH	54	13	67	81:19
50	CCl_4	water	64	3	67	96:4
50	CH_2Cl_2	water	65	3	68	96:4
50	CH_2Cl_2[b]	water	73	5	78	94:6

[a] Analysis by gas chromatography. [b] Disiamylborane added to 1-hexyne.

Results and Discussion

Bromination of (E)-1-Alkenyldisiamylborane Followed by Solvolysis. Disiamylborane[9] was first selected

(1) For Part 12 in this series, see: Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. *J. Org. Chem.*, preceding paper in this issue.

(2) For preliminary reports, see: (a) Brown, H. C.; Bowman, D. H.; Misumi, S.; Unni, M. K. *J. Am. Chem. Soc.* **1967**, *89*, 4531. (b) Brown, H. C.; Hamaoka, T.; Ravindran, N. *Ibid.* **1973**, *95*, 6456. (c) Brown, H. C.; Somayaji, V. *Synthesis* **1984**, 919.

(3) (a) Postdoctoral research associate (1980–1981) on Grant CHE 79-18881 and 6449 from the National Science Foundation. (b) Visiting scholar on funds provided by Fuji Photo Film Co., Ltd., Tokyo, Japan. (c) Postdoctoral research associate (1970–1972) on grants provided by G. D. Searle and Co., Chicago, IL, and the National Science Foundation (Grant 27742X). (d) Research assistant (1961–1963) on a project supported by the Ethyl Corporation at Purdue University. (e) Postdoctoral research associates (1963–1964) on Grant GM 10937 from the National Institutes of Health. (f) Postdoctoral research associate on Grant ARO DAAG 29-79-C-0027 from the U.S. Army Research Office. (g) Postdoctoral research associate on a National Science Foundation Grant CHE 8706102.

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

(5) Brown, H. C.; Zaidlewicz, M.; Negishi, E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1983; Vol. 7, pp 111–363.

(6) Pelter, A.; Smith, K. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, pp 687–940.

(7) Brown, H. C.; Lane, C. F. *Tetrahedron* **1988**, *44*, 2763.

(8) Brown, H. C.; Rathke, M. W.; Rogic, M. M.; De Lue, N. R. *Tetrahedron* **1988**, *44*, 2751.

(9) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834.

0022-3263/89/1954-6068$01.50/0

Table II. Vinyl Bromides from Acetylenes via (*E*)-1-Alkenyldisiamylborane

		solvolysis[a]		thermal decomposition[a]	
acetylene	product	yield, %	*Z*:*E*	yield, %	*Z*:*E*
1-pentyne	1-bromo-1-pentene	65	97:3	40	0:100
1-hexyne	1-bromo-1-hexene	67	95:5	75	12:88
1-heptyne	1-bromo-1-heptene	76	97:3	60	12:88
1-octyne	1-bromo-1-octene	68	98:2	50	6:94
phenylacetylene	β-bromostyrene	88	4:96	78	82:18
3-hexyne	3-bromo-3-hexene	14	43:57	11	100:0

[a] Yield and isomer distribution by GC analysis.

for the preparation of (*E*)-1-alkenylborane derivatives because this reagent hydroborates 1-alkynes cleanly to provide monohydroborated vinylboranes.

The rapid addition of 1-hexyne to disiamylborane at 0–2 °C in carbon tetrachloride or methylene chloride medium results in the formation of 1-hexenyldisiamylborane. Although disiamylborane is conveniently prepared by the addition of 2-methyl-2-butene to borane in tetrahydrofuran, the THF is replaced by CCl_4 or CH_2Cl_2 to provide a suitable medium for the subsequent bromination step.

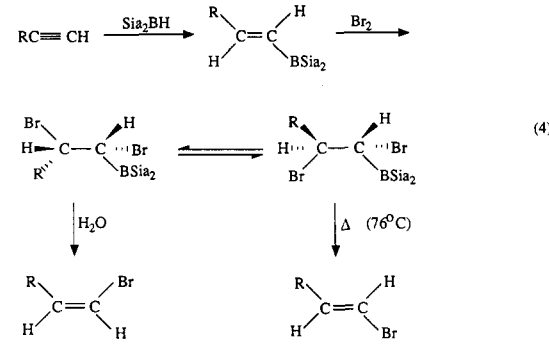
The bromination of the vinylborane was carried out by adding an equivalent amount of bromine in CCl_4 or other suitable solvent at 0 °C. The rate of addition of bromine is done as fast as it is decolorized and maintaining the temperature below 5 °C. The solvolysis of the dibromide is done with either ethanol or water at room temperature, and the progress of the solvolysis is easily followed by titrating the liberated hydrogen bromide with standard base by using phenolphthalein as indicator. The solvolysis is rapid (20 min) when alcohol is used but takes a longer period (~3 h) with water because of its insolubility in carbon tetrachloride medium. The results of varying the solvent during the bromination and solvolysis steps on the yields of (*Z*)- and (*E*)-1-bromo-1-hexenes are given in Table I.

It can be seen from Table I that very poor yields of (*Z*)-1-bromo-1-hexene are obtained when bromination is carried out in tetrahydrofuran or in the absence of a solvent. Also, poor yields resulted in an attempt to simplify the process by carrying out the bromination and solvolysis simultaneously in ethanol medium. However, in other solvents like ether, diglyme, pentane, carbon tetrachloride, or methylene chloride, a good yield (61–78%) of 1-bromo-1-hexene is obtained.

The solvolyzing agent has little effect on the yield or isomer distribution of the product. The use of water for hydrolysis of the dibromide, although it increases slightly the reaction time, has the advantage that at the end of the reaction the aqueous layer may be separated and the product isolated by a simple distillation.

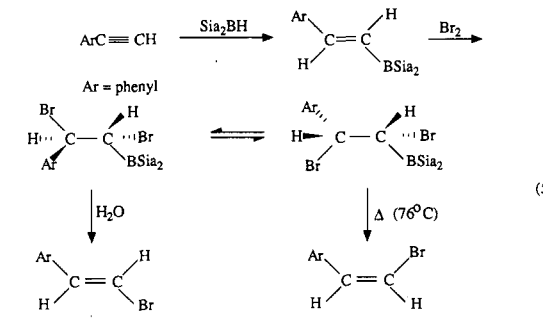
The reaction was extended to several terminal acetylenes, and a 65–75% yield of (*Z*)-1-bromo-1-alkene was realized in most cases; a 2–5% impurity of the *E* isomer was detected in all of the samples (Table II).

However, when this procedure was extended to phenylacetylene, we were surprised to note that in this case solvolysis of the intermediate yielded (*E*)-bromostyrene, the precise opposite of the geometrical isomer formed with 1-alkynes. The observation was checked repeatedly. We have not attempted to investigate the precise cause of this inversion of the geometrical isomer produced. The results may be rationalized as follows. Since the reaction of bromine presumably proceeds through the usual bromonium ion mechanism to give anti addition to the double bond, solvolysis must involve an anti elimination[10] to produce (*Z*)-1-bromo-1-alkene (eq 4).



(4)

However, it is possible that addition of bromine to phenyl-substituted vinylborane results in a syn addition rather than the usual anti (eq 5). Such a change has been observed previously in additions of chlorine, where the electron-deficient intermediate involves a benzylic center.[11]



(5)

Thermal Elimination. The action of heat on the dibromide produced the *E* isomer, presumably through syn elimination (eq 4). Heating at 200 °C was initially tried, but the reaction is found to proceed to near completion in refluxing carbon tetrachloride in 4 h. Several terminal and internal alkynes were subjected to the above sequence of reactions, and the results are presented in Table II.

Again, as in the solvolysis experiment, the formation of the product having the opposite configuration by thermal elimination of the dibromide was noticed in the case of phenylacetylene, where essentially (*Z*)-bromostyrene was formed (eq 5).

Table II indicated that the yields and stereochemical purities were not completely satisfactory. Therefore, we examined the utility of (*E*)-alkenylboronic acids for this purpose.

Bromination of (*E*)-Alkenylboronic Acids or Their Catechol Esters Followed by Treatment with Base. Catecholborane[12] hydroborates 1-alkynes to produce the catechol esters of (*E*)-1-alkenylboronic acids, and hydrolysis affords the corresponding acids. It was established[13] that the iodination of (*E*)-1-alkenylboronic acids in the presence of base provides the corresponding (*E*)-1-iodo-1-alkenes. We undertook to synthesize the corresponding bromide by a similar procedure utilizing bromine. However, the results proved unsatisfactory. For example, the addition of bromine to a solution of (*E*)-1-octenylboronic acid in the presence of aqueous sodium hydroxide at 0 °C provided a 65:35 mixture of (*Z*)- and (*E*)-1-bromo-1-octene in a yield of ~50%.[14] However, when the

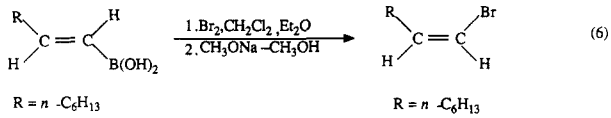
(10) Matteson, D. S.; Liedtke, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 1526.
(11) (a) Cristol, S. J.; Stermitz, F. R.; Ramey, P. S. *J. Am. Chem. Soc.* **1956**, *78*, 4939. (b) Buckles, R. E.; Knaak, D. F. *J. Org. Chem.* **1960**, *25*, 20.
(12) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370; **1975**, *97*, 5249.
(13) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.

Table III. Stereospecific Conversion of Alkynes to Alkenyl Bromides via (*E*)-Alkenylboronic Acids and Their Catechol Esters

alkyne	temp,[b] °C	temp,[b] °C	base used	stereochemical purity[c]	alkenyl bromide[c] yield, %
1-octyne	boronic acid (90)	−20	MeONa-MeOH	99% *Z*	94,[d] 85[e]
	catechol ester (90)	0	aq NaOH	99% *Z*	100,[d] 90[e]
cyclohexylethyne	boronic acid (93)	−40	MeONa-MeOH	99% *Z*	(91,[d] 82[e])
	catechol ester (93)	−40	MeONa-MeOH	99% *Z*	95,[d] 88[e]
phenylethyne	catechol ester	−40	MeONa-MeOH	99% *Z*	90[e]
3-hexyne	catechol ester (92)	−20	MeONa-MeOH	99% *Z*	92,[d] 85[e]
4,4-dimethyl-2-pentyne	catechol ester (97)	−20	MeONa-MeOH	98% *Z*	99,[d] 96[e]

[a] See ref 12. [b] At higher temperatures the stereochemical purity of the products is lower. [c] The alkenyl bromides were identified and characterized by GC, IR, NMR, and mass spectrometry. The stereochemistry of the internal alkenyl bromides was determined by preparation of the lithio derivatives,[29,33] followed by protonolysis and the identification of the resulting alkenes by GC. [d] Based on the intermediate boronic acid or its ester. [e] Based on the alkyne. The yields by isolation are given in parentheses.

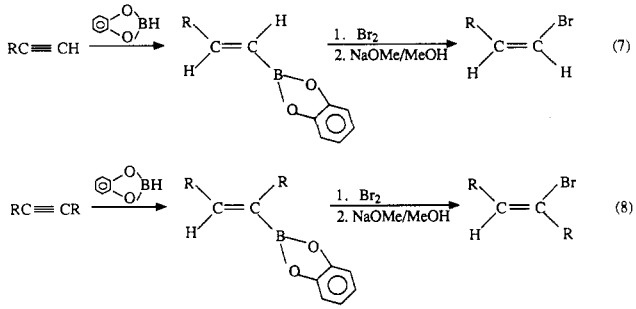
bromine was added first to the boronic acid, followed by a base, an essentially quantitative yield of the isomerically pure (*Z*)-1-bromo-1-octene[15] was obtained (eq 6).



(6)

The observation that the replacement of the boronic acid group by bromine proceeds with inversion of configuration whereas replacement by iodine[32] proceeds with retention of configuration was of major interest and stimulated a detailed study. The reaction appears to be general. Thus, *trans*-(2-cyclohexylethenyl)boronic acid also undergoes substitution with inversion (eq 6).

The catechol esters of (*E*)-1-alkenyl- and internal (*Z*)-alkenylboronic acids are conveniently prepared by the hydroboration of the corresponding alkynes with catecholborane.[12] There would be an obvious advantage in utilizing these catechol esters directly. Use of 1 mol equiv of bromine resulted in a low yield. Evidently the catechol moiety was reacting competitively with the bromine. However, use of 2 mol equiv of bromine solved this problem. Consequently, treatment of the catechol esters of the alkenylboronic acids with 2 mol equiv of bromine in methylene chloride, followed by treatment with base, provided a simple, practical procedure for the conversion of both terminal and internal alkynes into stereochemically pure vinyl bromides (eq 7 and 8). Representative results are summarized in Table III.



(7)

(8)

Thermolysis of the Dibromide Intermediate. Here also we studied the thermolysis of the borane, obtained after the addition of bromine to the (*E*)-1-alkenylboronic acids or catechol esters (Table IV). From Table IV, it was clear that (*Z*)-bromostyrene was obtained cleanly. But cyclohexenyl bromide was obtained as a mixture of *Z* and *E* isomers, indicating that thermolysis is not a general reaction. However, the possibility of obtaining 100% (*E*)-1-bromo-1-alkenes via thermal deboronobromination of dibromide derivative in a more systematic study is not ruled out.

Table IV. Bromination of (*E*)-1-Alkenylboronic Acids and the Corresponding Catechol Esters Followed by Thermolysis

alkyne	reacted derivative	temp, °C	time, h	*E* isomer,[a] % yield	*Z* isomer,[a] % yield
cyclohexylethyne	acid	25	24	38	17
cyclohexylethyne	ester	150	3	76	19
cyclohexylethyne	acid	76	18	43	57
phenylethyne	ester	100	1	87	9
phenylethyne	acid	35	1	100	0

[a] GC yields of 1-bromo-1-alkenes.

It is puzzling to note that phenylacetylene in the case of catecholborane gives (*Z*)-bromostyrene when the corresponding vinylborane was treated with bromine followed by base solvolysis and gives *E* derivative on the thermolysis of the dibromide intermediate while analogous reactions using disiamylborane provide opposite isomers. We did not attempt to look into the precise mechanism operating in both cases. However, this striking difference might be attributed to either difference in the mode of bromine addition (syn or anti) to the vinylborane or to the difference in the deboronobromination process (syn or anti) because the borane species involved are different.

Iodination of (*E*)-1-Alkenylboronic Acids or Their Catechol Esters Followed by Treatment with Base. The catechol esters of (*E*)-1-alkenyl- and (*Z*)-internal alkenylboronic acids are conveniently prepared by the hydroboration of the corresponding alkynes with catecholborane.[12] 1-Octyne was selected as representative alkyne, considering the availability of physical data of (*E*)-1-iodo-1-octene[13] and (*E*)-octenylmercurials[16] which were prepared in this laboratory. Preliminary study of the reaction of (*E*)-1-octenylboronic acid catechol ester with iodine indicated that excess iodine is necessary, as described in the literature.[17] However, even the use of 3 equiv of iodine to the ester proved unsatisfactory, giving a mixture of (*Z*)- and (*E*)-1-iodo-1-octenes [*E*/*Z* (75/25)] in a yield of approximately 70%, by stirring 12 h at 0 °C (eq 9).

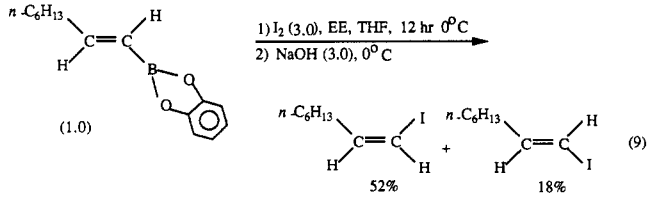
The use of interhalogens, IBr and ICl, proved unsatisfactory. A solution of interhalogens in carbon tetrachloride or other organic solvent was added to the catechol ester,

(14) Another product, more volatile than the bromides, was noted in the gas chromatogram. The reaction mixture revealed strong carbonyl group absorption in the IR spectrum. Possibly octanal is formed via oxidation of the vinylboronic acid by hypobromite (from bromine and the base).

(15) Hydroalumination–bromination of alkynes gives vinyl bromides of opposite stereochemistry. See: Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

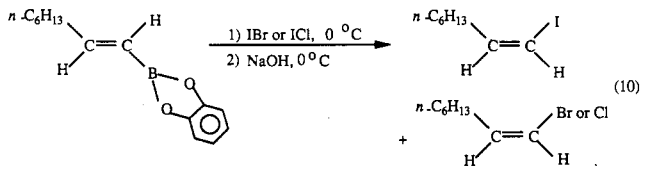
(16) Brown, H. C.; Gupta, S. K.; Larock, R. C. *J. Am. Chem. Soc.* **1972**, *96*, 4371.

(17) Caughley, F. G.; Robertson, P. W. *J. Am. Chem. Soc.* **1933**, 1323.



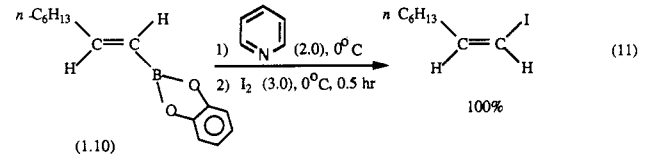
(9)

followed by treatment with base, giving a mixture of (*Z*)-1-iodo-1-octene and (*Z*)-1-bromo-1-octene, or chloride, depending on the interhalogens used (eq 10). The results are shown in Table V.



(10)

While investigating the effect of base on the formation of (*E*)-1-iodo-1-alkenes from corresponding catechol ester, we observed by chance that the catechol ester of (*E*)-1-octenylboronic acid added iodine in the presence of pyridine to give stereochemically pure (*Z*)-1-iodo-1-octene quantitatively (eq 11).

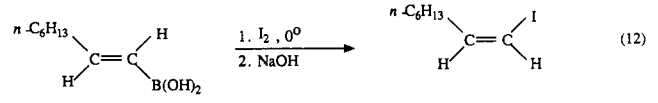


(11)

A series of catechol esters of (*E*)-1-alkenylboronic acids were treated with pyridine and iodine in a manner identical with that of (*E*)-1-octenylboronic acid catechol ester. The results were very interesting, as summarized in Table VI.

These catechol esters were distinctly classified into two groups—one giving only (*Z*)-1-iodo-1-alkenes and the other giving (*E*)-1-iodo-1-alkenes. It is well-known that catechol esters of alkenylboronic acids form the adduct with pyridine.[12] Then the reaction species might be the adduct with pyridine.

We investigated the reaction of (*E*)-1-alkenylboronic acids with iodine. It is said that *vic*-diiodo compounds are not so stable,[18] and an equilibrium between diiodo compounds and iodine is present.[17] We examined the reaction conditions, checking the solvent and the iodine amount, under which elemental iodine was added to a solution of (*E*)-1-octenylboronic acid in a given solvent, followed by treatment with base (eq 12). The best yield of (*Z*)-1-iodo-1-octene was realized in tetrahydrofuran with excess iodine. Table VII summarizes these experimental data.



(12)

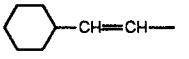
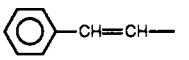
Considering the extraction procedure with ether, we adopted the conditions under which 200% excess of iodine was added to a solution of the acid in ether and THF at 0 °C. A series of (*E*)-1-alkenylboronic acids was treated in the manner mentioned above. The results are summarized in Table VIII.

Both (*E*)-3,3-dimethyl-1-butenylboronic acid and (*E*)-2-phenylboronic acid provided (*E*)-1-iodo-1-alkenes without treatment with base, respectively. (*E*)-(2-cyclohexylethenyl)boronic acid gave a mixture of (*E*)- and (*Z*)-1-iodo-1-alkenes.

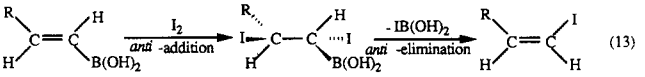
Table V. Preparation of (*Z*)-1-Iodo-1-octene by the Reaction of Catechol Ester of [*E*]-1-Octenylboronic Acid with Interhalogens

interhalogen	ratio (interhalogen/ester)	solvent	yield, of *Z* iodide, %
ICl	2.0	EE	20
ICl	2.0	CCl_4	19
ICl	2.0	CH_3CN	17
IBr	2.0	CH_2Cl_2	60
IBr	2.0	CH_3CN	76

Table VI. Reaction of Catechol Esters of (*E*)-1-Alkenylboronic Acids with Iodine in the Presence of Pyridine

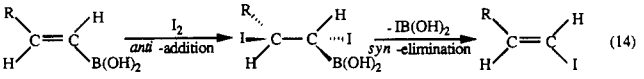
alkenyl moiety	pyridine/ester	iodine/ester	*Z* iodide, %	*E* iodide, %
n-C_4H_9CH=CH—	2.0	3.0	100	0
n-$C_6H_{13}CH$=CH—	2.0	3.0	100	0
$Cl(CH_2)_3CH$=CH—	2.0	3.0	100	0
	2.0	3.0	0	100
t-C_4H_9CH=CH—	2.0	3.0	0	100
	2.0	3.0	0	100

The iodination of (*E*)-1-alkenylboronic acids in the presence of base resulted in the formation of stereochemically pure (*Z*)-1-iodo-1-alkene, a mixture of (*Z*)- and (*E*)-1-iodo-1-alkenes or stereochemically pure (*E*)-1-iodo-1-alkene, depending on the substituents at the β-carbon to the boronic acid moiety (Table VIII). The *Z* isomer might arise by an anti addition of iodine followed by anti deboronoiodination[2a] as shown in eq 13. The formation



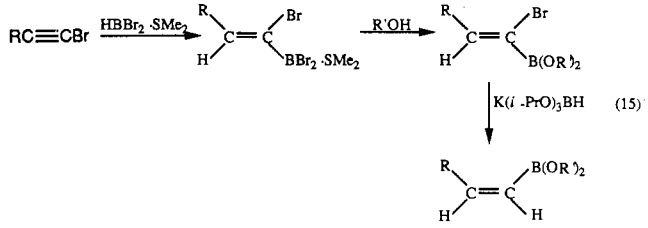
(13)

of the *E* isomer might be rationalized by an anti addition of iodine followed by syn elimination[2a] (deboronoiodination) as shown in eq 14.



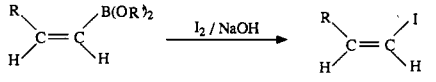
(14)

Base-Induced Iodination of (*Z*)-1-Alkenylboronic Esters. We recently reported the synthesis of pure (*Z*)-1-alkenylboronic esters from 1-bromo-1-alkynes[19] (eq 15). These (*Z*)-1-alkenylboronic esters reacted with iodine



(15)

in the presence of a base at 0 °C, giving the corresponding (*Z*)-1-iodo-1-alkenes (eq 16). A representative selection



(16)

of (*Z*)-1-iodo-1-alkenes was prepared by utilizing the above reaction sequence (Table IX). It is evident from Table

(18) (a) Skell, P. S.; Pavlis, R. R. *J. Am. Chem. Soc.* **1964**, *86*, 2956. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Part, CA, 1972; p 423.

(19) Brown, H. C.; Imai, T. *Organometallics* **1984**, *3*, 1392.

Table VII. Reaction of (*E*)-1-Octenylboronic Acid with Iodine Followed by Treatment with Sodium Hydroxide at 0 °C

solvent	acid, mol/L	I_2/acid	(*Z*)-1-octenyl iodide, % t^b = 0.5	t^b = 1.0	t^b = 3.0	t^b = 6.0	t^b = 120	t^b = 240
EE–THF[a]	1.0	1.2	45	50	59	65	69	70
THF	1.0	2.0	66	73	81	85	90	93
CH_3CN	1.0	2.0	65	73	81	85	90	92
EE–THF[a]	1.0	2.0	66	73	81	85	90	92
EE–THF[a]	1.0	3.0	86	90	96	>99		
THF	1.0	3.0	87	91	96	>99		
EE–THF[a]	1.0	4.0	90	94	>99			
THF	1.0	4.0	90	94	>99			
EE	0.2	5.0	75	86	91	96	>99	
THF	1.0	5.0	>99					

[a] EE and THF (1:1). [b] Time in hours.

Table VIII. Reaction of (*E*)-1-Alkenylboronic Acids with 3 Equiv of Iodine Followed by Treatment with Base

alkyne	*Z* iodide yield, %	*E* iodide yield, %
1-hexyne	>99	
1-octyne	>99	
5-chloro-1-pentyne	>99	
cyclohexylethyne	25	75
3,3-dimethyl-1-butyne	0	100
phenylethyne	0	100

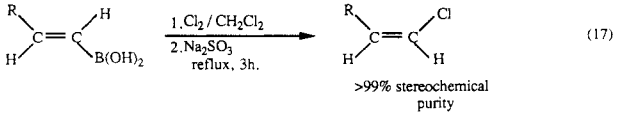
Table IX. Synthesis of (*Z*)-1-Iodo-1-alkenes: RCH=CHI

R[a]	bp,[a] °C/Hgmm	n^{25}_D	isolated yield,[b] %	isomeric purity,[c] %	M^+
n-C_4H_9	60–61/10[34]	1.5021	80	98	210
n-C_6H_{13}	48–50/0.3[35]	1.5002	82	98	238
c-C_6H_{11}	52–53/0.3[36]	1.4991	81	99	236
$(CH_3)C$	48–50/20[37]	1.5008	83	100	210
$Cl(CH_2)_3$[d]	64–65/0.5	1.5031	78	96	230

[a] Values agree with the literature values. [b] All of the reactions were carried out on a 25-mmol scale, and the yields are based on the starting (*Z*)-1-alkenylboronic esters. [c] Stereochemical purities were determined by GC analysis. [d] This compound appears to be new in the literature, and the ^1H NMR spectrum is given in the supplementary material.

IX that in these reactions not only are the yields high but also stereochemical purities are excellent. 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. It is also evident that these reactions are general as they worked equally well irrespective of the R group in (*Z*)-$RCH{=}CHB(OR')_2$.

Chlorination of (*E*)-1-Alkenylboronic Acids. Recently, Kabalka and co-workers developed a simple procedure for preparing stereochemically pure (*Z*)-1-chloro-1-alkenes based on (*E*)-1-alkenylboronic acids[20] (eq 17).



(17)

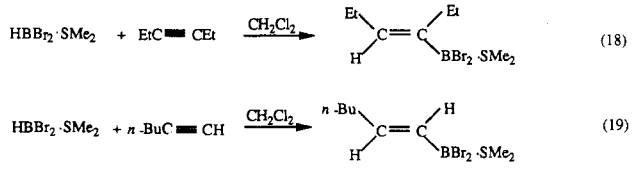
In a typical experiment, (*E*)-1-octenylboronic acid[12] in methylene chloride was reacted with chlorine in the dark at 0 °C. After refluxing with an aqueous solution of sodium sulfite, (*Z*)-1-chloro-1-octene was obtained in 78% yield and >99% stereochemical purity. We also have studied the application of dibromoborane–methyl sulfide complex ($BHBr_2{\cdot}SMe_2$), a new valuable hydroborating agent for the preparation of (*Z*)-1-bromo-1-alkenes.

Table X. Stereospecific Conversion of 1-Alkynes to (*Z*)-1-Bromo-1-alkenes via (*E*)-1-Alkenyldibromoborane–Dimethyl Sulfide Complexes

alkyne	product	isomeric purity	yield,[a] %
1-hexyne	1-bromo-1-hexene[31]	98% *Z*	93 (74)
1-heptyne	1-bromo-1-heptene[38]	99% *Z*	95 (84)
1-octyne	1-bromo-1-octene[34]	97% *Z*	92 (87)
cyclohexylethyne	1-bromo-2-cyclohexylethylene[26]	97% *Z*	92 (85)
5-chloro-1-pentyne	1-bromo-5-chloro-1-pentene[39]	99% *Z*	89 (85)[b]

[a] GC yields. The yields by isolation are given in parentheses. [b] Contains 9% of an unknown impurity.

Bromination of (*E*)-1-Alkenyldibromoborane–Methyl Sulfide Followed by Treatment with Base. Dibromoborane–methyl sulfide complex[21] ($BHBr_2{\cdot}SMe_2$) cleanly undergoes monohydroboration of both internal and terminal alkynes to afford alkenylboranes as their dimethyl sulfide adducts[22] (eq 18 and 19). These alkenyldibromoborane–dimethyl sulfide complexes undergo many of the characteristic reactions of alkenylboranes[4,5] with or without prior isolation.



The use of (*E*)-1-alkenyldibromoborane–dimethyl sulfide complexes without prior isolation in the bromination reaction looked quite attractive. Accordingly, the bromination and solvolysis of (*E*)-1-alkenyldibromoborane–dimethyl sulfide complexes were undertaken.

1-Hexyne was hydroborated with $HBBr_2{\cdot}SMe_2$ in CH_2Cl_2 as described previously.[22] Without purification, the complex was treated at −12 °C with 1 equiv of bromine in CH_2Cl_2 and aqueous NaOH or water. Gas chromatographic (GC) examination of the organic layer revealed the almost quantitative formation of (*Z*)-1-bromo-1-hexene. The reaction was extended to other (*E*)-1-alkenyldibromoborane–dimethyl sulfide complexes. All underwent the reaction in the same manner (eq 20). The results are summarized in Table X.

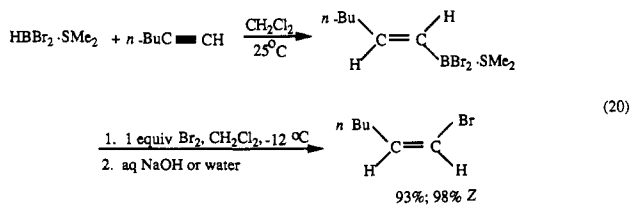
The corresponding reaction of internal alkenyldibromoborane–dimethyl sulfide complexes with bromine and base did not give clean products.

Mechanism of the Bromination Reaction. Matteson and Liedtke have established the stereospecific anti ad-

(20) Kunda, S. A.; Smith, T. L.; Hylarides, M. D.; Kabalka, G. W. *Tetrahedron Lett.* **1985**, *26*, 279.

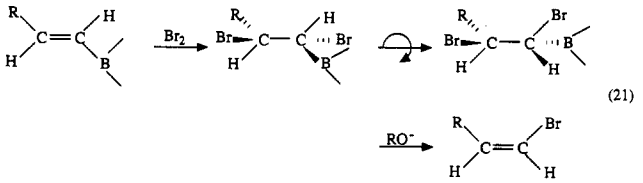
(21) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384.

(22) Brown, H. C.; Campbell, J. B., Jr. *J. Org. Chem.* **1980**, *45*, 389.



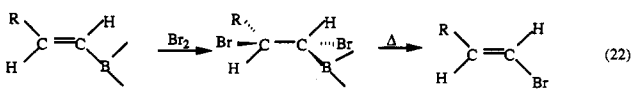
(20)

dition of bromine to the double bond of vinyl borate derivatives, followed by the stereospecific anti elimination (deboronobromination) under solvolytic conditions.[10] Consequently, it appears most reasonable to account for the inversion of configuration in the present reaction in terms of the usual anti addition of bromine to the double bond,[23] followed by a base-induced anti elimination of boron and bromine to give the product (eq 21).



(21)

As for the formation of (*E*)-1-bromo-1-alkenes, it is rationalized by the usual trans addition of bromine to the double bond, followed by a thermal syn elimination of boron and bromine to yield the products (eq 22).



(22)

(*Z*)-1-Halo-1-alkenes can also be obtained via hydroboration–protonolysis of 1-halo-1-alkynes.[1,24] Earlier methods for the preparation of these compounds involve the use of vinylsilanes[25,26] and alkynes.[27] The present studies, however, offer a simple one-pot process providing a stereospecific synthesis of (*Z*)-1-halo-1-alkenes in essentially quantitative yields.

Alkenyl bromides are readily converted into vinyl Grignard[28] and lithium[29] derivatives with retention of stereochemistry. Alkenyl bromides are finding important applications in the synthesis of insect pheromones.[30,31] The present studies offer a simple convenient method for the preparation of these valuable derivatives, thus demonstrating the synthetic utility of organoboranes. We have also achieved a general stereospecific synthesis of (*E*)-1-halo-1-alkenes utilizing either (*E*)- or (*Z*)-1-alkenylboronic acids or esters, and the results are discussed in the following paper.[32]

Experimental Section

Materials. All transformations of boron reagents were conducted under a nitrogen atmosphere by using extensively the techniques outlined in Chapter 9 of ref 4. A stock solution of borane in THF was prepared and stored in a cold room at 0 °C and standardized prior to use. Catechol esters of alkenylboronic acids were synthesized via the hydroboration of alkynes with catecholborane,[12] distilled under reduced pressure, and kept in the atmosphere of nitrogen. (*E*)-1-Alkenylboronic acids were prepared by the hydrolysis of these esters and recrystallized from water. (*Z*)-1-Alkenylboronic acids were prepared by the using literature procedure.[19] Dibromoborane–dimethyl sulfide was prepared from BBr_3 and borane–dimethyl sulfide (Aldrich) as described previously.[21] Alkynes used were commercial samples from Chemical Samples Co. and used without purification. Diglyme and tetrahydrofuran were used after distillation from lithium aluminum hydride. Diethyl ether was analytical reagent grade commercial product from Mallinckrodt and stored with 5-Å molecular sieves under nitrogen. Methyl alcohol was spectrometric grade solvent from Mallinckrodt. Sodium methoxide (3 M) solution in methanol was prepared by adding sodium to absolute methanol in the nitrogen atmosphere, standardized with hydrochloric acid by using phenolphthalein as indicator, and stored under nitrogen. Bromine was obtained from Fischer Scientific Co. Carbon tetrachloride and methylene chloride were freshly distilled from P_2O_5. 2-Methyl-2-butene (99% Phillips Pure Grade) was kept over calcium hydride and used without further purification.

Gas Chromatographic Analysis. GC analyses were carried out on a Hewlett-Packard gas chromatograph equipped with a thermal conductivity detector. The following columns were used: 20% tricresyl phosphate (TCP) on firebrick, 12 ft × 0.125 in. steel column, isothermally at 100 °C; 10% trixylyl phosphate (TXP) on 60–80 mesh, 12 ft × 0.125 in. steel column, isothermally at 150 °C. The 1-halo-1-alkenes were identified by comparison with authentic samples and by IR, ^1H NMR, and mass spectral data.

Spectral Analysis. ^1H NMR spectra (δ, relative to Me_4Si) were recorded on a Varian T-60 spectrometer. Both ^{13}C (δ, relative to Me_4Si) and ^{11}B (δ, relative to BF_3·OEt_2) spectra were recorded on a Varian FT-80A spectrometer equipped with a broad-band probe and a Hewlett-Packard 3335A frequency synthesizer. IR spectra were taken on a Perkin-Elmer 137B spectrometer.

(*Z*)-1-Bromo-1-alkenes: General Procedure via (*E*)-1-Alkenyldisiamylborane. A 100-mL, three-necked flask fitted with a reflux condenser, a thermometer, a rubber septum, and a pressure-equalized addition funnel was flushed with nitrogen. Disiamylborane (50 mmol) in tetrahydrofuran was prepared as previously described,[10] and the solvent was then removed under vacuum. Carbon tetrachloride (30 mL) was added to dissolve the reactant, and 50 mmol of the acetylene was added at a rate such that the temperature did not rise above 5 °C. Then a solution of 52.5 mmol of bromine in 30 mL of carbon tetrachloride was added, maintaining the temperature at 0–5 °C. The product underwent hydrolysis practically instantaneously upon the addition of 2 M sodium hydroxide. The carbon tetrachloride solution was separated, dried, and analyzed by GC, using a tricresyl phosphate column, with comparisons using authentic samples. Thus, 1-hexyne (4.11 g, 50 mmol) provided 5.17 g (64%) of (*Z*)-1-bromo-1-hexene, bp 42–43 °C/19 mmHg, n^{20}_D 1.4590. GC analysis indicated 96% isomeric purity (*Z*:*E* = 96:4).

(*E*)-1-Bromo-1-alkenes via Thermolysis: General Procedure via (*E*)-1-Alkenyldisiamylborane. In the thermal decomposition procedure, the carbon tetrachloride solution of the dibromide was refluxed for 6 h under nitrogen. Thus, (*E*)-1-bromo-1-hexene (4.3 g, 53%), bp 45–46 °C/20 mmHg, n^{20}_D 1.4615, was obtained from 1-hexyne (4.11 g, 50 mmol). GC indicated 86% isomeric purity (*Z*:*E* = 14:86).

(23) Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Holt, Rinehart & Winston: New York, 1959; pp 150, 523. Winstein, S. *J. Am. Chem. Soc.* **1942**, *64*, 2792. Barton, D. H. R.; Miller, E. *J. Am. Chem. Soc.* **1950**, *72*, 1066. Eliel, E. L.; Haber, R. G. *J. Org. Chem.* **1959**, *24*, 143.
(24) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086.
(25) Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, 543.
(26) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424.
(27) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.
(28) Normant, H. *Adv. Org. Chem.* **1960**, *2*, 1.
(29) Dreiding, A. S.; Pratt, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 1902.
(30) Rossi, R.; Carpita, A.; Quirici, M. G. *Tetrahedron* **1981**, *37*, 2617.
(31) Rossi, R.; Carpita, A.; Quirici, M. G.; Gaudenzi, L. *Tetrahedron* **1982**, *38*, 631.
(32) Brown, H. C.; Hamaoka, T.; Ravindran, N.; Subrahmanyam, C.; Somayaji, V.; Bhat, N. G. *J. Org. Chem.*, following paper in this issue.
(33) Curtin, D. Y.; Crump, J. W. *J. Am. Chem. Soc.* **1958**, *80*, 1922.
(34) On, H. P.; Lewis, W.; Zweifel, G. *Synthesis* **1981**, 999.
(35) Hudrlik, P. F.; Kulkarni, A. K.; Jain, S.; Hudrlik, A. M. *Tetrahedron* **1983**, *39*, 877.
(36) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1978**, *8*, 291.
(37) Westmeijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas.* **1977**, *96*, 168.
(38) Bloch, R.; Benecou, C.; Guibe-Jampel, E. *Tetrahedron Lett.* **1985**, *26*, 1301.
(39) Kabalka, G. W.; Sastry, K. A. R.; Knapp, F. F.; Srivastava, P. C. *Synth. Commun.* **1983**, *13*, 1027.

(Z)-1-Bromo-1-octene from (E)-1-Octenylboronic Acid. In a 100-mL flask were placed 20 mmol of (E)-1-octenylboronic acid[12] and 50 mL of absolute diethyl ether. The mixture was cooled to −20 °C in dry ice–carbon tetrachloride. Then, 20 mL of 1.0 M bromine solution in dichloromethane was added over 10 min at −20 °C. After this stirred for 15 min, 15 mL of 3.0 M sodium methoxide in methanol was added. The mixture was stirred 30 min at −20 °C and then brought up to room temperature. The product was extracted with 200 mL of dichloromethane and 100 mL of water saturated with sodium chloride. The organic layer was separated. The water phase was extracted twice, each with 100 mL of dichloromethane. The combined extracts were dried over anhydrous magnesium sulfate. After removal of the solvent, (Z)-1-bromo-1-octene was obtained by distillation at 90–91 °C/35 mmHg, yield 3.1 g (81%). The product was identified and characterized by infrared absorption at 700 cm^{-1} free from 960 cm^{-1} (E isomer); ^1H NMR ($CDCl_3$) δ 6.5–5.8 (m, 2 H), 2.9–1.8 (m, 2 H), 1.8–0.8 (m, 11 H); mass spectrum, M^+ m/e 190, 192.

(Z)-1-Bromo-1-octene from (E)-1-Octenylboronic Acid Catechol Ester. In a 500-mL flask equipped with a stopper, a joint having a stopcock, and magnetic stirrer were placed 11.0 g (100 mmol) of 1-octyne and 12 g (100 mmol) of catecholborane.[12] The mixture was heated for 2 h at 70 °C with stopcock closed. The reaction mixture was cooled to room temperature and with stopcock open diluted with 25 mL of methylene chloride. To this solution, 32 g of bromine in 40 mL of methylene chloride was added dropwise at 0 °C, and then 100 mL of 2.0 N sodium hydroxide solution in water was added and stirred for 1 h. The product was extracted with three portions, (44, 200, and 100 mL) of methylene chloride. The extracts were combined, washed with water saturated with sodium chloride, and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporator under reduced pressure. The residue was distilled to give 16.0 g (84%) of (Z)-1-bromo-1-octene, bp 90–91 °C/35 mmHg, n^{20}_D 1.4619. The stereochemical purity determined by gas chromatographic analysis is greater than 99%.

All other compounds were prepared in the same manner. GC yields were determined by using a suitable internal standard—for example, n-nonane was used for 1-octyne derivative on a 5-mmol scale reaction.

General Thermal Deboronobromination of Dibromide Intermediate Obtained via (E)-Alkenylboronic Acids or Catechol Esters. Thermal deboronobromination was carried out as follows. After the addition of bromine solution in dichloromethane or carbon tetrachloride to the vinylboronic acids or the catechol ester at 25 °C, the solvent was pumped off, and then the residue was heated under nitrogen as mentioned in Table IV.

(Z)-1-Iodo-1-octene. 1-Octyne (50 mmol) and catecholborane (50 mmol) were stirred in a 150 mL flask for 2 h under nitrogen at 70 °C. The mixture was cooled to room temperature and stirred with 50 mL of water for 2 h at 25 °C to effect the hydrolysis of the ester. The resulting white solid, (E)-1-octenylboronic acid, was collected by filtration and washed free of the catechol with ice cold water. The boronic acid was then dissolved in 50 mL of ether and tetrahydrofuran mixture (1:1) in a 500-mL flask and cooled to 0 °C. Elemental iodine (135 mmol) was added and stirred for 6 h at 0 °C. Then sodium thiosulfate solution in water was added until iodine color disappeared. From the product was extracted three portions of ether (200 × 3 mL), washed with water, saturated with sodium chloride and dried over anhydrous magnesium sulfate. After removal of solvent, the residue was distilled to give 36.5 mmol of (Z)-1-octenyl iodide (73%), bp 44–46 °C/0.2 mmHg.

The product was characterized: IR (neat) ν 1620, 690 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.30–6.18 (m, 2 H), 2.30–1.80 (m, 2 H), 1.60–1.20 (m, 8 H), 1.20–0.80 (m, 3 H); mass spectrum, M^+ m/e 238.

(Z)-5-Chloro-1-iodo-1-pentene. (E)-5-Chloro-1-pentenylboronic acid (5 mmol) in 5 mL of mixed solution of ether and tetrahydrofuran was cooled to 0 °C. Elemental iodine (15 mmol) was added. The reaction mixture was stirred 6 h at 0 °C. Aqueous sodium thiosulfate solution was added until the iodine color disappeared. The product was extracted with three portions of ether (50 mL × 3) and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was distilled under reduced pressure to give 0.920 g (80%) of (Z)-5-chloro-1-iodo-1-pentene, bp 63–65 °C/0.4 mmHg.

The product was characterized: IR (neat) ν 1605, 700 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.40–6.0 (2 H, m), 3.6 (2 H, t), 2.5–1.7 (4 H, m); mass spectrum, M^+ m/e 230, 232.

(Z)-2-Cyclohexyl-1-iodo-1-ethene. (E)-2-Cyclohexyl-1-ethyleneboronic acid (15 mmol) in 15 mL of ether and tetrahydrofuran mixed solution (1:1) was cooled to 0 °C. After addition of 45 mmol of elemental iodine, the mixture was stirred 6 h at 0 °C. Aqueous sodium thiosulfate solution was added until iodine color disappeared completely. The product was extracted with n-pentane and dried over anhydrous magnesium sulfate. After removal of the solvent, (Z)-2-cyclohexyl-1-iodo-1-ethene was isolated by preparative gas chromatography, F and M Model 300, using 20% SE-30 column. The product was characterized: IR (neat) ν 1610, 690 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ 6.2–5.8 (m, 2 H), 2.5–2.2 (m, 1 H), 2.0–1.0 (m, 10 H); mass spectrum, M^+ m/e 236.

Preparation of (Z)-1-Iodo-1-alkenes. (Z)-1-Alkenylboronic esters were prepared as described in literature. For the preparation of vinyl iodides, it was not necessary to isolate these esters since the byproduct, triisopropoxyborane, did not interfere with the reactions. Thus, the preparation of (Z)-1-iodo-1-octene is representative. Dimethyl (Z)-1-octenylboronate (25 mmol) in ether (25 mL) was added to a 100-mL round-bottom flask equipped with a stirring bar, septum inlet, and a stopcock-controlled outlet. With the flask cooled in an ice–water bath and the contents stirred, an ethereal solution of potassium triisopropoxyborohydride (25 mmol) was added over 5 min. After an additional 5 min the cold bath was removed and the sitrring continued for 0.5 h at room temperature. At this stage ^{11}B NMR indicated the complete conversion to the Z ester. The solid potassium bromide precipitated was removed by centrifugation. The centrifugate was cooled to 0 °C, and sodium hydroxide (25 mL, 3 N) was added to it. After a few minutes, a solution of iodine (30 mmol) in ether (~40 mL) was added to the reaction flask. After stirring for 1 h, the excess iodine was destroyed with a solution of sodium thiosulfate. The ether layer was separated, washed with brine, and dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The product, on distillation, gave pure (Z)-1-iodo-1-octene in 80% yield, bp 48–50 °C/0.2 mmHg. The results are given in Table IX.

(E)-1-Bromo-2-phenyl-1-ethene. (E)-2-Phenyl-1-ethenylboronic acid (10 mmol) and dichloromethane (50 mL) were placed in a 100-mL flask under nitrogen. Bromine (10 mmol, 10 mL of 1.0 M in CH_2Cl_2) was added at 25 °C. The reaction mixture was stirred 1 h at that temperature. The product was extracted with dichloromethane and water. The dichloromethane phase was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent, (E)-1-bromo-2-phenyl-1-ethene was isolated by preparative gas chromatography. The product was characterized: IR (neat) ν 1605, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (s, 5 H), 7.02 (d, 1 H, J = 14.2 Hz), 6.61 (d, 1 H, J = 14.2 Hz); mass spectrum, M^+ m/e 180, 182.

(Z)-1-Bromo-1-alkene via $BHBr_2$·SMe_2. The procedure for the synthesis of (Z)-1-bromo-1-heptene from 1-heptyne is representative. Hydroboration of 1-heptyne (6.56 mL, 50 mmol) with $BHBr_2$·SMe_2 (50 mmol, 14.7 mL, 3.4 M) to obtain (E)-1-heptenyldibromoborane–dimethyl sulfide was carried out according to known procedure.[22] Bromine (2.6 mL, 51 mmol) in CH_2Cl_2 (8 mL) was added to this vinylborane at −10 °C at such a rate that the inside temperature did not rise above 1 °C (15 min); a red solution resulted. This was stirred at −10 °C for 10 min and treated with 40 mL of 5 M NaOH (or 10 mL of water). The mixture was stirred at 0 °C to room temperature for 1 h, and the two layers were separated (in cases where water was used for hydrolysis, the reaction mixture was diluted with 20 mL of water before separating the two layers). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 layers were combined, and the total volume was made up to 100 mL by adding some more CH_2Cl_2. From this, 10 mL was withdrawn, 0.50 mL (4.75 mmol) of bromobenzene was added as internal standard, and the product was estimated by GC. It showed 47.50 mmol of the product, (Z)-1-bromo-1-heptene (95% yield).

From the remaining 90-mL extract, CH_2Cl_2 and SMe_2 were removed on rotary evaporator and the resulting dark liquid was

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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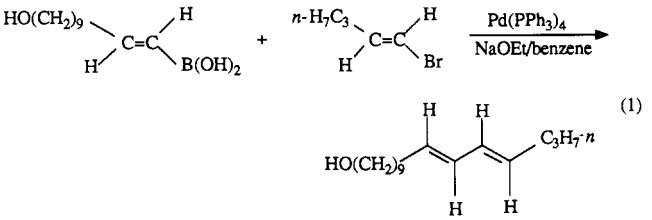
The reactions of (*E*)-1-alkenylboronic acids and their esters and (*E*)-1-alkenyldibromoborane–dimethyl sulfide complexes with iodine under various conditions were investigated. All of these compounds react with iodine in the presence of base, producing (*E*)-1-iodo-1-alkenes in excellent yields and 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.

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(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.

0022-3263/89/1954-6075$01.50/0