

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.63 (m, 1 H), 4.97 (d, 1 H,  $J = 5.6$  Hz), 4.40 (m, br, 1 H), 4.14 (m, 2 H), 2.94 (d, 1 H,  $J = 19.5$  Hz), 2.24 (s, 3 H), 2.04 (dd, 1 H,  $J = 19.5, 4.4$  Hz), 2.00-1.50 (m, 4 H), 0.00 (s, 9 H). Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{NO}_3\text{Si}$ : C, 60.98; H, 8.53; N, 4.74. Found: C, 61.14; H, 8.50; N, 4.67.

**2-Acetyl-8-azabicyclo[3.2.1]oct-2-ene (1c).**<sup>18b</sup> To a solution of 14 (0.074 g, 0.25 mmol) in THF (10 mL) was added tetrabutylammonium fluoride (0.25 mL, 0.25 mmol, 1 M), and the mixture was stirred under an argon atmosphere at room temperature for 12 h. The mixture was concentrated under reduced pressure and then purified by chromatography on neutral alumina (1/4 methanol/ether,  $R_f$  0.37) followed by bulb-to-bulb distillation (50 °C (0.8 mmHg)) to give 1c as a yellow liquid (0.028 g, 75%): IR (neat) 3160, 1660, 1600  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.63 (t, 1 H,  $J = 3.5$  Hz), 4.25 (d, br, 1 H,  $J = 4.4$  Hz), 3.70 (t, 1 H,  $J = 5.6$  Hz), 2.69 (d, br, 1 H,  $J = 19.6$  Hz), 2.24 (s, 3 H), 2.09-1.80 (m, 2 H), 2.03 (dd, 1 H,  $J = 19.6, 4.6$  Hz), 1.76 (s, br, 1 H), 1.60-1.48 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  196.9, 146.8, 136.8, 52.4, 52.0, 36.7, 36.2, 30.5, 24.8; MS  $m/z$  (rel intensity) 151 (22), 136 (15), 122 (100), 108 (25), 91 (11), 80 (28), 68 (30); HRMS calcd for  $\text{C}_9\text{H}_{13}\text{NO}$  151.0997, found 151.0995.

**8-Methyl-2-(methylcarbonyl)-8-azabicyclo[3.2.1]oct-2-ene (1d).**<sup>18b</sup> To a stirred mixture of 1c (0.1315 g, 0.87 mmol) and aqueous formaldehyde (0.35 mL, 4.35 mmol, 37%) in acetonitrile (15 mL) was added sodium cyanoborohydride (0.087 g, 1.39 mmol). After being stirred for 15 min the reaction was made acidic by addition of 1 M HCl (15 mL) over a 45-min period. The solution

was extracted with ether, and the aqueous layer was then made basic by the addition of aqueous sodium hydroxide. The aqueous solution was extracted with ethyl acetate (3 $\times$ ); the organic layer was then dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. The residue was purified by chromatography on basic aluminum oxide (1/19 methanol/ether) followed by bulb-to-bulb distillation (70 °C (0.4 mmHg)) to give 1d as a yellow liquid (0.1399 g, 97%): IR ( $\text{CDCl}_3$ ) 2940, 1645, 1610  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.68 (t, 1 H,  $J = 3.6$  Hz), 3.88 (d, 1 H,  $J = 5.2$  Hz), 3.23 (br t, 1 H,  $J = 5.6$  Hz), 2.67 (d, 1 H,  $J = 19.8$  Hz), 2.29 (s, 3 H), 2.23 (s, 3 H), 2.20-2.00 (m, 2 H), 1.89 (dd, 1 H,  $J = 19.8, 4.4$  Hz), 1.68 (t, 1 H,  $J = 9.3$  Hz), 1.45 (t, br, 1 H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  197.5, 143.7, 136.7, 57.5, 57.4, 37.3, 33.7, 33.0, 29.5, 24.9; MS  $m/z$  (rel intensity) 165 (62), 150 (24), 136 (100), 122 (40), 107 (6), 94 (15), 82 (30). HRMS calcd for  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$  165.1133, found 165.1133.

**Acknowledgment.** We thank Ms. Mary Uhrig from R. J. Reynolds Tobacco Company for some of the mass spectral determinations and Dr. F. Ivy Carrol for proton NMR spectra data of an authentic sample of 1b. Mass spectral determinations were also performed by the Midwest Center for Mass spectrometry, a National Science Foundation regional instrumentation facility (Grant No. CHE 8211164). Financial support of this work by the National Science Foundation (CHE 8517881) and R. J. Reynolds Tobacco Company is gratefully acknowledged.

## Notes

### Reaction of Vinylboronic Acids with Iodine on $\gamma$ -Alumina

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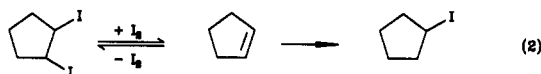
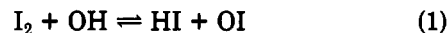
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#### Introduction

For many years we have explored organic reactions on solid surfaces such as  $\gamma$ -alumina with the intent of discovering new reactions, improving reaction characteristics, and understanding how these processes occur.<sup>1-8</sup> Notable in this work are the reactions of unsaturated substrates with halogens.<sup>3-7</sup> Alumina, for example, catalyzes the facile

iodination of aromatic compounds using molecular iodine,<sup>3,4,7</sup> a process that is difficult to carry out in solution. Alkynes, on the other hand, react with iodine on alumina by the stereospecific anti addition of the two iodine atoms to form (*E*)-diiodoalkenes.<sup>6,7</sup> Surprisingly, alkenes react with iodine to form monoiodoalkanes;<sup>4,5,7</sup> in this case, iodine adds reversibly to the double bonds, whereas hydrogen iodide (generated by reaction of iodine with surface hydroxyl groups) adds irreversibly to form the observed products.



Other iodination reactions should also be catalyzed by alumina, and we decided to investigate the reaction of vinylboronic acids with iodine as a representative example. In solution halogenation only occurs when the boron is complexed with hydroxide.<sup>9</sup> Because activated alumina has exposed oxides on its surface<sup>10</sup> that could serve the same function as hydroxide in solution, its surface should provide a good environment for the iodination reaction. In this vein, the reaction of vinylboronic acids with iodine on alumina was examined. The reactions in fact do occur

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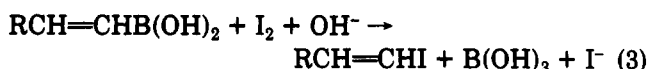
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**Table I. Product Yields and *E/Z* Ratios in the Reaction of Vinylboronic Acids (1 mmol) with 1 equiv of Iodine on Unactivated Alumina (10 g)**

RB(OH) <sub>2</sub> R =	% yield ( <i>E/Z</i> ) at 60 min	% yield ( <i>E/Z</i> ) at 120 min	% maximum yield ( <i>E/Z</i> ) (time)
( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CH-	50 (>99:1)	55 (>99:1)	96 (>99:1) (24 h)
( <i>E</i> )-(CH <sub>3</sub> ) <sub>3</sub> CCH=CH-	39 (100:0)	37 (100:0)	55 (100:0) (15 min)
( <i>E</i> )-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=CH-	40 (50:50)	46 (51:49)	61 (56:44) (24 h)
( <i>E</i> )-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH-	49 (54:46)	54 (55:45)	66 (60:40) (24 h)
( <i>E</i> )-ClCH <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=CH-	82 (74:26)	76 (75:25)	82 (74:26) (50 min)
( <i>E</i> )-HOCH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> CH=CH-	45 (49:51)	51 (54:46)	59 (58:42) (24 h)
C <sub>6</sub> H <sub>5</sub> -	no reaction	no reaction	
( <i>E</i> )-CH <sub>3</sub> CH <sub>2</sub> CH=C(CH <sub>2</sub> CH <sub>3</sub> )-	no reaction	no reaction	
( <i>E</i> )- <i>n</i> -PrCH=C( <i>n</i> -Pr)-	no reaction	no reaction	
( <i>E</i> )-(CH <sub>3</sub> ) <sub>3</sub> CCH=C(CH <sub>3</sub> )-	no reaction	no reaction	

but, as described below, the stereochemistry is quite different than that observed in solution.



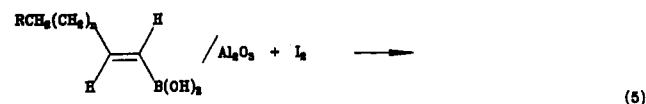
### Results

The first experiments were performed using unactivated Brockmann neutral alumina, which has a layer of exposed hydroxyl groups on the surface.<sup>10</sup> These groups can function as weak Lewis bases because of the presence of two nonbonding pairs of electrons on each oxygen atom. In fact, unactivated alumina is sufficiently basic to induce the iodination reactions. When (*E*)-2-phenyl-1-ethenylboronic acid, prepared by treating phenylacetylene with catecholborane followed by hydrolysis with water, was adsorbed onto the alumina from ether and then treated with 1 equiv of iodine in ether, a fairly rapid reaction ensued. (*E*)-1-Iodo-2-phenylethene was formed in 96% yield after 24 h (Table I). Only a trace of the *Z* isomer could be detected by gas chromatography/mass spectrometry (GC/MS). No reaction occurred in the absence of the alumina. These results parallel those reported by Brown for the solution reaction.<sup>9</sup> Likewise, treatment of (*E*)-3,3-dimethyl-1-butenylboronic acid with iodine on unactivated alumina gave results similar to those observed for the solution reaction,<sup>9</sup> generating the (*E*)-iodoalkene exclusively. Interestingly, the highest yield of product (55%) was obtained in 15 min after which time the product yield diminished.<sup>11</sup>

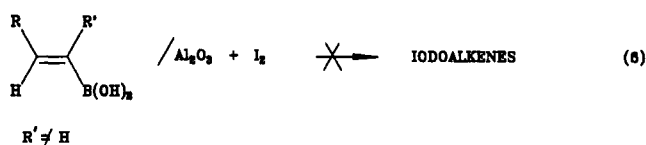


The results obtained in the reaction of straight-chained 1-alkenylboronic acids with iodine on alumina were strikingly different from those described above (Table I). For example, the reaction of the (*E*)-1-octenylboronic acid/alumina complex with iodine generated significant amounts of (*E*)- and (*Z*)-1-iodo-1-octene. Although the *E/Z* ratio of products did change somewhat over time, control experiments demonstrated that both iodoalkenes were initial products of the reaction. (*E*)-1-Decenylboronic acid, (*E*)-5-chloro-1-pentenylboronic acid, and (*E*)-11-hydroxy-1-undecenylboronic acid produced similar results using unactivated alumina (Table I). With the exception of (*E*)-5-chloro-1-pentenylboronic acid, where the *E/Z* ratio was approximately 3:1, the ratio of isomeric products was approximately 1:1. By comparison, most solution analogues of these reactions are highly stereoselective, although in most cases the order of addition of iodine and

hydroxide determines which isomeric iodoalkene is produced.<sup>9</sup> This interesting dichotomy of behavior will be discussed in more detail later.



The reaction of a few internal vinylboronic acids with iodine on unactivated alumina was also examined. Although chemical reactions occur, in no case was an iodoalkene, or any other volatile product, isolated from the procedure (Table I). Likewise, internal vinylboronic acids do not yield vinyl iodides when treated with iodine and base in solution.<sup>9a</sup> The difference in the behavior of terminal and internal boronic acids cannot currently be explained.



Because of the unusual stereochemistry observed in the reaction of vinylboronic acids with iodine on alumina, several additional experiments were performed in order to determine if the stereochemistry of the reactions could be altered. (*E*)-1-Octenylboronic acid was chosen as the model substrate in these studies.

The initial premise of this investigation was that the partially exposed oxide anions on the surface of alumina would induce the iodination of vinylboronic acids by complexation to the boron atoms. It was found that the surface hydroxyl groups of unactivated alumina were sufficiently basic to carry out this function. Because oxides exhibit greater basicity, they could be more effective in these reactions than hydroxyl. In fact, the opposite is true. Activated alumina (400 °C under vacuum for 15 h) is much less effective than unactivated alumina.<sup>12</sup> The reaction on activated alumina occurs approximately at a rate half as fast as the rate of reaction on unactivated alumina.

When the reaction of octenylboronic acid is run on unactivated alumina with 2 equiv of iodine, the reaction was considerably faster than when 1 equiv of iodine was used, yielding 100% of product after 20 min. However, the *E/Z* ratio of iodoalkenes was not altered. The reaction was also faster on activated alumina when 2 equiv of iodine were used but not as fast as reactions on the unactivated

(11) In no other case did the product yield diminish with time.

(12) Alumina activated at 400 °C is approximately 60% dehydroxylated. The surface consists of HO groups (40%), partially exposed aluminum cations (30%), and oxide anions (30%).<sup>10</sup>

solid. As before, the *E/Z* ratio was not affected.

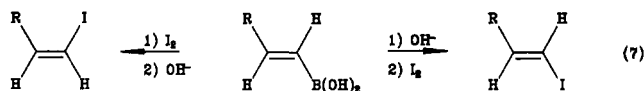
One of the intriguing aspects of the solution reaction is the fact that the order of addition of base and iodine determines the stereochemistry of the product in most cases.<sup>9</sup> This factor has no effect on the stereochemistry of 1-octenylboronic acid reactions on alumina. The same ratio of products was obtained whether iodine was added to the boronic acid/alumina complex or alumina was added to a mixture of iodine and vinylboronic acid.

The only variable that influenced the stereoselectivity of the reaction was the surface area available to the boronic acid. All the reactions described above were run with 1 mmol of boronic acid on 10 grams of alumina. In the case of (*E*)-1-octenylboronic acid this yielded an *E/Z* ratio of 60:40 after a 1-day reaction time. When  $1/3$  mmol of octenylboronic acid was used on the same amount of solid, the *E/Z* ratio diminished by 20%, whereas when 3 mmol of boronic acid was used, the ratio went up by 40%. In other words, the more boronic acid one had on a given weight of alumina, the more (*E*)-iodoalkene was generated in the reaction.

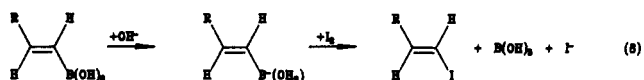
### Discussion

To understand the iodination reactions on alumina, one must examine the reactions that occur in solution.

What is most striking about the solution reactions is that the stereochemistry can be altered by changing the order of addition of iodine and aqueous hydroxide.<sup>9</sup> If hydroxide is added to the vinylboronic acid prior to the iodine, the iodination proceeds with retention of configuration. If iodine is added prior to the base, the reaction proceeds with inversion of configuration. Only with the boronic acids derived from phenylacetylene and 3,3-dimethyl-1-butyne does one get retention of configuration regardless of the order of addition of the two reagents.<sup>9</sup>

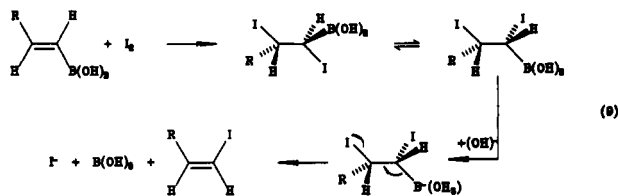


Although the mechanisms for these transformations have never been discussed in detail in the literature,<sup>13</sup> reasonable pathways are available. Consider first the reaction proceeding with retention of configuration. Reaction of the vinylboronic acid with hydroxide will, of course, generate the corresponding borate anion. If this species then reacts with iodine by a  $S_{\text{E}}2$  mechanism proceeding with retention of configuration, the observed product will be produced. Many  $S_{\text{E}}2$  reactions at carbon metal bonds are known to occur with retention of configuration.<sup>14</sup>

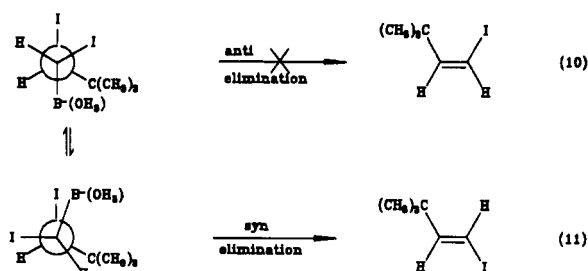


The reaction occurring with inversion of configuration proceeds by a completely different pathway. Iodine is known to add to double bonds reversibly to make vicinally substituted diiodoalkanes via the anti addition of the two iodine atoms. In the case of a vinylboronic acid, addition of iodine will generate a saturated diiodoboronic acid that is in a position to undergo anti elimination of boric acid and iodide once the trivalent boron is converted into a tetravalent form by reaction with hydroxide.

Why then do the (*E*)-vinylboronic acids derived from phenylacetylene and 3,3-dimethyl-1-butyne yield only the corresponding (*E*)-iodoalkene under both modes of addi-



tion? When hydroxide is added first, the mechanism of iodination presumably is the same as that of the other boronic acids. However, when iodine is added first, the mechanism must change in some respect. It is reasonable to assume that the first step, the addition of iodine, is identical with that observed in the other examples. If this is true, one will arrive at the correct product only by syn elimination of boric acid and iodide. This pathway will only occur if the normally favorable anti elimination pathway is inhibited. The large size of the phenyl and *tert*-butyl groups in these compounds might prohibit proper alignment of the carbon iodine and carbon boron bonds for anti elimination.



To understand how the surface reactions occur, it is important to know that no vinyl iodides are generated in the absence of the alumina. Thus, both isomeric iodoalkenes must arise by surface-mediated processes. We believe that this requires that the species generating the observed products contain tetracoordinate boron atoms. Evidence that the product-forming steps in the surface reactions involve species with tetracoordinated boron atoms came from a  $^{11}\text{B}$  NMR spectrum taken of (*E*)-1-octenylboronic acid adsorbed on unactivated alumina, the medium that gave the highest yields of products in this study.  $^{11}\text{B}$  is a quadrupolar nucleus with a spin equal to  $3/2$ . Because of this fact  $^{11}\text{B}$  spectra of species with restricted motions such as those attached to solid materials are very broad when the boron atoms are trivalent.<sup>15</sup> When the boron atoms are in a more symmetric environment, however, as they are when tetravalent, the peaks are relatively sharp. Thus, solid-state NMR offers a method for distinguishing these two types of boron in species adsorbed on solids. In the present case, the sample produced a relatively sharp peak (width at half height = 6 ppm) at 7 ppm (relative to  $(\text{C}_6\text{H}_5)_4\text{B}^-$  at  $\delta = 0$  ppm). By way of comparison, solid sodium (*E*)-1-octenylborate, prepared by reaction of (*E*)-1-octenylboronic acid with 1-equiv of NaOH in water followed by removal of the water, gave a similar  $^{11}\text{B}$  spectrum:  $\delta = 6.54$  ppm and width at half height = 8 ppm. Solid (*E*)-1-octenylboronic acid, on the other hand, gave an uninterpretable broad  $^{11}\text{B}$  spectrum with numerous spinning sidebands, although its solid-state  $^{13}\text{C}$  NMR spectrum was well resolved, showing all eight carbon resonances. One can conclude that the "observable" boron on the solid is coordinated to the oxygen atoms of

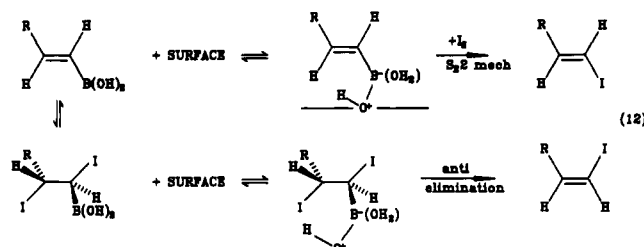
(13) A few mechanistic ideas have been discussed in ref 9.

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the surface hydroxy groups. Any uncomplexed boronic acid would not be detected in the spectrum.

One can invoke special geometric arrangements of surface hydroxyl groups and the adsorbed vinylboronic acids to explain the unusual stereochemistry of the surface reactions, but this is not necessary. The results can be explained simply, if there is an equilibrium admixture of complexed and uncomplexed vinylboronic acid. In this scheme the complexed boronic acid with its tetracoordinate boron reacts with iodine on the surface with retention of configuration via the  $S_E2$  mechanism. The uncomplexed boronic acid, on the other hand, reacts reversibly first with iodine to produce a saturated boronic acid and then with surface hydroxyl groups to form a surface bound species that yields the (*Z*)-iodoalkene by the anti elimination of boric acid and iodide. The boronic acids derived from phenylacetylene and 3,3-dimethyl-1-butyne react highly stereoselectively on the surface of alumina because their complexed and uncomplexed boronic acids yield the same products by different mechanisms, as they do in solution. Lastly, the ratio of *E/Z* products decreases as the ratio of alumina to vinylboronic acid increases because the two reversible reactions involving the surface shift, but to differing degrees.



### Experimental Section

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL FX-90Q and Nicolet NT 200 spectrometers in  $\text{CDCl}_3$  using tetramethylsilane as the internal standard ( $\delta = 0$  ppm). The  $^{11}\text{B}$  NMR spectra were obtained using the Nicolet spectrometer. GC/MS were recorded on a Hewlett-Packard 5970 series instrument. Gas chromatographs were recorded on a Hewlett-Packard 5890A instrument using a 30 m  $\times$  1/8 in. column packed with 30% by weight SE-30 on Chromasorb W. Product yields were obtained from peak areas after calibration with known compounds. (*E*)-Alkenylboronic acids were prepared, via the procedure of Brown,<sup>9</sup> by reacting the corresponding alkyne with catecholborane followed by hydrolysis of the resulting organoborane with water. Unactivated Brockmann neutral alumina was ordinary used in the iodination reactions. When activated alumina was needed, it was prepared according to the procedure of Pagni, Kabalka, et al.<sup>1b</sup>

**Preparation of the Alumina-Boronic Acid Complex.** To a stirred slurry of alumina (10 g) and ether (15 mL) was added a solution of vinylboronic acid (1.00 mmol) in 15 mL of ether. After stirring for 5 min, the ether was removed in vacuo. If the boronic acid complexes to all surface sites, this concentration corresponds to 1.4% surface coverage if the solid has a surface area of 300  $\text{m}^2/\text{g}$ .<sup>1b</sup>

**Reaction of Alumina-Boronic Acid Complex with Iodine.** The following is a representative example of the reaction of a vinylboronic acid with  $\text{I}_2$  on alumina. To a stirred slurry of the (*E*)-1-octenylboronic acid complex in ether (15 mL) containing decane ( $5 \times 10^{-4}$  mol; GC standard) was added a solution of iodine (1.00 mmol) in 15 mL of ether. The reaction was monitored using GC by removal of 1-mL aliquots at convenient time intervals. After 24 h, the ether was separated from the alumina; evaporation left behind an oily residue. GC analysis showed that a 65% yield of a 56:44 admixture of (*E*)- and (*Z*)-1-iodo-1-octene had been formed in the reaction. The *E* and *Z* isomers were separated by preparatory GC and were identical with independently synthesized compounds.

**(*E*)-1-Iodo-1-octene.** This compound was synthesized from 1-octyne by the procedure of Brown.<sup>9</sup>

**(*Z*)-1-Iodo-1-octene.** This compound was synthesized from 1-iodo-1-octyne by the procedure of Brown.<sup>16</sup>

**Control Experiments.** Several experiments were performed in order to determine if the two 1-iodo-1-alkenes were the initial products of the reaction. In all cases both products were present at very early reaction times. Extrapolation of the *E/Z* ratio of products to zero time clearly indicated that both products were initial products of the reaction.

In the case of the reaction of the (*E*)-1-octenylboronic acid with iodine, additional experiments were performed. The less stable (*Z*)-1-iodo-1-octene was subjected to alumina, iodine on alumina, and (*E*)-1-octenylboronic acid on alumina for extended periods of time. In no case did the *Z* isomer isomerize to the *E* isomer.

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**Registry No.** (*E*)- $\text{C}_6\text{H}_5\text{CH}=\text{CHB}(\text{OH})_2$ , 6783-05-7; (*E*)- $(\text{CH}_3)_3\text{CCH}=\text{CHB}(\text{OH})_2$ , 86595-37-1; (*E*)- $\text{CH}_2(\text{CH}_2)_8\text{CH}=\text{CHB}(\text{OH})_2$ , 42599-16-6; (*E*)- $\text{CH}_2(\text{CH}_2)_7\text{CH}=\text{CHB}(\text{OH})_2$ , 86883-77-4; (*E*)- $\text{ClCH}_2(\text{CH}_2)_2\text{CH}=\text{CHB}(\text{OH})_2$ , 37490-32-7; (*E*)- $\text{HOCH}_2(\text{CH}_2)_2\text{CH}=\text{CHB}(\text{OH})_2$ , 87096-18-2;  $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$ , 98-80-6; (*E*)- $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_2\text{CH}_3)\text{B}(\text{OH})_2$ , 134849-01-7; (*E*)-*n*-PrCH= $\text{C}(\text{CH}_3)_2\text{B}(\text{OH})_2$ , 81793-07-9; (*E*)- $(\text{CH}_3)_3\text{CCH}=\text{C}(\text{CH}_3)\text{B}(\text{OH})_2$ , 134849-02-8; (*E*)- $\text{C}_6\text{H}_5\text{CH}=\text{CHI}$ , 42599-24-6; (*E*)- $(\text{CH}_3)_3\text{CCH}=\text{CHI}$ , 61382-45-4; (*E*)- $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CHI}$ , 42599-17-7; (*Z*)- $\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CHI}$ , 52356-93-1; (*E*)- $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CHI}$ , 66291-52-9; (*Z*)- $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CHI}$ , 66291-51-8; (*E*)- $\text{ClCH}_2(\text{CH}_2)_2\text{CH}=\text{CHI}$ , 78461-58-2; (*Z*)- $\text{ClCH}_2(\text{CH}_2)_2\text{CH}=\text{CHI}$ , 95835-51-1; (*E*)- $\text{HOCH}_2(\text{CH}_2)_2\text{CH}=\text{CHI}$ , 87096-20-6; (*Z*)- $\text{HOCH}_2(\text{CH}_2)_2\text{CH}=\text{CHI}$ , 134849-03-9; Alumina, 1344-28-1.

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### Direct Electrochemical Synthesis of Diaryl Dichalcogenides by $S_{RN}1$ Reactions Using Sacrificial Se and Te Cathodes

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Diaryl diselenides and ditellurides are useful starting materials for many Se- and Te-containing compounds and reagents.<sup>1,2</sup> In the field of  $S_{RN}1$  reactions,<sup>3</sup> it was shown

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