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Electrochemical Properties and Reactions of Organoboronic Acid Esters Containing Unsaturated Bonds at Their α-Position

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Electrochemical analyses of 2-(cynnamyl)boronic acid pinacol ester and (3-phenyl-2-propynyl)boronic acid pinacol ester, and their trimethylsilyl analogues as well as their parent compounds were comparatively studied by cyclic voltammetry measurements. We found remarkable negative shifts of the oxidation potentials of the organoboronic acid pinacol esters in the presence of fluoride ions compared to those in the absence of fluoride ions. The negative shift observed was more pronounced than that of the corresponding trimethylsilyl compounds. Such marked negative shift seems to be derived from the formation of negatively charged boron-ate complex with fluoride ions as well as β-effect of organoborate. Anodic acetoxylation of organoboronic acid pinacol esters was achieved in NaOAc/AcOH, while their alkoxylation was successfully carried out in the presence of fluoride ions.
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Organoboron compounds are highly useful in various fields such as synthetic organic chemistry, pharmaceutical chemistry, and materials chemistry[1–7] as well as analytical chemistry.[8–16] For example, much attention has been paid to electrochemistry and electrogenerated chemiluminescence of BODIPY (boron dipyrromethene) dyes[13] and also recently, a new class of fluorescence PET sensors based on anthraceneboronic acid ester for detection of a trace amount of water in organic solvents has been developed.[14] The preferential boron-ate complex formation with fluoride ions is applicable to fluoride ion sensors.[8–11,15] Shinkai and his co-worker reported the molecular design of artificial sugar sensing systems.[16] Electrodes modified with carotenoids bearing a $B(OH)_2$ group were also shown to be potential sugar sensors.[12] Furthermore, carboranes exhibit reversible reduction behavior and their reduction potential is easily tunable with functional groups on the carbon atoms.[7,17] We have recently found that carboranes are high-performance electrocatalysts for cathodic dehalogenation of alkyl halides.[18,19] Waldvogel and his co-workers reported quite unique boron-templated electrosynthesis of 2,2′-biphenols from sodium tetraphenoxy borates.[20] However, this report does not deal with carbon-boron bond cleavage.

On the other hand, limited examples of electrochemical reaction of triorganoboranes have been reported to date.[6,17,21,22] Anodic oxidation of triorganoboranes generally requires the activation with nucleophiles to generate negatively charged boron-ate complex.[23–26] Schäfer and Koch reported anodic oxidation of trihexylborane in NaOMe/MeOH in the presence of butadiene.[23] They proposed that electron transfer takes place from trihexylmethoxyborate formed in situ to generate hexyl radical intermediates, which reacts with butadiene. However, in this reaction, many products were formed by methoxylation and dimerization.

Anodic oxidation of alkylboronic acids was also carried out in an aqueous NaOH solution to afford the corresponding dimers or olefins via radical or cation intermediates.[27–29] Becker and his coworkers reported anodic oxidation of arylboronic acid esters in the presence of bromide ions leading to the cleavage of the carbon-boron bond to provide the corresponding aryl bromides in moderate yields.[30] In this reaction, the generation of bromonium ion was proposed for the bond cleavage. Mitsudo, Tanaka and their co-workers developed a facile electrooxidative method for synthesizing biaryls from arylboronic acids or arylboronic esters using a catalytic amount of $Pd(OAc)_2$ and TEMPO.[31] On the other hand, we have reported cathodic selective hydroxylation of various substituted phenylboronic acids under oxygen atmosphere to provide phenol derivatives.[32] In this case, electrogenerated superoxide ions caused the C-B bond cleavage.

Quite recently, we found marked negative shifts of the oxidation potentials of alkyl and arylboronic acids in the presence of fluoride ions compared with those in the absence of fluoride ions.[33] It was also clarified that the negative shift was derived from the formation of negatively charged boron-ate complex with fluoride ions.[33] On the other hand, it is well-known that allylsilane and benzylsilane exhibit less positive oxidation potentials compared with the parent compounds devoid of a silyl group owing to effective C-Si σ orbital overlapping with a neighboring π orbital, which causes a significant increase in the HOMO level (β-effect).[34,35] The presence of a silyl group also assists anodically selective cleavage of a C-Si bond.[34,35]

These facts prompted us to investigate the anodic oxidation behavior of organoboronic acid pinacol esters having a neighboring double or triple bond such as 2-(cynnamyl)boronic acid pinacol ester and (3-phenyl-2-propynyl)boronic acid pinacol ester in organic solvents in the absence and presence of fluoride ions using cyclic voltammetry as well as anodic substitution reaction in this work. Furthermore, anodic oxidation behavior of their trimethylsilyl analogues was also comparatively studied.

Experimental

General.—^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on JEOL JNM EX-270 (^{1}H: 270 MHz, ^{13}C: 67.8 MHz, ^{19}F: 254.05 MHz) spectrometer in $CDCl_3$. The chemical shifts for ^{1}H, ^{13}C and ^{19}F NMR spectra were given in δ (ppm) from internal TMS (0.00), $CDCl_3$ (77.0) and monofluorobenzene (−36.5), respectively. Cyclic voltammetry measurement was performed using BAS ALS Instruments model 600 A. Preparative electrolysis experiments were carried out with Metronnix Corp. (Tokyo) constant current power supply model 5944 by monitoring electricity with Hokutodenko Coulomb/Ampere-hour meter HF-201.

Measurement of cyclic voltammetry.—Cyclic voltammetry measurement was carried out in a glass cell. A platinum disk electrode ($\phi = 0.8$ mm) was used as a working electrode. A platinum plate (1 cm × 1 cm) was used as a counter electrode. A saturated calomel electrode was used as a reference electrode. Electrolyte solutions for cyclic voltammetry were deoxygenated with bubbling N_2 gas before use.

Materials.—4,4,5,5-Tetramethyl-2-cinnamyl-1,3,2-dioxaborolane (**1**) was prepared in a similar manner to the reported procedure.[36,37] The spectral data were identical to those of the authentic sample.[38] Tetra-*n*-butylammonium cinnamyltrifluoroborate (**2**) was prepared by the cation exchange reaction of the corresponding potassium salts[39] similarly to our previous report[40] according to the literature method.[41]

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Tetra-n-butylammonium cinnamyltrifluoroborate (2).—Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.25–7.13 (m, 4H), 7.00–6.95 (m, 1H), 6.61–6.55 (m, 1H), 6.07–6.01 (m, 1H), 3.42 (t, $J = 8.6$ Hz, 8H), 1.83–1.74 (m, 8H), 1.49–1.41 (m, 8H), 1.35 (br, 2H), 0.97 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 139.4, 136.2, 128.2, 124.9, 124.8, 57.9, 53.4, 23.5, 19.4, 13.5; ^{19}F NMR (254 MHz, $CDCl_3$) δ −62.4; HRMS calcd. for $C_{23}H_{45}BF_3N$: 427.3597. Found; 427.3594.

Synthesis of 4,4,5,5-tetramethyl-(3-phenylpropyn-2-yl)-1,3,2-dioxaborolane (4).—To a stirred solution of THF (20 ml) containing ethynylbenzene (20 mmol), *n*-buthyl lithium in hexane (20 mmol) was added dropwise at −78°C. The resulting solution was stirred at the same temperature for 1 h, and then (bromomethyl)pinacolborane (20 mmol) was added dropwise and the mixture was stirred at room temperature for 2 h. After the reaction, 1 M HCl was added to the reaction mixture at 0°C, and the solution was stirred for 20 min. The solution was mixed with water and the product was extracted repeatedly with ether. The extracts were washed with brine and the ether layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation and the residue was distilled under reduced pressure to give the product (bp: 130–135°C/0.3 mmHg), which was further purified with silica gel column chromatography (eluent: hexane/AcOEt = 5:1) provide a pure product **4** as a yellow oil in 12% yield.

^{1}H NMR (270 MHz, $CDCl_3$) δ 7.48–7.38 (m, 3H), 7.30–7.22 (m, 2H), 2.04 (s, 2H), 1.32 (s, 12H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 132.4, 131.5, 128.2, 127.1, 84.1, 83.2, 65.5, 24.8; MS: m/z = 242 (M^+), 227 (M^+-Me), 198, 169, 143, 128, 115, 89; HRMS calcd. for $C_{15}H_{19}BO_2$: 242.1478. Found; 242.1480.

A typical procedure for anodic acetoxylation and alkoxylation.—Constant current anodic oxidation of **1**, **4** or **5** (0.3 mmol) was carried out with a graphite anode (2 cm × 2 cm) and a platinum cathode (2 cm × 2 cm) in 10 ml of 0.2 M NaOAc/AcOH, 0.1 M NaOMe/MeOH, 0.1 M Et_4NOTs/MeOH, or 0.3 M Et_3N-3HF/alcohol in an undivided cell at room temperature. After electrolysis, 80 ml of water was added to the mixture and extracted with ether (40 ml × 3). The organic phase was washed with an aqueous solution of $NaHCO_3$ and brine, and then dried over $MgSO_4$. The solution was evaporated under reduced pressure and the product was isolated by silica gel column chromatography (eluent: hexane/AcOEt = 20∼5:1). ^{1}H NMR yields were estimated using nitromethane or dichloromethane as an internal standard.

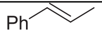
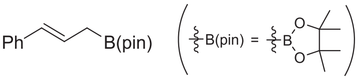
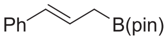
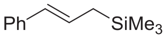
The known products (**6a**, **6b**,[42] **7a**,[43] **7b**,[44] **7c**,,[44] **7d**,[45] **8a**,[46] **8b**,[44] **8c**,[44] **9**, **10**,[47] **11a**,[48] **11b**,[49] **11c**,[50] **12**, and **13**) were identified by comparison with the spectral data of commercially available or reported authentic samples.

Results and Discussion

Cyclic voltammetry measurement.—At first, cyclic voltammetry measurement of 2-(cinnamyl)boronic acid pinacol ester **1**, tetra-*n*-butylammonium cinnamyltrifluoroborate (**2**), cinnamyltrimethylsilane (**3**), and β-methylstyrene was carried out in 0.1 M *n*-Bu_4NClO_4/MeCN. Their oxidation peak potentials are summarized in Table I.

The oxidation potentials of β-methylstyrene and cinnamylboronic acid pinacol ester **1** are almost the same, which indicates the introduction of a boryl group does not affect the oxidation potential. Interestingly, when the supporting electrolyte was changed from *n*-Bu_4NClO_4 to Et_4NF-4HF, the oxidation peak potential of **1** was dramatically shifted from 1.85 V to 0.95 V vs. SCE. Thus, it was found that the presence of fluoride ions markedly decreased the oxidation potential of **1** by 0.9 V. Notably, the oxidation potential of cinnamyltrifluoroborate **2** was found to be almost the same as that of **1** in the presence of fluoride ions. Previously, we clarified the facile formation of trifluoroborate species from organoboronic acid and HF salts by ^{19}F NMR and ^{11}B NMR spectroscopic study.[33] Therefore, the remarkable negative shift of the oxidation potential of **1** seems to be attributable to negatively charged trifluoroborate **2** derived from **1** and fluoride ions.

Table I. Oxidation peak potentials ($E_p{}^{ox}$) of cynnamyl boronate ester, borate and related compounds.[a]

Compound		$E_p{}^{ox}$ (V vs. SCE)
		1.90
	1	1.85
	1	0.95[b]
	2	0.94
	3	1.40

[a]0.1 M Bu_4NClO_4/MeCN, Pt disk electrode (ϕ = 0.8 mm), scan rate: 100 mV/s.

[b]0.1 M Et_4NF-4HF/MeCN.

Similar marked negative shift of the oxidation potentials was also observed in the case of oxygen-containing organoboronic acid pinacol esters.[51] As already mentioned, it is well-known that allylsilane and benzylsilane exhibit less positive oxidation potentials compared with their corresponding compounds devoid of a silyl group. Therefore, the oxidation potential of cinnamyltrimethylsilane (**3**) was also measured under the same conditions as the measurement of **2**. The oxidation potential of **3** was found to be 1.40 V vs. SCE, which is less positive compared with β-methylstyrene probably due to a β-effect of the silyl group. However, **3** showed much more positive oxidation potential compared with cinnamyltrifluoroborate **2** although allyltrimethylsilane and allyltrifluoroborate exhibited quite similar oxidation potentials (around 1.40 V vs. SCE).[52]

In order to further understand the difference in oxidation potentials of **1**, **2** and **3**, DFT calculation was carried out using Gaussian 03 with the B3LYP/6-31G(d,p) method (Figure 1). The highest occupied molecular orbitals (HOMO) of these compounds were mainly located on the C-C double bonds. The optimized structures indicate that the orbital on the C-B bond or C-Si bond can overlap that of the C-C double bond. This result strongly supports that the oxidation potentials of the substrates are decreased by the β-effect. Moreover, the

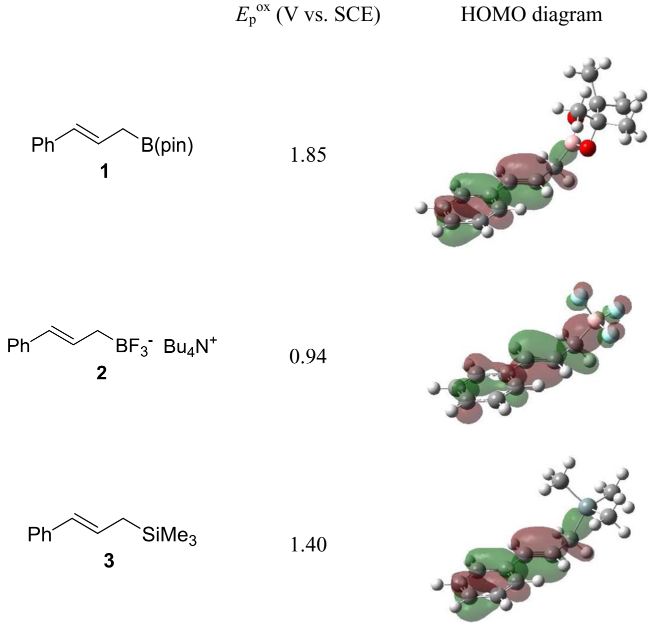


Figure 1. Left: Oxidation peak potentials ($E_p{}^{ox}$) of cynnamyl derivatives recorded in Bu_4NClO_4/MeCN and right: HOMO diagrams of **1**, **2**, and **3**.

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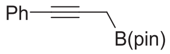
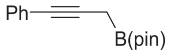
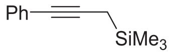
Table II. Oxidation peak potentials (E_p^{ox}) of boronate ester having a triple bond, and related compounds[a]

Compound		E_p^{ox} (V vs. SCE)
Ph—≡—Me		2.32
	**4**	2.30
	**4**	1.28[b]
	**5**	1.72

[a] 0.1 M Bu_4NClO_4/MeCN, Pt disk electrode (ϕ = 0.8 mm), scan rate: 100 mV/s.
[b] 0.1 M Et_4NF-4HF/MeCN.

observed oxidation potentials well corresponded to the contribution of the orbital on C-B or C-Si bond to the HOMO diagrams.

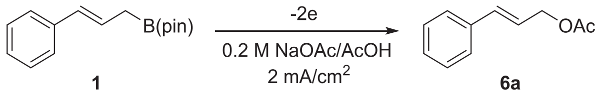
Next, cyclic voltammetry measurement of boronic acid pinacol ester having a triple bond like (3-phenyl-2-propynyl)boronic acid pinacol ester **4**, its trimethylsilyl analogue **5**, and 1-methyl-2-phenylacetylene was carried out similarly. The observed oxidation potentials are summarized in Table II.

The oxidation potentials of boronic acid pinacol ester **4** and 1-methyl-2-phenylacetylene were found to be rather positive and quite similar each other. The introduction of a boryl group to the α-position of 1-methyl-2-phenylacetylene did not affect the oxidation potential similarly to the case of the corresponding cinnamyl analogue **1**. In sharp contrast, the oxidation potential of silyl derivative **5** decreased significantly to 1.72 V vs. SCE by 0.6 V compared with 1-methyl-2-phenylacetylene, which was quite similar to the case of cinnamyl analogues **1** and α-methylstylene. Interestingly, the oxidation potential of boronic acid pinacol ester **4** was changed dramatically from 2.30 to 1.28 V vs. SCE in the presence of fluoride ions similar to the case of **1**. It is notable that such large negative shift of the oxidation potentials of **1** and **4** was observed regardless of neighboring π-systems.

Again, DFT calculation for **4**, **5** and BF_3 analogue of **4** was performed using the same method as discussed above. The HOMOs were delocalized through the π-system and the C-B or C-Si bond in a similar manner to the result shown in Figure 1 (data not shown). The level of oxidation potential was dependent on the degree of β-effect observed with different functional groups.

Anodic substitution reactions of organoborates with oxygen nucleophiles.—Anodic acetoxylation of 2-(cynnamyl)boronic acid pinacol ester **1** was carried out at a constant current using graphite and platinum anodes in 0.2 M NaOAc/AcOH. The results are summarized in Table III.

Table III. Anodic acetoxylation of 1 under various conditions.



1 **6a**

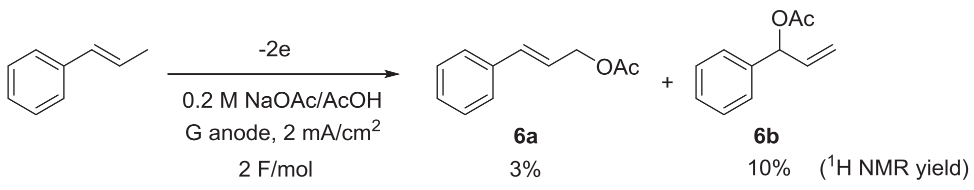
Entry	Anode material	Electricity (F/mol)	Yield (%)[a]
1	Pt	2	2[b]
2	G	2	17
3	G	2.5	20
4	G	3	26
5	G	4	15

[a] Isolated yield.
[b] Determined by ^1H NMR.

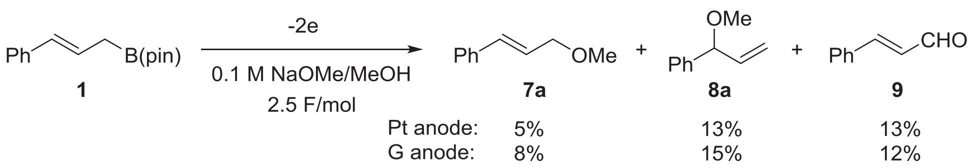
When a theoretical amount of electricity (2 F/mol) was passed at a graphite anode, acetoxylation proceeded with eliminating a boryl group. However, expected acetoxylated product **6a** was obtained in poor yield (entry 2). Platinum was not suitable as an anode material for the acetoxylation (entry 1). Since considerable amount of starting material **1** remained at 2 F/mol of electricity, the amount of charge was increased. As expected, the yield of **6a** increased up to 26% with increase of electricity (entries 2–4). However, at 4 F/mol of electricity, the yield decreased probably due to the overoxidation of the product **6a** even though starting compound **1** remained. Interestingly, **6a** was obtained solely and regioisomer was not formed at all. In comparison, anodic acetoxylation of β-methylstyrene was carried out using a graphite anode under the same conditions. The electrolysis at 2 F/mol provided two acetoxylated products **6a** and **6b** as a regioisomeric mixture as shown in Scheme 1. In this case, 1-phenylallyl acetate (**6b**) was mainly formed and **6a** was a minor product. Since a benzylic cation is more stable than a terminal cation, **6b** seems to be formed mainly. These results indicate that a boryl group would control the regioselectivity for the anodic acetoxylation.

Next, anodic methoxylation of **1** was investigated. When a neutral supporting electrolyte like Et_4NOTs was used, the reaction did not proceed at all and starting material **1** was mostly recovered. In this case, methanol was oxidized predominantly due to the high oxidation potential of **1**. It was expected that **1** would form a boron-ate complex with a base resulting in decrease of its oxidation potential as reported by Shäfer and Koch.[23] Therefore, NaOMe was used as a basic supporting electrolyte, and anodic oxidation of **1** was carried out at platinum and graphite anodes. As expected, the methoxylation proceeded regardless of anode materials to afford methoxylated products **7a** and **8a** as a regioisomeric mixture as well as cinnamylaldehyde **9** as shown in Scheme 2. However, the total yield was unsatisfactory.

Since we found that the oxidation potentials of **1** was decreased significantly in the presence of fluoride ions, anodic methoxylation was performed using Et_3N-3HF as a supporting electrolyte, which has been



Scheme 1. Anodic acetoxylation of β-methylstyrene.



Scheme 2. Anodic methoxylation of **1** with different anode materials.

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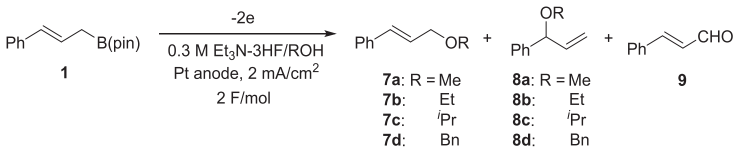
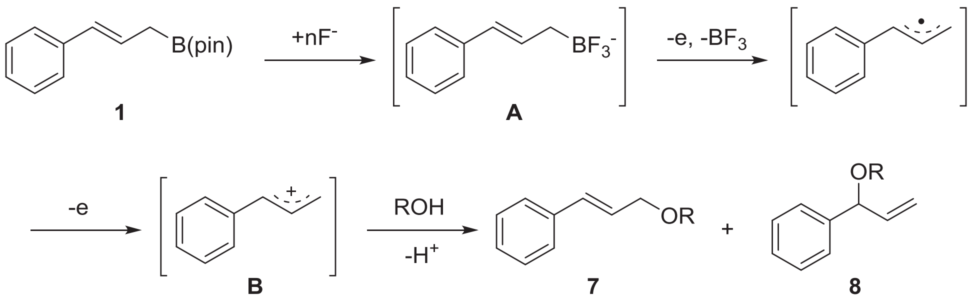
Table IV. Anodic alkoxylation of 1 in the presence of fluoride ions.

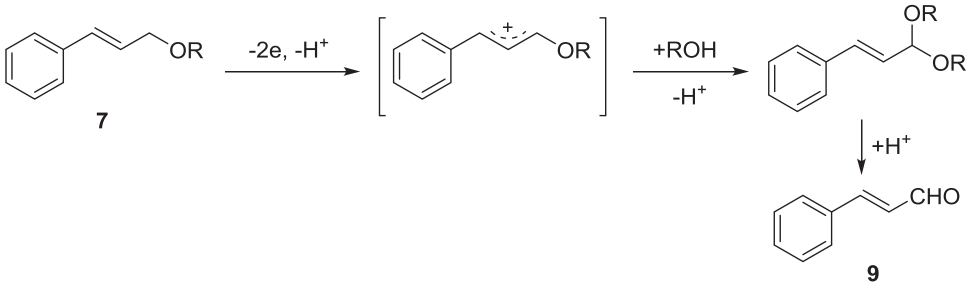


		Yield (%)[a]					
Entry	R	7		8		9	Total
1	Me	15	**(7a)**	18	**(8a)**	17	50
2	Et	12	**(7b)**	12	**(8b)**	21	35
3	^{i}Pr	13	**(7c)**	9	**(8c)**	12	34
4[b]	Bn	13	**(7d)**	0	**(8d)**	20	33

[a] Determined by ^{1}H NMR.
[b] 0.3 M BnOH/MeCN.



Scheme 3. Plausible reaction mechanism for anodic alkoxylation of **1** in the presence of fluoride ions.



Scheme 4. Formation of **9** via anodic alkoxylation of **7** and hydrolysis.

used for anodic fluorination of various organic compounds.[40,53–57] As expected, methoxylation proceeded well, and products, **7a**, **8a**, and **9** were obtained in moderate total yield (50%) at 2F/mol as shown in Table IV (entry 1). In order to investigate scope and limitation as well as regioselectivity of alkoxylation, we carried out anodic alkoxylation similarly, using various alcohols. The results are summarized in Table IV. Regardless of alcohols, alkoxylation proceeded to provide three kinds of products in moderate yields except for benzyl alcohol. In all cases, starting compound **1** remained appreciably. When benzyl alcohol was used as a nucleophile, benzylic substituted regioisomer **8d** was not formed at all. This is interesting from a mechanistic aspect. In all cases, no fluorinated product was formed at all.

The anodic alkoxylation of **1** seems to proceed as shown in Scheme 3. At first, a fluoride ion coordinates to the boron atom to form a

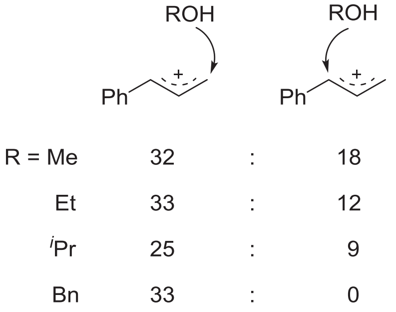
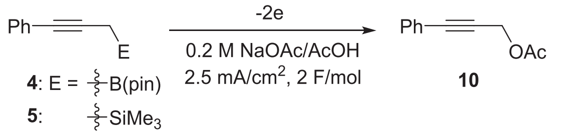


Figure 2. Regioselectivity of anodic alkoxylation of **1**.

Table V. Anodic acetoxylation of 4 and 5 having a triple bond.



Entry	Substrate	Anode material	Yield (%)[a]
1	**4**	Pt	4[b]
2	**4**	G	44
3	**5**	Pt	trace
4	**5**	G	53

[a] Isolated yield.
[b] Determined by ^{1}H NMR.

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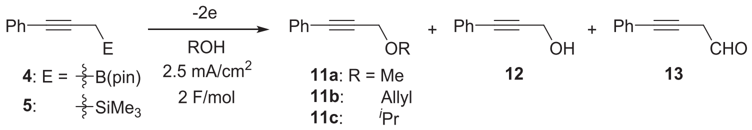
Table VI. Anodic alkoxylation of 4 and 5 under various conditions.



				Yield (%)[a]				
Entry	Substrate	R	Supporting electrolyte	11		12	13	Total
1	**4**	Me	0.1 M Et$_4$NOTs	9	**(11a)**	4	0	13
2	**5**	Me	0.1 M Et$_4$NOTs	3	**(11a)**	3	4	10
3	**4**	Me	0.3 M Et$_3$N-3HF	32	**(11a)**	10	11	53
4	**4**	Allyl	0.3 M Et$_3$N-3HF	28	**(11b)**	7	9	44
5	**4**	^{i}Pr	0.3 M Et$_3$N-3HF	8	**(11c)**	12	7	27

[a]Determined by ^{1}H NMR.

boron-ate complex **A** like trifluoroborate. As already mentioned, we confirmed the formation of trifluoroborate from organoboronic acid and fluoride ions by ^{19}F NMR and ^{11}B NMR spectroscopic studies.[33] The boron-ate complex **A** is readily oxidized at an anode to generate a radical intermediate, followed by one more electron oxidation to generate cationic intermediate **B** in a manner similar to anodic oxidation of trifluoroboate compounds as reported.[52] An alcohol attacks the terminal carbon or inner carbon of **B** to form **7** or **8**, respectively. Further anodic oxidation of **7** affords acetal products, which are an equivalent to cinnamyl aldehyde **9** (Scheme 4). Even in the presence of fluoride ions in the anodic alkoxylation, any fluorinated products were not formed at all. This can be explained in terms with much lower nucleophilicity of a fluoride ion compared with methanol. Supporting this, we have reported fluoride ion mediated anodic methoxylation of organosulfur and organoselenium compounds.[58–60]

In consideration to both Table IV and Scheme 3, the regioselectivity of anodic alkoxylation can be summarized in Figure 2, and the regioselectivity was found to depend on the bulkiness of alcohols. Namely, it was found that the selectivity of terminal alkoxylation increased with an increase of bulkiness of alkyl group of alcohols.

Next, anodic acetoxylation of (3-phenyl-2-propynyl)boronic acid pinacol ester **4** and its trimethylsilyl analogue **5** was comparatively investigated in NaOAc/AcOH using platinum and graphite anodes. As shown in Table V (entry 2), anodic acetoxylation of **4** at a graphite anode proceeded with eliminating a bory group to afford the desired acetoxylated product **10** in moderate yield (44%). Anodic acetoxylation of **5** at a graphite anode also proceeded with eliminating a silyl group to provide **10** in better yield (53% in Table V, entry 4) compared with the case of **4**. In both cases of **4** and **5**, a platinum anode was not suitable due to anodic passivation (formation of non-conducting polymer film on the anode surface).

Finally, anodic methoxylation of **4** and **5** was comparatively investigated at a platinum anode in Et$_4$NOTs/MeOH (Table VI). Quite different from **1**, **4** underwent anodic methoxylation even in a neutral electrolytic solution to afford methoxylated product **11a** mainly in low yield (entry 1) although the oxidation potential of **4** is much higher compared with **1**. In contrast to **4**, anodic methoxylation of **5** gave three products including **11a** without product selectivity (entry 2). In both cases, considerable amount of starting materials remained due to their high oxidation potentials. Therefore, anodic methoxylation **4** was carried out in the presence of fluoride ions similarly to the anodic methoxylation of **1**. As shown in Table VI (entry 3), methoxylation proceeded well to provide α-methoxylated product **11a** mainly as well as α-hydroxyl product **12** and aldehyde derivative **13** in moderate total yield (53%). Next, anodic oxidation of **4** in allyl alcohol and isopropyl alcohol was also performed similarly. Although allyl alcohol is readily oxidized, anodic substitution with allyl alcohol proceeded to give the desired product **11b** in reasonable yield (entry 4). Anodic isopropoxylation also took place although the yield of **11c** was low. In all cases, α-hydroxylated product **12** was formed considerably or mainly (entry 5). A small amount of water contaminated in an electrolytic solution seems to be a reason for the anodic hydroxylation.

Anodic alkoxylation and hydroxylation of **4** in the presence of fluoride ions seem to proceed through electron transfer from the corresponding trifluoroborate derivative in situ formed from **4** and fluoride ions in a similar manner to the case of **1**. Aldehyde derivative **13** seems to be formed by further anodic oxidation of **11** and **12**.

Conclusions

We examined the electrochemical properties of organoboronic acid pinacol esters having a double or triple bond at the α-position. Their oxidation potentials are much higher than those of the corresponding trimethylsilyl compounds. However, it was found that the presence of fluoride ions markedly decreased the oxidation potentials of the organoboronic acid pinacol esters. Such remarkable cathodic shift of the oxidation potentials can be explained by a negatively charged trifluoroborate moiety in situ formed as well as β-effect due to well overlapping of a C-B σ bond with unsaturated bond, which was confirmed by calculations. These effects enabled to achieve regioselective anodic acetoxylation and alkoxylation. Thus, we found that a boronic acid ester group in a molecule having a neighboring unsaturated bond serves as an efficient electroauxiliary similar to a well-known silyl group.

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