Electrochimica Acta xxx (2015) xxx-xxx



Contents lists available at ScienceDirect

### Electrochimica Acta



journal homepage: www.elsevier.com/locate/electacta

### Electrochemical Properties and Reactions of Sulfur-Containing Organoboron Compounds

### Masahiro Tanigawa, Yu Kuriyama, Shinsuke Inagi<sup>1</sup>, Toshio Fuchigami<sup>1,\*</sup>

Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

#### ARTICLE INFO

Article history: Received 8 January 2016 Received in revised form 8 February 2016 Accepted 9 February 2016 Available online xxx

Keywords: Electrosynthesis Anodic substitution reaction Organoboron compound β-Effect Electrochemical fluorination

#### 1. Introduction

Organoboron compounds have been widely used in the fields of synthetic organic chemistry toward both materials chemistry and pharmaceutral sciences [1]. The unique behaviors of organoboron compounds are mainly due to the Lewis acidity, arising from their vacant p-orbital on the boron atom. For example, it induces the formation of the key intermediate, borane-alkene complex, in hyrdoboration reaction [2,3]. In addition, it allows easy formation of a boronate complex, which is also an important step in homologation [4,5] and Suzuki-Miyaura coupling reaction [6,7]. The preferential ate complex formation with fluoride ion due to the large bond energy between boron and fluorine atoms is potentially applicable to fluoride ion sensors [8–11].

On the other hand, only limited examples of electrochemical reaction of organoboron compounds have been reported so far. Anodic oxidation of alkylboronic acids in aqueous NaOH solution resulted in formation of the corresponding dimers or olefins via radical or cation intermediates [12–15]. Suzuki and his co-workers also reported that anodic oxidation of trialkylboranes in NaOMe/MeOH and NaOAc/AcOH generated alkyl radical or cation species, followed by radical coupling or nucleophilic substitutions with methoxide and acetate ions depending on anode materials [16–19]. These reports imply the possibility of the

#### ABSTRACT

Electrochemical analyses of 4,4,5,5-tetramethyl-2-phenylsulfanylmethyl-[1,3,2]dioxaborolane and tetra*n*-butylammonium phenylthiomethyltrifluoroborate were comparatively studied by cyclic voltammetry measurements and we found for the first time the  $\beta$ -effect of organoborate, which was indicated by experimental and theoretical aspects. The organoborate was found to have a much lower oxidation potential compared to the organoborane. Anodic substitution reaction of organoboronate ester and organoborate was successfully carried out in the presence of nucleophiles to afford the selectively substituted products in good yields.

© 2016 Elsevier Ltd. All rights reserved.

application of organoboron compounds, especially their ate complex form, to electroorganic synthesis. However, they did not show the detailed electrochemical analyses and reaction mechanisms. Becker et al. exhibited the carbon-boron bond cleavage by electrogenerated bromonium ion [20]. Unfortunately, the reactive bromonium ion could not control the selectivity of the reaction. Furthermore, Waldvogel and his co-workers reported unique boron-templated electrosynthesis of 2,2'-biphenols from sodium tetraphenoxy borates [21]. However, this report does not deal with carbon-boron cleavage.

Besides the development of typical borane chemistry, recent progress in chemistry of organotrifluoroborate compounds is noticeable because their exceptional stability at ambient conditions, and their inherent ate complex forms are widely available in synthetic chemistry [22,23]. However, to the best of our knowledge, there have been no reports on the investigation of organotrifluoroborate by electrochemical approach. Moreover, no reports dealing with anodic oxidation of organoboron compounds containing a heteroatom like sulfur have been published so far.

Herein, we report the first investigation of electrochemical behaviors of organotrifluoroborate together with the application to anodic substitution reactions.

#### 2. Experimental

#### 2.1. General Information

\* Corresponding author. Tel.: +81 45 924 5407; fax: +81 45 924 5407.

http://dx.doi.org/10.1016/j.electacta.2016.02.051 0013-4686/© 2016 Elsevier Ltd. All rights reserved. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on JEOL JNM EX-270 (<sup>1</sup>H: 270 MHz, <sup>13</sup>C: 67.8 MHz, <sup>19</sup>F: 254.05 MHz) spectrometer in

E-mail address: fuchi@echem.titech.ac.jp (T. Fuchigami).

<sup>&</sup>lt;sup>1</sup> ISE member.

#### M. Tanigawa et al./Electrochimica Acta xxx (2015) xxx-xxx

CDCl<sub>3</sub>. The chemical shifts for <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were given in  $\delta$  (ppm) from internal TMS, CDCl<sub>3</sub> and monofluorobenzene, respectively. Cyclic voltammetry 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.

#### 2.2. Measurement of cyclic voltammetry

Cyclic voltammetry 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<sub>2</sub> gas before use.

#### 2.3. Materials

Thioanisole (1), 4,4,5,5-tetramethyl-2-phenylsulfanylmethyl-[1,3,2]dioxaborolane (2), and allyltrimethylsilane were purchased and used without purification. Potassium phenylthiomethyltrifluoroborate [24] and tetra-*n*-butylammonium allyltrifluoroborate [25] were prepared according to the literatures. The known methoxylated, ethoxylated, acetoxylated, allylated and fluorinated products (**4a,4b**, **4c**, **5** and **6**) were identified by comparison with the spectral data of their authentic samples [26–28].

## 2.4. Synthesis of tetra-n-butylammonium phenylthiomethyltrifluoroborate (**3**)

To a stirred solution of potassium phenylthiomethyltrifluoroborate (5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), tetra-*n*-butylammonium hydroxide (5 mmol) in water (40%) was added and the reaction mixture was stirred for 2 h at room temperature. The mixture was added brine and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over MgSO<sub>4</sub> and evaporated under reduced pressure. A clear crystal was obtained in 100% yield. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.24–7.14 (m, 4H), 6.97 (t, *J* = 7.1 Hz, 1H), 3.19 (t, *J* = 8.3 Hz, 8H), 2.00 (q, *J* = 5.4 Hz, 2H), 1.65–1.53 (m, 8H), 1.48–1.35 (m, 8H), 0.98 (t, *J* = 7.2 Hz, 12H); <sup>13</sup>C NMR (67.8 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  143.4, 128.0, 125.1, 122.7, 58.5, 23.9, 19.7, 13.7; Anal. Calcd. for C<sub>23</sub>H<sub>43</sub>BF<sub>3</sub>NS: C, 63.73; H, 10.00; N, 3.23; S, 7.40. Found: C, 63.89; H, 10.24; N, 3.17; S, 7.35. The ammonium salt shows higher solubility in organic solvents than the precursor potassium salt.

2.5. A typical procedure for anodic methoxylation, ethoxylation and acetoxylation

Constant current  $(5 \text{ mA/cm}^2)$  anodic oxidation of **2** or **3** (1 mmol) was carried out with a graphite anode  $(2 \text{ cm} \times 2 \text{ cm})$  and a platinum cathode  $(2 \text{ cm} \times 2 \text{ cm})$  in 10 mL of alcohol with and without 0.1 M Et<sub>4</sub>NOTs or in 0.5 M NaOAc/AcOH in an undivided cell. After electrolysis, to the mixture was added water and extracted with CHCl<sub>3</sub>. The organic phase was washed with an aqueous solution of NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>. The solution was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography.

#### 2.6. A typical procedure for anodic allylation

Constant current (5 mA/cm<sup>2</sup>) anodic allylation of **3** (0.2 mmol) was carried out with a graphite anode (2 cm  $\times$  2 cm) and a platinum cathode (2 cm  $\times$  2 cm) in 10 mL of tetra-*n*-butylammonium allyltrifluoroborate (2.0 mmol)/MeNO<sub>2</sub> in an undivided cell at 50 °C. After electrolysis, the electrolytic solution was passed

through a short column filled with silica gel using *n*-hexane as an eluent to remove excess allyltrifluoroborate. The yield of **5** in the eluent was estimated by <sup>1</sup>H NMR using nitromethane as an internal standard.

#### 2.7. A typical procedure for anodic fluorination

A constant current (5 mA/cm<sup>2</sup>) was passed for anodic fluorination of **2** (1.0 mmol) in a plastic undivided cell equipped with platinum anode and cathode (2 cm × 2 cm) containing 10 mL of 1 M Et<sub>3</sub>N-3HF/DME. After electrolysis, the electrolytic solution was passed through a short column with silica gel to remove salts. The yield of **6** was estimated by <sup>19</sup>F NMR using monofluorobenzene as an internal standard.

#### 3. Results and discussion

#### 3.1. $\beta$ -Effect of trifluoroborate

At first, cyclic voltammetry measurements of thioanisole (1), 4,4,5,5-tetramethyl-2-phenylsulfanylmethyl-[1,3,2]-dioxaborolane (2) and tetra-*n*-butylammonium phenylthiomethyltrifluoroborate (3) were carried out (Fig. 1). The introduction of boron atom into the  $\alpha$ -position of the sulfur atom of thioanisole did not influence the oxidation peak potential. However, the oxidation peak potential of **3** was markedly decreased by ca. 0.5 V. This cathodic shift was caused by the existence of a trifluoroborate moiety in the molecule.

DFT calculation was performed using Gaussian 03 suit of programs [29] for further understanding the CV results. The structures of boronate ester 2 and borate 3 were optimized using the B3LYP/6-31G(d,p) method. The orbital diagrams were generated by using the GaussView program [30]. The highest occupied molecular orbital (HOMO) of 3 was mainly located on the sulfur atom and the C-B  $\sigma$  bond as shown in Fig. 1. The observed welloverlapping of these two orbitals seemed to result in the marked decrease of the oxidation potential. Such  $\beta$ -effect of organoborane compounds has never been observed so far although it is wellknown in organosilicon chemistry [31–34]. Therefore, this is the first example of  $\beta$ -effect of organoboranes. Yoshida et al. found the marked decrease of oxidation potentials of  $\alpha$ -silylorganooxygen compounds due to the  $\beta$ -effect. However, they observed only slight decrease of the oxidation potentials of organosulfur analogues. They employed the  $\beta$ -effect of a silvl group in electrochemical



**Fig. 1.** Oxidation peak potentials  $(E_p^{\text{ox}})$  of sulfides, measured in Bu<sub>4</sub>NClO<sub>4</sub>/MeCN and HOMO diagrams of **2** and **3**. Isovalue is 0.02.

. .

2

Please cite this article in press as: M. Tanigawa, et al., Electrochemical Properties and Reactions of Sulfur-Containing Organoboron Compounds, Electrochim. Acta (2016), http://dx.doi.org/10.1016/j.electacta.2016.02.051

M. Tanigawa et al./Electrochimica Acta xxx (2015) xxx-xxx

reactions and developed the new concept of electroauxiliaries, which assist the reaction proceeding in a more selective manner [35,36]. We independently reported that a silyl group bearing at the  $\alpha$ -position of thioanisole acted as a good leaving group in electrochemical reaction to achieve the selective anodic substitution reactions [37–39]. Since a silyl group is well-known to be a good leaving group as a cation, we became very much interest to know a boryl group is also a good leaving group or not. These facts and our results prompted us to investigate the potential use of boronate ester **2** and borate **3** in anodic substitution reactions.

#### 3.2. Anodic substitution reactions

Anodic methoxylation of **2** was carried out with a graphite anode  $(2 \text{ cm} \times 2 \text{ cm})$  and a platinum cathode  $(2 \text{ cm} \times 2 \text{ cm})$  in Et<sub>4</sub>NOTs/MeOH (Table 1). A theoretical amount of electricity (2 F/mol) afforded the desired methoxylated product in 78% yield (entry 1). Similarly, anodic ethoxylation of **2** using Et<sub>4</sub>NOTs/EtOH successfully proceeded (entry 2). On the other hand, it is noted that anodic methoxylation of 3 proceeded smoothly in a neutral MeOH solution without intentionally added supporting electrolyte (entry 3). Furthermore, anodic acetoxylation of 3 in NaOAc/AcOH was also successful (entry 4). In this case, a supporting electrolyte and high temperature (50 °C) were necessary in order to provide sufficient electrical conductivity to the solution and enhance the nucleophilicity of the acetate ion. Even though 2 showed the higher oxidation potential than **3** as shown in Fig. 1, there is little difference in reactivity for the substitution reaction. During the electrolysis, the cathodically generated alkoxide and acetate ion probably attacked 2 to form an ate complex, which decreased the oxidation potential of **2** significantly.

The plausible reaction mechanism of anodic substitution reaction of **2** and **3** is shown in Scheme 1. One-electron oxidation of the ate complexes at an anode and subsequent selective cleavage of carbon-boron bond generates the radical intermediate. Recently there have been a lot of reports on oxidative radical formation processes from organoborates with chemical oxidants [40,41] and photoredox catalysts [42–45], supporting the electrochemical process above. Further oxidation generates cation species of thioanisole, which reacts with coexisting nucleophiles such as alkoxide ion and acetate ion to give selectively substituted products.

#### Table 1

Anodic methoxylation, ethoxylation and acetoxylation of 2 and 3.

3

3



NaOAc/AcOH (0.5 M)

MeOH

<sup>a</sup> Isolated yield.

3

4



Scheme 1. Plausible mechanism for anodic methoxylation, ethoxylation and acetoxylation of 2 and 3.

Next, we investigated anodic substitution of 2 with allyltrimethylsilane. However, the reaction was unsuccessful since both substrates have the same oxidation potential ( $E_p^{\text{ox}} = 1.4 \text{ V}$  vs SCE). Then, we carried out anodic substitution of easily oxidizable **3**  $(E_p^{\text{ox}} = 0.9 \text{ V vs SCE})$  with allyltrimethylsilane  $(E_p^{\text{ox}} = 1.4 \text{ V vs SCE})$  or allyltrifluoroborate ( $E_p^{\text{ox}} = 1.4 \text{ V vs SCE}$ ) as nucleophiles to obtain the corresponding homoally/sulfide 5 without supporting electrolyte (Table 2). When allyltrimethylsilane was used as the nucleophile, the desired homoallylsulfide was detected in low yield (entries 1 and 2). The silyl group of allylsilane seemed to trap the fluoride ion of **3** [46,47], which resulted in the prohibition of both the preferential oxidation of 3 and selective elimination of trifluoroborate. On the other hand, the use of allyltrifluoroborate as the nucleophile afforded 5 in good yields although the reaction temperature had to be raised to dissolve high concentration of allyltrifluoroborate in nitromethane. In this case, the higher oxidation potential of resulting homoally lsulfide **5** ( $E_p^{\text{ox}} = 1.5 \text{ V}$  vs SCE) than those of both the substrate and trapping reagent effectively prevented the overoxidation of the product even after an excess amount of charge was passed (entry 7).

To further investigate the scope of the anodic substitution, anodic fluorination [48–50] of **2** was carried out using a poly (hydrogen fluoride) salt, Et<sub>3</sub>N-3HF as a supporting electrolyte and a fluorine source (Table 3). The fluoride ion can also assist the formation of an active ate complex for electrochemical oxidation. Constant current electrolysis of **2** at 2 F/mol with a graphite anode in MeCN gave the corresponding fluorinated product **6** in 39% yield (entry 1). When DME was used as a solvent, the yield of **6** was

4a

4c

Yield (%)<sup>a</sup>

78

55

66

65

Please cite this article in press as: M. Tanigawa, et al., Electrochemical Properties and Reactions of Sulfur-Containing Organoboron Compounds, Electrochim. Acta (2016), http://dx.doi.org/10.1016/j.electacta.2016.02.051

rt

50

#### M. Tanigawa et al./Electrochimica Acta xxx (2015) xxx-xxx

4

**Table 2**Anodic allylation of **3** under various conditions.



Entry	R	Solvent	Temperature ( °C)	Electricity (F/mol)	Yield (%) <sup>a</sup>
1 2 3	–SiMe <sub>3</sub> –SiMe <sub>3</sub> ⊖ ⊕ -BF <sub>3</sub> Bu₄N	MeCN DME MeNO <sub>2</sub>	rt rt 50	3 3 1	10 trace 25
4	$\ominus \oplus \oplus$ -BF <sub>3</sub> Bu <sub>4</sub> N	MeNO <sub>2</sub>	50	3	58
5	⊖ ⁻BF <sub>3</sub> Bu₄N	MeNO <sub>2</sub>	50	5	67
6	⊖ −BF <sub>3</sub> Bu <sub>4</sub> N	MeNO <sub>2</sub>	50	10	73
7	⊖ −BF <sub>3</sub> Bu <sub>4</sub> N	MeNO <sub>2</sub>	50	13	69

<sup>a</sup> Determined by <sup>1</sup>H NMR.

#### Table 3

Anodic fluorination of **2** under various conditions.



Entry	Anode material	Solvent	Yield (%) <sup>a</sup>
1	Graphite	MeCN	39
2	Graphite	DME	57
3	Platinum	DME	58
4	Platinum	neat	20

<sup>a</sup> Determined by <sup>19</sup>F NMR.

increased due to the solvent effect of DME on the enhancement of nucleophilicity of fluoride ions (entry 2) [51]. Platinum was also available as an anode material to afford moderate yield of **6** (entry 3). In entry 4, the use of neat  $Et_3N$ -3HF without solvent resulted in giving lower yield of **6** compared to the former cases.

#### 4. Conclusion

We clarified for the first time the electrochemical behaviors of sulfur-containing organoborane and organotrifluoroborate. It was demonstrated that both boryl and trifluoroborate groups were

Please cite this article in press as: M. Tanigawa, et al., Electrochemical Properties and Reactions of Sulfur-Containing Organoboron Compounds, Electrochim. Acta (2016), http://dx.doi.org/10.1016/j.electacta.2016.02.051

#### M. Tanigawa et al./Electrochimica Acta xxx (2015) xxx-xxx

good leaving groups.  $\beta$ -Effect in the trifluoroborate was also confirmed for the first time by experimental and calculations, which made it possible to achieve the selective anodic substitution reactions without intentionally added supporting electrolyte. These results exhibit the potentials of organoboron compounds in electroorganic synthesis.

#### Acknowledgments

We thank Prof. Jun-ichi Yoshida at Kyoto University and Prof. Toshiki Tajima at Shibaura Institute of Technology for their valuable suggestions.

#### References

- A. Pelter, K. Smith, H.C. Brown, Borane Reagents, Academic Press London, 1988.
   H.C. Brown, B.C. Subba Rao, A new technique for the conversion of olefins into
- organoboranes and related alcohols, J. Am. Chem. Soc. 78 (1956) 5694. [3] H.C. Brown, I.R. Schwier, B. Singaram, Simple synthesis of
- monoisopinocampheylborane of high optical purity, J. Org. Chem. 43 (1978) 4395.
- [4] H.C. Brown, S.M. Singh, M.V. Rangaishenvi, Organoboranes. 46. New procedures for the homologation of boronic esters: A critical examination of the available procedures to achieve convenient homologation of boronic esters, J. Org. Chem. 51 (1986) 3150.
- [5] H.C. Brown, A.S. Phadke, M.V. Kangaishenvi, Ring enlargement of boracyclanes via sequential one-carbon homologation. The first synthesis of boracyclanes in the strained medium ring range, J. Am. Chem. Soc. 110 (1988) 6263.
- [6] N. Miyaura, A. Suzuki, Palladium-catalyzed cross-coupling reactions of organoboron compounds, Chem. Rev. 95 (1995) 2457.
   [7] A. Suzuki, Pacent advances in the cross coupling reactions of accurate the second coupling reaction of accurate the second coupl
- [7] A. Suzuki, Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998, J. Organomet. Chem. 576 (1999) 147.
- [8] S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, Dibenzoborole-containing  $\pi$ -electron systems: remarkable fluorescence change based on the "on/off" control of the  $p\pi$ - $\pi$ \* conjugation, J. Am. Chem. Soc. 124 (2002) 8816. [9] S. Solé, F.P. Gabbaï, A bidentate borane as colorimetric fluoride ion sensor,
- [9] S. Solé, F.P. Gabbaï, A bidentate borane as colorimetric fluoride ion sensor, Chem. Commun. (2004) 1284.
   [0] X.V. in D.P. as S. Mage Cheme transfer prelimination and the sense of the
- [10] X.Y. Liu, D.R. Bai, S. Wang, Charge-transfer emission in nonplanar threecoordinate organoboron compounds for fluorescent sensing of fluoride, Angew. Chem. Int. Ed. 45 (2006) 5475.
- [11] M. Miyata, Y. Chujo,  $\pi$ -Conjugated organoboron polymer as an anion sensor, Polym. J. 34 (2002) 967.
- [12] A.A. Humffray, LF.G. Williams, Anodic oxidation of *n*-butylboronic acid, Chem. Commun. (1965) 616.
- [13] J.T. Keating, P.S. Skell, Free carbonium ions in the anodic oxidations of alkanecarboxylates, alkaneboronates, and alkyl halides, J. Org. Chem. 34 (1969) 1479.
- [14] A.A. Humffray, L.F.G. Williams, The anodic oxidation of boronic acids–I. *n*-Butaneboronic acid: product yields and comparison with pentanoic acid, Electrochim. Acta 17 (1972) 401.
- [15] L.F.G. Williams, A.A. Humffray, The anodic oxidation of boronic acids–II. *n*-Butaneboronic acid: electrode kinetics, Electrochim. Acta 17 (1972) 409.
- [16] T. Taguchi, M. Itoh, A. Suzuki, Anodic oxidation of trialkylboranes. A new procedure of alkyl coupling reaction of organoboranes, Chem. Lett. (1973) 719.
  [17] T. Taguchi, Y. Takahashi, M. Itoh, A. Suzuki, Anodic oxidation of trialkylboranes
- using graphite as the anode. Novel reaction of organoboranes proceeding through a carbonium ion mechanism, Chem. Lett. (1974) 1021.
- [18] Y. Takahashi, M. Tokuda, M. Itoh, A. Suzuki, A new electrochemical synthesis of nitroalkanes from organoboranes, Synthesis (1976) 616.
- [19] Y. Takahashi, M. Tokuda, M. Itoh, A. Suzuki, Electrochemical reaction of trialkylboranes with acetone, Chem. Lett. (1978) 669.
- [20] D.-Q. Shi, A. Gitkis, J.Y. Becker, Anodic carbon–boron bond cleavage through the intermediacy of electrogenerated bromonium ion, Electrochim. Acta 53 (2007) 1824.
- [21] I.M. Malkowsky, C.E. Rommel, R. Fröhlich, U. Griesbach, H. Pütter, S.R. Waldvogel, Novel template-directed anodic phenol-coupling reaction, Chem. Eur. J. 17 (2006) 7482.
- [22] S. Darses, J.-P. Genet, Potassium organotrifluoroborates: new perspectives in organic synthesis, Chem. Rev. 108 (2008) 288.
- [23] S. Darses, J.-P. Genet, Potassium trifluoro(organo) borates: new perspectives in organic chemistry, Eur. J. Org. Chem. (2003) 4313.
- [24] E. Vedejs, R.W. Chapman, S.C. Fields, S. Lin, M.R. Schrimpf, J. Org. Chem. 60 (1995) 3020.
- [25] A.N. Thadani, R.A. Batey, A mild protocol for allylation and highly diastereoselective syn or anti crotylation of aldehydes in biphasic and aqueous media utilizing potassium allyl- and crotyltrifluoroborates, Org. Lett. 4 (2002) 3827.

- [26] O. Itoh, T. Numata, T. Yoshimura, S. Oae, Intermolecular pummerer rearrangement reactions of alkyl phenyl and dialkyl sulfoxides with acetic anhydride, Bull. Chem. Soc. Jpn. 56 (1983) 343.
- [27] G.A. Russel, P. Ngoviwatchai, H.I. Tashtoush, A. Pla-Dalmau, R.K. Khanna, Reactions of alkylmercurials with heteroatom-centered acceptor radicals, J. Am. Chem. Soc. 110 (1988) 3530.
- [28] T. Umemoto, G. Tomizawa, α-Fluorination of sulfides with N-fluoropyridinium triflates, Bull. Chem. Soc. Jpn. 59 (1986) 3625.
- [29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.É. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision E.O1, Gaussian, Inc., Wallingford, CT, 2004.
- [30] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W.L. Hovell, R. Gilliland, GaussView, Version 4.1, Semichem, Inc., Shawnee Mission, KS, 2003.
- [31] J.B. Lambert, R.B. Finzel, The modes of β-silyl involvement in solvolysis, J. Am. Chem. Soc. 104 (1982) 2020.
- [32] S.G. Weierschke, J. Chandrasekhar, W. Jorgensen, Magnitude and origin of the β-silicon effect on carbenium ions, J. Am. Chem. Soc. 107 (1985) 1496.
- [33] E. Block, J.A. Yencha, M. Aslam, V. Eswarakrishnan, J. Luo, A. Sano, Gas-phase determination of the geometric requirements of the silicon β-effect. Photoelectron and Penning ionization electron spectroscopic study of silylthiiranes and -oxiranes. Synthesis and chemistry of *trans*-2,3-bis (trimethylsilyl)thiirane, J. Am. Chem. Soc. 110 (1988) 4748.
- [34] J.B. Lambert, Y. Zhao, R.W. Emblidge, L.A. Salvador, X. Lio, J. So, E.C. Chelius, The  $\beta$  effect of silicon and related manifestations of  $\beta$  conjugation, Acc. Chem. Res. 32 (1999) 183.
- [35] J. Yoshida, K. Nishiwaki, Redox selective reactions of organo-silicon and -tin compounds, J. Chem. Soc. Dalton Trans. (1998) 2589.
- [36] J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, Modern strategies in electroorganic synthesis, Chem. Rev. 108 (2008) 2265.
- [37] T. Koizumi, T. Fuchigami, T. Nonaka, A novel synthesis of phenylthiomethyl (PTM) ethers and esters by anodic oxidation of phenyl trimethylsilylmethyl sulfide, Chem. Lett. (1987) 1095.
- [38] T. Koizumi, T. Fuchigami, T. Nonaka, Anodic oxidation of  $\alpha$ , $\alpha'$ -bis (trimethylsilyl) xylenes in alcohols, Electrochim. Acta 33 (1988) 1635.
- [39] T. Koizumi, T. Fuchigami, T. Nonaka, Anodic oxidation of (trimethylsilyl) methanes with  $\pi$ -electron substituents in the presence of nucleophiles, Bull. Chem. Soc. Jpn. 62 (1989) 219.
- [40] G. Sorin, R.M. Malloquin, Y. Contie, A. Baralle, M. Malacria, J.-P. Goddard, L. Fensterbank, Oxidation of alkyl trifluoroborates: an opportunity for tin-free radical chemistry, Angew. Chem. Int. Ed. 49 (2010) 8721.
- [41] G.A. Molander, V. Colombel, V.A. Braz, Direct alkylation of heteroaryls using potassium alkyl- and alkoxymethyltrifluoroborates, Org. Lett. 13 (2011) 1852.
- [42] Y. Yasu, T. Koike, M. Akita, Visible light-induced selective generation of radicals from organoborates by photoredox catalysis, Adv. Synth. Catal. 354 (2012) 3414.
- [43] K. Miyazawa, Y. Yasu, T. Koike, M. Akita, Visible-light-induced hydroalkoxymethylation of electron-deficient alkenes by photoredox catalysis, Chem. Commun. 49 (2013) 7249.
- [44] H. Huang, G. Zhang, L. Gong, S. Zhang, Y. Chen, Visible-light-induced chemoselective deboronative alkynylation under biomolecule-compatible conditions, J. Am. Chem. Soc. 136 (2014) 2280.
- [45] J.C. Tellis, D.N. Primer, G.A. Molander, Single-electron transmetalation in organoboron cross-coupling by photoredox/nickel dual catalysis, Science 345 (2014) 433.
- [46] E. Vedejs, R.W. Chapman, S.C. Fields, S. Lin, M.R. Schrimpf, Conversion of Arylboronic Acids into Potassium Aryltrifluoroborates: convenient precursors of arylboron difluoride lewis acids, J. Org. Chem. 60 (1995) 3020.
- [47] E. Vedejs, S.C. Fields, R. Hayashi, S.R. Hitchcock, D.R. Powell, M.R. Schrimpf, Asymmetric memory at labile, stereogenic boron: enolate alkylation of oxazaborolidinones, J. Am. Chem. Soc. 121 (1999) 2460.
- [48] T. Fuchigami, S. Inagi, Selective electrochemical fluorination of organic molecules and macromolecules in ionic liquids, Chem. Commun. 47 (2011) 10211.
- [49] T. Fuchigami, S. Inagi, Fluorination, in: O. Hammerich, B. Speiser (Eds.), Organic Electrochemistry, Ch. 20, 5th ed., CRC Press, Boca Raton, FL, 2015, pp. 807.
- [50] T. Fuchigami, S. Inagi, Organic electrosynthesis, in: T. Fuchigami (Ed.), Fundamentals and Applications of Organic Electrochemistry, Ch. 5, Wiley, West Sussex, 2015, pp. p. 83.
- [51] Y. Hou, T. Fuchigami, Electrochemical partial fluorination of organic compounds XL. Solvent effects on anodic fluorination of heterocyclic sulfides, J. Electrochem. Soc. 147 (2000) 4567.

Please cite this article in press as: M. Tanigawa, et al., Electrochemical Properties and Reactions of Sulfur-Containing Organoboron Compounds, Electrochim. Acta (2016), http://dx.doi.org/10.1016/j.electacta.2016.02.051