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Electrochemical Properties and Reactions of Sulfur-Containing Organoboron Compounds

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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 β-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.

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 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

^{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

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$CDCl_3$. The chemical shifts for ^{1}H, ^{13}C and ^{19}F NMR spectra were given in δ (ppm) from internal TMS, $CDCl_3$ 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 ($\varphi = 0.8$ 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.

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_2Cl_2 (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_2Cl_2. The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. A clear crystal was obtained in 100% yield. ^{1}H NMR (270 MHz, $CDCl_3$, ppm): δ 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); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm): δ 143.4, 128.0, 125.1, 122.7, 58.5, 23.9, 19.7, 13.7; Anal. Calcd. for $C_{23}H_{43}BF_3NS$: 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 mA/cm^2) anodic oxidation of **2** or **3** (1 mmol) was carried out with a graphite anode (2 cm × 2 cm) and a platinum cathode (2 cm × 2 cm) in 10 mL of alcohol with and without 0.1 M Et_4NOTs or in 0.5 M NaOAc/AcOH in an undivided cell. After electrolysis, to the mixture was added water and extracted with $CHCl_3$. The organic phase was washed with an aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. 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^2) anodic allylation of **3** (0.2 mmol) was carried out with a graphite anode (2 cm × 2 cm) and a platinum cathode (2 cm × 2 cm) in 10 mL of tetra-*n*-butylammonium allyltrifluoroborate (2.0 mmol)/$MeNO_2$ 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 ^{1}H NMR using nitromethane as an internal standard.

2.7. A typical procedure for anodic fluorination

A constant current (5 mA/cm^2) 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_3N-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 ^{19}F NMR using monofluorobenzene as an internal standard.

3. Results and discussion

3.1. β-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 α-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 σ bond as shown in Fig. 1. The observed well-overlapping of these two orbitals seemed to result in the marked decrease of the oxidation potential. Such β-effect of organoborane compounds has never been observed so far although it is well-known in organosilicon chemistry [31–34]. Therefore, this is the first example of β-effect of organoboranes. Yoshida et al. found the marked decrease of oxidation potentials of α-silylorganooxygen compounds due to the β-effect. However, they observed only slight decrease of the oxidation potentials of organosulfur analogues. They employed the β-effect of a silyl group in electrochemical

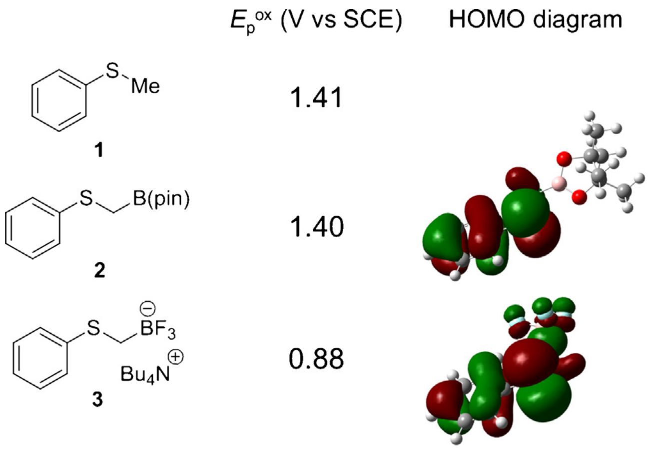

Fig. 1. Oxidation peak potentials (E_p^{ox}) of sulfides, measured in Bu_4NClO_4/MeCN and HOMO diagrams of **2** and **3**. Isovalue is 0.02.