

# Anodic Methoxylation of 2-Acyloxy-3,3,3-trifluoropropyl Sulfides Accompanying with [1,2]-Rearrangement of the Acyloxy Group and Anodic Cyclization of 2-(*t*-Butoxycarbonyl)oxy-3,3,3-trifluoropropyl Sulfide

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Anodic methoxylation of 2-acyloxy-3,3,3-trifluoropropyl sulfides was carried out in methanol containing Et<sub>3</sub>N-3HF as a supporting electrolyte and mediator using an undivided cell to provide the corresponding  $\alpha$ -methoxylated products and unexpected  $\beta$ -methoxylated products owing to [1,2]-rearrangement of the acyloxy group in the latter case. It was also found that the regioselectivity and diastereoselectivity of the anodic methoxylation were greatly affected by the concentration of methanol in an electrolytic solvent, electrolytic temperature, and bulkiness of acyloxy group. This is the first example of anodic methoxylation of sulfides accompanying with rearrangement of an acyloxy group. Furthermore, anodic intramolecular cyclization of 2-(*t*-butoxycarbonyl)oxy-3,3,3-trifluoropropyl sulfide was achieved in 0.01 M Et<sub>3</sub>N-3HF/MeCN eliminating a *t*-butyl cation to provide the corresponding trifluoromethylated ethylene carbonate derivative in good yield.

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Anodic substitution is known to be one of characteristic organic electrochemical reactions. For example, anodic a-methoxylation of organonitrogen compounds has been well-established.<sup>1-3</sup> However, the analogous  $\alpha$ -methoxylation of organosulfur compounds is rather limited.<sup>3</sup> Namely, the methoxylation proceeds only when organosulfur compounds have a strongly electron-withdrawing  $group^{4-6}$  or a good leaving group like sily1 $^{7-13}$  and boryl groups  $^{14-19}$  at the  $\alpha$ position to the sulfur atom. On the other hand, we have found that a fluoride ion markedly promotes anodic  $\alpha$ -methoxylation of sulfides even when the sulfides have relatively weak electron-withdrawing and electron-donating groups as shown in Scheme 1.<sup>20–22</sup> It was also shown that Et<sub>3</sub>N-3HF was more effective than tetrabutylammonium fluoride. Since a fluoride ion mediator is highly effective for the anodic generation of α-carbocation to a sulfur atom, a fluoride ion mediator was successfully applied to anodic intramolecular cyclization of  $\alpha$ -(phenylthio)acetamides to provide indole and 3-oxotetrahydroisoquinoline derivatives.<sup>23</sup>

On the other hand, organofluorine compounds are highly useful for development of novel functional materials, pharmaceuticals and agrochemicals. However, methods for their synthesis are strictly limited in many cases because of specific properties of fluorine atoms. For example, nucleophilic substitution at  $\alpha$ - and  $\beta$ -positions to a CF<sub>3</sub> group is generally difficult because of its strongly electron-withdrawing nature.<sup>24-27</sup>

With these facts in mind, we applied the fluoride ion-mediator to anodic methoxylation of 2-acyloxy-3,3,3-trifluoropropyl sulfides and intramolecular cyclization of 2-(*t*-butoxycarbonyl)oxy-3,3,3trifluoropropyl sulfide to form cyclic carbonate derivative. Since all of the starting sulfides have a stereogenic center, the stereoselectivity of the products would be interesting.

## Experimental

**General.**—<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 CDCl<sub>3</sub>. The chemical shifts for <sup>1</sup>H and <sup>13</sup>C were given in  $\delta$  (ppm) downfield from internal TMS (0.00) and <sup>19</sup>F NMR chemical shifts are given in  $\delta$  (ppm) upfield from external trifluoroacetic acid, respectively. Preparative electrolysis experiments were carried out with Hokuto Denko HABF 501 potentiostat/galvanstat. Mass spectra and high-resolution mass spectra were obtained with a Shimazu



R = Me, CH<sub>2</sub>F, CHF<sub>2</sub>, CF<sub>3</sub>CH<sub>2</sub>, CF<sub>3</sub>CH(OMe), CF<sub>3</sub>CH(COOEt)

Scheme 1. Fluoride ion-mediated anodic  $\alpha$ -methoxylation of sulfides.

GCMS-QP-2000A or JEOL JMS-700 mass spectrometer. <sup>19</sup>F NMR yields and diastereomeric excess (d.e.) were estimated using  $\alpha$ , $\alpha$ , $\alpha$ -trifluorotoluene as an internal standard.

*Materials.*—2-Acyloyl-3,3,3-trifluoropropyl phenyl sulfides 1a-1e.—Acid anhydride (60 mmol) was added dropwise to a stirred solution of 2-hydroxy-3,3,3-trifluoropropyl phenyl sulfide.<sup>34</sup> (50 mmol) derived from thiophenol and 3,3,3-trifluoropropene oxide in 50 ml of CH<sub>2</sub>Cl<sub>2</sub> containing Et<sub>3</sub>N (60 mmol) at 0°C and the solution was stirred for 1 h at 0°C. After the solution was stirred at room temperature overnight, water was added to the solution, followed by addition of sat. aq. NaHCO<sub>3</sub> solution to neutralize, and then the product (oily layer) was extracted repeatedly with CH<sub>2</sub>Cl<sub>2</sub>. The extracts were dried over anhydrous MgSO<sub>4</sub> and the solvent was removed by evaporation under reduced pressure. The products **1a-1e** were isolated by silica gel column chromatography (eluent: hexane/AcOEt = 12:1). The yields of **1a-1e** were 96%, 87%, 79%, 94%, and 93% yield, respectively.

**2-Acetoxy-3,3,3-trifluoropropyl phenyl sulfide** (1a) colorless oil; <sup>1</sup>H NMR  $\delta$  7.25-7.44 (m, 5H), 5.37-5.50 (m, 1H), 3.15-3.30 (m, 2H), 2.04 (s, 3H); <sup>13</sup>C NMR  $\delta$  168.88, 131.20, 129.25, 129.22, 127.51, 123.03, 68.47, 32.92, 20.02; <sup>19</sup>F NMR  $\delta$  –0.12 (d, *J* = 6.21 Hz); MS: m/z = 264 (M<sup>+</sup>); analysis calculated for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>O<sub>2</sub>S: C, 49.99; H, 4.20; F, 21.57; S, 12.13. Found: C, 49.71; H, 4.09; F, 21.47; S, 12.01.

**2-**(*n***-Propylcarbonyloxy)-3,3,3-trifluoropropyl phenyl sulfide** (**1b**) colorless oil; <sup>1</sup>H NMR  $\delta$  7.28-7.43 (m, 5H), 5.43-5.48 (m, 1H), 3.08-3.29 (m, 2H), 2.28 (t, J = 3.3 Hz, 2H), 1.59-1.72 (m, 2H), 0.95 (t, J = 7.26 Hz, 3H); <sup>13</sup>C NMR  $\delta$  171.12, 133.42, 130.73, 127.03, 122.05, 67.70, 34.97, 32.63, 17.70, 12.92; <sup>19</sup>F NMR  $\delta$  0.08 (d, J = 6.82Hz); MS: m/z = 292 (M<sup>+</sup>); analysis calculated for C<sub>13</sub>H<sub>15</sub>F<sub>3</sub>O<sub>2</sub>S: C, 53.41; H, 5.17; F, 19.50; S, 10.97. Found: C, 53.44; H, 5.17; F, 19.99; S, 10.73.

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**2-**(*t*-Butylcarbonyloxy)-**3**,**3**,**3**-trifluoropropyl phenyl sulfide (**1c**) colorless oil; <sup>1</sup>H NMR  $\delta$  7.29- 7.42 (m, 5H), 5.36-5.43 (m, 1H), 3.08-3.32 (m, 2H), 1.27 (s, 9H); <sup>13</sup>C NMR,  $\delta$  171.12, 133.42, 130.73, 128.73, 127.03, 122.05, 67.70, 34.97, 32.63, 17.70, 12.92; <sup>19</sup>F NMR  $\delta$  -0.22 (d, *J* = 6.20 Hz); MS: m/z = 306 (M<sup>+</sup>); analysis calculated for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>2</sub>S: C, 54.89; H, 5.9; F, 18.60; S, 10.47. Found: C, 54.87; H, 5.78; F, 18.91; S, 10.27.

**2-Benzoyloxy-3,3,3-trifluoropropyl phenyl sulfide** (1d) colorless oil; <sup>1</sup>H NMR  $\delta$  7.02- 8.00 (m, 10H), 5.66-5.71 (m, 1H), 3.25-3.42 (m, 2H), <sup>13</sup>C NMR  $\delta$  134.27, 134.20, 131.91, 131.73, 130.55, 129.70, 128.93, 128.05, 123.69, 69.52, 33.95; <sup>19</sup>F NMR  $\delta$  0.13 (d, J = 6.82 Hz); MS: m/z = 326 (M<sup>+</sup>); analysis calculated for C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub>S: C, 58.89; H, 4.02; F, 17.47; S, 9.83. Found: C, 59.16; H, 4.16; F, 17.48; S, 9.83.

**2-**(*p*-Methoxybenzoyloxy)-**3**,**3**,**3**-trifluoropropyl phenyl sulfide (1e) colorless oil; <sup>1</sup>H NMR  $\delta$  7.93 (d, *J* = 2.31 Hz, 2H), 7.20-7.92 (m, 5H), 6.92 (d, *J* = 2.30 Hz, 2H), 5.66-6.93 (m, 1H), 3.86 (s, 3H), 3.23-3.39 (m, 2H); <sup>13</sup>C NMR  $\delta$  164.29, 164.00, 133.94, 132.22, 131.38, 129.21, 127.49, 123.32, 120.70, 113.73, 68.72, 55.47, 33.8; <sup>19</sup>F NMR  $\delta$  0.14 (d, *J* = 6.82 Hz); MS: m/z = 356 (M<sup>+</sup>); analysis calculated for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>S: C, 57.30; H, 4.24; F, 15.99; S, 9.0. Found: C, 57.24; H, 4.24; F, 15.99; S, 8.63.

2-Acetoxy-3-fluoropropyl phenyl sulfide (1f). A solution of sec-BuLi (1.04 M in cyclohexane/hexane, 50 ml) in dry THF was slowly added dropwise to a solution of thioanisole (6.5 ml, 55 mmol) in a minimun amount of dry THF at -78°C. After 1 h ethyl fluoroacetate (4.8 ml, 50 mmol) was added, and the mixture was stirred for 1 h. Then water was added, it was rosen slowly to room temperature. After the reaction mixture was neutralized by 2 M HCl aqueous solution, the product was extracted with ethyl acetate and washed with water, and brine. The extract was dried over MgSO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel using hexane to hexane/ethyl acetate (10/1) as an eluent to give 1.0 g (11%) of 3-fluoro-1- phenylthiopropan-2-one as a colorless oil. Then, a NaBH<sub>4</sub> (0.4 g, 10 mmol) was added dropwise to 3-fluoro-1phenylthiopropan-2-one (0.9 g, 5 mmol) in MeOH (10 ml) at 0°C for 1 h and stirred at room temperature for 24 h. After the reaction mixture was neutralized by 2 M HCl aqueous solution, it was concentrated, the product was extracted with ethyl acetate and washed with water, and brine. The extract was dried over MgSO4 and concentrated. The residue was purified by column chromatography on silica gel using hexane to hexane/ethyl acetate (4/1) as an eluent to give 0.8 g (86%) of 2-hydroxy-3-fluoropropyl phenyl sulfide as a colorless oil. Next, 2-hydroxy-3-fluoropropyl phenyl sulfide (0.7 g, 4 mmol) and triethylamine (0.7 ml, 5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was slowly added acetyl chloride (1.4 ml, 20 mmol) at 0°C for 1 h and stirred at room temperature for 24 h. After the reaction mixture was concentrated, water was added, and then the product was extracted with ethyl acetate and washed with water, and brine. The extract was dried over MgSO4 and concentrated. The residue was purified by column chromatography on silica gel using hexane to hexane/ethyl acetate (7/1) as an eluent to give 0.8 g (85%) of 1f as a colorless oil. <sup>1</sup>H NMR & 2.03 (s, 3H), 3.10-3.26 (m, 2H), 4.56 (ddd, J = 48.7 Hz, 10.3 Hz, 3.0 Hz, 1H), 4.64 (ddd, J =45.8 Hz, J = 12.4 Hz, J = 4.1 Hz, 1H), 5.01-5.15 (m, 1H), 7.19-7.43 (m, 5H); <sup>19</sup>F NMR  $\delta$  -156.10 (td, J = 47.3 Hz, J = 23.0 Hz); <sup>13</sup>C NMR  $\delta$  20.9, 32.9 (d, J = 6.2 Hz), 71.3 (d, J = 19.5 Hz), 82.1 (d, J =173.5 Hz), 126.7, 129.3, 129.8, 134.8, 170.1; MS m/z 228 (M<sup>+</sup>), 123 (M<sup>+</sup> -CH(OAc)CH<sub>2</sub>F); HRMS: m/z calcd for C<sub>11</sub>H<sub>13</sub>FO<sub>2</sub>S 228.0620, found 228.0609.

**2-Acetoxypropyl phenyl sulfide (1g)** Sulfide **1g** was prepared from 2-hydroxypropyl phenyl sulfide derived from propyrene oxide and thiophenol in a similar manner to the preparation of **1a–1e**. Colorless oil; <sup>1</sup>H NMR  $\delta$  7.41-7.19 (m, 5H), 5.08-5.01 (m, 1H), 3.20-2.94 (m, 2H), 1.96 (s, 3H), 1.33 (d, J = 5.70 Hz, 3H); MS: m/z = 210 (M<sup>+</sup>); HRMS calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>S: 210.0715. Found; 210.0697.

**2-**(*t*-**Butoxycarbonyl)oxy-3,3,3-trifluoropropyl phenyl sulfide** (4).— $K_2CO_3$  was added slowly to a stirred solution of pyrocarbonic acid di-tert-butyl ester (50 mmol) and 2-hydroxy-3,3,3-trifluoropropyl phenyl sulfide<sup>40</sup> (50 mmol) in 50 ml of THF cooled in an ice bath, and then the mixture was stirred for 1 h. After that, the mixture was stirred at room temperature over night, and then water was added and neutralized with 2 M HCl. The resulting solution was extracted with ethyl acetate repeatedly, and the extracts were dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by evapolation under reduced pressure, and the remaining oil was purified by silica gel column chromatography (eluent: hexane/AcOEt = 9:1) to provide **4** as a light yellow oil in 54% yield.

<sup>1</sup>H NMR δ 7.45-7.25 (m, 5H), 5.10-5.25 (m, 1H), 3.4-3.26 (m, 2H), 1.51 (s, 9H); <sup>13</sup>C NMR δ 151.5, 135.6, 131.23, 129.1, 127.9, 122.9 (q, J = 270 Hz), 83.9, 71.3 (q, J = 32 Hz), 33.5, 27.6; <sup>19</sup>F NMR δ -0.26 (d, J = 7.4 Hz); MS: m/z = 322 (M<sup>+</sup>); HRMS: m/z calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>3</sub>S 322.0846, found 322.0809.

A typical procedure for anodic methoxylation.-Constant current (6.25 mA/cm<sup>2</sup>) anodic oxidation of 1 (1.0 mmol) was carried out with a platinum anode and cathode (2 cm  $\times$  2 cm) in an undivided cell containing 25 ml of MeOH or MeOH/MeCN containing 0.13 M Et<sub>3</sub>N-3HF (10 eq. of F- to 1) under a dry nitrogen atmosphere. After 4 F/mol of electricity was passed, the electrolytic solution was neutralized with a saturated aqueous solution of NaHCO3, and organic solvent was removed on a rotary evaporator. The residue was extracted repeatedly with AcOEt and the extracts were dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed under reduced pressure, the NMR yield and diastereomeric excess (d.e.) of product 2 were estimated from <sup>19</sup>F NMR spectra using CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub> as an internal standard. After the estimation, the crude mixture was passed through a silica gel column (eluent: hexane/AcOEt = 13:1), and then  $\alpha$ -methoxylated and rearrangement products 2 and 3 were isolated by medium-pressure liquid chromatography (silica gel Merk Lichroprep Si 60; 37  $\varphi \times 440$ mm) on elution with hexane/2-propanol (99.9:0.1).

**2-Acetoxy-1-methoxy-3,3-trifluoropropyl phenyl sulfide (2a)** (less polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.32-7.48 (m, 5H), 5.29 (dq, J = 8.25 Hz, J = 6.20 Hz, 1H), 4.76 (d, J = 8.25 Hz, 1H), 3.56 (s, 3H), 2.16 (s, 3H); <sup>19</sup>F NMR  $\delta$  3.47 (d, J = 6.20 Hz); MS: m/z = 294 (M<sup>+</sup>); HRMS calcd. for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S: 294.0537. Found; 294.0528.

**2-Acetoxy-1-methoxy-3,3,3-trifluoropropyl phenyl sulfide (2a)** (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.33-7.54 (m, 5H), 5.63 (dq, J = 6.60 Hz, J = 3.63 Hz, 1H), 4.84 (d, J = 3.30 Hz, 1H), 3.61 (s, 3H), 2.06 (s, 3H); <sup>19</sup>F NMR  $\delta$  3.32 (d, J = 6.82 Hz); MS: m/z = 294 (M<sup>+</sup>); MS: m/z = 294 (M<sup>+</sup>); HRMS calcd. for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S: 294.0537. Found; 294.0529.

**1-Acetoxy-2-methoxy-3,3-trifluoropropyl phenyl sulfide (3a)** (less polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.36-7.76 (m, 5H), 5.65 (d, *J* = 6.27 Hz, 1H), 4.28 (dq, *J* = 6.27, 5.58 Hz, 1H), 3.33 (s, 3H), 1.65 (s, 3H); <sup>19</sup>F NMR  $\delta$  0.33 (d, *J* = 5.58 Hz); MS: m/z = 294 (M<sup>+</sup>); HRMS calcd. for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S: 294.0537. Found; 294.0533.

**1-Acetoxy-2-methoxy-3,3,3-trifluoropropyl phenyl sulfide** (**3**a) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.34-7.64 (m, 5H), 5.59 (d, J = 5.61 Hz, 1H), 4.53 (dq, J = 5.94, 5.61 Hz, 1H), 3.38 (s, 3H), 1.65 (s, 3H); <sup>19</sup>F NMR  $\delta$  = -1.13 (d, J = 6.20 Hz); MS: m/z = 294 (M<sup>+</sup>); MS: m/z = 294 (M<sup>+</sup>); HRMS calcd. for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S: 294.0537. Found; 294.0530.

**2-**(*n***-Propylcarbonyloxy)-1-methoxy-3,3,3-trifluoropropyl** phenyl sulfide (2b) (less polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$ 7.31-7.47 (m, 5H), 5.32 (dq, J = 1.45, 6.60 Hz, 1H), 4.77 (d, J = 7.92 Hz, 1H), 3.59 (s, 3H), 2.39 (t, J = 7.26 Hz, 2H), 1.71 (qt, J = 7.26, 14.56 Hz, 2H), 0.99 (t, J = 7.26 Hz, 3H); <sup>19</sup>F NMR  $\delta$  3.45 (d, J = 6.82 Hz); MS: m/z = 322 (M<sup>+</sup>); calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>3</sub>S: 322.0851. Found; 322.0858

**2-**(*n***-Propylcarbonyloxy**)**-1-methoxy-3,3,3-trifluoropropyl phenyl sulfide (2b)** (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$ 7.32-7.54 (m, 5H), 5.32 (dq, J = 2.97, 6.60 Hz, 1H), 4.85 (d, J = 3.63Hz, 1H), 3.60 (s, 3H), 2.31 (t, J = 6.93 Hz, 2H), 1.68 (qt, J = 7.26, 14.52 Hz, 2H), 0.96 (t, J = 7.26 Hz, 3H); <sup>19</sup>F NMR  $\delta$  4.05 (d, J =7.34 Hz); MS: m/z = 322 (M<sup>+</sup>); calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>3</sub>S: 322.0851. Found; 322.0855.

## 1-(*n*-Propylcarbonyloxy)-2-methoxy-3,3,3-trifluoropropyl

**phenyl sulfide** (**3b**) (less polar isomer) Colorless oil; <sup>T</sup>H NMR δ 7.20-7.65 (m, 5H), 5.64 (d, J = 6.40 Hz, 1H), 4.27 (dq, J = 5.94, 12.21 Hz, 1H), 3.32 (s, 3H), 1.85 (t, J = 7.26 Hz, 2H), 1.22 (qt, J = 6.93, 13.86 Hz, 2H), 0.93 (t, J = 7.26 Hz, 3H); <sup>19</sup>F NMR δ -0.77 (d, J = 5.58 Hz); MS: m/z = 322 (M<sup>+</sup>); calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>3</sub>S: 322.0851. Found; 322.0823.

## 1-(n-Propylcarbonyloxy)-2-methoxy-3,3,3-trifluoropropyl

**phenyl sulfide** (**3b**) (highly polar isomer) Colorless oil; <sup>19</sup>F NMR & 0.38 (d, J = 5.58 Hz); MS: m/z = 322 (M<sup>+</sup>); calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>O<sub>3</sub>S: 322.0851. Found; 322.0833.

## 2-(t-Butylcarbonyloxy)-1-methoxy-3,3,3-trifluoropropyl

**phenyl sulfide** (**2c**) (less polar isomer) Colorless oil; <sup>1</sup>H NMR & 7.31-7.34 (m, 5H), 5.28 (dq, J = 6.60, 8.25 Hz, 1H), 4.81 (d, J = 8.57 Hz, 1H), 3.54 (s, 3H), 1.27 (s, 9H); <sup>19</sup>F NMR & 3.36 (d, J = 6,82 Hz); MS: m/z = 336 (M<sup>+</sup>); calcd for C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>O<sub>3</sub>S: 336.1002. Found; 336.1012.

2-(t-Butylcarbonyloxy)-1-methoxy-3,3,3-trifluoropropyl

**phenyl sulfide** (**2c**) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR & 7.44-7.53 (m, 5H), 5.57 (dq, J = 4.61, 6.92 Hz, 1H), 4.89 (d, J = 4.29 Hz, 1H), 3.55 (s, 3H), 1.26 (s, 9H); <sup>19</sup>F NMR & 3.70 (d, J = 6.82 Hz); MS: m/z = 336 (M<sup>+</sup>); calcd for C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>O<sub>3</sub>S: 336.1002. Found; 336.1010.

## 1-(t-Butylcarbonyloxy)-2-methoxy-3,3,3-trifluoropropyl

**phenyl sulfide** (**3c**) (less polar isomer) Colorless oil; <sup>1</sup>H NMR & 7.34-7.39 (m, 5H), 5.51 (d, J = 8.25 Hz, 1H), 4.46 (dq, J = 5.61, 8.25 Hz, 1H), 3.36 (s, 3H), 0.88 (s, 9H); <sup>19</sup>F NMR & 1.24 (d, J = 5.58); MS: m/z = 336 (M<sup>+</sup>); calcd for C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>O<sub>3</sub>S: 336.1002. Found; 336.9985.

## 1-(t-Butylcarbonyloxy)-2-methoxy-3,3,3-trifluoropropyl

**phenyl sulfide** (**3c**) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.53-7.58 (m, 5H), 5.66 (d, J = 8.25 Hz, 1H), 4.29 (dq, J = 5.28, 8.25 Hz, 1H), 3.29 (s, 3H), 1.03 (s, 9H); <sup>19</sup>F NMR  $\delta$  1.49 (d, J = 5.58 Hz); MS: m/z = 336 (M<sup>+</sup>); calcd for C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>O<sub>3</sub>S: 336.1002. Found; 336.1000.

**2-Benzoyloxy-1-methoxy-3,3,3-trifluoropropyl phenyl sulfide** (2d) (less polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.28-8.07 (m, 10H), 5.53 (dq, J = 3.60, 6.20 Hz, 1H), 4.94 (d, J = 3.30 Hz, 1H), 3.61 (s, 3H); <sup>19</sup>F NMR  $\delta$  3.66 (d, J = 6.20 Hz); MS: m/z = 356 (M<sup>+</sup>); HRMS calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>S: 356.0694. Found; 356.0690.

**2-Benzoyloxy-1-methoxy-3,3,3-trifluoropropyl phenyl sulfide** (2d) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.23-8.07 (m, 10H), 5.86 (dq, J = 3.96, 6.60 Hz, 1H), 4.98 (d, J = 3.96 Hz, 1H), 3.62 (s, 3H); <sup>19</sup>F NMR  $\delta$  3.77 (d, J = 6.73 Hz); MS: m/z = 356 (M<sup>+</sup>); HRMS calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>S: 356.0694. Found; 356.0692.

**1-Benzoyloxy-2-methoxy-3,3,3-trifluoropropyl phenyl sulfide** (**3d**) (less polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.31-7.59 (m, 10H), 5.79 (d, J = 6.83 Hz, 1H), 4.33 (dq, J = 6.83, 5.94 Hz, 1H), 3.36 (s, 3H); <sup>19</sup>F NMR  $\delta$  0.71 (d, J = 6.20 Hz); MS: m/z = 356 (M<sup>+</sup>); calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>S: 356.0694. Found; 356.0686.

**1-Benzoyloxy-2-methoxy-3,3,3-trifluoropropyl phenyl sulfide** (**3d**) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$  7.20-8.01 (m, 10H), 5.71 (d, J = 5.94 Hz, 1H), 4.71 (dq, J = 3.30, 5.94 Hz, 1H), 3.33 (s, 3H); <sup>19</sup>F NMR  $\delta$  –0.52 (d, J = 6.21 Hz); MS: m/z = 356 (M<sup>+</sup>); calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>S: 356.0694. Found; 356.0690.

**2-**(*p*-Methoxybenzoyloxy)-1-methoxy-3,3,3-trifluoropropyl phenyl sulfide (2e) (less polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$ 7.99-8.03 (m, 2H), 7.27-7.44 (m, 5H), 6.93-6.97 (m, 2H,), 5.52 (dq, J = 6.60, 7.27 Hz, 1H), 4.93 (d, J = 7.91 Hz, 1H), 3.89 (s, 3H), 3.60 (s, 3H); <sup>19</sup>F NMR  $\delta$  3.64 (d, J = 6.20 Hz); MS: m/z = 386 (M<sup>+</sup>); calcd for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>O<sub>4</sub>S: 386.0800. Found; 386.0794.

**2-**(*p*-Methoxybenzoyloxy)-1-methoxy-3,3,3-trifluoropropyl phenyl sulfide (2e) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$ 7.98-8.03 (m, 2H), 7.50-7.53 (m, 5H), 6.89-6.95 (m, 2H,), 5.83 (dq, J = 3.53, 6.96 Hz, 1H), 4.97 (d, J = 3.96 Hz, 1H), 3.87 (s, 3H), 3.61 (s, 3H); <sup>19</sup>F NMR  $\delta$  3.76 (d, J = 6.82 Hz); MS: m/z = 386 (M<sup>+</sup>); calcd for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>O<sub>4</sub>S: 386.0800. Found; 386.0796.

**1-(***p***-Methoxybenzoyloxy)-2-methoxy-3,3,3-trifluoropropyl phenyl sulfide** (3e) (less polar isomer) Colorless oil; <sup>19</sup>F NMR δ 0.76 (d, J = 5.58 Hz); MS: m/z = 386 (M<sup>+</sup>); calcd for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>O<sub>4</sub>S: 386.0800. Found; 386.0796.

**1-**(*p*-Methoxybenzoyloxy)-2-methoxy-3,3,3-trifluoropropyl phenyl sulfide (3e) (highly polar isomer) Colorless oil; <sup>1</sup>H NMR  $\delta$ 7.50-7.59 (m, 5H), 7.36 (d, *J* = 5.61 Hz, 2H), 6.91 (d, *J* = 8.90 Hz, 2H), 5.71 (d, *J* = 5.60 Hz, 1H), 4.69 (dq, *J* = 5.41, 5.94 Hz, 1H), 3.82 (s, 3H), 3.33 (s, 3H); <sup>19</sup>F NMR  $\delta$  0.57 (d, *J* = 6.20 Hz); MS: m/z = 386 (M<sup>+</sup>); calcd for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>O<sub>4</sub>S: 386.0800. Found; 386.0789.

**2-Acetoxy-1-methoxy-3-fluoropropyl phenyl sulfide (2f) (less polar isomer).** <sup>1</sup>H NMR  $\delta$  7.57-7.27 (m, 5H), 5.32-5.23 (m, 1H), 4.79 (d, J = 6.3 Hz, 1H), 4.86-4.48 (m, 2H), 3.53 (s, 3H), 2.05 (s, 3H); <sup>19</sup>F NMR  $\delta$  -156.66 (td, J = 20.2 Hz, 46.9 Hz); MS m/z 258 (M<sup>+</sup>), 153 (M<sup>+</sup> -CH(OAc)CH<sub>2</sub>F); calcd for C<sub>12</sub>H<sub>15</sub>FO<sub>3</sub>S: 258.09447. Found; 258.09551.

**2-Acetoxy-1-methoxy-3-fluoropropyl phenyl sulfide (2f)** (highly polar isomer). <sup>1</sup>H NMR  $\delta$ 7.49-7.22 (m, 5H), 5.13-5.00 (m, 1H), 4.77 (d, J = 7.3 Hz, 1H), 4. 72–4.51 (m, 2H), 3.52 (s, 3H), 2.13 (s, 3H); <sup>19</sup>F NMR  $\delta$  -159.08 (td, J = 23.9 Hz, 47.1 Hz); MS m/z 258 (M<sup>+</sup>), 153 (M<sup>+</sup>-CH(OAc)CH<sub>2</sub>F); calcd for C<sub>12</sub>H<sub>15</sub>FO<sub>3</sub>S: 258.09447. Found; 258.09632.

**2-Acetoxy-1-methoxypropyl phenyl sulfide (2g)** (less polar isomer) <sup>1</sup>H NMR  $\delta$  7.52-7.26 (m, 5H), 5.15-5.08 (m, 1H), 4.67-4.60 (m, 1H), 3.49 (s, 3H), 1.99 (s, 3H), 1.34 (d, J = 2.60 Hz, 3H); MS: m/z = 222 (M<sup>+</sup>).

**2-Acetoxy-1-methoxypropyl phenyl sulfide (2g)** (highly polar isomer) <sup>1</sup>H NMR  $\delta$  7.52-7.26 (m, 5H), 5.15-5.08 (m, 1H), 4.67-4.60 (m, 1H), 3.52 (s, 3H), 2.06 (s, 3H), 1.36 (d, J = 2.60 Hz, 3H); MS: m/z = 222 (M<sup>+</sup>).

Anodic cyclization of sulfide 4.—Constant current  $(10 \text{ mA/cm}^2)$  anodic oxidation of 4 (1.0 mmol) was carried out with platinum electrodes (2 cm × 2 cm) in an undivided cell containing 20 ml of MeCN containing various supporting electrlytes (Table III) at various temperatures. When 3 F/mol of electricity was passed, the electrolysis was stopped, and then work up and estimation of product yields were performed similarly to the anodic methoxylation of 1. Isolation of cyclized product 5 and fluoro by-product 6 was carried out by using silica gel columun chromatography (eluent:hexane/AcOEt = 8:1).

*trans*-4-Phenylthio-5-trifluoromethyl-1,3-dioxolan-2-one (5) <sup>1</sup>H NMR  $\delta$  7.59-7.43 (m, 5H), 5.86 (d, 1H, J = 4.1 Hz), 4.41 (dq, J = 5.9, 5.6 Hz, 1H); <sup>19</sup>F NMR  $\delta$  -2.39 (d, 3F, J = 5.6 Hz); MS m/z 264 (M<sup>+</sup>); <sup>13</sup>C NMR  $\delta$  150.8, 134.8, 130.5, 129.9, 121.6 (q, J = 281 Hz), 82.1, 76.5 (q, J = 35 Hz), 29.7; calcd for C<sub>10</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>S: 264.0068. Found; 264.0060.

## 2-(t-Butoxycarbonyl)oxy-1-fluoro-3,3,3-trifluoropropyl

phenyl sulfide (6) (diastereomeric mixture) <sup>1</sup>H NMR δ 7.62-7.31 (m, 5H), 5.86 (dd, 1H, J = 6.8, 5.1 Hz), 5.26 (m, 1H), 1.54 (s, 9H); <sup>19</sup>F NMR δ -85.9 (m, 1F), -81.7 (m, 1F), 3.04 (dd, 3F, J = 7.4, 5.6 Hz), 2.88 (dd, 3F, J = 7.4, 5.6 Hz); MS m/z 340 (M<sup>+</sup>), 321 (M<sup>+</sup>-F); calcd for C<sub>14</sub>H<sub>14</sub>F<sub>4</sub>O<sub>3</sub>S: 340.0756. Found; 340.0750.

#### **Results and Discussion**

Anodic methoxylation of 2-acetoxy-3,3,3-trifluoropropyl phenyl sulfides using a fluoride ion-mediator.—Anodic methoxylation of 2-acetoxyl sulfide 1a was carried out at various temperatures in MeOH and MeOH/MeCN containing Et<sub>3</sub>N-3HF. The results are summarized in Table I.

Anodic oxidation of **1a** at 25°C in MeOH containing Et<sub>3</sub>N-3HF as a supporting salt provided the corresponding  $\alpha$ -methoxylated product **2a** mainly and unexpected  $\beta$ -methoxylated product **3a** was also formed (Entry 1). The total yield was 68% and the both products were diastereisomeric mixture. The product **3a** seems to be formed owing to [1,2]-rearrangement of the acetoxy group of **1a**. In comparison, anodic oxidation of **1a** was carried out similarly using Et<sub>4</sub>NOTs instead of Et<sub>3</sub>N-3HF as a supporting salt, **2a** was formed solely in much lower yield (23%) with similar diastereoselectivity (30% d.e.). When the electrolytic solvent was changed to MeOH/MeCN (1:1), **2a** and **3a** were formed in almost same yield (Entry 2). Furthermore, when the



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

<sup>b</sup>Diastereomeric excess (d.e, %) is shown in parentheses.

ratio of MeOH to MeCN was reduced to 1:9,  $\beta$ -methoxylated product **3a** was formed mainly and the total yield was also increased to 90% (Entry 3). Notably, the diastereoselectivity of **2a** also increased with decrease of the ratio of MeOH to MeCN, while the diastereselectivity of **3a** was not appreciably affected by the solvent ratio (Entries 1–3).

Next, temperature effect on the rearrangement of acetoxy group was also examined. The rearrangement did not take place at a low temperature as 15°C (Entry 4). In this case, the diastereselectivity of **2a** was slightly decreased. With increase of temperature, the product selectivity ratio of  $\beta$ -methoxylated product **3a** to  $\alpha$ -methoxylated product **2a** increased (Entries 3, 5, 6). However, the total yield was decreased with increase of temperature.

Effects of acyloxy groups on the anodic [1,2]-rearrangement of 2acyloxy-3,3,3-trifluoropropyl phenyl sulfides.—In order to clarify the effects of acyloxy groups on the anodic [1,2]-rearrangement, anodic methoxylation of other sulfides **1b-1e** having various acyloxy groups at the  $\beta$ -position was carried out similarly in MeOH/MeCN (10/90). The results are summarized in Table II.

As shown in Table II, acyloxy groups affected the anodic rearrangement considerably. In a series of RCOO groups, the rearrangement of an acyloxy group occurs more easily in the following order: MeCOO >*p*-MeOC<sub>6</sub>H<sub>4</sub> > PhCOO = *n*-PrCOO >>*t*-BuCOO. Namely, in the case of sulfide **1a** having a sterically smallest acetoxy group, acetoxy rearrangement takes place more preferentially than  $\alpha$ -methoxylation (Entry 1). On the other hand, sulfide **1c** having a bulky *t*-BuCOO group undergoes anodic  $\alpha$ -methoxylation more favorably compared to acyloxy rearrangement (Entry 3). Anodic  $\alpha$ -methoxylation of sul-



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

<sup>b</sup>Diastereomeric excess (d.e, %) is shown in parentheses.



Scheme 2. Anodic methoxylation of sulfides 1f and 1g.

fide **1b** having an *n*-PrCOO group proceeded to give  $\alpha$ -methoxylated product **2b** with the highest diastereoselectivity as 72% d.e. On the other hand, the diastereoselectivity of the  $\beta$ -methoxylated products **3a-3d** is much lower than that of  $\alpha$ -methoxylated products **2a-2d**.

The results thus obtained indicate that the diastereoselectivity of  $\alpha$ -methoxylated products **2** and the product selectivity of  $\beta$ -methoxylated products **3** are affected by the concentration of MeOH, electrolytic temperature, and bulkiness of acyloxy group.

Effects of  $\beta$ -fluoroalkyl group of sulfides on the anodic [1,2]rearrangement of acyloxy group.—In order to disclose the effects of fluoroalkyl groups at the  $\beta$ -position of sulfides on the anodic [1,2]rearrangement of acyloxy group, we comparatively investigated anodic methoxylation of 2-acetoxy-3-fluoropropyl phenyl sulfide (1f) and nonfluorinated analogue 1g in Et<sub>3</sub>N-3HF/MeOH-MeCN (10:90) similarly. In sharp contrast to the case of sulfides 1a-1e, these sulfides did not undergo rearrangement at all, and  $\alpha$ -methoxylated products 2f and 2g were formed solely although the yield was quite low (23% and 8%) (Scheme 2). These results clearly indicate that a strongly electronwithdrawing CF<sub>3</sub> group significantly contributes to the rearrangement to result in  $\beta$ -methoxylation.

**Reaction mechanism for anodic methoxylation and [1,2]**rearrangement of acyloxy group.—More than 75 years ago, Winstein and his co-workers reported a number of papers dealing with roles of neighboring groups in nucleophilic substitution reactions.<sup>28–32</sup> For example, the solvolysis of *trans*-2acetoxycyclohexyl *p*-toluenesulfonate in acetic acid proceeds via *cis*cyclohexaneacetoxonium ion to provide 1,2-diacetoxycyclohexane as shown in Scheme 3.<sup>33</sup>

Paulsen and his co-workers also reported simple synthesis of acyloxonium salts by the reaction of 1,2-diol esters with  $SbCl_5$  in  $CH_2Cl_2$ as shown in Scheme 4.<sup>33,34</sup> This indicates that cyclic acyloxonium cations are generally stable enough.

Moreover, it is well-known that neighboring group participation of an acetoxy group plays an important role to control stereochemical pathway in nucleophilic substitutions of carbohydrates.<sup>35–37</sup>

In consideration to these reports and the mechanism of anodic methoxylation of sulfides via a fluorosulfonium ion intermediate (Scheme 1),<sup>20-23</sup> a plausible mechanism can be illustrated as shown in Scheme 5.

One electron oxidation of sulfide 1 generates radical cation intermediate A followed by reaction with a fluoride ion to form fluorosulfonium ion B. Elimination of HF from B generates cation intermediate C. Since C is destabilized by the strongly electron-withdrawing  $CF_3$ group, the acyloxy group would stabilize the cathionic intermediate



Scheme 3. Solvolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate in acetic acid.

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Scheme 4. Synthesis of acyloxonium Salts.

C to form cyclic cationic intermediate D (i.e. neighboring group participation). When a methanol electrolytic solution is used without co-solvent, methanol should attack mainly C immediately after the generation of intermediate C (Path 1), namely before such neighboring group participation. This should result in favorable formation of 2 and lower diastereoselectivity. On the other hand, when the methanol concentration in the electrolytic solution is reduced by using acetonitrile co-solvent, methanol seems to attack **D** preferentially after the neighboring group participation. Acyloxonium cation intermediate **D** has two reactive sites, which react with MeOH to afford  $\alpha$ - and  $\beta$ methoxylated products 2 and 3 (Path 2 and 3, respectively). Since the  $\beta$ -position to the sulfur atom of intermediate **D** is also adjacent to strongly electron-withdrawing  $CF_3$  group, the  $\beta$ -position is more positive compared to the  $\alpha$ -position. Therefore, the methoxylation at the  $\beta$ -position should occur more preferentially than that at the α-position. To support this, sulfides devoid of a strongly electronwithdrawing group 1f and 1g provided  $\alpha$ -methoxylated products solely and [1,2]-rearrangement did not take place at all (Scheme 2). This result clearly indicates that a strongly electron-withdrawing CF<sub>3</sub> group is neccessary for the [1,2]-rearrangement.

Intermediate **C** might also undergo [1,2]-rearrangement via intermediate **D** to generate another open-chain cation intermediate **E**, which may react with MeOH to give a  $\beta$ -methoxylated product (Path 4). However, it is well known that the generation of  $\alpha$ -cation to a CF<sub>3</sub> group is particularly difficult and S<sub>N</sub>1 reaction via a trifluoroethyl carbenium ion has been unsuccessful<sup>26</sup> unless a sulfur or nitrogen atom exists at  $\alpha$ -position to the CF<sub>3</sub> group.<sup>5,38</sup> Therefore, Path 4 is not likely.

In order to verify further more  $\beta$ -methoxylation via cation intermediate **D**, optically active **1a** was subjected to anodic methoxylation



**Scheme 6.** Temperature dependency on the structure of anodically generated cation intermediate.

in Et<sub>3</sub>N-3HF/MeOH and obtained  $\beta$ -methoxy product **3a** was found to be optically active.<sup>39</sup> This clearly suggests that  $\beta$ -methoxylation proceeds mainly via **D** in a similar way to S<sub>N</sub>2 type reaction. Thus, major  $\beta$ -methoxylation via acyloxonium cation intermediate **D** can be reasonably explained.

In the case of sulfide **1c**, the formation of **D** seems to be less favorable compared to other sulfide derivatives owing to a bulky *t*-BuCOO group. This is probably one of main reasons for less preferable rearrangement of the *t*-BuCOO group.

β-Methoxylation derived from rearrangement of an acyloxy group is also enhanced by increase of electrolytic temperature. This can be explained in terms of preferential formation of cyclic cationic intermediate **D** at higher temperature as shown in Scheme 6. However, at high temperature like 45°C, free Et<sub>3</sub>N is released from Et<sub>3</sub>N-3HF and generated Et<sub>3</sub>N is anodically oxidized prior to oxidation of sulfide **1a**. Therefore, conversion of **1a** decreased significantly (Table I, Entry 6).

It is notable that the diastereoseletivity of  $\alpha$ -methoxylation is much higher than that of  $\beta$ -methxylation, however the reason is not clear at present time.

*Anodic cyclization of 2-(t-butoxycarbonyl)oxy-3,3,3-trifluoropropyl phenyl sulfide using a fluoride ion-mediator.*—In consideration to the mechanism for [1,2]-rearrangement of an acyloxy group via an acyloxonium ion, we expected that anodic intramolecular cyclization of 2-(*t*-butoxycarbonyl)oxy-3,3,3-trifluoropropyl phenyl sulfide (**4**) would be achieved by using a fluoride ion-mediator to



**Scheme 5.** Plausible mechanism for anodic methoxylation and [1,2]-rearrangement of an acyloxy group of sulfides.



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

<sup>b</sup>Diastereomeric excess (d.e. %) is 57–61%.

<sup>c</sup>Isolated yields are shown in parentheses.

provide the corresponding ethylene carbonate derivative. The anodic oxidation of **4** was carried out in MeCN under various conditions. When of Et<sub>3</sub>N-3HF was used as a supporting electrolyte, expected intramolecular cyclization took place eliminating a *t*-butyl group to provide 1-phenylthio-2-trifluoromethylethylene carbonate derivative **5** as well as the corresponding  $\alpha$ -fluorosulfide **6** (Table III, Entry 1–5). Regardless of electrolytic conditions, *trans* form of **5** was always formed exclusively. At a high concentration (1.0 M) of Et<sub>3</sub>N-3HF, a large amount of  $\alpha$ -fluorosulfide **6** was formed as a by-product considerably (Entry 1). In order to avoid the formation of **6**, the concentration of Et<sub>3</sub>N-3HF was reduced and eventually desired product **5** was obtained in good yield (73%) at a low concentration (0.01 M) of Et<sub>3</sub>N-3HF (Entry 5). In this case, the formation of by-product **6** was suppressed considerably. At a low temperature (0°C), the yield of **5** was decreased significantly (Entry 3) while at a



Scheme 7. Reaction mechanism for anodic cyclization of sulfide 4.

high temperature (45°C), the yield was almost same as that at room temperature (Entries 2 and 4). Therefore, the electrolysis at a room temperature was found to be suitable for the formation of **5**. In sharp contrast to these results, other supporting electrolytes like  $Et_4NClO_4$  and  $Bu_4N$ -HSO<sub>4</sub> were not effective at all or much less effective (Entries 6 and 7). The product **5** seems to be a useful fluorobuilding block.

Based on the results and the proposed mechanism for the [1,2]rearrangement of acyloxy group, a plausible reaction mechanism can be illustrated as shown in Scheme 7.

Fluoride ion effectively promotes anodic generation of  $\alpha$ -cation intermediate **F** of sulfide **4**. Then, neighboring participation takes place to form cyclic cation intermediate **G** and **H**. Since *t*-butyl cation is a good leaving group, elimination of *t*-butyl cation from **G** and **H** takes place to give **5**. On the other hand, nucleophilic attack of fluoride ion to **F**, **H**, and **G** affords **6**. Regarding the stereoselectivity of **5**, a CF<sub>3</sub> group is much more bulky than a CH<sub>3</sub> group, therefore, exclusive formation of *trans* form of **5** is reasonable.

## Conclusions

We found the first example of anodic methoxylation of sulfides accompanying with [1,2]-rearrangement of acyloxy group. Furthermore, electrochemical synthesis of trifluoromethylated ethylene carbonate derivative was achieved by anodic cyclization of sulfide having a carbonate moiety using a fluoride ion mediator. Thus, we have shown that a fluoride ion-mediator is highly useful for electrochemical molecular conversion of organosulfur compounds.

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