JOC Article

Electrolytic Partial Fluorination of Organic Compounds. 64.[1] Anodic Mono- and Difluorination of Thiazolyl Sulfides

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The anodic fluorination of 2-thiazolyl methyl sulfide, 2-thiazolyl propargyl sulfide, and 2-thiazolyl acetonyl sulfide was successfully carried out to provide the corresponding 5-fluorothiazole and 2,5,5-trifluorothiazoline derivatives. The latter products were readily hydrolyzed to give isolable 5,5-difluoro-2-hydroxythiazoline derivatives. On the other hand, anodic fluorination of 2-thiazolyl cyanomethyl sulfide afforded 5-fluorothiazole and α-fluorinated thiazole derivatives. Thus, the product selectivity was found to be greatly changed by the electron-withdrawing ability of substituents at the side chain of the thiazole ring. This is the first report of a successful anodic fluorination of a thiazole ring.

Introduction

Thiazole derivatives have attracted a great deal of interest owing to their antifungal,[2] antiinflammatory,[3] and antiviral[4] activities. They are also useful as anti-allergic,[5] anthelmintic[6] agents. The incorporation of a thiazole ring system into antibacterial agents of the sulfanilimide series furnishes substances of considerable clinical value and provides the most familiar example of the utilization of the thiazole ring in chemotherapeutic agents.[7] In addition to being used in the pharmaceutical industry, thiazoles also find a wide application in the dye and photographic industry.[8] On the other hand, the synthesis of heterocyclic compounds containing fluorine has become an important part of fluoro organic chemistry.[9] Among nitrogen-containing heterocyclic compounds, azoles take such a pivotal place due to their biological activities: the attachment of fluorine-containing substituents to an azole generally considerably increases its biological activity.[10] In addition, it is well-known that introduction of a difluoromethylene unit into organic molecules[11] can lead to a wide range of biologically interesting difluoromethylene compounds such as the anticancer agent gemcitabine,[12] HIV-1 protease inhibitors,[13] and phosphotyrosine mimetics.[14]

However, the selective direct fluorination of heterocyclic compounds is not straightforward, because conventional direct fluorination usually requires hazardous, poisonous, or costly fluorinating reagents.[15] Moreover, the chemical direct fluorination of five-membered heteroaromatic compounds such as pyrroles and thiophenes produces extremely low yields (less than 6%) along with an unsatisfactory level of selectivity.[16,17] From this viewpoint, electrochemical fluorination is a promising method, since it can be performed under safe conditions using fluoride anion as a fluoride source and supporting electrolyte. Nevertheless, limited examples of anodic partial fluorination of heterocyclic compounds have been reported to date and the yields and/or selectivities are generally quite low.[18−23]

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SCHEME 1

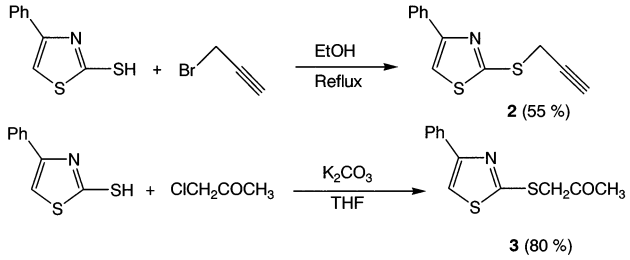
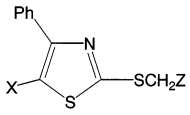


TABLE 1. Oxidation Potentials (peak potentials, E_p^{ox}) of Thiazolyl Sulfides and the Corresponding Monofluoro Derivatives



no.	X	Z	E_p^{ox} (V vs SCE)[a]	no.	X	Z	E_p^{ox} (V vs SCE)[a]
1	H	H	1.47	**1a**	F	H	1.37
2	H	C≡CH	1.57	**2a**	F	C≡CH	1.57
3	H	$COCH_3$	1.61	**3a**	F	$COCH_3$	1.52
4	H	CN	1.72	**4a**	F	CN	1.71

[a] Substrate (0.01 M) in 0.1 M $Bu_4N{\cdot}BF_4$/MeCN; Sweep rate 100 mV/s.

With these facts in mind, the anodic fluorination of thiazolyl sulfides has been attempted. The reactions give the corresponding 5-fluorothiazole derivatives in addition to 5,5-difluoro-2-hydroxythiazoline or α-fluorinated sulfides, depending on the nature of the side chain on the thiazole ring. This paper presents the first example of the direct electrochemical fluorination of a thiazole ring.

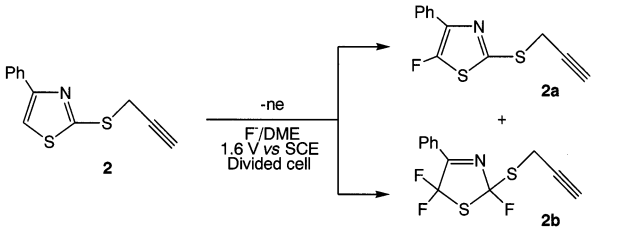
Results and Discussion

Preparation of Thiazolyl Sulfides 1−4. Methyl 2-thiazolyl sulfide **1**[24] and cyanomethyl 2-thiazolyl sulfide **4**[25] were prepared according to literature procedures. Propargyl 2-thiazolyl sulfide **2** was prepared by refluxing the corresponding 2-mercaptothiazole with propargyl bromide in boiling EtOH. On the other hand, acetonyl 2-thiazolyl sulfide **3** was prepared in good yield by the reaction of 2-mercaptothiazole with chloroacetone in boiling THF in the presence of K_2CO_3, as shown in Scheme 1.

Oxidation Potentials of Thiazolyl Sulfides 1−4. The anodic peak potentials of thiazolyl sulfides having an electron-withdrawing group (**2**−**4**) and methyl thiazolyl sulfide **1** were measured by cyclic voltammetry using a platinum anode in an anhydrous acetonitrile solution containing $Bu_4N{\cdot}BF_4$ (0.1 M) using SCE as a reference electrode. These sulfides showed irreversible anodic waves. The first peak potentials E_p^{ox} are summarized in Table 1.

A strong electron-withdrawing cyano group at the position α to the sulfur atom greatly increases the oxidation potential E_p^{ox} (ca. 0.3 V) when compared to methyl thiazolyl sulfide, while other α-electron-withdrawing groups such as acetylenyl and acetyl groups cause a slight increase of the oxidation potentials, ca. 0.1 and 0.14 V, respectively.

TABLE 2. Anodic Fluorination of 2-(4-Phenylthiazolyl) Propargyl Sulfide under Different Electrolytic Conditions



run	supporting electrolyte	charge passed, F/mol	% yield[a] 2a	% yield[a] 2b
1[b]	$Et_4NF{\cdot}4HF$	3	10	15
2	$Et_4NF{\cdot}4HF$	3	20	32
3	$Et_4NF{\cdot}5HF$	3	18	28
4	$Et_3N{\cdot}5HF$	3	25 (20)	28
5	$Et_4NF{\cdot}4HF$	6	10	40
6	$Et_4NF{\cdot}5HF$	6	7	37
7	$Et_3N{\cdot}5HF$	6	5	50

[a] Determined by ^{19}F NMR, and the isolated yield is shown in parentheses. [b] Under constant current.

Anodic Fluorination of Thiazolyl Sulfides 1−3. Anodic fluorination of 2-(4-phenylthiazolyl) propargyl sulfide (**2**) was carried out mainly at constant potential (1.6 V vs SCE) in DME containing various fluoride salts, and the results are summarized in Table 2.

Regardless of the electrolytic conditions, monofluorinated thiazole derivative **2a** and trifluorinated thiazoline derivative **2b** were always formed. Although constant current electrolysis provided both products in low yields due to the formation of a considerable amount of unidentified fluorinated products (run 1), constant potential electrolysis afforded them in moderate total yield. Electrolysis in $Et_3N{\cdot}5HF$/DME at 3 F/mol gave the highest yield (25%) of **2a** (run 4), while similar electrolysis at 6 F/ mol afforded the highest yield (50%) of **2b** (run 7). Thus, $Et_3N{\cdot}5HF$ was found to be the most suitable for the formation of both **2a** and **2b**.

As mentioned above, monofluoro **2a** and trifluoro **2b** were always formed, regardless of supporting fluoride salts. This is quite different from our previous finding: anodic fluorination of *N*-methylpyrrole provided monofluoro and/or trifluoro products, depending on the fluoride salts and solvent used.[26] In all cases, the side chain was not fluorinated at all. This is in sharp contrast to the anodic fluorination of 2-propargylthiobenzothiazole, which provided the corresponding α-fluorinated product.[27]

The relationships between the yields of fluorinated products **2a** and **2b** and the charge passed were investigated.

As shown in Figure 1, the yield of **2a** increased to 25% with an increase of electricity up to 3 F/mol, and then the yield decreased. On the other hand, trifluorinated

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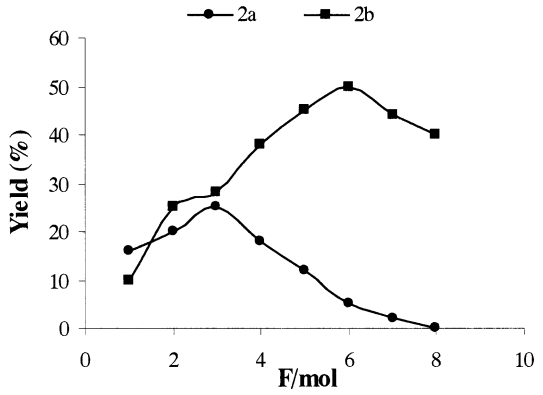
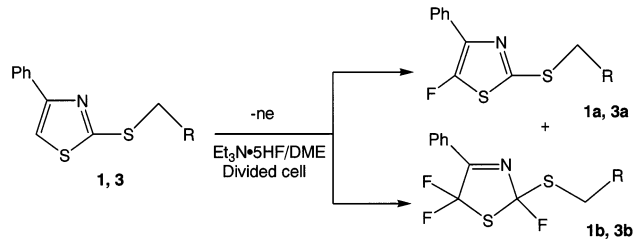


FIGURE 1. Relationships between the yields of the fluorinated products **2a** and **2b** and the electricity passed.

TABLE 3. Anodic Fluorination of 2-(4-phenylthiazolyl) Sulfides 1 and 3



run	no.	R	charge passed, F/mol	anodic potential (V vs SSCE)	% yield[a] a	b
1	**1**	H	3	1.5	25 (20)	28
2	**1**	H	6	1.5	10	55
3	**3**	$COCH_3$	3	1.65	20 (18)	23
4	**3**	$COCH_3$	6	1.65	8	50

[a] Determined by ^{19}F NMR; the isolated yields are shown in parentheses.

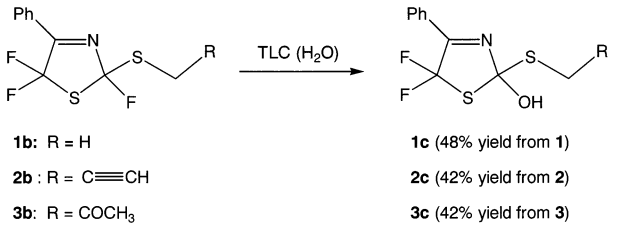
product **2b** was formed even at the early stage of the electrolysis and the yield of **2b** increased linearly with amount of electricity and 50% yield was obtained at 6 F/mol. However, after 6 F/ mol, the yield decreased. At 8 F/mol, **2b** was obtained exclusively. These facts suggest that **2a** is easily oxidized to give **2b** immediately after **2a** is formed during the electrolysis.

Next, the anodic fluorination of other thiazolyl sulfides **1** and **3** was carried out similarly in $Et_3N{\cdot}5HF$/DME.

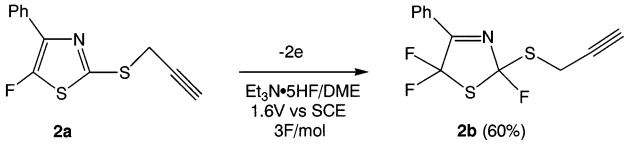
As shown in Table 3, regardless of substituent groups (R), fluorination took place smoothly to provide 5-fluorothiazoles **1a** and **3a** together with 2,5,5-trifluorothiazolines **1b** and **3b**. The product ratio depended on the electricity passed. The monofluorinated products **1a**−**3a** were easily isolated by column chromatography, while trifluorinated products **1b**−**3b** were too unstable to be isolated by preparative thin-layer chromatography. Instead of **1b**−**3b**, the hydrolyzed 5,5-difluoro-2-hydroxythiazoline derivatives **1c**−**3c** were obtained following chromarography, as shown in Scheme 2.To clarify the reason for the lower yields of monofluorothiazole **1a**−**3a** compared with those of trifluorinated products **1b**−**3b**, the oxidation potentials of monofluorinated products **1a**−**4a** were measured.

As shown in Table 1, it was found that the oxidation potentials of monofluorinated thiazoles were almost the same (**2a**, **4a**) or slightly less positive (**1a**, **3a**) compared with the corresponding nonfluorinated starting sulfides **1**−**4**, although a fluorine atom has an electron-withdrawing effect. Next, we carried out the electrolysis of **2a** at constant potential (1.6 V vs SCE) in $Et_3N{\cdot}5HF$/DME as an electrolytic solution and found that **2b** was formed selectively in good yield as shown in Scheme 3.

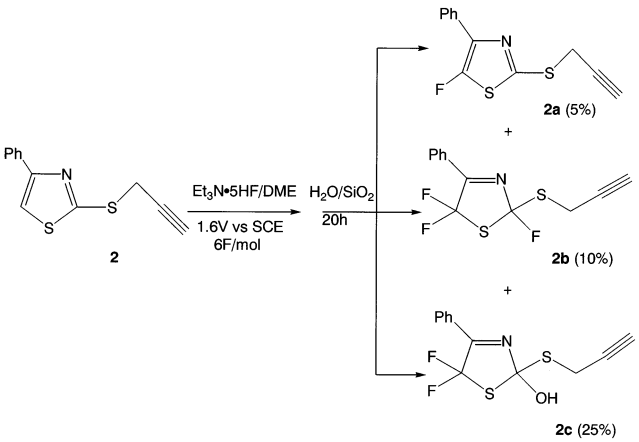
SCHEME 2



SCHEME 3



SCHEME 4



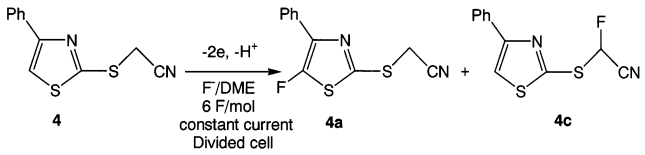
As mentioned, the trifluorinated thiazoline derivative **2b** was too unstable to be isolated by preparative thin-layer chromatography. Therefore, immediately after the electrolysis of **2** in $Et_3N{\cdot}5HF$/DME, an excess of water was added to the electrolytic solution in the presence of SiO_2, and then the reaction mixture was stirred at room temperature to hydrolyze **2b**, which resulted in the formation of the isolable difluorinated product **2c** in reasonable yield, as shown in Scheme 4.

These results indicate that monofluorinated thiazole derivatives **1a**−**3a** were found to be the precursors of trifluorinated thiazoline derivatives **1b**−**3b**. On the other hand, trifluorothiazolines **1b**−**3b** were the precursors of difluorinated thiazoline derivatives **1c**−**3c**.

Anodic Fluorination of Cyanomethyl 2-Thiazolyl Sulfide 4. In contrast to the cases of **1**−**3**, anodic fluorination of cyanomethyl 2-thiazolyl sulfide **4** gave α-fluorocyanomethyl 2-thiazolyl sulfide **4c** in addition to 5-fluorothiazolyl sulfide **4a**. The results are summarized in Table 4.

Although constant potential electrolysis gave low yields of both **4a** and **4c**, constant current electrolysis provided

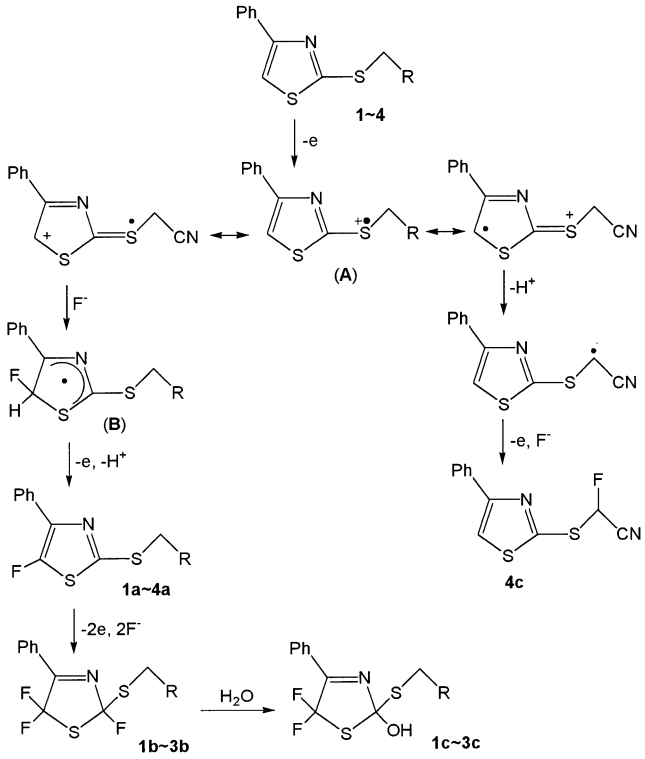
TABLE 4. Anodic Fluorination of Cyanomethyl 2-(4-Phenylthiazolyl) Sulfide 4



run	supporting electrolyte	% yield[a] 4a	4c
1[b]	$Et_4NF{\cdot}4HF$	10	20
2	$Et_4NF{\cdot}4HF$	20 (18)	65 (60)
3	$Et_4NF{\cdot}5HF$	15	60
4	$Et_3N{\cdot}5HF$	15	58

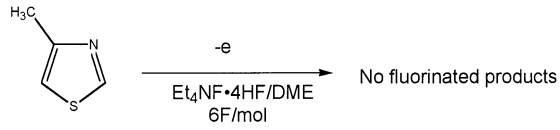
[a] Determined by ^{19}F NMR; the isolated yields are shown in parentheses. [b] Under constant potential (1.75 V vs SCE).

SCHEME 5



4a and **4c** in reasonable and moderate yields, respectively (runs 2−4). Among the supporting fluoride salts used, the use of $Et_4NF{\cdot}4HF$ was the most suitable for the monofluorination of **4**. As compared with other thiazolyl sulfides **1**−**3**, cyanomethyl 2-thiazolyl sulfide **4** has the highest oxidation potential (Table 1); therefore, its corresponding 5-fluorothiazole **4a** should be the most difficult to oxidize. In fact, **4a** was found to have the highest oxidation potential, as shown in Table 1. This seems to be one of the main reasons why **4a** was not susceptible to further oxidation, leading to the 2,5,5-trifluoro thiazoline derivative. Meanwhile, a strongly electron-withdrawing cyano group was responsible for the exclusive anodic fluorination at the α-position toward the sulfur atom, leading to α-monofluorinated sulfide **4c** in rather good yield, particularly when $Et_4NF{\cdot}4HF$/DME was used as the electrolytic solution (Table 4 run 2).

SCHEME 6



From these results, a possible reaction mechanism was proposed, as shown in Scheme 5.

This reaction can be explained by a conventional ECEC process: One-electron oxidation of starting sulfides **1**−**4** generates radical cation **A**, which reacts with a fluoride ion to give the corresponding radical **B**, and further oxidation of the radical **B** followed by deprotonation affords monofluorothiazole derivatives **1a**−**4a**. Since **1a**−**3a** are more easily oxidized than **1**−**3**, trifluorinated products **1b**−**3b** are preferentially formed by further electrochemical oxidative fluorination. Moreover, hydrolysis of **1b**−**3b** produces difluorinated compounds **1c**−**3c**. On the other hand, the formation of α-monofluorocyanomethyl 2-thiazolyl sulfide **4c** can be explained as follows. The deprotonation from the α-position of the radical cation **C** is facilitated by the strongly electron-withdrawing cyano group to generate the α-radical intermediate, followed by further oxidation and fluoride ion attack.

To disclose the role of a thioalkyl group, anodic fluorination of 4-methyl thiazole was attempted. However, no fluorinated products were formed, as shown in Scheme 6. Therefore, the presence of thioalkyl group is essential for this regioselective anodic fluorination.

Conclusion

In conclusion, we have successfully carried out for the first time the anodic fluorination of thiazolyl sulfides. The products **1b**−**3b** and **1c**−**3c** have a biologically interesting *gem*-difluoromethylene unit in the heterocyclic thiazoline ring and the products **1a**−**4a** have a fluorine atom on the aromatic thiazole ring. Therefore, **1a**−**4a**, **1b**−**3b**, and **1c**−**3c** seem to be useful fluorinated building blocks.

Experimental Section

CAUTION. $Et_4NF{\cdot}4HF$ and $Et_3N{\cdot}5HF$ are toxic and contact with skin causes serious burns, so proper safety precautions should be taken all the time. It is therefore recommended to protect hands with rubber gloves.[28]

Materials. Methyl 2-thiazolyl sulfide **1**[24] and cyanomethyl 2-thiazolyl sulfide **4**[25] were prepared according to the literature methods. $Et_4NF{\cdot}4HF$ and $Et_3N{\cdot}5HF$ were obtained from Morita Chemical Industries Co. Ltd. (Japan).

Preparation of 2-(4-Phenylthiazolyl) Propargyl Sulfide 2. To a stirred solution of 4-phenyl-2-mercaptothiazole (10 mmol) in ethanol (50 mL) was added propargyl bromide (10 mmol) dropwise. The mixture was refluxed for 5 h. After evaporation of the solvent and pouring the residue onto crushed ice, the precipitated solid was filtered and purified by column chromatography on silica gel using hexane/AcOEt (5:1) as an eluent to give the pure product **2**: ^1H NMR δ 2.32 (t, 1 H, J = 2.6 Hz), 4.07 (d, 2 H, J = 2.6 Hz), 7.25−7.45 (m, 4 H), 7.93 (d, 2 H, J = 8 Hz); MS m/z 231 (M^+), 230 ($M^+ - H$). Anal. Calcd for $C_{12}H_9NS_2$: C, 62.30; H, 3.92; N, 6.05; S, 27.72. Found: C, 62.54; H, 4.07; N, 6.29; S, 27.58.

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Preparation of Acetonyl 2-(4-Phenylthiazolyl) Sulfide 3. To a stirred solution of 4-phenyl-2-mercaptothiazole (10 mmol) in THF (50 mL) in the presence of anhydrous K_2CO_3 (15 mmol), was added α-chloroacetone (10 mmol). The reaction mixture was refluxed for 2 h and then left to cool to room temperature. The inorganic salts were filtered off, and the filtrate was evaporated under vacuum. The obtained product was purified by column chromatography on silica gel using benzene as an eluent to give the pure product **3**: ^{1}H NMR δ 2.27 (s, 3 H), 4.02 (s, 2 H), 7.25−7.34 (m, 4 H), 7.93 (d, 2 H, J = 8 Hz); MS m/z 249 (M^+), 206 ($M^+ - COCH_3$). Anal. Calcd for $C_{12}H_{11}NOS_2$: C, 57.80; H, 4.45; N, 5.62; S, 25.72. Found: C, 57.83; H, 4.54; N, 5.81; S, 25.62.

Anodic Fluorination of Thiazolyl Sulfides 1−3. The electrolyses were carried out with platinum plate electrodes (3 × 3 cm^2) in 0.37 M Et_3N·5HF/DME (30 mL) containing a sulfide (**1**−**3**, 1 mmol) using a divided cell under nitrogen atmosphere at room temperature. Constant potential was applied until the starting material was consumed (checked by TLC). After the electrolysis, the electrolytic solution was passed through a short column filled with silica gel using AcOEt as an eluent to remove fluoride salts. The eluent was evaporated under reduced pressure. The yields of the fluorinated products were estimated by means of ^{19}F NMR by using a known amount of monofluorobenzene as an internal standard: The yields were calculated on the basis of the integral ratios between the monofluorobenzene and the fluorinated products. The residue was further purified by column chromatography on silica gel using hexane/AcOEt (1:10) as an eluent.

5-Fluoro-2-methylthio-4-phenylthiazole (1a): ^{1}H NMR δ 2.72 (s, 3 H), 7.35−7.93 (m, 5 H); ^{19}F NMR δ −63.8 (s); MS m/z 225 (M^+), 210 ($M^+ - CH_3$). Anal. Calcd for $C_{10}H_8FNS_2$: C, 53.31; H, 3.58; N, 6.22; S, 28.46. Found: C, 53.04; H, 3.33; N, 6.35; S, 28.33.

5-Fluoro-4-phenyl-2-propargylthiothiazole (2a): ^{1}H NMR δ 2.32 (t, 1 H, J = 2.6 Hz), 4.07 (d, 2 H, J = 2.6 Hz), 7.35−7.91 (m, 5 H); ^{19}F NMR δ −64.2 (s). MS m/z 249 (M^+), 248 ($M^+ - H$); HRMS m/z calcd for $C_{12}H_8FNS_2$ 249.0082, found 249.0076. Anal. Calcd for $C_{12}H_8FNS_2$: C, 57.81; H, 3.23; N, 5.62; S, 25.72. Found: C, 57.68; H, 3.13; N, 5.45; S, 25.53.

2-Acetonylthio-5-fluoro-4-phenylthiazole (3a): ^{1}H NMR δ 2.33 (s, 3 H), 4.06 (s, 2 H), 7.35−7.93 (m, 5 H); ^{19}F NMR δ −67.33 (s). MS m/z 267 (M^+), 224 ($M^+ - COCH_3$); HRMS m/z calcd for $C_{12}H_{10}FNOS_2$ 267.0188, found 267.0190. Anal. Calcd for $C_{12}H_{10}FNOS_2$: C, 53.91; H, 3.77; N, 5.24; S, 23.99. Found: C, 53.77; H, 3.53; N, 5.05; S, 23.78.

2-Methylthio-4-phenyl-2,5,5-trifluoro-2,5-dihydrothiazole (1b): ^{1}H NMR δ 2.72 (s, 3 H), 7.35−7.88 (m, 5 H); ^{19}F NMR δ 3.23 (dd, J = 200, 5 Hz), −22.98 (dd, J = 205, 3 Hz), −43.50 (t, J = 3 Hz); MS m/z 263 (M^+), 248 ($M^+ - CH_3$); HRMS m/z calcd for $C_{10}H_8F_3NS_2$ 263.0188, found 263.0190.

4-Phenyl-2-propargylthio-2,5,5-trifluoro-2,5-dihydrothiazole (2b): ^{19}F NMR δ 4.63 (dd, J = 205, 3 Hz), −21.61 (dd, J = 205, 3 Hz), −42.75 (t, J = 3 Hz).

2-Acetonylthio-4-phenyl-2,5,5-trifluoro-2,5-dihydrothiazole (3b): ^{19}F NMR δ 4.72 (dd, J = 205, 3 Hz), −20.66 (dd, J = 205, 3 Hz), −43.67 (t, J = 3 Hz).

5,5-Difluoro-2-hydroxy-2-methylthio-4-phenyl-2,5-dihydrothiazole (1c): ^{1}H NMR δ 2.65 (s, 3 H), 3.62 (s, 1 H), 7.35−7.59 (m, 5 H). ^{19}F NMR δ −22.3 (d, J = 200 Hz), 3.25 (d, J = 200 Hz); MS m/z 261 (M^+), 244 ($M^+ - OH$). Anal. Calcd for $C_{10}H_9F_2NOS_2$: C, 45.96; H, 3.47; N, 5.36; S, 24.54. Found: C, 45.89; H, 3.21; N, 5.28; S, 24.33.

5,5-Difluoro-2-hydroxy-4-phenyl-2-propargylthio-2,5-dihydrothiazole (2c): ^{1}H NMR δ 2.32 (t, 1 H, J = 2.6 Hz), 3.44 (s, 1 H), 4.11 (d, 2 H, J = 2.6 Hz), 7.35−7.61 (m, 5 H); ^{19}F NMR δ −22.7 (d, J = 200 Hz), 3.66 (d, J = 200 Hz); MS m/z 285 (M^+), 284 ($M^+ - H$); HRMS m/z calcd for $C_{12}H_9F_2NOS_2$ 285.0144, found 285.0145. Anal. Calcd for $C_{12}H_9F_2NOS_2$: C, 50.51; H, 3.18; N, 4.91; S, 22.48. Found: C, 50.28; H, 3.11; N, 4.77; S, 22.31.

2-Acetonylthio-5,5-difluoro-2-hydroxy-4-phenyl-2,5-dihydrothiazole (3c): ^{1}H NMR δ 2.35 (s, 3 H), 3.66 (s, 1 H), 4.10 (s, 2 H), 7.35−7.63 (m, 5 H). ^{19}F NMR δ −22.5 (d, J = 200 Hz), 3.62 (d, J = 200 Hz); MS m/z 303 (M^+), 286 ($M^+ - OH$); HRMS m/z calcd for $C_{12}H_{11}F_2NO_2S_2$ 303.0199, found 303.0216. Anal. Calcd for $C_{12}H_{11}F_2NO_2S_2$: C, 47.51; H, 3.65; N, 4.62; S, 21.14. Found: C, 47.38; H, 3.41; N, 4.47; S, 21.02.

Anodic Fluorination of Cyanomethyl 2-(4-Phenylthiazolyl) Sulfide 4. The electrolysis were carried out with platinum plate electrodes (3 × 3 cm^2) in 0.37 M Et_4NF·4HF/DME (30 mL) containing a sulfide **4** (1 mmol) using a divided cell under nitrogen atmosphere at room temperature. Constant current (5 mA/cm^2) was passed until the starting material **4** was consumed (checked by TLC).

α-[2-(5-Fluoro-4-phenylthiazolyl)thio]acetonitrile (4a): ^{1}H NMR δ 3.99 (s, 2 H), 7.35−7.90 (m, 5 H); ^{19}F NMR δ −68.5 (s); MS m/z 250 (M^+), 210 ($M^+ - CH_2CN$). Anal. Calcd for $C_{11}H_7FN_2S_2$: C, 52.78; H, 2.82; N, 11.19; S, 25.62. Found: C, 52.56; H, 3.07; N, 11.12; S, 25.48.

α-Fluoro-α-[2-(4-Phenylthiazolyl)thio]acetonitrile (4c): ^{1}H NMR δ 6.22 (d, 1 H, J = 58.6 Hz), 7.35−7.55 (m, 4 H), 7.64 (d, 2 H, J = 8 Hz); ^{19}F NMR δ −72.28 (d, J = 58.6 Hz); MS m/z 250 (M^+); HRMS m/z calcd for $C_{11}H_7FN_2S_2$ 250.0035, found 250.0015. Anal. Calcd for $C_{11}H_7FN_2S_2$: C, 52.78; H, 2.82; N, 11.19; S, 25.62. Found: C, 52.62; H, 2.71; N, 11.05; S, 25.49.

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Note Added after ASAP. The version posted ASAP on November 28, 2002, had the following errors: the supporting electrolyte in runs 4 and 7 of Table 2 and run 4 of Table 4; the products listed in columns 3 and 4 of Table 4 and the Supporting Information paragraph. The corrected version was posted December 4, 2002.

Supporting Information Available: Copies of ^{1}H and ^{19}F NMR of **1b**. This material is available free of charge via Internet at http://pubs.acs.org.

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