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# ELECTROLYTIC REACTIONS OF FLUORO ORGANIC COMPOUNDS. 8.[1] FURTHER STUDY ON ANODIC METHOXYLATION AND ACETOXYLATION OF ARYL FLUOROALKYL SULFIDES

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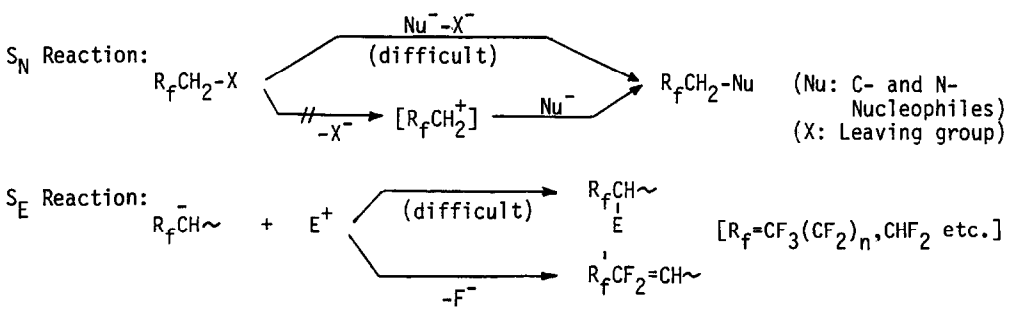
Abstract – Anodic α-methoxylation and α-acetoxylation of substituted phenyl 2,2,2-trifluoroethyl sulfides and various fluoroalkyl phenyl sulfides were studied from both synthetic and mechanistic aspects. These anodic reactions were greatly affected by both substituent groups at the benzene ring and fluoroalkyl groups. Electron-donating substituents interfered with the reactions significantly. Strong electron-withdrawing perfluoroalkyl groups($C_nF_{2n+1}$: n = 1-3) remarkably promoted these anodic substitutions while difluoro- and monofluoromethyl groups showed much less substitution.

Fluoro organic compounds have specific chemical and physical properties. A great deal of recent interest has been focused on partially fluorinated compounds because of their potential biological activities.[2] However, methods for their synthesis are strictly limited in many cases.[3] For example, nucleophilic or electrophilic substitution at the position α to a perfluoroalkyl group generally occurs with difficulty.[4-6] The former problem arises from the strong electron-withdrawing effect of the perfluoroalkyl group and the latter is due to extremely facile defluorination of anionic intermediates prior to trapping them with electrophiles.




(Scheme 1)

Therefore, the realization of substitution at the α-position is the one of the most important subjects in modern organo fluorine chemistry. Electrochemical reactions have recently been shown to be powerful new tools in organic synthesis.[7] With regard to fluoro organic compounds, extensive studies on the electrofluorination of organic compounds[8] and the synthesis of trifluoromethylated compounds by the anodic oxidation of trifluoroacetic acid in the presence of the appropriate unsaturated compounds[9] have been performed. Although anodic substitution is known to be a characteristic of certain electrochemical reactions, no results pertaining to the electrolytic substitution of trifluoromethylated compounds have been reported so far.

From these viewpoints, we have made efforts to solve such problems by using electrochemical techniques.[1,10-15] For example, we have investigated anodic α-substitution of 2,2,2-trifluoroethyl sulfides with oxygen-nucleophiles and (we) have found that the trifluoromethyl group remarkably promoted anodic α-methoxylation and α-acetoxylation of the sulfides.[1,10]

In this work, we have examined the anodic methoxylation of various substituted phenyl 2,2,2-trifluoroethyl sulfides 1 in more detail and also have extended the α-substitution to other fluoroalkyl phenyl sulfides 2.

In addition, the oxidation potentials of these fluorinated sulfides 1 and 2 were measured in order to investigate the effect of substituents X and fluoroalkyl groups $R_f$ on their oxidation potentials. So far, the oxidation potentials of a limited number of fluoro organic compounds have been reported.[16]

## Results and Discussion

### Effects of Substituents at the Benzene Ring on the Oxidation Potentials of Aryl 2,2,2-Trifluoroethyl Sulfides and Anodic Methoxylation

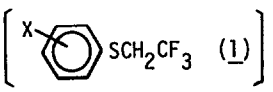
Although extensive studies on the substituent effects on the reduction potentials of diaryl sulfides have been done,[17,18] the effect of substituents on the oxidation potentials of sulfides has been scarcely investigated. Therefore, oxidation potentials of various substituted phenyl 2,2,2-trifluoroethyl sulfides 1 were first measured by cyclic voltammetry using a platinum anode in acetonitrile.

These sulfides 1 exhibited irreversible multiple anodic waves. The first oxidation peak potentials $E_p^{ox}$ are summarized in Table 1. As shown in Fig. 1, a linear correlation of $E_p^{ox}$ with Hammett's σ values of X was obtained except for a p-chloro substituent.

The substitution effects are essentially polar, namely, electron-donating groups make the oxidation potential less positive while electron-withdrawing groups show the opposite effect. This fact indicates that the first electron transfer from the substrate to the anode may be the oxidation-potential determining step.

Next, their anodic methoxylation was carried out in a manner similar to the previous report.[1,10] The results are summarized in Table 2.

Table 1. Oxidation Potentials(Peak Potentials, $E_p^{ox}$) of Substituted Phenyl Trifluoroethyl Sulfides 1[a].



| Sulfide | | $E_p^{ox}$/V vs SCE |
|---|---|---|
| No | X | |
| 1a | H | 1.78 |
| 1b | p-Cl | 1.82 |
| 1c | p-F | 1.86 |
| 1d | m-Me | 1.75 |
| 1e | p-Me | 1.66 |
| 1f | p-MeO | 1.49 |

a) 1 mM of 1 in 0.1 M $Bu_4NBF_4$/MeCN. Sweep rate: 100 mV $s^{-1}$.

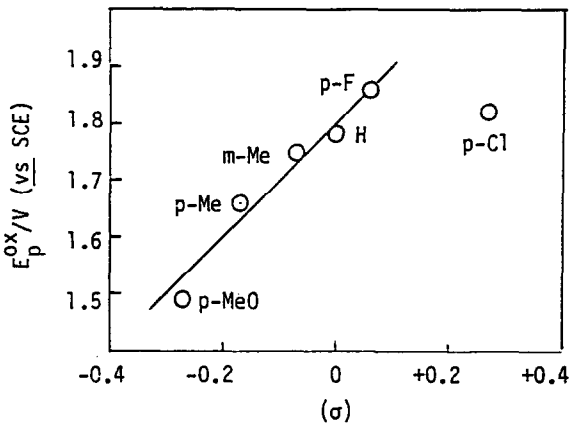
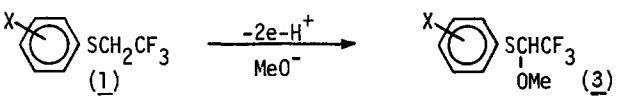



Fig. 1. Relationship between oxidation peak potentials($E_p^{ox}$) of sulfides 1 and Hammett's substituent constants(σ)

Table 2. Anodic Methoxylation of Substituted Phenyl Trifluoroethyl Sulfides 1




| Run | Sulfide | | Electricity passed | Conversion | Yield |
|---|---|---|---|---|---|
| | No | X | F $mol^{-1}$ | % | % |
| 1 | 1a | H | 10 | 100 | 3a (93) |
| 2 | 1b | p-Cl | 10 | 100 | 3b (80) |
| 3 | 1c | p-F | 10 | 86 | 3c (43)[a] |
| 4 | 1d | m-Me | 20 | 51 | 3d (28)[a] |
| 5 | 1e | p-Me | 20 | 100 | 3e (18) |
| 6 | 1f | p-MeO | 10 | 97 | 3f (13) |

a) Based on consumed 1.

It was found that the anodic methoxylation was greatly affected by the substituents at the benzene ring. Thus, an electron-withdrawing group such as a chlorine atom remarkably promoted this anodic methoxylation (Run 2) while electron-donating groups significantly interfered with the methoxylation (Runs, 4-6). It should be noted that a fluorine substituent also caused a considerable decrease in the yield of the product 3 (Run 3) although a fluorine atom is similar to a chlorine atom.

As a main reason for decrease in the product yields of 3c - 3f, we firstly considered that the expected methoxylated products 3 might be reoxidized due to their oxidation potentials being lower than the corresponding starting sulfides 1 except for unsubstituted and p-chloro-substituted sulfides 1a and 1b. Thus, the oxidation potentials of the methoxylated products 3 were measured. Their first peak potentials $E_p^{ox}$ and those of the corresponding starting sulfides 1 are summarized in Table 3.

Table 3. Oxidation Potentials(Peak Potentials, $E_p^{ox}$) of α-Methoxylated Sulfides 3[a]

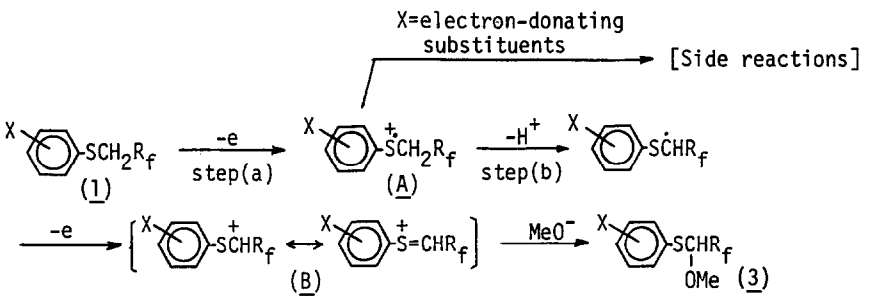
| Sulfide | $E_p^{ox}$/V vs SCE[b] |
|---|---|
| 3a | 2.02 (1.78) |
| 3b | 1.89 (1.82) |
| 3c | 1.91 (1.86) |
| 3d | 1.98 (1.75) |
| 3f | 1.58 (1.49) |

a) 1 mM of 3 in 0.1 M $Bu_4NBF_4$/MeCN. Sweep rate: 100 mV $s^{-1}$.

b) Figures in parentheses are oxidation potentials of the corresponding starting sulfides 1.

As shown in Table 3, each product has a higher oxidation potential than the corresponding starting sulfide. Therefore, the reoxidation of the desired methoxylated products is not the main reason for the decreased yield.

In our previous work,[1] it was confirmed that this anodic methoxylation is initiated by direct electron transfer from the substrate sulfides and the most probable process, a so-called ECEC mechanism was tentatively proposed as shown in scheme 2.




(Scheme 2)

It is reasonable to assume that the rate-determining step in this reaction should be the deprotonation step (b) of the cation radical intermediate A. When the substituent X is electron-donating, the cation radical intermediate A should be so stabilized that the deprotonation may be suppressed and side reactions would occur. Consequently, the efficiency for the anodic methoxylation should be decreased. Considering these points, the relationship of the yields of the methoxylated sulfides with Hammett's σ and $\sigma^+$ values was investigated. These values and the product yields are summarized in Table 4.

Here, the negative values of σ and $\sigma^+$ mean the magnitude of the electron-donating effect of the substituents X in the neutral molecules and cationic intermediates, respectively[19] or vice versa. The product yields seem to be better correlated to $\sigma^+$ values than σ values. Namely, as the $\sigma^+$ value becomes more negative, the yield of the methoxylated sulfide 3 decreases. Therefore, the reaction is not governed by the stability of the cationic intermediates A or B. Since the electron-withdrawing substituent (X= Cl) did not inter-

fere with this reaction and promoted remarkably the methoxylation as observed in the case of non-substituted phenyl sulfide 1a, this reaction seems to be highly controlled by the ease of deprotonation of A.

Table 4. Efficiency of Anodic Methoxylation and Hammett's σ and $\sigma^+$ Values of Substituents(X)

| X | p-Cl | H | p-F | m-Me | p-Me | p-MeO |
|---|---|---|---|---|---|---|
| Yield/% | 80 | 93 | 43 | 28 | 18 | 13 |
| $\sigma^+$ | +0.11 | 0 | -0.07 | -0.07 | -0.31 | -0.78 |
| σ | +0.23 | 0 | +0.66 | -0.07 | -0.17 | -0.27 |

In support of this, for example, many by-products substituted with two or three methoxy groups at the tolyl group were detected by $^1$H NMR spectroscopy in the case of the methoxylation of p-tolyl sulfide 1e.[20] However, it was found that no methoxy groups were introduced into the α-positions of these by-products by $^1$H NMR spectral study.

The results obtained strongly support our proposed reaction mechanism.

Effect of Fluoroalkyl Groups on the Oxidation Potentials of Sulfides and Anodic Substitutions with Oxygen-nucleophiles

First of all, in order to investigate the effect of fluoroalkyl groups on the oxidation potentials of fluorinated sulfides 2, their oxidation peak potentials $E_p^{ox}$ were measured similarly. The sulfides 2 showed irreversible multiple anodic waves. The first oxidation peak potentials $E_p^{ox}$ are summarized in Table 5.

Table 5. Oxidation Potentials(Peak Potentials, $E_p^{ox}$) of Fluoroalkyl Phenyl Sulfides 2[a]

$$\left[\ PhSCH_2R_f \quad (2)\ \right]$$

| Sulfide No | $R_f$ | $E_p^{ox}$/V vs SCE |
|---|---|---|
| 2a | $CF_3$ | 1.78 |
| 2b | $CF_3CF_2$ | 1.82 |
| 2c | $CF_3CF_2CF_2$ | 1.84 |
| 2d | $CHF_2$ | 1.69 |
| 2e | $CH_2F$ | 1.58 |
| 2f | CHClF | 1.69 |
| 2g | $CH_3$ | 1.48 |

a) 1 mM of 2 in 0.1 M $Bu_4NBF_4$/MeCN. Sweep rate: 100 mV $s^{-1}$.

As shown in Fig. 2, a linear correlation of the oxidation potentials $E_p^{ox}$ with Taft's $\sigma^*$[19] values of fluoromethyl groups was obtained. This clearly indicates that the polar effect of the fluoroalkyl group plays a significant role in the step of the electron-transfer from the sulfides to anode. Namely, the oxidation potential increases linearly as the number of fluorine atoms of the fluoroalkyl group increases. However, interestingly the oxidation potential was not appreciably affected by the length of the perfluoroalkyl group (Table 5).

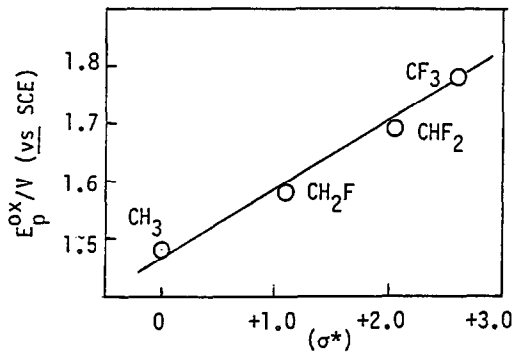



Fig. 2. Relationship between oxidation peak potentials($E_p^{ox}$) of sulfides 2 and Taft's substituent constants(σ*)

Next, the effects of fluoroalkyl groups on the anodic methoxylation and acetoxylation of fluorosulfides were investigated. The results are summarized in Table 6.

Table 6. Anodic Methxoylation and Acetoxylation of Fluoroalkyl Phenyl Sulfides 2

$$\underset{(2)}{PhSCH_2R_f} \xrightarrow[YO^-]{-2e-H^+} \underset{OY}{PhSCHR_f} \quad (4):Y=Me \quad (5):Y=Ac$$

| Sulfide | | Anodic Methoxylation[a] | | Anodic Acetoxylation[b] | |
|---|---|---|---|---|---|
| No | $R_f$ | Conversion/% | Yield of 4/% | Conversion/% | Yield of 5/%[c] |
| 2a | $CF_3$ | 100 | 93 | 80 | 53 |
| 2b | $CF_3CF_2$ | 87 | 72[c] | 89 | 46 |
| 2c | $CF_3CF_2CF_2$ | 83 | 58[c] | 80 | 43 |
| 2d | $CHF_2$ | 99 | 19 | 77 | 28 |
| 2e | $CH_2F$ | - | 0 | 95 | 20 |
| 2f | CHClF | - | 0 | 81 | 16 |

a) Electricity passed:10F $mol^{-1}$. b) Electricity passed:4F $mol^{-1}$.
c) Based on consumed 2.

Strong electron-withdrawing perfluoroalkyl groups promoted the anodic methoxylation. Interestingly, the longer perfluoroalkyl group exhibited less substitution when compared with the trifluoromethyl group although these longer perfluoroalkyl groups showed almost the same effect on the oxidation potentials of the sulfides as the trifluoromethyl group.

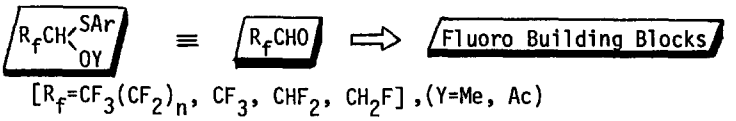
On the contrary, a difluoromethyl group caused a drastic decrease in the yield of 4d and monofluoromethyl and chlorofluoromethyl groups did not promote the methoxylation.

On the other hand, the anodic acetoxylation took place regardless of the fluoroalkyl group. It was found that the promotion effect on the acetoxylation was ordered as $CF_3 > C_2F_5 > C_3F_7 \gg CHF_2 > CH_2F >$ CHClF. This order is similar to that of the methoxylation. This order can be rationalized as being due to the ease of the deprotonation from A in Scheme 2 (MeO ⟶ AcO), since the stronger the acidity of the methylene hydrogen, the easier the deprotonation.

Thus, the anodic methoxylation and acetoxylation of aryl fluoroalkyl sulfides were greatly affected by both substituent groups at the benzene ring and fluoroalkyl groups.

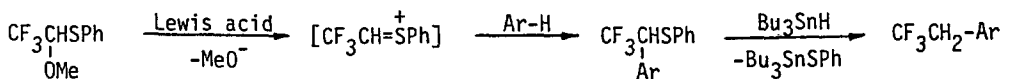
Utilization of Anodically Methoxylated and Acetoxylated Fluorosulfides

The products obtained are equivalents of fluoroalkylaldehyde, which are useful fluorobuilding blocks.[10,21]



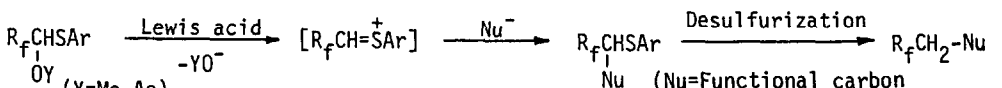

$[R_f=CF_3(CF_2)_n,\ CF_3,\ CHF_2,\ CH_2F]$, (Y=Me, Ac)

Furthermore, the products are also α-fluoroalkyl O,S-acetals. Lewis acid mediated substitution of acetals with various carbon-nucleophiles is an important part of modern synthetic methodology.[22] In fact, we have demonstrated that α-trifluoromethyl O,S-acetal is a useful starting material for the preparation of 2,2,2-trifluoroethylaromatics as shown in Scheme 3.[1]




(Scheme 3)

Therefore, the anodically prepared α-fluoroalkyl O,S-acetals should be promising versatile building blocks for the construction of a carbon-carbon bond at the α-positions to the fluoroalkyl groups.




(Scheme 4)

## Experimental

$^1$H NMR spectra were measured in $CCl_4$ at 60 MHz on JEOL PMX-60SI NMR spectrometers. The chemical shifts for $^1$H are given in δ ppm downfield from internal $Me_4Si$. IR spectra were obtained with Hitachi 295 infrared spectrometer. Mass spectra were obtained with a JEOL JMS-D100 GC-mass spectrometer. Cyclic voltammetric and preparative electrolysis experiments were carried out using a Hokutodenko HA-501 Potentiostat/Galvanostat equipped with a Hokutodenko HF-201 digital coulometer.

### Substituted Phenyl 2,2,2-Trifluoroethyl Sulfides 1.

Sulfides 1 were prepared from 2,2,2-trifluoroethyl p-toluenesulfonate and the corresponding substituted benzenethiols similar to the reported procedure.[1,23,24]

*p*-Fluorophenyl 2,2,2-trifluoroethyl sulfide (1c): $^1$H NMR: 3.29 (q, 2H, $CH_2$, $J_{H-F}$ = 10 Hz), 6.7-7.7 (m, 4H, $C_6H_4$). Mass: m/e 210 ($M^+$), 141 ($M^+ - CF_3$), 127 ($M^+ - CF_3CH_2$), 83 ($CF_3CH_2^+$); Calcd. for $C_8H_6F_4S$: m/e 210.0126, Found: 210.0125.

*m*-Tolyl 2,2,2-trifluoroethyl sulfide (1d): $^1$H NMR: 2.27 (s, 3H, $CH_3$), 3.32 (q, 2H, $CH_2$, $J_{H-F}$ = 10 Hz), 6.8-7.5 (m, 4H, $C_6H_4$). Mass: m/e 206 ($M^+$), 137 ($M^+ - CF_3$), 123 ($M^+ - CF_3CH_2$); Calcd. for $C_9H_9F_3S$: m/e 206.0377, Found: 206.0302.

*p*-Tolyl 2,2,2-trifluoroethyl sulfide (1e): $^1$H NMR: 2.23 (s, 3H, $CH_3$), 3.32 (q, 2H, $CH_2$, $J_{H-F}$ = 10 Hz), 6.9-7.5 (m, 4H, $C_6H_4$). Mass: m/e 206 ($M^+$), 123 ($M^+ - CF_3CH_2$), 92 ($PhMe^+$); Calcd. for $C_9H_9F_3S$: m/e 206.0377, Found: 206.0370.

*p*-Methoxyphenyl 2,2,2-trifluoroethyl sulfide (1f): bp 165 °C / 22 Torr. $^1$H NMR: 3.26 (q, 2H, $CH_2$, $J_{H-F}$ = 9 Hz), 3.82 (s, 3H, $OCH_3$), 6.6-7.7 (m, 4H, $C_6H_4$). Mass: m/e 222 ($M^+$), 139 ($M^+ - CF_3CH_2$); Calcd. for $C_9H_9F_3OS$: m/e 222.0326, Found: 222.0356.

### Fluoroalkyl phenyl sulfides 2.

Sulfides 2 were similarly prepared from the corresponding fluoroalkyl p-toluenesulfonates and benzenethiol.

2,2-Difluoroethyl *p*-toluenesulfonate: mp 30.0-31.0 °C. $^1$H NMR: 2.50 (s, 3H, $CH_3$), 4.16 (dt, 2H, $CH_2$, $J_{H-H}$ = 4 Hz, $J_{H-F}$ = 12.4 Hz), 5.91 (tt, 1H, $CHF_2$, $J_{H-H}$ = 4 Hz, $J_{H-F}$ = 55 Hz), 7.1-8.0 (m, 4H, $C_6H_4$). IR(KBr): 1370(S=O), 1180 cm$^{-1}$. Mass: m/e 236 ($M^+$), 155 ($Ts^+$), 92 ($PhMe^+$); Calcd. for $C_9H_{10}F_2O_3S$: C, 45.76; H, 4.26%, Found: C, 46.02; H, 4.23%.

2-Chloro-2-fluoroethyl *p*-toluenesulfonate: $^1$H NMR: 2.50 (s, 3H, $CH_3$), 4.26 (m, 2H, $CH_2$), 6.23 (m, 1H, CHClF), 7.1-7.9 (m, 4H, $C_6H_4$). IR(neat): 1360(S=O), 1170 cm$^{-1}$. Mass: m/e 254 ($M^+$ + 2), 252 ($M^+$), 155 ($Ts^+$), 92 ($PhMe^+$); Calcd. for $C_9H_{10}ClFO_3S$: m/e 252.0023, Found: 252.0018.

2,2-Difluoroethyl phenyl sulfide (2d): bp 80-81 °C / 6 Torr. $^1$H NMR: 3.10 (dt, 2H, $CH_2$, $J_{H-H}$ = 5 Hz, $J_{H-F}$ = 14.5 Hz), 5.73 (tt, 1H, $CHF_2$, $J_{H-H}$ = 5 Hz, $J_{H-F}$ = 55 Hz), 7.0-7.5 (m, 5H, Ph). Mass: m/e 174 ($M^+$), 123 ($M^+ - CHF_2$), 109 ($PhS^+$); Calcd. for $C_8H_8F_2S$: m/e 174.0314, Found: 174.0318.

2-Chloro-2-fluoroethyl phenyl sulfide (2e): bp 180 °C / 25 Torr. $^1$H NMR: 3.1-3.7 (m, 2H, $CH_2$), 6.16 (m, 1H, CHClF), 7.0-7.6 (m, 5H, Ph). Mass: m/e 192 ($M^+$ + 2), 190 ($M^+$), 123 ($M^+ - CHClF$), 109 ($PhS^+$); Calcd. for $C_8H_8ClFS$: m/e 190.0019, Found: 189.9990.

2-Fluoroethyl phenyl sulfide (2f): From benzenethiol and 1-bromo-2-fluoroethane, 2f was prepared. bp 110-128 °C / 10 Torr. $^1$H NMR: 3.22 (dt, 2H, $CH_2$, $J_{H-H}$ = 7.4 Hz), 4.47 (dt, 2H, $CH_2F$, $J_{H-H}$ = 7.4 Hz, $J_{H-F}$ = 46.4 Hz), 7.1-7.5 (m, 5H, Ph). Mass: m/e 156 ($M^+$), 123 ($M^+ - CH_2F$); Calcd. for $C_8H_9FS$: m/e 156.0409, Found: 156.0404.

### Electrolysis and Product Analysis.

Electrolysis was carried out at a constant current using platinum plates(3x2 cm) as an anode and a cathode in an undivided cylindrical cell equipped with a magnetic stirrer. Electrolytic conditions in each electrolysis are shown in Tables 2 and 6.

(a) Anodic Methoxylation: Constant current (3.3 A/dm$^2$) electrolysis of sulfide 1 and 2 (2 mmol) was carried out in 0.2 M $Et_4NOTs$-MeOH (30 ml) at room temperature. After passing 10 F/mol or 20 F/mol of electricity [monitoring unreacted 1 and 2 by GC(PEG 20M)], the electrolyte was concentrated under reduced pressure. The residue was mixed with 20 ml of water and extracted three times with 20 ml-portions of ether and then washed with 50 ml of brine. The extracts were dried over anhydrous sodium sulfate and solvent was

evaporated. The remaining oil was chromatographed on silica gel (hexane–AcOEt, 40:1 - 4:1 or hexane) to provide α-methoxy products 3 and 4.

(b) Anodic Acetoxylation: Constant current (1.2 A/dm$^2$) electrolysis of sulfides 2 (2 mmol) was carried out in 0.3 M AcOK/AcOH (30 ml) at room temperature. After passing 4 F/mol of electricity, the electrolyte was concentrated under reduced pressure. The residue was mixed with 20 ml of water and extracted three times of 20 ml-portions of ether. The extracts were washed with sodium bicarbonate, water, and brine and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–AcOEt, 20:1 - 4:1) to provide α-acetoxy products 5.

p-Fluorophenyl 1-methoxy-2,2,2-trifluoroethyl sulfide (3c): $^1$H NMR: 3.56 (s, 3H, $OCH_3$), 4.56 (q, 1H, CH, $J_{H-F}$ = 6 Hz), 6.7-7.6 (m, 4H, $C_6H_4$). IR(neat): 970 cm$^{-1}$(C-O). Mass: m/e 240 ($M^+$), 171 ($M^+ - CF_3$), 127 ($M^+ - CF_3CH(OCH_3)$), 113 ($CF_3CH(OCH_3)^+$); Calcd. for $C_9H_8F_4OS$: m/e 240.0231, Found: 240.0230.

1-methoxy-2,2,2-trifluoroethyl m-tolyl sulfide (3d): $^1$H NMR: 2.40 (s, 3H, $CH_3$), 3.63 (s, 3H, $OCH_3$), 4.8 (q, 1H, CH, $J_{H-F}$ = 6.5 Hz), 7.0-7.4 (m, 4H, $C_6H_4$). IR(neat): 980 cm$^{-1}$(C-O). Mass: m/e 236 ($M^+$), 167 ($M^+ - CF_3$), 123 ($M^+ - CF_3CH(OCH_3)$), 113 ($CF_3CH(OCH_3)^+$); Calcd. for $C_{10}H_{11}F_3OS$: m/e 236.0482, Found: 236.0479.

1-methoxy-2,2,2-trifluoroethyl p-tolyl sulfide (3e): $^1$H NMR: 2.32 (s, 3H, $CH_3$), 3.52 (s, 3H, $OCH_3$), 4.58 (q, 1H, CH, $J_{H-F}$ = 7 Hz), 6.9-7.4 (m, 4H, $C_6H_4$). Mass: m/e 236 ($M^+$), 167 ($M^+ - CF_3$), 123 ($M^+ - CF_3CH(OCH_3)$), 113 ($CF_3CH(OCH_3)^+$); Calcd. for $C_{10}H_{11}F_3OS$: m/e 236.0482, Found: 236.0463.

p-Methoxyphenyl 1-methoxy-2,2,2-trifluoroethyl sulfide (3f): $^1$H NMR: 3.58 (s, 3H, α-$OCH_3$), 3.79 (s, 3H, p-$OCH_3$), 4.60 (q, 1H, CH, $J_{H-F}$ = 6 Hz), 6.6-7.7 (m, 4H, $C_6H_4$). IR(neat): 980 cm$^{-1}$(C-O). Mass: m/e 252 ($M^+$), 139 ($M^+ - CF_3CH(OCH_3)$), 113 ($CF_3CH(OCH_3)^+$); Calcd. for $C_{10}H_{11}F_3O_2S$: m/e 252.0431, Found: 252.0425.

1-Methoxy-2,2-difluoroethyl phenyl sulfide (4d): $^1$H NMR: 3.63 (s, 3H, $OCH_3$), 4.56 (dt, 1H, CH, $J_{H-H}$ = 5 Hz, $J_{H-F}$ = 9 Hz), 5.50 (dt, 1H, $CHF_2$, $J_{H-H}$ = 5 Hz, $J_{H-F}$ = 55 Hz), 7.2-7.7 (m, 5H, Ph). IR(neat): 980 cm$^{-1}$(C-O). Mass: m/e 204 ($M^+$), 153 ($M^+ - CF_2H$), 109 ($PhS^+$); Calcd. for $C_9H_{10}F_2OS$: m/e 204.0420, Found: 204.0421.

1-Acetoxy-2,2-difluoroethyl phenyl sulfide (5e): $^1$H NMR: 2.13 (s, 3H, $CH_3$), 5.70 (dt, 1H, $CHF_2$, $J_{H-H}$ = 4.6 Hz, $J_{H-F}$ = 56 Hz), 5.96 (dt, 1H, CH, $J_{H-H}$ = 4.6 Hz, $J_{H-F}$ = 10 Hz), 7.2-7.8 (m, 5H, Ph). IR(neat): 1780 cm$^{-1}$(C=O). Mass: m/e 232 ($M^+$), 110 ($PhSH^+$), 43 ($CH_3CO^+$); Calcd. for $C_{10}H_{10}F_2O_2S$: m/e 232.0369, Found: 232.0400.

1-Acetoxy-2-fluoroethyl phenyl sulfide (5d): $^1$H NMR: 3.56 (s, 3H, $CH_3$), 4.43 (m, 2H, $CH_2F$), 6.15 (m, 1H, CH), 7.2-7.7 (m, 5H, Ph). IR(neat): 1770 cm$^{-1}$(C=O). Mass: m/e 214 ($M^+$), 110 ($PhSH^+$), 43 ($CH_3CO^+$); Calcd. for $C_{10}H_{11}FO_2S$: m/e 214.0463, Found: 214.0475.

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