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Electrochemical Properties and Fluorination of Cyclopropane Derivatives Bearing Arylthio Groups

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Electrochemical analyses of phenylthiocyclopropane derivatives and bis(arylthio)cyclopropanes were comparatively studied by cyclic voltammetric measurements. Based on the substituent effects on their oxidation potentials, a cyclopropane ring was confirmed to have a double bond system as reported. Anodic fluorination of phenylthiocyclopropanes resulted in the formation of sulfoxide and/or ring opening fluorinated products while 1,1-bis(arylthio)cyclopropanes afforded mainly desulfurative monofluorinated cyclopropanes and sulfoxides together with ring opening fluorinated products. This is the first successful electrochemical fluorination of a cyclopropane ring.

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A cyclopropane group is a common structural motif in biologically active compounds and cyclopropanol derivatives are often applied to pharmaceuticals and agrochemicals.1,2 On the other hand, organofluorine compounds are also widely applied to medicinal chemistry, agrochemistry, and materials science.3–8 Among aliphatic organofluorine compounds, monofluorocyclopropanes are highly useful for modification of biological activities such as antibacterial, antibiotic, and neurochemical activities.8,9 Moreover, gem-difluoro cyclopropane derivatives are expected to be useful functional polymers, liquid crystals, and building blocks.9,10,11 However, their preparation is not so easy and remains an important challenge. There are several synthetic methods of monofluorocyclopropanes such as addition of carbene to fluoroalkanes, addition of fluorocarbenes to alkenes, Michael initiated ring closure, and nucleophilic fluorination of a cyclopropane ring.9–12 Furthermore, fluoroxyolation of alkylidenecyclopropanes using N-fluorosuccinimide (NFS), fluorination of arylcyclopropyl silyl ether with diethylaminosulfur trifluoride (DAST), and halogen exchange reaction with a fluoride ion also provide fluorocyclopropane derivatives in moderate to good yields (Schemes 1–3).13–15 Although the halogen exchange reaction affords high yield, high reaction temperature as 120 °C is required.

Among them, direct fluorination is one of the ideal methods; however, it requires hazardous and/or costly reagents and yield is generally unsatisfactory. For example, Toyota et al. reported the fluorination of cyclopropyl phenyl sulfoxide with 5% F2/N2 affording fluorocyclopropyl phenyl sulfone in 12% yield as shown in Scheme 4.16 In this case, nonfluorinated cyclopropyl phenyl sulfone was mainly formed.

On the other hand, we have systematically studied electrochemical fluorination of various organic molecules and macro-molecules so far, and we have published a number of papers dealing with electrochemical α-fluorination of organosulfur compounds and heterocyclic compounds as exemplified by Scheme 5.17–20 Electrochemical oxidation of a cyclopropane ring is of much interest because of its olefin-like character. Shono and his co-workers reported the oxidation potentials and anodic methoxylation of cyclopropanes having multi-methyl groups.31,32 They found that the oxidation potential decreased by 0.25 V with increase of the number of the methyl group. Arnold and Wong also reported the oxidation potential of trans-1,2-diphenycyclopropane was lower by 0.24 V than that of cis-form.33 Such trend is similar to that observed in an olefin system.

Torii and his co-workers reported that anodic methoxylation of cyclopropanes and fused cyclopropanes having a phenylthio group to provide methoxylated products accompanied with ring opening regardless of the structures of cyclopropanes (Scheme 6).34 However, there have been no reports on cyclic voltammetry study of cyclopropanes having phenylthio groups and anodic fluorination of cyclopropane rings to date.

With these facts in mind, we have studied electrochemical properties and fluorination of various cyclopropanes having phenylthio groups.

**Experimental

**General.—1H, 13C, and 19F NMR spectra were recorded on a JEOL JNM EX-270 (1H: 270 MHz, 13C: 67.8 MHz, 19F: 254.05 MHz) spectrometer in CDCl3. The chemical shifts for 1H and 13C are given in δ (ppm) downfield from internal TMS and CDC13, respectively.19F NMR chemical shifts are given in δ (ppm) upfield from external trifluoroacetic acid. Oxidation potentials (E°) were measured in 0.1 M Bu4NClO4/McCN at a scan rate of 100 mV s−1 by cyclic voltammetry using ALS Instruments model 600 A. A platinum disk electrode (φ = 1 mm) and a platinum plate (1 cm × 1 cm) were used as working and counter electrodes, respectively. A saturated calomel electrode (SCE) was used as a reference electrode. Preparative electrolysis experiments were carried out with a Hokuto Denko HABF 501 potentiosat/galvanostat. Mass spectra and high resolution-mass spectra were obtained with a Shimadzu GCMS-QP-2000A or JEOL JMS-700 mass spectrometer. 19F NMR yields were estimated with α,α,α-trifluorotoluene as an internal standard.

**Materials.—Cyclopropyl phenyl sulfide (1a) was obtained from TCI and used without further purification. Dry solvents were purchased and used as received. Et3N-NH2 (n = 3, 5) and Et4NF-3HF were kindly supplied by Morita Chemical Industries Co. Ltd. Japan).

**Trans-1-phenyl-2-phenylthiocyclopropane (1b),35 trans-1-bromo-2-phenylthio-cyclopropane (1c),40 methyl trans-2-phenylthiocyclopropanecarboxylate (1d),51 1,2-diphenyl-3-phenylthiocyclopropane (1f),52 1-phenylthio-2,2,3,3-tetramethylcyclopropane (1g),53 1,1-bis(phenylthio)cyclopropane (1h),54 were synthesized according to the literature method.

**1,1-Diphenyl-2-phenylthio-cyclopropane (1e).—To a vigorous stirred solution of 1,1-diphenylethylene (5.6 mmol) and benzyltrimethylammonium chloride (1.0 mmol) in a mixture of CH2Cl2 (30 ml) and 50% aq. NaOH (5 ml), α-chlorothioanisole (15 mmol)
was added at room temperature, and vigorously stirred at room temperature for 2 d. The reaction mixture was diluted with CHCl3 (10 ml) and washed with water (30 ml), 1 M HCl (10 ml), and brine (30 ml). The organic layer was separated and dried over anhydrous Na2SO4, and then the solution was removed by evaporation under reduced pressure. The crude product was purified by silica gel chromatography (SiO2 300 g, hexane/ethyl acetate = 10:1) as an eluent. A solution of 1,1,3-tri(μ-chloro)iodo-2-phenyl-3-phenylthiocyclopropane thus obtained (6.2 mmol) and 1,1-Bis(p-methoxyphenyl)iodocyclopropane (1k)—This substrate was prepared similarly to 1k. Colorless cubic; mp. 59 °C–60 °C; 1H NMR δ = 7.25–7.37 (m, 8H), 1.44 (s, 4H); 13C NMR δ =133.66, 132.94, 131.26, 128.92, 32.83, 20.65; MS m/z 332 (M+ + 2), 326 (M+ + 2), 183 (M+–CIC5H4S); HRMS: calcd for C15H12Cl2S: 294.0037; found; 294.0025.

**General procedure for electrochemical fluorination.**—Constant current anodic oxidation of substrate (0.5 mmol) was carried out with platinum plate electrodes (2 × 2 cm2) in an undivided glass or polyethylene cell containing 10 ml of 1 M Et3N-nHF or Et4NF-nHF/DME, MeCN or CHCl3 until the starting material was consumed (monitored by silica gel TLC). After the electrolysis, the electrolytic solution was extracted with hexane or passed through a short column filled with silica gel using CHCl3 as an eluent to evaporate the solvent. The residue was further purified by silica gel column chromatography or preparative thin-layer silica gel chromatography with hexane or hexane/ethyl acetate (50:1) as an eluent.

1.3-Difluoro-3,3-diphenyl-1-phenylsulfonylpropane (5e)—HRM

δ = 7.91–7.24 (m, 15H), 5.28 (ddd, J = 1.0, 9.2, 49 Hz, 1H), 3.36 (ddd, J = 1.0, 16, 26, 42 Hz, 1H), 2.98 (ddd, J = 9.2, 16, 21, 34 Hz, 1H); 13C NMR δ = 141.78, 141.17, 134.89, 134.59, 124.95, 122.22, 128.64, 128.30, 128.08, 128.05, 125.21, 124.99, 95.96, 93.76, 37.86; 19FN M R: δ = –71.86 (ddd, J = 11, 20, 33 Hz, 1F); –98.58 (ddd, J = 11, 18, 35 Hz, 1F); MS m/z 372 (M+), 211 (M+–PhSO–HF), 185 (PhSCF2); HRMS: calcd for C15H12F2O2S: 329.0971, found: 329.0986.

1.1-Dichloro-3-fluoro-2-phenyl-3-phenylthiophene (6)—HRM

δ = 7.42–7.14 (m, 11H), 6.75 (d, J = 46 Hz, 1H); 1F NMR δ = –98.86 (d, J = 46 Hz, 1F); MS m/z 316 (M+ + 4), 314 (M+ + 2), 312 (M+); HRMS: calcd for C15H11F2S: 311.0843, found: 311.0850.

1.1-Dichloro-3,3-difluoro-2-phenyl-3-phenylthiophene (7)—HRM

δ = 7.64–7.19 (m, 10H); 1F NMR δ = –10.44 (s, 2F); MS m/z 334 (M+ + 4), 332 (M+ + 2), 330 (M+); 221 (M+–PhS); HRMS: calcd for C15H11Cl2F2S: 329.9848, found: 329.9844.
1-Fluoro-1-phenylthiocyclopropane (8i). —^1H NMR: δ = 7.51–7.25 (m, 5H), 2.17–1.45 (m, 2H), 1.55–1.12 (m, 2H); ^13C NMR: δ = 134.25, 129.69, 128.88, 127.01, 83.84, 16.15; ^19F NMR: δ = −75.97 (ddddd, J = 7.4, 7.4, 15, 15 Hz, 1 F); MS m/z 168 (M^+), 109 (PhS^+), 91 (M^+–Ph).

1-Fluoro-1-(p-phenylthiophenyl)cyclopropane (8j). —^1H NMR: δ = 7.43–7.25 (m, 4H), 1.55–1.45 (m, 2H), 1.18–1.10 (m, 2H); ^13C NMR: δ = 133.24, 132.73, 131.06, 129.06, 83.86, 16.16; ^19F NMR: δ = −75.97 (ddddd, J = 7.4, 7.4, 15, 15 Hz, 1 F); MS m/z 204 (M^+ + 2), 202 (M^+), 167 (M^+–Cl), 143 (ClC(6)H(5)S^-); HRMS: calcd for C_{17}H_{18}O_{3}S_{2}: 334.0697, found; 334.0694.

δ = −7.44 (1H, t, J = 4.95, 1H, t, J = 4.95, 4H, t, J = 4.95), 3.85 (s, 3H), 3.79 (s, 3H), 1.24–1.09 (m, 2H); ^13C NMR: δ = 162.08, 159.39, 133.36, 133.24, 127.41, 123.88, 114.48, 55.42, 55.30, 51.00, 11.85; MS m/z 334 (M^+), 179 (M^+–MeOCMe), 139 (MeOCMe); HRMS: calcd for C_{13}H_{18}O_{2}S: 334.0697, found; 334.0694.

Results and Discussion

Oxidation potentials of phenylthiocyclopropanes.—At first, the oxidation potentials (E_p^ox) of various monosubstituted phenylthiocyclopropanes, 1a–Id were measured by cyclic voltammetry in Bu4NClO4/MeCN using a Pt disk electrode. The oxidation potentials are summarized in Table I.

Cyclopropane with a phenyl group (1b) was most easily oxidized while that with a carbomethoxy group (1d) was found to have the highest oxidation potential. We have already reported a good linear correlation of the oxidation potentials of fluoroethyl phenyl sulfides and N-(fluoroethyl)amines with Taft’s σ^* values for the fluoromethyl groups.41,42 However, a linear relationship between the oxidation potentials E_p^ox and the Hammett’s σ values or Taft’s σ^* values of substituent groups was not observed in the case of substituted phenylthiocyclopropanes. Instead, a linear correlation of the oxidation potentials E_p^ox with Hammett’s σ^* values of substituent groups was obtained as shown in Fig. 1. Brown and Okamoto also reported that Hammett equation could be applied to substituted cyclopropanes.43 The good relationship in Fig. 1 suggests that the cyclopropane ring has a double bond nature as reported.41

To theoretically understand the electronic properties of the cyclopropane derivatives, the density functional theory (DFT) calculation of 1a–Id was carried out (Fig. 2). The highest occupied molecular orbital (HOMO) of 1a–Id was mainly located on the sulfur atom regardless of substituents as shown in Fig. 2. This indicates the electron transfer of I takes place from the sulfur atom.

Next, the oxidation potentials of multi-substituted phenylthiocyclopropane derivatives, 1e–1h were measured by cyclic voltammetry similarly. As shown in Table II, gem-diphenyl substituted cyclopropane derivative 1e showed lower oxidation potential compared to the corresponding mono phenyl substituted cyclopropane 1b significantly, while the oxidation potential of 1f bearing diphenyl groups at different positions of the cyclopropane ring is almost same as that of 1b. Introduction of four methyl groups to the cyclopropane decreased little the oxidation potential (1a vs 1g) while introduction of two chloro groups increased the oxidation potential considerably (1b vs 1h). These results also suggest that a cyclopropane ring has a double-bond nature.

The HOMO of 1e and 1h was mainly located on the sulfur atom regardless of substituents as shown in Fig. 3. Again, in these cases, the first electron transfer should take place from the sulfur atom regardless of the substituents.

Next, the oxidation potentials of 1,1-bis(phenylthio)cyclopropanes 1i–1k were measured by cyclic voltammetry. The oxidation potentials are summarized in Table III.

It was expected that the introduction of an additional phenylthio group to the cyclopropane ring would decrease their oxidation potentials. However, unexpectedly 1i bearing gem-phenylthio groups has a considerably higher oxidation potentials than 1a having a single phenylthio group (E_p^ox = 1.46 V). Similar trend has been observed in the oxidation potentials of dithioacetals bearing α-electron-withdrawing substituents.36 These results and facts indicate that the additional phenylthio group does not act as an electroattract, but acts as an electron-withdrawing group. Cyclopropane derivative 1k having gem-(p-methoxyphenyl) group has much lower oxidation potentials than 1i bearing gem-phenyl group. Since a p-methoxy group has an electron-donating effect, the decrease of the oxidation potential of 1k is reasonable.

**Table I. Oxidation potentials (E_p^ox) of monosubstituted phenylthiocyclopropane derivatives, 1a–Id.**

| Substrate | R  | E_p^ox (V vs SCE) |
|-----------|----|-----------------|
| 1a        | H  | 1.46            |
| 1b        | Ph | 1.39            |
| 1c        | Br | 1.54            |
| 1d        | COOMe | 1.61         |

a) Pt disk electrode (δ = 1 mm), 0.1 M Bu4NClO4/MeCN, scan rate: 100 mV s^-1.

**Figure 1. Relationship between oxidation potentials (E_p^ox) of 1 and the Hammett’s σ^* values.**

Electrochemical fluorination of cyclopropane derivatives 1.— At first, anodic fluorination of unsubstituted phenylthiocyclopropane 1a was carried out at a platinum anode in various solvents containing...
Et$_3$N-3HF using an undivided glass cell. However, no fluorination took place and the corresponding sulfoxide 2a was obtained in ca. 50% yield regardless of electrolytic solvents as shown in Scheme 7.

As already mentioned, it has been reported that fluorination of phenylsulfonylcyclopropane with F$_2$/N$_2$ gas resulted in formation of the corresponding fluorinated and unfluorinated sulfone derivatives (Scheme 4). Next, we carried out anodic fluorination of 2-bromo-1-phenylthiocyclopropane (1c) similarly to the case of 1a. However, the desired fluorinated product was not obtained and the corresponding sulfoxide 2c was formed as shown in Scheme 7. In this case, unidentified byproducts were formed considerably.

Then, anodic fluorination of 1,1-diphenyl derivative 1e was carried out similarly in Et$_3$N-3HF/DME. In this case, fluorination proceeded; however, ring opening of the cyclopropane took place to form the corresponding difluoro product 3e as shown in Scheme 8. However, the attempt of isolation of 3e using silica gel column chromatography resulted in hydrolysis of 3e to form enone derivative 4e (Scheme 8).

Therefore, 3e was converted to the corresponding sulfone derivative 5e by the treatment with mCPBA immediately after the electrolysis of 1e. Thus, stable α,γ-difluoro product 5e was obtained in moderate yield (53%). Then, anodic fluorination of 1e was investigated using various solvents and supporting fluoride salts. However, ring opening fluorination always took place to afford 3e, and the use of Et$_3$N-3HF/DME was found to give the highest yield of 5e as shown in Table IV.

Next, anodic fluorination of 1,1-dichloro-2-phenyl-3-phenylthiocyclopropane (1h) was also carried out in DME and MeCN containing Et$_3$N-3HF. As shown in Scheme 9, mono and difluorinated ring opening products 6 and 7 were formed in reasonable yields. In both cases, a considerable amount of unidentified byproduct was formed.

### Table II. Oxidation potentials of multi-disubstituted phenylthiocyclopropane derivatives, 1e–1h$^{a,b}$.

| Substrate | R$^1$ | R$^2$ | R$^3$ | R$^4$ | $E_{P}^{ox}$ (V vs SCE) |
|-----------|-------|-------|-------|-------|---------------------|
| 1e        | Ph    | Ph    | H     | H     | 1.21                |
| 1f        | Ph    | H     | Ph    | H     | 1.37                |
| 1g        | Me    | Me    | Me    | Me    | 1.35                |
| 1h        | Ph    | H     | Cl    | Cl    | 1.61                |

a) Pt disk electrode ($\phi = 1$ mm), 0.1 M Bu$_4$NClO$_4$/MeCN, scan rate: 100 mV s$^{-1}$.

Et$_3$N-3HF using an undivided glass cell. However, no fluorination took place and the corresponding sulfoxide 2a was obtained in ca. 50% yield regardless of electrolytic solvents as shown in Scheme 7.

### Table III. Oxidation potentials of 1,1-bis(phenylthio)cyclopropane derivatives$^{a,b}$.

| Substrate | X   | $E_{P}^{ox1}$ (V vs SCE) | $E_{P}^{ox2}$ (V vs SCE) | $E_{P}^{ox3}$ (V vs SCE) |
|-----------|-----|-------------------------|-------------------------|-------------------------|
| 1i        | H   | 1.69                    | —                       | —                       |
| 1j        | Cl  | 1.64                    | 1.90                    | —                       |
| 1k        | OMe | 1.27                    | 1.43                    | 1.62                    |

a) Pt disk electrode ($\phi = 1$ mm), 0.1 M Bu$_4$NClO$_4$/MeCN, scan rate: 100 mV s$^{-1}$.
Other phenylthio cyclopropane derivatives 1b and 1g also provided difluorinated ring opening products, which were detected by $^{19}$F NMR. However, the products could not be fully identified.

**Reaction mechanism for anodic fluorination of phenylthiocyclopropane derivatives 1e and 1h.**—As shown in Scheme 10, one electron transfer takes place from the sulfur atom of cyclopropane 1e to generate radical cation, which undergoes ring opening and then reacts with a fluoride ion followed by one more electron oxidation to generate fluorinated cation intermediate A. The resulting A reacts with a fluoride ion to form 1,3-difluoro derivative 3e, which is readily hydrolyzed to give the corresponding aldehyde B. Since a proton at α to the aldehyde group of B is acidic, deprotonation readily takes place to form anion intermediate, which undergoes elimination of a fluoride ion to give 4e. On the other hand, the treatment of 3e with mCPBA provides the corresponding stable sulfone derivative 5e.

Anodic fluorination of 1h proceeds similarly as shown in Scheme 11. The cation intermediate C undergoes readily deprotonation to give monofluoro product 6 since the β-proton of C is highly acidic owing to electron-withdrawing fluorine and chlorine atoms. Monofluoro product 6 is further oxidized to generate cation intermediate D, which reacts with a fluoride ion to give gem-difluoro product 7.

**Anodic fluorodesulfurization of 1,1-bis(phenylthio)cyclopropane 1i.**—As explained above, regardless of substituents on the cyclopropane having a phenylthio group, the corresponding fluorinated cyclopropanes were not formed at all. Previously, we studied anodic fluorodesulfurization of various dithioacetals to provide gem-difluoro or monofluoro products depending on electrolytic methods, supporting fluoride salts, and the molecular structures of dithioacetals. Therefore, we investigated anodic fluorination of cyclopropane derivative 1i bearing gem-phenylthio groups.

Anodic fluorination of 1i was performed in Et$_3$N-5HF/DME under various conditions. The results are summarized in Table V.

As shown in Table V, fluorodesulfurization of 1i took place selectively to provide monofluoro product 8i in reasonable to moderate yields regardless of electrolytic conditions. Notably, in this case, gem-difluorodesulfurization of dithioacetals of diaryl ketones affords generally

### Table IV. Anodic fluorination of 2,2-diphenyl-1-phenylthiocyclopropane 1e.

| Run | Supporting Electrolyte | Solvent | Electricity (F mol$^{-1}$) | Yield of 5e (%) |
|-----|------------------------|---------|---------------------------|----------------|
| 1   | Et$_3$N-3HF            | DME     | 3.0                       | 53$^{(a)}$     |
| 2   | Et$_3$N-3HF            | CH$_2$Cl$_2$ | 3.0                       | 13$^{(a)}$     |
| 3   | Et$_3$N-3HF            | MeCN    | 3.0                       | 12$^{(a)}$     |
| 4   | Et$_3$N-5HF            | DME     | 3.5                       | 38$^{(a)}$     |
| 5   | Et$_3$NF-3HF           | DME     | 3.5                       | 33$^{(a)}$     |

a) Isolated yield. b) Determined by $^{19}$F NMR.
gem-difluorinated products except for dithiaoacetals bearing an electron-withdrawing group. The electrolysis at 5 mA cm \(^{-2}\) and 10 mA cm \(^{-2}\) gave the almost same yield, 33% and 32% (Runs 2 and 3). Next, the effects of electrolytic cell materials was investigated. The use of an undivided polyethylene cell results in little higher yield (Run 5: 37%) compared to the use of an ordinary glass cell (Run 2: 33% yield). High content of HF such as Et,N-5HF causes corrosion of a glass cell, which seems to decrease the fluorination yield. Therefore, by using the polyethylene cell, we also investigated the effects of substrate concentration on the yield. Notably, the yield of 8i was affected by the concentration of substrate II significantly and 58% yield was obtained at 0.1 M concentration of II (Run 6). However, the reason is not clear. Although 8i is isolable, it is not stable enough. Therefore, 8i was converted to the corresponding stable sulfoxide and sulfone derivatives 9 and 10 respectively as shown in Scheme 12.

Next, effects of substituents of the phenylthio group on the fluorination was investigated. Anodic fluorination of 1,1-dichloro-2-phenyl-3-phenylthiocyclopropane 1h was carried out, and the anodic fluorination of 1,1-bis(p-chlorophenylthio)cyclopropane (1j) provided fluorodesulfurizative product 8j and sulfoxide of 11j mainly as well as ring opening vic-difluorothioster 12j as shown in Scheme 13. In addition, the corresponding disulfide was also formed. Anodic fluorination of 1,1-bis(p-methoxyphenyl)cyclopropane 1k afforded fluorodesulfurizative product 8k and sulfoxide 11k similarly to the case of 1j. As
Table V. Anodic fluorination of 1,1-bis(Phenylthio)cyclopropane (1i).

| Run | Concentration of 1i (M) | Current Density (mA cm$^{-2}$) | Electricity (F mol$^{-1}$) | Yield (%)$^a$ |
|-----|-------------------------|---------------------------------|---------------------------|--------------|
| 1$^{b)}$ | 0.05                    | 2.5                            | 2                         | 26           |
| 2$^{b)}$ | 0.05                    | 5.0                            | 3                         | 33           |
| 3$^{b)}$ | 0.05                    | 10                             | 3                         | 32           |
| 4$^{b)}$ | 0.05                    | 20                             | 3                         | 11           |
| 5$^{b)}$ | 0.05                    | 5.0                            | 3                         | 37           |
| 6$^{c)}$ | 0.1                     | 10                             | 3                         | 58$^{d)}$    |
| 7$^{c)}$ | 0.2                     | 10                             | 3                         | 37$^{d)}$    |

$^a$ Determined by $^{19}$F NMR $^b$ Undivided glass cell. $^c$ Undivided polyethylene cell. $^d$ Isolated yield.

Scheme 13. Anodic fluorination of 1,1-bis($p$-chlorophenylthio)cyclopropane 1j and 1,1-bis($p$-methoxyphenylthio)cyclopropane 1k.

Scheme 14. Reaction mechanism for anodic fluorination of 1,1-bis(phenylthio)cyclopropanes 1i–1k.
already mentioned, anodic fluorination of dithioacetals usually provides gem-difluoro products, and only when a halogen mediator or a KF-PEG/MeCN electrolytic solution was used, monofluoro products were formed selectively. However, in the case of dithioacetals of cyclopropane, gem-difluorination did not occur at all. Thus, we achieved electrochemical fluorination of cyclopropanes for the first time although the yield was moderate to low.

Reaction mechanism for the anodic fluorination of II-1k is shown in Scheme 14. Electron transfer takes place from the sulfur atom of II-1k generates radical cation E followed by desulfurization to give cation intermediate F, which is stabilized by an ArS group to avoid the ring opening. Then, a fluoride ion attacks F to form the corresponding monofluoroproduct 8i-8k. The radical cation E reacts with water contaminated in the electrolytic solution, and further oxidation and deprotonation gives the corresponding sulfoxide 11j and 11k. On the other hand, E reacts with a fluoride ion accompanying ring opening followed by further oxidations, fluorinations, elimination of HF, further oxidative fluorination, and eventually hydrolysis of H to form vic-difluoro product 12j as shown in Scheme 14.

Conclusions

We disclosed electrochemical properties of phenylthiocyclopropane derivatives bearing various substituents by cyclic voltammetric studies, and we confirmed that the cyclopropane ring has a double bond system electrochemically. Furthermore, we achieved electrochemical fluorination of a cyclopropane ring for the first time.

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