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Toward the synthesis of novel fluorinated building blocks: 3,4-difluorothiophene-1,1-dioxide

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Abstract

Addition of elemental fluorine to 2,5-dihydrothiophene-1,1-dioxide (**4**) provided a mixture of isomeric 3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxides (**5**) in moderate yield. Photochemical chlorination of each of these isomers gave the same product mixture consisting mainly of *trans*-3-chloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**9a**) and *trans*-3,4-dichloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**11b**). Dehydrohalogenation of the former gave 3,4-difluoro-4,5-dihydrothiophene-1,1-dioxide (**12**) as the main product, whereas dehydrohalogenation of the latter gave 3,4-difluorothiophene-1,1-dioxide (**3**) as the main product.

Keywords: Chlorination; Dehydrohalogenation; Difluorothiophene dioxide; Fluorodiene; Elemental fluorine; Fluorination

1. Introduction

Although the parent thiophene dioxide **1** is an unstable material [1–3], more substituted derivatives can be isolated as stable, crystalline compounds. Most of the chemistry of substituted thiophene dioxides has been focused on their use in cycloaddition reactions. A great range of such adducts was prepared [4–8] most notably by the Raasch [4] and Nakayama groups [7,8].

In a recent paper, one of us (I.N.) described the synthesis and reactivity of 3-chloro-4-fluorothiophene-1,1-dioxide (**2**) [9]. As a part of our continuing interest in the synthesis of fluorinated thiophene dioxides which may have potential as useful fluorinated building blocks, we describe herein the synthesis of 3,4-difluorothiophene-1,1-dioxide (**3**).

2. Results and discussion

The compound 2,5-dihydrothiophene-1,1-dioxide (**4** or 3-sulfolene) served as a cheap and readily accessible starting material for the syntheses reported herein. Since the methylene hydrogen atoms adjacent to a sulfonyl group are reluctant to be involved in a radical process, it appeared possible to saturate smoothly the double bond with elemental fluorine. Thus, fluorine diluted with nitrogen was slowly passed through a vigorously stirred, aqueous solution of 2,5-dihydrothiophene-1,1-dioxide (**4**) at ambient temperature. Since the use of water caused foaming and the formation of a film on the surface of the solution, a mixture of water and acetonitrile (4:1) was used instead. The reaction was halted after the complete consumption of the starting material, which was monitored by ^{1}H NMR spectroscopy. A variety of products was isolated from the reaction mixture; 3-fluoro-2,3-dihydrothiophene-1,1-dioxide (**6**) [10] and 3,4-epoxy-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**7**) [11] were formed along with the expected *cis*- and *trans*-difluoroadducts **5a** and **5b**, respectively (see Scheme 1). In an attempt to minimize the formation of epoxide **7**, a fluorination was carried out in acetonitrile at −30°C, but the presence of considerable amounts of compound **7** was again detected spectroscopically.

The assignment of the *cis* structure to adduct **5a** was based on a single-crystal X-ray analysis [2]. As can be seen in Fig. 1, the five-membered ring is distorted considerably from planarity with the C–F bonds being in a synclinal (gauche)

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[2]Crystal data for **5a**, $C_4H_6F_2O_2S$: $M = 156.15$; triclinic, space group $P1$; $a = 5.6334(8)$, $b = 6.3970(9)$, $c = 9.3893(13)$ Å, $\alpha = 82.278(3)$, $\beta = 78.067(3)$, $\gamma = 65.062(2)^\circ$, $V = 299.76(7)$ Å^3; $Z = 2$; $\rho_{calc} = 1.730$ Mg m^{-3}; $\mu(\mathrm{Mo}K_\alpha) = 0.500$ mm^{-1}; $R1 = 0.065$ and $wR2 = 0.162$.

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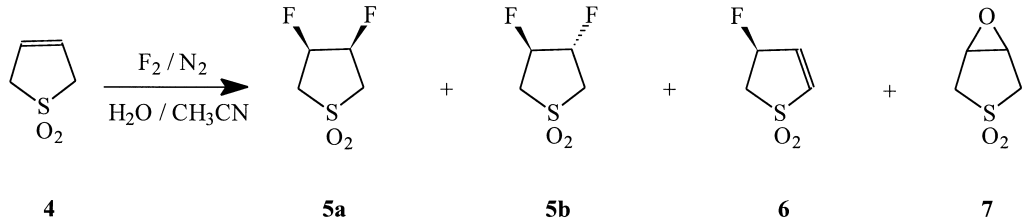


Scheme 1.

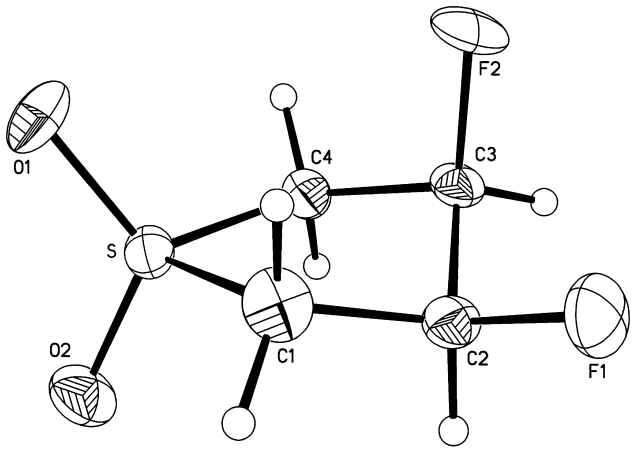
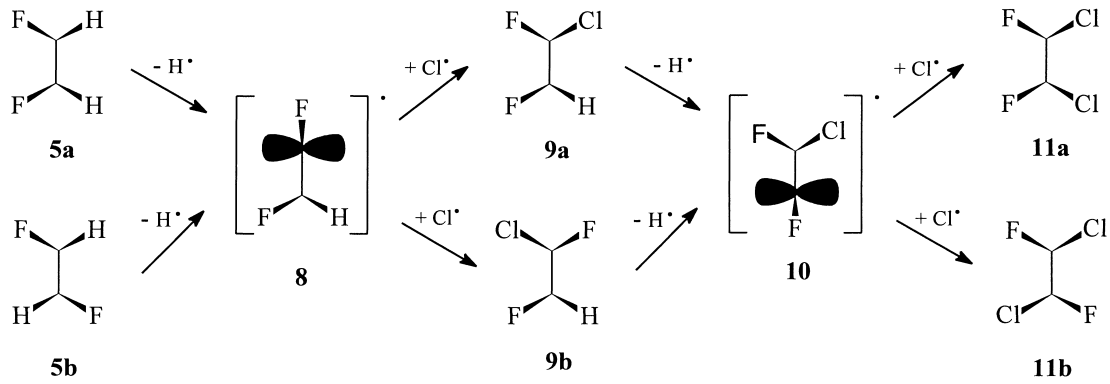


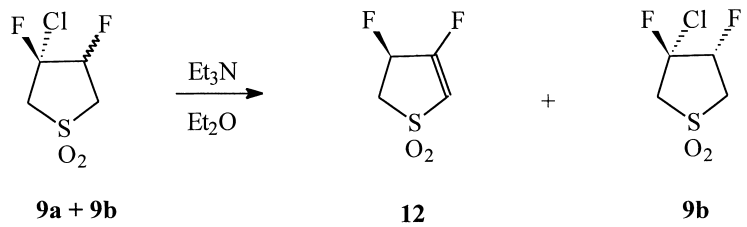
Fig. 1. ORTEP diagram of **5a**. Displacement ellipsoids are drawn at 50% probability level and hydrogen atoms have been given arbitrarily reduced radii for clarity.

arrangement. This assignment is also consistent with the previous work of Yagupol'skii et al. where compound **5a** was prepared from the ring opening reaction of epoxide **7** with sulfur tetrafluoride [10]. Although Yagupol'skii and co-workers did not assign the stereochemistry (*cis* or *trans*) of their product, the reaction of epoxides with DAST (and thus presumably with SF_4) is reported to give vicinal *cis*-difluorides [12]. In addition, Yagupol'skii reported a melting point of 129°C for **5a** versus 131–133°C found herein, both of which are in stark contrast to the 89–91°C melting point found for the *trans*-isomer **5b**.

Photochlorination of either the *cis* or *trans* isomer of **5** in carbon tetrachloride, after 7 h, gave the same mixture of mono and dichloro products. This result strongly suggests that the same intermediate, presumably radical **8** is involved in the reaction pathway. After removal of the solvent and subsequent purification over a silica gel column, compounds **9** and **11** were isolated as **9a** : **9b** = 30:10% and **11a** : **11b** = 5:30% mixtures, respectively (see Scheme 2). Pure isomers **9a** and **11b** were isolated after several additional recrystallizations of the obtained fractions. Reasonably pure (85%) isomer **9b** was recovered unchanged after reacting a mixture of isomers **9** with triethylamine (see Scheme 3); this reaction also resulted in the formation of 3,4-difluoro-4,5-



Scheme 2.



Scheme 3.

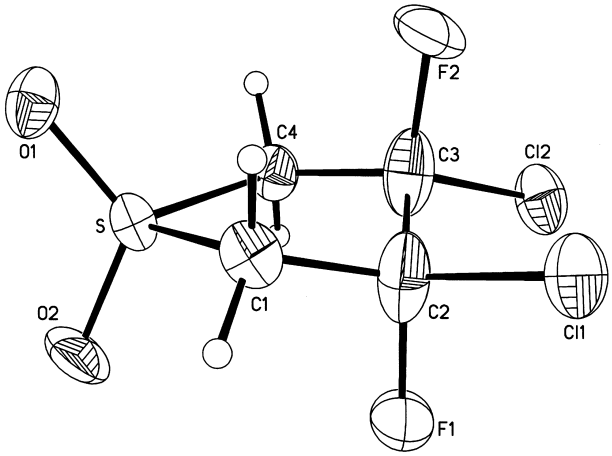


Fig. 2. ORTEP diagram of **11b**. Displacement ellipsoids are drawn at 50% probability level and hydrogen atoms have been given arbitrarily reduced radii for clarity.

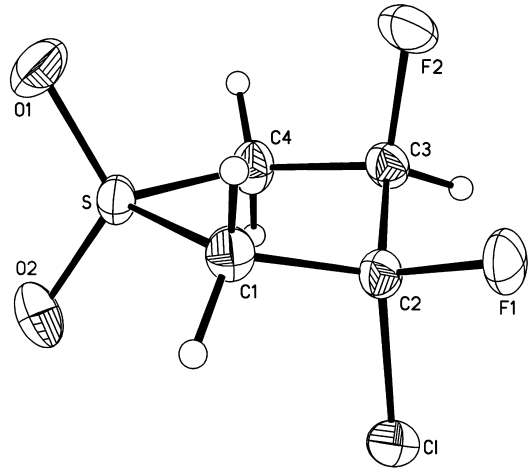
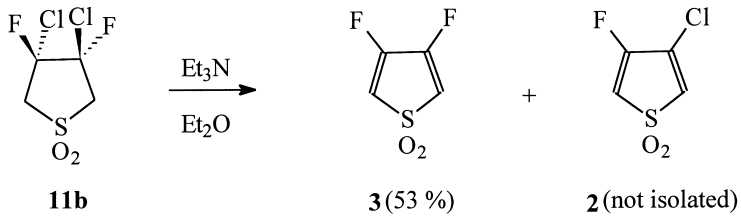


Fig. 3. ORTEP diagram of **9a**. Displacement ellipsoids are drawn at 50% probability level and hydrogen atoms have been given arbitrarily reduced radii for clarity.



11b **3** (53 %) **2** (not isolated)

Scheme 4.

dihydrothiophene-1,1-dioxide (**12**) in 53% yield. Irradiation of the sulfones **5** for a longer period of time (24 h) was necessary to complete the chlorination, thereby giving dichlorosulfones **11a** and **11b** in a total yield of 68% and a ratio of 1:5, respectively.

Due to uncertainty in the stereochemical assignments of compounds **9** and **11** based solely on the NMR data, the stereochemistry of the dominating isomers **9a** and **11b** was established by single-crystal X-ray analysis (see Figs. 2 and 3). Compound **11b** (Fig. 2) is the *trans* isomer with C–F bonds directed to opposite sides of the ring [3]. In contrast, X-ray analysis for the major isomer **9a** (Fig. 3) revealed that a *cis* arrangement of fluorine atoms is present [4]. The change of stereochemistry at the carbon atom after the introduction of second chlorine can be attributed to the existence of radical intermediate **10**. Once formed, radical **10** can combine with a chlorine atom under formation of the more stable *trans* isomer **11b** (see Scheme 3).

A well-established method for the generation of thiophene dioxide and its derivatives involves the double dehydrohalogenation of dihalothiolane dioxides [13,14]. In the case of compounds **11a** and **11b** the possibility of obtaining a mixture of both fluorinated as well as chlorinated products was quite obvious. However, our previous experience with selective elimination of hydrogen chloride in preference to hydrogen fluoride [9] gave us some hope that such a selectivity might be obtained again. Indeed, we have found that the addition of triethylamine to a diethyl ether solution of **11b** gave the expected 3,4-difluorothiophene-1,1-dioxide (**3**) and 3-chloro-4-fluorothiophene-1,1-dioxide (**2**) [9] as a minor product, in a ratio of 4:1 (Scheme 4). The reaction proceeds smoothly at room temperature within minutes. The elimination can also be carried out in other solvents like ethyl acetate, benzene or tetrahydrofuran, with the ratio of elimination products **3** and **2** being unchanged. This dehydrohalogenation reaction was also carried out on a mixture of isomers **11a** and **11b** (both analytical and laboratory scales), and no discernible difference in the ratio of products **3** and **2** was observed versus starting with just isomer **11b**. It is remarkable that the dehydrohalogenation proceeds with high chemoselectivity producing difluorinated compound **3** as a main product.

The considerable volatility of 3,4-difluorothiophene-1,1-dioxide (**3**) makes it possible to isolate it simply by sub-

[3]Crystal data for **11b**, $C_4H_4Cl_2F_2O_2S$: $M = 225.03$; monoclinic, space group $P2_1/c$; $a = 11.839(2)$, $b = 5.9558(8)$, $c = 10.9294(14)$ Å, $\beta = 99.404(2)^\circ$, $V = 760.3(2)$ Å^3; $Z = 4$; $\rho_{calc} = 1.966$ Mg m^{-3}; μ(Mo K_α) = 1.107 mm^{-1}; $R1 = 0.057$ and $wR2 = 0.141$.

[4]Crystal data for **9a**, $C_4H_5ClF_2O_2S$: $M = 190.59$; monoclinic, space group $P2_1/c$; $a = 5.7182(2)$, $b = 10.9121(4)$, $c = 10.8784(3)$ Å, $\beta = 95.910(2)^\circ$, $V = 675.18(4)$ Å^3; $Z = 4$; $\rho_{calc} = 1.875$ Mg m^{-3}; μ(Mo K_α) = 0.845 mm^{-1}; $R1 = 0.056$ and $wR2 = 0.134$.

limation under reduced pressure followed by recrystallization. The structure of compound **3** was confirmed by the presence of a single vinylic hydrogen signal in the ^{1}H NMR spectrum and a single vinylic fluorine signal in the ^{19}F NMR spectrum. The mass spectrum exhibited strong peaks for the molecular ion as well as the ions $(M–CHO)^+$ and $(M–CHO–F)^+$, which are also characteristic for 3-chloro-4-fluorothiophene-1,1-dioxide (**2**) [9].

3. Experimental

Melting points were determined in open capillaries and are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO, with Bruker AM360 and AM500 spectrometers at the frequency indicated. Chemical shifts are quoted in ppm from internal TMS for ^{1}H (positive downfield; same for ^{13}C) and from internal $CFCl_3$ for ^{19}F (positive downfield). Preliminary ^{13}C NMR spectra were taken to assure consistency with the structures proposed herein, but high quality spectra were not recorded; this may be the subject of a future study. GC-MS analyses were performed with a Hewlett-Packard 5890 GC-MS (70 eV) using a 30 m capillary column coated with HP1 oil. Column chromatography was carried out on 70–230 mesh silica gel.

Crystals of compounds **5a**, **9a**, and **11b** were mounted on fibers, transferred to the goniometer, and cooled to −100°C using a stream of nitrogen gas. Crystallographic data were collected using a Siemens CCD area detector-equipped diffractometer, and all calculations were performed using the SHELXTL suite of programs [15]. All crystallographic data, including structure factor tables, have been submitted as supplementary information and can be obtained by following the instructions on the current masthead page of this journal.

3.1. Reaction of 2,5-dihydrothiophene-1,1-dioxide (4) with fluorine

Elemental fluorine (ca. 30 g, 0.79 mol) diluted with nitrogen (1:3 ratio) was passed very slowly through a vigorously stirred solution of 2,5-dihydrothiophene-1,1-dioxide (**4**) (30 g, 0.25 mol) in a mixture with water (200 ml) and acetonitrile (50 ml) at ambient temperature. The reaction mixture was then evaporated in vacuo until aqueous hydrogen fluoride started to distill. The organic material was subjected to column chromatography on silica with chloroform as an eluent. Analytical samples of **5a**, **5b**, **6** and **7** were obtained after recrystallization of collected fractions from methanol. Yields: 18%, 13%, 15%, and 6%, respectively.

Cis-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**5a**): m.p. 131–133°C. *Anal*. Found: C, 30.84; H, 4.00; F, 21.86; S, 20.72%. $C_4H_6F_2SO_2$ requires: C, 30.77; H, 3.87; F, 24.33; S, 20.54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.46 (m, 2H, CHF), 3.60 (m, 4H, CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ: −199.3 (m). GC-MS (*m/z*) [relative intensity, ion]: 156 [3%, M^+], 77 [15, $(C_3H_3F_2)^+$], 46 [100, $(C_2H_3F)^+$].

Trans-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**5b**): m.p. 89–91°C. *Anal*. Found: C, 30.90; H, 3.99; F, 21.86; S, 20.54%. $C_4H_6F_2SO_2$ requires: C, 30.77; H, 3.87; F, 24.33; S, 20.54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.45 (m, 2H, CHF), 3.55 (m, 4H, CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ: −186.8 (m). GC-MS (*m/z*) [relative intensity, ion]: 156 [3%, M^+], 77 [15, $(C_3H_3F_2)^+$], 46 [100, $(C_2H_3F)^+$].

3-Fluoro-2,3-dihydrothiophene-1,1-dioxide (6): m.p. 66–68°C ([10], 68–69°C). *Anal*. Found: C, 35.36; H, 3.82; F, 13.36; S, 23.76%. $C_4H_5FSO_2$ requires: C, 35.29; H, 3.70; F, 13.95; S, 23.55%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.85 (ddd, 1H vinylic, $^3J_{HH} = 6.8$ Hz, $^4J_{HF} = 2.8$ Hz, $^4J_{HH} = 0.9$ Hz); 6.81 (ddd, 1H vinylic, $^3J_{HH} = 6.8$ Hz, $^4J_{HF} = 4.5$ Hz, $^3J_{HH} = 3.0$ Hz); 5.81 (ddddd, 1H, CHF, $^2J_{HF} = 50.3$ Hz, $^3J_{HH} = 7.3$ Hz, $^3J_{HH} = 3.0$ Hz, $^3J_{HH} = 2.8$ Hz, $^4J_{HH} = 0.9$ Hz); 3.64 (ddd, 1H, CH_2, $^2J_{HH} = 14.4$ Hz, $^3J_{HF} = 12.1$ Hz, $^3J_{HH} = 7.3$ Hz); 3.36 (ddd, 1H, CH_2, $^3J_{HF} = 22.8$ Hz, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 2.8$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ: −171.5 (ddddd, CHF, $^2J_{HF} = 50.3$ Hz, $^3J_{HF} = 22.8$ Hz, $^3J_{HF} = 12.1$ Hz, $^4J_{HF} = 4.5$ Hz, $^4J_{HF} = 2.8$ Hz). GC-MS (*m/z*) [relative intensity, ion]: 136 [10%, M^+], 107 [20, $(M–CHO)^+$], 64 [45, SO_2^+], 46 [100, $C_2H_3F^+$].

3,4-Epoxy-1,2,3,4-tetrahydrothiophene-1,1-dioxide (7): m.p. 159–161°C ([11], 157–159°C). ^{1}H NMR (360 MHz, $CDCl_3$) δ: 3.92 (m, 2H), 3.65 and 3.46 (AB pattern, 4H, $^2J_{AB} = 14.4$ Hz). GC-MS (*m/z*)) [relative intensity, ion]: 70 [30%, $(M–SO_2)^+$], 64 [20, $(SO_2)^+$], 42 [100, $(C_2H_2O)^+$].

3.2. Photochemical chlorination of 3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxides (5)

Method A: A 3 l, four-necked flask equipped with a reflux condenser (protected from atmospheric moisture with a bubbler containing concentrated sulfuric acid), a Teflon-coated stirring bar, and a chlorine gas inlet valve, was charged with either difluorosulfone **5a** or **5b** (8 g, 0.05 mol) and carbon tetrachloride (1500 ml). Elemental chlorine was slowly passed through this vigorously stirred mixture. The resulting solution was subsequently irradiated with a Hanau Heraeus (15 W) immersion lamp (UV) for 7 h while monitoring the progress of the reaction by GC-MS. The solvent was removed on a rotary evaporator, and the residue was separated by column chromatography (100 g silica, toluene as eluent). Fractions containing mixtures of **9a**, **9b** and **11a**, **11b** were collected. Analytically pure samples of **9a** and **11b** were obtained after recrystallization of the collected fractions from methanol. Yields: 30% and 30%, respectively.

Method B: The procedure described above was used, but the time of irradiation was prolonged to 24 h. After column chromatography, a mixture of compounds **11a** and **11b** (1:5 ratio) was obtained in a 68% yield.

Trans-3-chloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**9a**): m.p. 64–66°C. *Anal*. Found: C, 25.17; H, 2.67; F, 13.15; Cl, 19.29; S, 16.79%. $C_4H_5ClF_2SO_2$ requires: C, 25.21; H, 2.64; F, 19.94; Cl, 18.60; S, 17.01%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.48 (dm, $^2J_{HF} = 49.6$ Hz, 1H, CHF); 3.70–4.17 (m, 4H, 2×CH_2). ^{19}F NMR (470 MHz, $CDCl_3$) δ: −120.6 (m, 1F, CFCl); −183.6 (ddddd, $^2J_{HF} = 49.6$ Hz, $J = 29.3$, 18.3, 16.2, 2.7 Hz, 1F, CHF). GC-MS (*m/z*) [relative intensity, ion]: 190 [2, M^+], 80 [100, $(C_2H_2FCl)^+$].

Trans-3,4-dichloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**11b**): m.p. 150–152°C. *Anal*. Found: C, 21.55; H, 1.91; Cl, 31.99; S, 14.30%. $C_4H_4Cl_2F_2SO_2$ requires: C, 21.35; H, 1.79; Cl, 31.51; S, 14.22%. ^{1}H NMR (360 MHz, $CDCl_3$) δ: 3.88–4.18 (m). ^{19}F NMR (470 MHz, DMSO-d_6) δ: −110.1 (m). GC-MS (*m/z*) [relative intensity, ion]: 224 [2, M^+], 160 [5, $(M–SO_2)^+$], 125 [30, $(M–SO_2–Cl)^+$], 111 [35, $C_3H_2F_2Cl^+$], 80 [100, $C_2H_2FCl^+$].

Cis-3,4-dichloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**11a**): ^{19}F NMR (470 MHz, DMSO-d_6) δ: −111.8 (m).

3.3. Reaction of a mixture of 3-chloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxides (9) with triethylamine

To a solution of 3-chloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**9**) (3 g, 0.016 mol) in diethyl ether (100 ml) was added triethylamine (3 g, 0.030 mol), and the mixture was stirred at room temperature. The progress of the reaction was monitored by GC-MS, which indicated that the elimination was complete after 15 min. The reaction mixture was then filtered, the precipitate washed with ether, and the filtrate concentrated. The remaining yellow residue was subjected to column chromatography using toluene as an eluent. Compounds **9b** and **12** were isolated in 20% and 53% yield, respectively.

Cis-3-chloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (**9b**): (oil, 85% purity); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.6–4.1 (m, 4H); 5.35 (dm, 1H, $^2J_{HF} = 47.8$ Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ: −114.0 (m, 1F, CFCl); −180.4 (dddddd, 1F, $^2J_{HF} = 47.8$ Hz, $^3J_{FF} = 35.4$ Hz, $J = 19.7$, 16.6, 2.1, 0.5 Hz, CHF). GC-CIMS (CH_4, *m/z*) [relative intensity, ion]: 191 [100, $(M+H)^+$], 171 [10, $(M–HF)^+$].

3,4-Difluoro-4,5-dihydrothiophene-1,1-dioxide (**12**): m.p. 67–69°C. *Anal*. Found: C, 31.08; H, 2.66; F, 23.16; S, 21.06%. $C_4H_4F_2SO_2$ requires: C, 31.17; H, 2.61; F, 24.65; S, 20.76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.70 (ddm, 1H, $^3J_{HF} = 22.5$ Hz, $^2J_{HH} = 14.7$ Hz); 3.90 (ddd, 1H, $^3J_{HF} = 15.2$ Hz, $^2J_{HH} = 14.7$ Hz, $^3J_{HH} = 7.5$ Hz); 5.73 (ddt, 1H, $^2J_{HF} = 52.7$ Hz, $^3J_{HH} = 7.5$ Hz, $J = 2.1$ Hz); 7.20 (m, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ: −111.3 (dm, 1F, $^3J_{FF} = 30.2$ Hz); −181.1 (ddddd, 1F, $^2J_{HF} = 52.1$, $^3J_{FF} = 30.2$ Hz, $^3J_{HF} = 22.8$, 15.2 Hz, $J_{HF} = 3.4$ Hz). GC-MS (*m/z*) [relative intensity, ion]: 154 [45, M^+], 125 [100, $(M–CHO)^+$], 106 [100, $(M–F–CHO)^+$].

3.4. Elimination of hydrogen chloride from 3,4-dichloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide (11)

To a solution of *trans*-3,4-dichloro-3,4-difluoro-2,3,4,5-tetrahydrothiophene-1,1-dioxide **11b** (3.0 g, 0.013 mol) in diethyl ether (100 ml) was added triethylamine (3.0 g, 0.030 mol), and the mixture was stirred at room temperature. The progress of the reaction was monitored by GC-MS, which indicated that the elimination was complete in ca. 30 min. The reaction mixture was then filtered, the precipitate washed with ether (3×30 ml), and the combined filtrates were concentrated (30% of the starting volume). This mixture was passed through silica with ether as an eluent. Evaporation of the solvent gave a red oil (2.5 g). Subsequent sublimation (70°C @20 Torr) and recrystallization from methanol gave 3,4-difluorothiophene-1,1-dioxide (**3**) as a colorless solid in 53% yield. Reactions with a mixture of **11a** and **11b** were done on both an analytical and laboratory scale with no discernible difference between the ratio of products **3** and **2** [9].

3,4-Difluorothiophene-1,1-dioxide (**3**): m.p. 107–109°C. *Anal*. Found: C, 31.55; H, 1.32; F, 24.40; S, 21.14%. $C_4H_2F_2SO_2$ requires: C, 31.58; H, 1.31; F, 24.98; S, 21.08%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.31 (m). ^{19}F NMR (470 MHz, $CDCl_3$) δ: −128.8 (m). GC-MS (*m/z*) [relative intensity, ion]: 152 [50, M^+], 123 [40, $(M–CHO)^+$], 104 [100, $(M–CHO–F)^+$].

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