



# Reactions of polyfluorinated thietanes

## Selective synthesis of 4-R-2,2-bis(trifluoromethyl)thietane-1-S-oxides and 2-substituted 5-fluoro-4-(trifluoromethyl)-2,3-dihydrothiophenes

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### ABSTRACT

Oxidation of 4-substituted 2,2-bis(trifluoromethyl)thietanes by *m*-chloroperoxybenzoic acid results in selective formation of the corresponding S-oxides in 65–86% yield. Oxidation of 4-C<sub>2</sub>H<sub>5</sub>S-2,2-bis(trifluoromethyl)thietane under mild conditions led to selective formation of 4-C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub>-2,2-bis(trifluoromethyl)thietane, which under more rigorous conditions was selectively converted into *trans*-4-C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub>-2,2-bis(trifluoromethyl)thietane-1-S-oxide. Reaction of 4-substituted 2,2-bis(trifluoromethyl)thietanes with activated aluminum powder results in a highly selective ring expansion process, producing the corresponding 5-fluoro-4-(trifluoromethyl)-2,3-dihydro-2-alkoxythiophenes in 58–93% yield. These compounds were also prepared in 61–85% yield using a “one-pot” procedure, starting from sulfur, hexafluoropropene and the corresponding vinyl ether without isolation of any intermediates. Both 2-*i*-C<sub>3</sub>H<sub>7</sub>O- and 2-*t*-C<sub>4</sub>H<sub>9</sub>O- 5-fluoro-4-(trifluoromethyl)-2,3-dihydrothiophenes were converted into 2-fluoro-3-trifluoromethylthiophene by reaction with P<sub>2</sub>O<sub>5</sub>.

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## 1. Introduction

Discovered by W. Middleton in 1960s, polyfluorinated thietanes were originally prepared by [2 + 2] cycloaddition reaction of monomeric hexafluoroacetone (HFTA) with vinyl ethers or vinyl sulfides [1]. Later the Ishikawa group introduced a system based on a readily available [2] 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (cyclic dimer of HFTA)/dry KF and vinyl ether, which significantly simplified the synthesis of 4-alkoxy-2,2-bis(trifluoromethyl)thietanes [3]. So far, only four representatives of 4-R-2,2-bis(trifluoromethyl)thietanes (R = CH<sub>3</sub>O-, C<sub>2</sub>H<sub>5</sub>O-, CH<sub>3</sub>S-, (CH<sub>3</sub>)<sub>3</sub>CS-) [1,3], and one perfluorinated analog along with 2,2,4,4-tetrakis(trifluoromethyl)-3,3-difluorothietane [4] were prepared. Examples of polycyclic fluorinated thietanes include adducts of HFTA with dihydropyrane and dioxene [1] or by the cycloadducts of fluorinated thiocarbonyls and quadricyclanes. For example, the reaction of HFTA with quadricyclane gives 3-thia-4,4-bis(trifluoromethyl)-tricyclo[5.2.1.0<sup>2,5</sup>]non-7-ene in a high yield [5]; bis(trifluoromethyl)thioetene also undergoes cycloaddition with quadricyclane and its derivatives forming norbornenethietanes containing exocyclic double bond [6,7].

Additional information on reactions and synthetic applications of HFTA and its cyclic dimer, along with chemical transformations of other polyfluorinated sulfur containing heterocycles can be found in recently published review article [8].

Despite the fact that fluorinated thietanes have been known for a long time, the information on chemical transformation of these materials is limited to ring opening reactions of 4-RO-2,2-bis(trifluoromethyl)thietanes (R = CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>) under action of R'-M (M = Li or -MgX) resulting in the formation of ring opening products CF<sub>2</sub> = C(CF<sub>3</sub>)CH<sub>2</sub>CH(OR)S-R' [3] and a similar transformation of 3-thia-4,4-bis(trifluoromethyl)-tricyclo[5.2.1.0<sup>2,5</sup>]non-7-ene resulting in high yield formation of 3-[(perfluoroprop-1-en-2-yl)bicyclo[2.2.1]-hept-5-en-2-yl]sulfanes in reaction with organo-lithium or magnesium derivatives [9]. The only reported example of ring expansion is a base catalyzed insertion of sulfur into of 4-alkoxy-2,2-bis(trifluoromethyl)thietanes leading to the formation of 5-alkoxy-3,3-bis(trifluoromethyl)-1,2-dithiolanes in moderate yield [3].

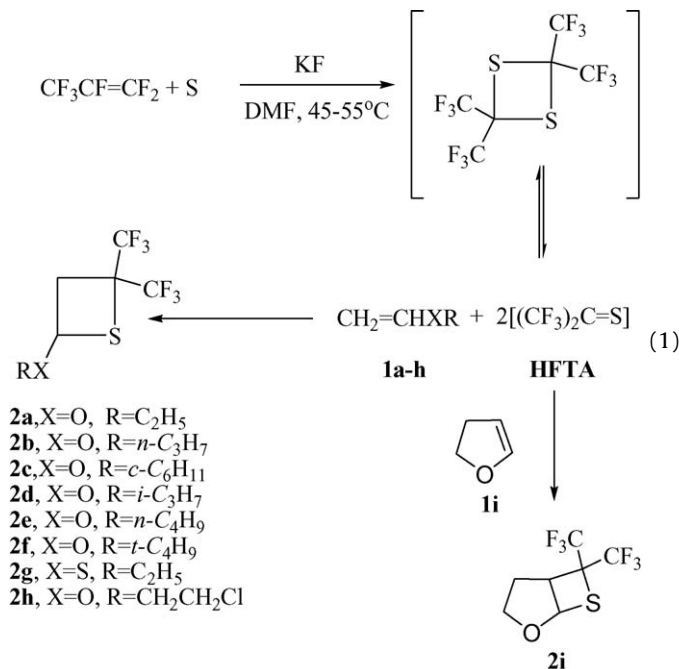
This paper describes two new transformations of 4-R-2,2-bis(trifluoromethyl)thietanes—a highly selective oxidation by *m*-chloroperoxybenzoic acid (MCPBA) with the formation of the corresponding S-oxides and a new reductive ring expansion process, leading to 2-substituted 5-fluoro-4-(trifluoromethyl)-2,3-dihydrothiophenes.

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## 2. Results and discussion

4-R-2,2-Bis(trifluoromethyl)thietanes **2a–i** used in this study were prepared using a reported KF catalyzed reaction of 2,2,4,4-tetrakis-(trifluoromethyl)-1,3-dithietane with vinyl ethers [3]. The reaction was extended and used for the synthesis of new thietanes thietanes **2b–h** and **2i** (Eq. (1)).



In the process of synthesis of thietanes **2a–i** it was discovered that the course of reaction is significantly affected by the nature of the catalyst and reaction conditions and a detailed study of this reaction will be the subject of separate publication.

**Table 1**

Yields, boiling points, IR and MS data for new materials.

Entry	Comp. no.	Yield (%)	B.p., °C/mmHg (m.p.)	IR (cm <sup>-1</sup> )	MS (m/z)
1	<b>3a</b>	77	41–45/1.7	1064, 1090 (S=O)	241 [C <sub>5</sub> H <sub>3</sub> F <sub>6</sub> O <sub>2</sub> S <sup>+</sup> , M–C <sub>2</sub> H <sub>5</sub> ] <sup>+</sup> , 222[C <sub>7</sub> H <sub>8</sub> F <sub>6</sub> O <sup>+</sup> , (M–SO) <sup>+</sup> ]
2	<b>3b</b>	79	51–55/0.7	1069, 1090 (S=O)	236 [C <sub>8</sub> H <sub>10</sub> F <sub>6</sub> O <sup>+</sup> , (M–SO) <sup>+</sup> ]
3	<b>3c</b>	76	88–91/0.8 <sup>a</sup>	1076, 1090 <sup>b</sup> (S=O)	–
4	<b>3d</b>	86	58–62/0.7	1073, 1090 (S=O)	250 [C <sub>9</sub> H <sub>12</sub> F <sub>6</sub> O <sup>+</sup> , (M–SO) <sup>+</sup> ]
5	<b>3e</b>	65	(59–61) <sup>c</sup>	1070, 1092 (S=O)	250 [C <sub>9</sub> H <sub>12</sub> F <sub>6</sub> O <sup>+</sup> , (M–SO) <sup>+</sup> ]
6	<b>3f</b>	88	64–67/1	1031, 1072 (S=O)	220 [(M–SO) <sup>+</sup> , C <sub>7</sub> H <sub>6</sub> F <sub>6</sub> O <sup>+</sup> ]
7	<b>3g</b>	60	(112.5–113) <sup>c</sup>	1422 (SO <sub>2</sub> )	302 (M <sup>+</sup> , C <sub>7</sub> H <sub>8</sub> F <sub>6</sub> O <sub>2</sub> S <sup>+</sup> )
8	<b>3h</b>	75	(84–84.5) <sup>c</sup>	1078 (S=O), 1422 (SO <sub>2</sub> )	–
9	<b>4a</b>	76	66–67/20	1678 (C=C)	216 (M <sup>+</sup> , C <sub>7</sub> H <sub>8</sub> F <sub>4</sub> OS <sup>+</sup> )
10	<b>4b</b>	63	80–82/50	1678 (C=C)	230 (M <sup>+</sup> , C <sub>8</sub> H <sub>10</sub> F <sub>4</sub> OS <sup>+</sup> )
11	<b>4c</b>	74	57–58/6	1677 (C=C)	270 (M <sup>+</sup> , C <sub>11</sub> H <sub>14</sub> F <sub>4</sub> OS <sup>+</sup> )
12	<b>4d</b>	58	27–28/0.2	1677 (C=C)	230 (M <sup>+</sup> , C <sub>8</sub> H <sub>10</sub> F <sub>4</sub> OS <sup>+</sup> )
13	<b>4e</b>	80	36–37/0.01	1678 (C=C)	244 (M <sup>+</sup> , C <sub>9</sub> H <sub>12</sub> F <sub>4</sub> OS <sup>+</sup> )
14	<b>4f</b>	85	32–33/0.02	1678 (C=C)	244 (M <sup>+</sup> , C <sub>9</sub> H <sub>12</sub> F <sub>4</sub> OS <sup>+</sup> )
15	<b>4g</b>	73	50–52/1.8	1677 (C=C)	232 (M <sup>+</sup> , C <sub>7</sub> H <sub>8</sub> F <sub>4</sub> S <sub>2</sub> <sup>+</sup> )
16	<b>4h</b>	68	116–118/0.8 (80–80.5) <sup>c</sup>	1454 (SO <sub>2</sub> ), 1677 (C=C)	264 (M <sup>+</sup> , C <sub>7</sub> H <sub>8</sub> F <sub>4</sub> O <sub>2</sub> S <sub>2</sub> <sup>+</sup> )
17	<b>4i</b>	83	76–77/2	1679 (C=C)	250 (M <sup>+</sup> , C <sub>7</sub> H <sub>7</sub> ClF <sub>4</sub> OS <sup>+</sup> )
18	<b>6a</b>	71	77–78/20	1670 (C=C)	214 (M <sup>+</sup> , C <sub>7</sub> H <sub>6</sub> F <sub>4</sub> OS <sup>+</sup> )
19	<b>6b</b>	93	60–61/0.2	1668 (C=C)	236 (M <sup>+</sup> , C <sub>10</sub> H <sub>8</sub> F <sub>4</sub> S <sup>+</sup> )
20	<b>6c<sup>d</sup></b>	50	–	1638, 1655 (C=C)	286 (M <sup>+</sup> , C <sub>11</sub> H <sub>8</sub> F <sub>6</sub> S <sup>+</sup> )
21	<b>7d<sup>e</sup></b>	12	–	1745 (C=C)	–
22	<b>7e<sup>f</sup></b>	11	100–105/0.05	1746 (C=C)	–
23	<b>8</b>	35–50	99–100	1611 (sh), 1589	170 (M <sup>+</sup> , C <sub>5</sub> H <sub>2</sub> F <sub>4</sub> S <sup>+</sup> )

<sup>a</sup> Sample crystallized upon standing at ambient temperature.

<sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub> solvent.

<sup>c</sup> Crystallized from CCl<sub>4</sub>.

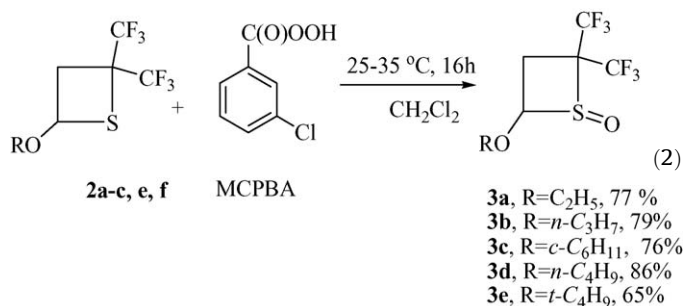
<sup>d</sup> Reaction was run using 1 g of **5c**, purity of **6c**–95%.

<sup>e</sup> Purity 95%, mixture of diastereomers, ratio 1:1.

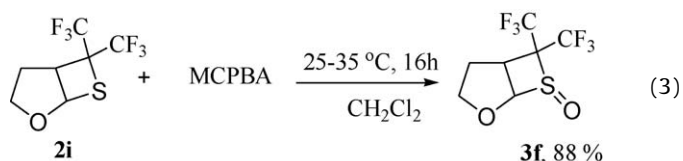
<sup>f</sup> Purity 99%, mixture of diastereomers, ratio 2:1.

### 2.1. Oxidation of 4-R-2,2-bis(trifluoromethyl)thietanes

Due to the presence of two strong electron withdrawing groups in  $\alpha$ -position a sulfur atom in 2,2-bis(trifluoromethyl)thietanes carries significant positive charge, which makes possible a direct attack of soft nucleophiles, such as Grignard reagents, on sulfur of the thietane ring [3]. Despite the electron-deficiency of sulfur in these materials, they still have an ability to react with oxidizers. We found that the reaction of thietanes **2a–c**, **e–f** with *m*-chloroperoxybenzoic acid (MCPBA) proceeds rapidly and is surprisingly selective. The addition of thietanes **2a–c**, **e–f** in CH<sub>2</sub>Cl<sub>2</sub> to a solution of an excess of MCPBA results in an exothermic reaction, leading to the formation of the corresponding thietane-1-S-oxides **3a–f** (Eq. (2); Tables 1 and 2).



The oxidation of bicyclic thietane **2i** results in rapid and selective formation of S-oxide **3f** (mixture *trans*-, *cis*- isomers, Eq. (3), Table 1).



**Table 2**  
 $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$  NMR data for new materials.

Entry	Comp. no.	$^1\text{H}$ NMR <sup>a</sup>	$^{19}\text{F}$ NMR <sup>a</sup>	$^{13}\text{C}$ NMR <sup>a</sup>
1	<b>3a<sup>b</sup></b>	1.29 (q), 2.31 (1H, m), 2.82 (3H, m), 3.7–4.1 (2H, m), 6.14 (t, $J = 5.4$ ), 6.48 (dd, $J = 7.3, 4.6$ )	Major: –64.04 (3F, $q, J = 9.2$ ), –66.70 (3F, $q, J = 9.2$ ); minor: –63.00 (3F, $q, J = 9.9$ ), –66.45 (3F, $q, J = 9.9$ )	
2	<b>3b<sup>b</sup></b>	0.95 (t), 1.67 (m), 2.33 (m), 3.9–3.9 (m), 6.14t, $J = 5.2$ ), 6.48 (dd, $J = 7.3, 4.7$ )	Major: –64.00 (3F, $q, J = 9.2$ ), –66.70 (3F, $q, J = 9.2$ ); minor: –63.00 (3F, $q, J = 9.7$ ), –66.44 (3F, $q, J = 9.7$ )	
3	<b>3c<sup>c</sup></b>	1.2–2.0, 2.81 (m), 3.78 (m), 6.26 (t, $J = 5.4$ ), 6.60 (dd, $J = 7.7, 4.5$ )	Major: –64.02 (3F, $q, J = 9.0$ ), –66.82 (3F, $q, J = 9.0$ ); minor: –62.95 (3F, $q, J = 9.7$ ), –66.35 (3F, $q, J = 9.7$ )	
4	<b>3d<sup>d</sup></b>	0.93 (t), 1.39 (m), 1.63 (m), 2.32 (m), 2.82 (m), 3.69 (m), 3.94 (m), 6.13 (t, $J = 5.2$ ), 6.48 (dd, $J = 7.3, 4.7$ )	Major: –63.01 (3F, $q, J = 9.5$ ), –66.45 (3F, $q, J = 9.5$ ); minor: –64.02 (3F, $q, J = 9.2$ ), –66.72 (3F, $q, J = 9.2$ )	
5	<b>3e<sup>e</sup></b>	1.33 (s), 1.34 (s), 2.27 (1H, m), 2.73 (m), 2.84 (m), 6.33 (t, $J = 5.7$ ), 6.72 (dd, $J = 7.9, 4.4$ )	Major: –64.00 (3F, $q, J = 9.2$ ), –66.98 (3F, $q, J = 9.2$ ); minor: –62.87 (3F, $q, J = 9.7$ ), –66.21 (3F, $q, J = 9.7$ )	
6	<b>3f<sup>f</sup></b>	2.15 (m), 2.25 (m), 2.56 (m), 3.29 (m), 3.37 (m), 4.16–4.35 (m), 6.67 (d, $J = 5.0$ ), 7.01 (d, $J = 4.0$ )	Major: –58.56 (3F, $q, J = 11.3$ ) –65.42 (3F, $q, J = 11.2$ ); minor: –60.75 (3F, $q, J = 10.1$ ), –63.69 (3F, $q, J = 10.1$ )	
7	<b>3g</b>	1.39 (3H, t, $J = 7.6$ ), 3.06 (2H, m), 3.20 (1H, dd, $J = 15.0, 9.1$ ), 3.68 (1H, ddq, 15.0, 7.6, 1.3), 4.74 (1H, t, $J = 8.0$ )	–73.12 (3F, $q, J = 10$ ), –74.63 (3F, $q, J = 10$ )	6.50, 28.73, 44.90, 48.03 (sept., $J = 33.5$ ), 49.50, 122.90 (q, $J = 280$ ), 126.00 (q, $J = 280$ )
8	<b>3h<sup>g</sup></b>	1.49 (3H, t, $J = 7.4$ ), 3.20 (4H, m), 4.80 (1H, t, $J = 8.0$ )	–65.24 (3F, $q, J = 8.2$ ), –68.50 (3F, $q, J = 8.2$ )	6.70, 17.53, 48.41, 56.55 (sept., $J = 30$ ), 63.20, 121.92 (q, $J = 282$ ), 122.40 (q, $J = 280$ )
9	<b>4a</b>	1.27, (3H, t, $J = 7.6$ ), 3.0 (1H, dd, $J = 15.6, 5.2$ ), 3.28 (1H, m), 3.45 (1H, qd, $J = 7.6, 2.1$ ), 3.73 (1H, qd, $J = 7.6, 1.8$ ), 5.41 (1H, t, $J = 6.1$ )	–60.94 (3F, d, $J = 17.2$ ), –106.25 (1F, qq, $J = 17.2, 5.7$ )	13.86, 38.08, 64.74, 87.63, 97.41 (qq, $J = 34.9, 3.9$ ), 121.00 (qd, $J = 269.3, 2.9$ ), 161.22 (d, $J = 307$ )
10	<b>4b<sup>h</sup></b>	0.96 (3H, t, $J = 7.2$ ), 1.66 (2H, sext, $J = 7.6$ ), 3.01 (1H, ddm, $J = 16.3, 5.4, 1.1$ ), 3.30 (1H, m), 3.36 (1H, dt, $J = 9.0, 6.3$ ), 5.42 (1H, dd, $J = 6.8, 1.3$ )	–60.99 (3F, dm, $J = 17.3, 1.4$ ), –106.20 (1F, qq, $J = 17.3, 5.7$ )	10.85, 23.36, 39.14, 72.01, 99.06 (qq, $J = 35.8, 4.8$ ), 122.44 (q, $J = 269.3$ ), 162.27 (d, q, $J = 307, 3.9$ )
11	<b>4c</b>	1.1–2.0 (10H, m), 2.97 (1H, dd, 15.9; 5.3), 3.25 (1H, d, m; $J = 15.9$ ), 3.47 (1H, m), 5.58 (1H, dt, $J = 6.8, 1.5$ )	–60.40 (3F, d, $J = 16.5$ ), –105.58 (1F, qq, $J = 16.5; 5.5$ )	
12	<b>4d</b>	1.20 (3H, d, $J = 6.3$ ), 1.24 (3H, d, $J = 6.3$ ), 2.96 (1H, ddm, $J = 15.9, 5.5$ ), 3.26 (1H, dm, $J = 15.9$ ), 3.78 (1H, sept., $J = 6.3$ ), 5.52 (1H, dd, $J = 5.3, 1.5$ )	–60.91 (3F, d, $J = 17.3$ ), –106.12 (1F, qq, $J = 17.2, 5.7$ )	20.09, 22.39, 38.45, 71.61, 85.49, 97.71 (qd, $J = 34.9, 4.8$ ), 121.38 (q, $J = 268.4$ ), 161.25 (dq, $J = 306.0, 4.8$ )
13	<b>4e</b>	0.96 (3H, t, $J = 7.5$ ), 1.41 (2H, sext, $J = 7.9$ ), 1.61 (2H, sext, $J = 7.9$ ), 3.00 (1H, dd, $J = 16.9, 5.6$ ), 3.20 (1H, m), 3.40 (1H, dt, 16.0, 7.0), 3.63 (1H, dt, 16.0, 6.1), 5.42 (1H, ddd, $J = 6.7, 5.4, 1.5$ )	–60.98 (3F, dt, $J = 17.2, 1.1$ ), –106.23 (1F, qqq, $J = 17.2, 9.3, 5.7$ )	13.07, 19.04, 31.00, 38.00, 69.00, 87.80, 97.70 (qd, $J = 35.0, 3.9$ ), 121.20 (qd, $J = 269.0, 2.9$ ), 162.32 (dq, $J = 307.0, 3.9$ )
14	<b>4f</b>	1.30, (9H, s), 2.96 (1H, dm, $J = 17.7$ ), 3.26 (1H, dm, $J = 17.7$ ), 5.70 (1H, m, $J = 7.8$ )	–60.81 (3F, dt, $J = 17.2, 1.1$ ), –105.33 (1F, qm, $J = 17.2$ )	27.63, 40.18 77.50, 81.72, 97.10 (q, $J = 35.0$ ), 121.70 (q, $J = 270.0$ ), 161.40 (dq, $J = 307.0, 4.8$ )
15	<b>4g</b>	1.29, (3H, t, $J = 7.5$ ), 2.72 (2H, m), 2.91 (1H, dt, $J = 15.8, 4.8$ ), 3.35 (1H, dm, $J = 15.8$ ) 4.94 (1H, ddd, $J = 7.8, 4.7, 3.1$ )	–60.79 (3F, dt, $J = 17.1, 1.4$ ), –104.81 (1F, qm, $J = 17.1$ )	14.00, 25.5, 38.52, 12, 98.41 (qq, $J = 34.9, 3.9$ ), 121.00 (qd, $J = 269.3, 2.9$ ), 161.22 (d, $J = 307$ )
16	<b>4h</b>	1.45, (3H, t, $J = 1.5$ ), 3.04 (1H, dm, $J = 13.5$ ), 3.27 (1H, dm, $J = 13.5$ ), 3.46 (2H, m) 4.71 (1H, ddd, $J = 8.8, 4.2, 2.2$ )	–61.29 (3F, dt, $J = 17.1, 1.0$ ), –103.81 (1F, qtd, $J = 17.1, 5.6, 2.2$ )	5.86, 30.75, 42.76, 63.05, 99.31 (qd, $J = 35.6, 3.5$ ), 120.79 (q, $J = 270$ ), 158.90 (d, $J = 318$ )
17	<b>4i</b>	3.03 (1H, dd, $J = 16.3, 5.0$ ), 3.30 (1H, mdtq, $J = 16.3, 6.0, 1.9$ ), 3.65 (3H, m), 3.90 (1H, m), 5.45 (1H, t, $J = 6.0$ )	–60.56 (3F, d, $J = 17.2$ ), –106.00 (1F, qq, $J = 17.0, 5.7$ )	38.04, 41.02, 68.75, 87.24, 98.14 (qd, $J = 35.7, 4.5$ ), 121.00 (qd, $J = 270, 2.7$ ), 160.22 (dq, $J = 310, 4.2$ )
18	<b>6a</b>	2.16 (2H, m), 3.28 (1H, m), 3.96 (2H, m), 4.15 (1H, m), 6.33 (1H, dd, $J = 7.6, 4.6$ Hz)	–59.40 (3F, d, $J = 16.6$ ), –99.65 (1F, qt, $J = 16.6, 4.6$ ).	30.85 (d, $J = 2.9$ ), 48.54, 66.40, 89.78, 99.62 (qd, $J = 39.9, 2.9$ ), 121.06 (qd, $J = 269.3, 2.9$ ), 161.06 (d, $J = 310, 3.9$ )
19	<b>6b</b>	1.69 (1H, d quint., $J = 9.8, 1.8$ ), 2.06 (1H, d, $J = 9.8$ ), 2.98 (1H, s), 3.11 (1H, s), 3.18 (1H, dd, $J = 8.9, 6.1$ ), 3.64 (1H, d quint., $J = 8.9, 1.8$ ), 6.05 (1H, dd, $J = 5.8, 3.4$ Hz), 6.20 (1H, dd, $J = 5.8, 3.1$ )	–59.78 (3F, d, $J = 17.2$ ), –97.03 (1F, qdd, $J = 17.2, 5.7, 2.3$ )	42.03, 47.51, 47.55, 49.10, 50.24, 100.30 (q, $J = 33.0$ ), 121.88 (q, $J = 270$ ), 135.49, 138.22, 163.57 (dq, $J = 311, 6.8$ )
20	<b>6c</b>	1.63 (1H, dm, $J = 9.6, 1.5$ ), 1.96 (1H, dm, $J = 9.5$ ), 2.96 (1H, s), 3.14 (1H, s), 3.50 (1H, d, $J = 9.6$ ), 3.68 (1H, dd, $J = 9.6, 1.6$ ), 6.0 (1H, dd, $J = 5.7, 2.7$ ), 6.12 (1H, dd, $J = 5.7, 3.0$ )	–58.61 (3F, q, $J = 10.2$ ) –59.24 (3F, qd, $J = 10.2, 2.9$ )	
21	<b>7d<sup>h</sup></b>	0.94 (3H, t, $J = 7.0$ ), 1.389 (2H, m), 1.56, (2H, m), 2.63 (1H, dm, $J = 15.5$ ), 2.93 (1H, m), 3.36 (1H, m), 3.88 (1H, m), 4.49 (1H, dt, $J = 9.6, 4.4$ )	–60.46 (3F, m), –75.13 (m), –78.81 (1F, m, $J = 12.2$ Hz)	
22	<b>7e<sup>h</sup></b>	1.28 (9H, s), 2.79 (2H, m), 4.78 (t, $J = 6.9$ ), 4.85, dd, $J = 9.2, 3.9$ )	–60.008 (3F, dd, $J = 20.0, 10.7$ ), –60.14 (3F, dd, $J = 20.0, 10.7$ ), –74.96 (m), –77.81 (quint, q, $J = 10.7, 2.4$ ), –78.03 (quint, q, $J = 10.7, 2.4$ )	
23	<b>8</b>	6.75 (1H, dd, $J = 6.3, 3.8$ ) 6.87 (1H, dd, $J = 6.3, 3.3$ )	–58.63 (3F, d, $J = 12$ ), –126.56 (1F, qt, $J = 12.0, 4.0$ )	112.75 (qd, $J = 36.8, 4.8$ ), 113.50 (d, $J = 3.0$ ), 121.50 (q, $J = 272$ ), 121.60 (d, $J = 3.0$ ), 165.25 (dq, $J = 298, 4.0$ )

<sup>a</sup>  $\delta$ , ppm,  $J$ , Hz; in  $\text{CDCl}_3$  unless it mentioned otherwise.

<sup>b</sup> Mixture of two isomers, ratio ~1:1.

<sup>c</sup> Mixture of two isomers, ratio 58:42.

<sup>d</sup> Mixture of two isomers, ratio 63:37.

<sup>e</sup> Single isomer.

<sup>f</sup> Mixture of two isomers, ratio 52:48 in crude; 62:38 in distilled material.

<sup>g</sup>  $^{13}\text{C}$  NMR spectrum was acquired in  $\text{DMF-d}_6$ .

<sup>h</sup> Mixture of diastereomers, most resonances in  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra are overlapped.

It should be pointed out, that despite relatively high reaction temperature and excess of oxidizing agent we could not find any evidence for the formation of the corresponding 1-S-dioxides, previously prepared by Smart and Middleton [10] by reaction of  $(CF_3)_2C=SO_2$  with vinyl ethers. Such high selectivity is quite unusual, since the oxidation of hydrocarbon analogs, such as 2,2,4,4-tetramethyl-3-aminothietane by MCPBA under similar conditions leads to high yield formation of the corresponding S-dioxides [11] and the oxidation of a close fluorinated analog 3-thia-4,4-bis(trifluoromethyl)-tricyclo[5.2.1.0<sup>2,5</sup>]non-7-ene also proceeds with complete oxidation [12]. The only reported example of selective oxidation of fluorinated heterocycle is the reaction of 2,2,3,3-tetrakis-(trifluoromethyl)thiirane with  $CF_3SO_2OOH$  leading to the corresponding -1-S-oxide [13].

The S-oxides **3a–f** were purified by short-path distillation under reduced pressure and were fully characterized by NMR, IR and mass- spectroscopy. The <sup>1</sup>H and <sup>19</sup>F NMR spectra oxides **3a–f** suggest that these compounds form as a mixture of isomers with *trans*- and *cis*- orientation of oxygen and alkoxy groups. While the oxidation of thietanes **3a,b,d,f** results in the formation of approximately equal amount of two isomers, in the case of thietanes carrying bulky cyclohexyl-O- and *t*-BuO- groups (**3c** and **e**, respectively), a noticeable difference in the ratio of two isomers was observed, in favor of the less hindered *trans*-isomer (ratios 58:46 and 69:31, respectively). A reasonable correlation of the ratio of isomers with an increase in the value of the Tafts steric parameters ( $E_s$ ; *n*-Bu – 0.39; *c*-Hex – 0.79; *t*-Bu – 1.54 [14]) of the substituent connected to oxygen is another argument in favor of steric influence of the substituent on oxidation (see also discussion below on oxidation of compound **2g**).

<sup>19</sup>F NMR spectra of sulfoxides **3a–f** typically contain four resonances around –63 to –69 ppm, which are significantly shifted (by ~10 ppm) upfield compared to the corresponding resonances of  $CF_3$ - groups in starting thietanes. It should be pointed out, that similar trend was previously reported for 4-alkoxy-2,2-bis(trifluoromethyl)-1-thietane-1,1-dioxides, [10] 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane -1- oxide and -1,3-dioxide [13,15].

The presence of two bands in IR spectra of **3a–f** in 1070–1090  $cm^{-1}$  region is consistent with the presence of two isomeric S-oxides and these values agree well with values reported for 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithiethane-1-oxide, -1,3-dioxide [13,15] and S-oxide of 3-thia-4,4-bis(trifluoromethyl)tricyclo[5.2.1.0<sup>2,5</sup>]non-7-ene [12].

The outcome of the reaction of thietane **2g** (bearing a  $C_2H_5S$ -substituent) with MCPBA can vary depending on reaction conditions. The “electron-rich” sulfur of  $C_2H_5S$ - group is oxidized first and this process leads to the formation of sulfone **3g**.

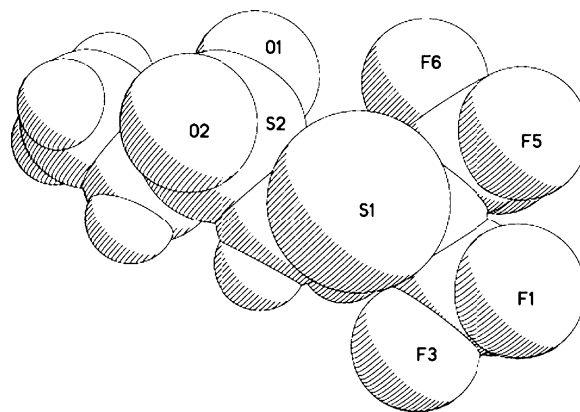
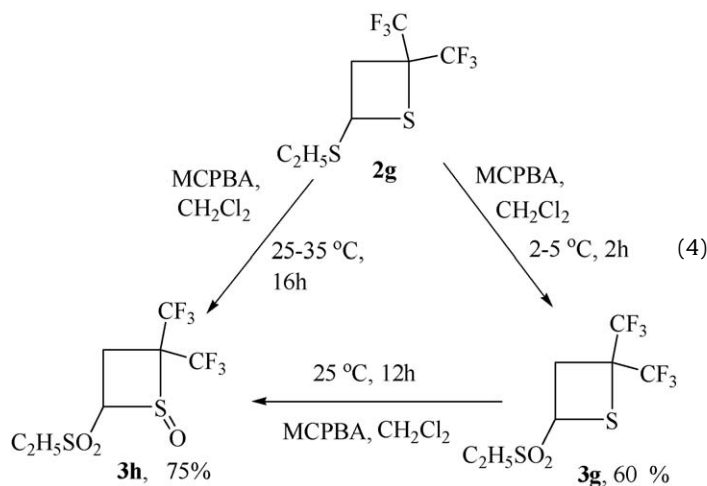


Fig. 1. Space-filled drawing of thietane **3g**.

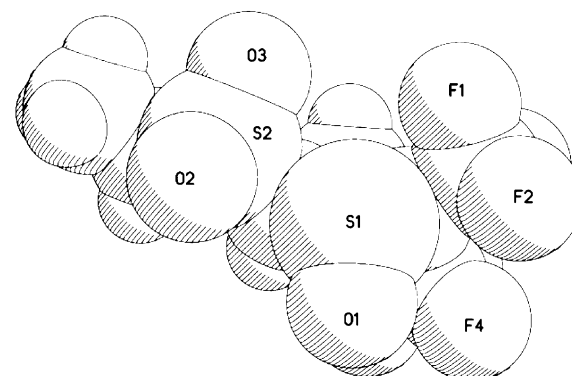


Fig. 2. Space-filled drawing of **3h**.

The structure of **3g** was firmly established by X-ray diffraction (see Fig. 1).

This compound seems to be the first representative of fluorinated thietanes containing a sulfone group of established structure. In 1965, Middleton has reported the oxidation of 4-*t*-butyl-2,2-bis(trifluoromethyl)thietane by peroxyacetic acid and isolated the material containing two oxygens, but the structure of the product was not reported [1]. It should be pointed out, that the selective formation of compound **3g** in this reaction is a clear indication of a significant difference in the reactivity of the sulfur atom in the  $C_2H_5S$ - group and thietane ring.

The oxidation of a sulfur atom of thietane ring in compound **3g** can be achieved, when the reaction with MCPBA is carried out at ambient temperature. It leads to exclusive formation of S-oxide **3h**. In sharp contrast to thietanes **3a–f**, the oxidation of **3g** has surprisingly high stereoselectivity resulting in the formation of a single isomer of S-oxide **3h** (NMR) with *trans*-relationship of oxygen and  $C_2H_5SO_2$ - group (single crystal X-ray diffraction, see Fig. 2).

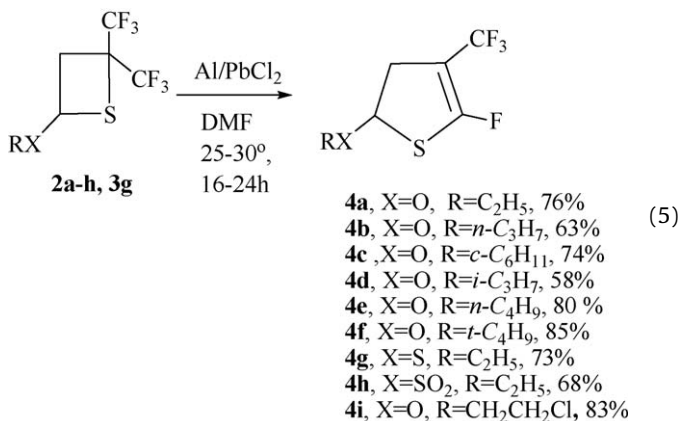
It is believed that the stereoselectivity of oxidation of **3g** by MCPBA is controlled by a steric bulk of  $C_2H_5SO_2$ - and  $CF_3$ -substituents, which are effectively blocking one side of the thietane ring (for space-filled drawing of thietane **3g** see Fig. 1) and forcing the attack of MCPBA on sulfur of the ring from less hindered side of the molecule, leading to selective formation of *trans*-isomer **3h**.

## 2.2. Reductive ring expansion of 4-substituted 2,2-bis(trifluoromethyl)thietanes

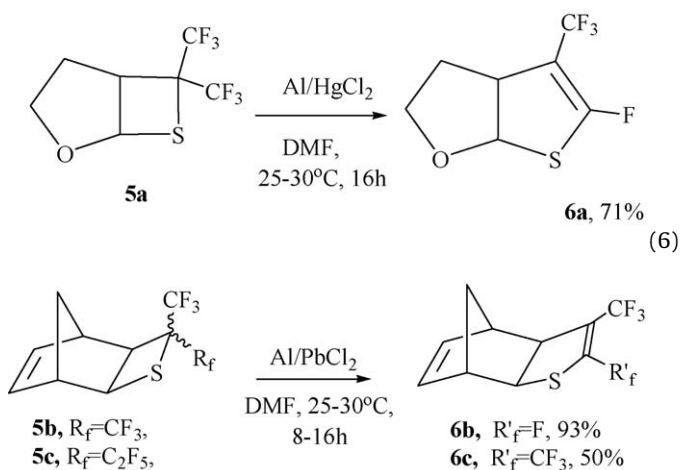
Another very interesting feature of thietanes **2a–h** and **3g** is an ability to undergo unusual ring expansion under the action of



certain reducing agents. For example, the treatment of fluorinated thietanes **2a–h** and **3g** by aluminum powder activated by a small amount of  $MCl_2$  ( $M = \text{Hg}$  or  $\text{Pb}$ , 10–20 mol%) in DMF solvent results in an exothermic reaction and a high yield formation of dihydrothiophenes **4a–i** (Eq. (5))



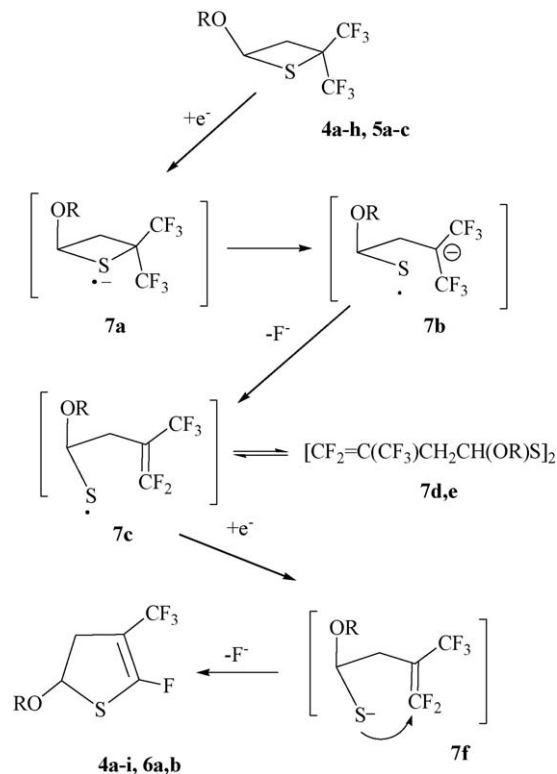
Polycyclic thietanes **5a–c** were also converted into the corresponding fused dihydrothiophenes **6a–c** under action of aluminum/ $MCl_2$  system (Eq. (6)).



We believe that the reductive ring expansion is a multistep process which is initiated by single electron transfer (SET) from a metal to the sulfur atom of the thietane ring (Scheme 1), leading to the formation of the radical-anion **7a**, which further undergoes ring opening isomerization into a radical-anion **7b**. This intermediate forms unsaturated radical **7c** after fluoride anion elimination, which further undergoes either dimerization (forming disulfides **7d,e**) or a reduction into anion **7f**. Nucleophilic intramolecular attack of the sulfide anion on the positively charged carbon of the CF<sub>2</sub><sup>+</sup> group of **7f** results in the formation of dihydrothiophenes **4a–i**, **6a–c**.

Indeed, reducing agents such as Al/ $PbX_2$  [16–20] or  $P[N(C_2H_5)_3]_3$  [21,22] are known to activate C–Hal bonds in  $CCl_4$ ,  $FCCl_3$ ,  $CF_3CCl_3$  through SET mechanism. For example, recently Zeifman and Postovoi employed an Al/ $HgCl_2$  system for alkylation of polyfluorinated ketones [20,23–25] and esters [26] by  $CCl_4$ ,  $FCCl_3$  and  $CF_3CCl_3$  and also reported a very interesting reductive defluorination process under action of Al/ $HgCl_2$  on fluorinated ketones leading to the formation of polyfluorinated enols after acidic hydrolysis [27,28].

It should be pointed out that in the reaction of thietanes **4a–i** with activated Al the formation of disulfide similar to **7d,e**



Scheme 1.

sometimes can be observed at early stages of the reaction by NMR. Disulfides **7d,e** ( $R = n\text{-Bu}$  and  $t\text{-Bu}$ ) were actually isolated in reaction of thietanes **4e,f**. Due to the presence of two asymmetrical centers, both compounds **7d,e** exist as a mixture of diastereomers (see Table 1, entries 19, 20). Rather complicated <sup>19</sup>F NMR spectra of disulfides **7d,e** contain multiplets around –60, –74 and –79 ppm (ratio 3:1:1), attributed to  $CF_2=C(CF_3)-$  group [3,9] and IR spectra exhibit a strong band at  $\sim 1747\text{ cm}^{-1}$  which is also consistent with the presence in the molecule of a fluorinated terminal double bond [29].

On the contrary, well resolved <sup>19</sup>F NMR spectra of dihydrothiophenes **4a–i**, **6a,b** exhibit only two resonances around –60 and between –105 and –110 ppm (relative intensity 3:1) assigned to CF<sub>3</sub><sup>–</sup> and –F substituents, respectively. <sup>13</sup>C NMR spectra of **4a–i**, **6a,b** along with other signals, exhibit a doublet, at  $\sim 160$  ppm ( $J \sim 310$  Hz) and a quartet at  $\sim 100$  ppm ( $J \sim 35$  Hz) assigned to  $=\underline{C}F$  and  $=\underline{C}CF_3$ , respectively. The IR spectra of dihydrothiophenes **4a–i**, **6a,b** contain an intense band  $\sim 1675\text{–}1700\text{ cm}^{-1}$  typical for a trisubstituted double bond in fluorinated olefins [29].

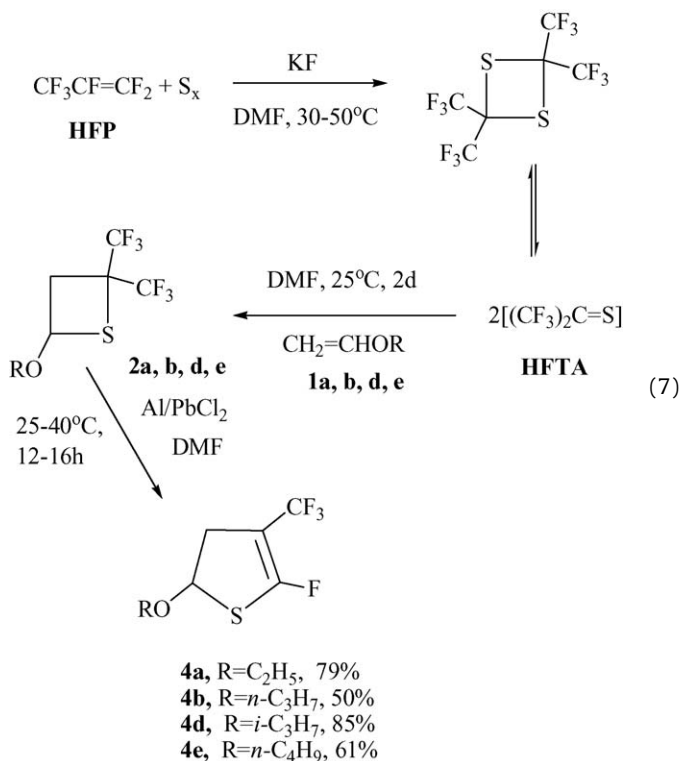
Lead dichloride was found to be more efficient promoter for the ring expansion of fluorinated thietanes, compared to  $HgCl_2$ . In general, reactions in the presence of  $PbCl_2$  are more exothermic, faster and produce less disulfide by-products. The ring expansion proceeds well in amide-like solvents such as DMF, dimethylacetamide or *N*-methylpyrrolidone, but no reaction between fluorinated thietanes and Al/ $MCl_2$  ( $M = \text{Hg}$  or  $\text{Pb}$ ) was observed in ether type solvents, such as THF, monoglyme or diglyme. Among other reducing agents which were tried in this study,  $P[N(C_2H_5)_3]_3$  also was found to be effective for the conversion of bicyclic thietane **5a** and **b** into dihydrothiophene **6a** and **b** (>95% yield after 1–2 h at 25 °C in DMF-*d*<sub>6</sub> solvent, NMR). It should be pointed out, that monocyclic thietanes **4a–e**, **i** in the reaction with phosphines behave differently and this transformation will be reported in forthcoming publication. Although  $Mg/[(CH_3)_3SiCl]$  system was widely employed by the Uneyama group for defluorination

reactions of hexafluoroacetone and its derivatives [30], we found that it has a relatively low activity for the conversion of **5b** into **6b** (conversion <10%, after 3d at 25 °C, in THF or DMF solvents).

Some interesting examples of this new reductive defluorination process are reaction of thietanes **2g** or **3g**, bearing C<sub>2</sub>H<sub>5</sub>S<sup>-</sup> and C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub><sup>-</sup> substituents, respectively (Eq. (5)). The reaction of **2g** with Al/PbCl<sub>2</sub> system resulted in clean formation of **4g** (73% isolated yield, Eq. (5)). In sharp contrast to reaction with MCPBA, which starts with oxidation of C<sub>2</sub>H<sub>5</sub>S<sup>-</sup> group (see Eq. (4)), a highly selective ring expansion process involves exclusively a sulfur of the thietane ring, while the C<sub>2</sub>H<sub>5</sub>S<sup>-</sup> group remains intact. The reaction of thietane **3g**, containing in the same position an electron deficient C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub><sup>-</sup> group with Al/PbCl<sub>2</sub> system is another striking example. In general RSO<sub>2</sub> group is sensitive towards action of reducing agents and can be readily replaced by hydrogen. For example, Na/Hg or activated Mg metal is widely employed for the reduction of a PhSO<sub>2</sub><sup>-</sup> group in fluorinated organic molecules [31–33]). Interestingly, in the reaction of **3g** with the Al/PbCl<sub>2</sub> system only the S(II) atom of the fluorinated thietane ring, is involved in the process, leading to a selective formation of dihydrothiophene **4h**, containing C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub><sup>-</sup> group. The structure of this compound was firmly established by single crystal X-ray diffraction (Fig. 3).

### 2.3. “One-pot” type synthesis of 2-alkoxy-5-fluoro-4-(trifluoromethyl)-2,3-dihydrothiophenes

Recently, we reported that 3-thia-4,4-bis(trifluoromethyl)-tricyclo[5.2.1.0<sup>2,5</sup>]non-7-ene [5] and other cycloadducts of HFTA can be prepared by a direct reaction of sulfur/HFP and hydrocarbon substrate without isolation of HFTA dimer intermediate [34]. In the present work this “one-pot” methodology was extended for the synthesis of fluorinated dihydrothiophenes **4a,b,d,e** (Eq. (7)).



The synthesis of dihydrothiophenes **4a,b,d,e**, which does not require the isolation of either 2,2,4,4-tetrakis(trifluoromethyl)-

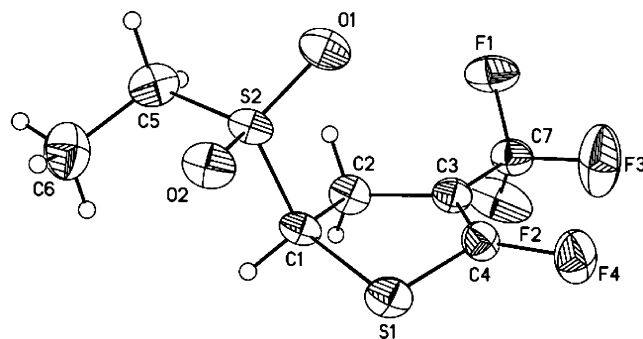


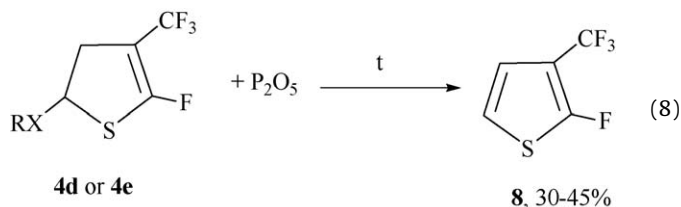
Fig. 3. ORTEP drawing of **4h** with thermal ellipsoids drawn to the 50% probability level.

1,3-dithietane or thietanes **2a,b,d,e** includes three consecutive steps (see Eq. (7)):

- the generation of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane by KF catalyzed reaction of sulfur with HFP in DMF solvent;
- the synthesis of the corresponding thietane by the reaction of the corresponding vinyl ether with 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane;
- the ring expansion step, which is carried out by slow addition of the crude reaction mixture containing thietane to a suspension of Al/PbCl<sub>2</sub> in DMF solvent.

Using these protocol compounds **4a,b,d,e** were prepared in a 50–85% yield (see Section 3.3). Overall, this procedure significantly simplifies the preparation of 5-fluoro-4-(trifluoromethyl)-2,3-dihydro-2-alkoxythiophenes, by avoiding the isolation of either 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane and or 4-alkoxy-2,2-bis(trifluoromethyl)thietane intermediates.

Due to the presence of the highly electrophilic double bond, dihydrothiophenes **4a–h** are a valuable synthetic intermediates. The synthetic utility of this group of materials was widely explored by the Burger group [35–37]. In this work it was demonstrated that compounds **4d,e** can serve as precursors for the synthesis of 2-fluoro-3-trifluoromethylthiophene. Using the procedure developed by the Sizov group for conversion of fluorinated sulfides into thiols [38], dihydrothiophenes **4d,e** were converted into previously unknown 2-fluoro-3-trifluoromethylthiophene **8** in moderate yield (Eq. (8)).



### 3. Experimental

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on Bruker DRX-500 (499.87 MHz) and DRX-400 (376.8485 MHz) instruments, respectively, using CFCl<sub>3</sub> or TMS as an internal standards and CDCl<sub>3</sub> as a lock solvent. IR spectra were recorded on a PerkinElmer 1600 FT spectrometer (KCl plates, liquid film or in KBr pellet for solids). Moisture sensitive materials were handled in a glove box. The purity of isolated materials was established using NMR and GC. GC and GC/MS analysis were carried out on a HP-6890 instrument,

using HP FFAP capillary column and either TCD (GC) or mass selective (GS/MS) detector. MCPBA (Aldrich, 65%), DMF (Aldrich, anhydrous), CH<sub>2</sub>Cl<sub>2</sub>, Al powder (Aldrich, 99.5%, ~200 mesh), HgCl<sub>2</sub> and PbCl<sub>2</sub> (Aldrich), sulfur (sublimed, 99.5%, ~100 mesh, Alfa Aesar), hexafluoropropene (DuPont) were obtained from commercial sources and used without further purification. KF (Aldrich, 99%) was dried under dynamic vacuum at 100–130 °C for 3–4 h and was stored and handled inside of dry box.

**Caution:** Dryness of DMF solvent and especially KF is crucial for successful preparation of thietanes and dihydrothiophenes, since the presence of insignificant amount of water severely effects the activity of the catalyst.

Compounds **2a–i**, **5b**, **c** were prepared using literature procedures [3,5]. Due to a high ratio of sulfur to fluorine, elemental analyses were not attempted for new materials. The purity of all isolated compounds was >98%, with exception of compounds **6c** and **7d,e** (>95%; GC and/or NMR spectroscopy).

### 3.1. Crystallography

X-ray data for **3g,h** and **4h** were collected at –100 °C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator.

The structures were solved and refined using the Shelxtl [39] software package, refinement by full-matrix least squares on  $F^2$ , scattering factors from Int. Tab. Vol C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #721667, #721668 and #721669. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

### 3.2. Oxidation of thietanes 2a–c,e–f,i

To a vigorously agitated suspension of 10–12 g of MCPBA in 75–100 mL of CH<sub>2</sub>Cl<sub>2</sub>, placed in 250 mL round-bottomed flask, equipped with thermocouple, dry-ice condenser and addition funnel, it was slowly added over ~1 h period a solution of 5–7 g of **2a–c,e–f,i** in 10–20 mL of CH<sub>2</sub>Cl<sub>2</sub> with the rate, which allow to maintain the internal temperature at 30–35 °C. The reaction mixture was agitated overnight and next morning was filtered. The filter cake was washed with ~10 mL of cold CH<sub>2</sub>Cl<sub>2</sub> and combined filtrate was treated in a separatory funnel with 1 M solution of sodium thiosulfate (2 × 200 mL). Organic layer was separated, checked for the presence of peroxides using wet KI/starch paper, washed with 300 mL of saturated solution of NaHCO<sub>3</sub> to bring pH of to ~7–8. Organic layer was separated, dried over MgSO<sub>4</sub>, filtered, solvent was removed under reduced pressure at 25–40 °C and the residue was distilled under vacuum using micro distillation column with a short deflegmator to give 4–6 g of clear colorless liquid. In case of sulfoxides **3c,e,g** distilled material crystallized upon standing at ambient temperature. Yields, boiling and melting points, IR, mass and NMR spectroscopy data of sulfoxides **3a–e** are given in Tables 1 and 2.

### 3.3. Preparation of sulfone 3g

To a vigorously agitated suspension of 12 g of MCPBA in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> a solution of 6 g of **2g** in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was slowly added at 2–4 °C. The reaction mixture was agitated at this temperature for 2 h and was worked up as it was described in the previous experiment. It was isolated 4.5 g (60%) of **3g**. Data of IR, mass and NMR spectroscopy are given in Tables 1 and 2.

### 3.4. Preparation of dihydrothiophenes 4a–i, 6a–c

#### 3.4.1. From thietanes 2a–h, 3g, 5a–c

In a dry 100 mL flask equipped with thermocouple, reflux condenser and addition funnel 1–3 g of aluminum powder and 50–70 mL of dry DMF was placed under nitrogen atmosphere. To a vigorously agitated reaction mixture 0.2–0.6 g of PbCl<sub>2</sub> was added and after ~1–5 min induction period an exothermic reaction started and the temperature rose to 27–30 °C. The solution of ~10–12 g of the corresponding thietane in 20 mL of dry DMF was slowly added to reaction mixture over ~1–1.5 h period with the rate which was sufficient to keep internal temperature of the reaction mixture <35 °C. An agitated reaction mixture was left overnight. Next morning the reaction mixture was filtered, filter cake was washed with hexane (20 mL) and filtrate was diluted with 300 mL of 10% hydrochloric acid, extracted with hexane (3 × 50 mL). Combined organic solution was washed by 10% hydrochloric acid (3 × 300 mL), dried over MgSO<sub>4</sub>, a solvent was removed under vacuum and the residue was distilled under reduced pressure to afford dihydrothiophenes **4a–i**, **6a–c** of 98–99.8% purity (GC, NMR). Yields, boiling and melting points, IR, mass and NMR spectroscopy data of **4a–i**, **6a–c** are given in Tables 1 and 2.

#### 3.4.2. “One-pot” procedure for the preparation of 5-fluoro-4-(trifluoromethyl)-2,3-dihydro-2-alkoxythiophenes 2a,b,d,e

In a dry 250 mL dry flask equipped with thermocouple, dry ice condenser and gas inlet tube under nitrogen blanket it was placed 2–3 g of dry KF, 100–150 mL of dry DMF and of 3.2–6.4 g (0.1–0.2 mol) of sublimed sulfur. The addition of sulfur resulted in the appearance of green or blue color of the solution. Vigorously agitated reaction mixture was brought up to ~30–35 °C and the addition gaseous hexafluoropropene (HFP) was started with the rate, which allows to maintain internal temperature at 35–45 °C, but at the same time to avoid the condensation of excessive amount of HFP on dry ice condenser. After required amount of HFP was added and all sulfur went into solution, the reaction mixture was agitated for an hour without additional heating. One equivalent of vinyl ether **2a,b,d,e** was added to the reaction mixture and it was agitated at ambient temperature for 24–48 h, till the conversion of starting materials would exceed 90% (GC). The agitation was stopped and the reaction mixture was decanted into addition funnel (reaction mixture A). In a separate 500 mL flask equipped with thermocouple, reflux condenser and addition funnel aluminum powder (1–3 g) and dry DMF (50–100 mL) were added under nitrogen blanket. To a vigorously agitated reaction mixture it was added 0.2–0.6 g of PbCl<sub>2</sub>, after ~1–5 min induction period an exothermic reaction started and the internal temperature rose to 27–30 °C. At this point the addition of the reaction mixture A was started with the rate, sufficient to maintain internal temperature at 30–35 °C. After addition was finished (1–2 h), the reaction mixture was agitated for 12–16 h at ambient temperature and worked up using hexane extraction, as it was described above. The isolated yields of dihydrothiophenes **4a,b,d,e** were 50–85%.

### 3.5. Preparation of thiophene 8

A mixture of 10–15 g P<sub>2</sub>O<sub>5</sub> and 6–8 g of **4d** or **4f** was slowly heated to ~200 °C in the flask equipped with short-path distillation column and the product was distilled out. It was collected 3.5–4.0 g of clear liquid, b.p. 99–100 °C. Data of IR, mass and NMR spectroscopy are given in Tables 1 and 2.

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