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Thermal Transformations of 2,5-Difluoro-3,4,6-trichlorobenzenethiol with Tetrafluoroethylene

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Abstract—Pyrolysis of a mixture of 2,5-difluoro-3,4,6-trichlorobenzenethiol with tetrafluoroethylene leads to 2,2,3,3,4,7-hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene (the major reaction product) along with 2,2,3,3,4,6-hexafluoro-5,7-dichloro-2,3-dihydrobenzo[*b*]thiophene. Schemes of their formation with the participation of intermediate radicals are proposed. Oxidation of a mixture of the synthesized compounds gave 2,2,3,3,4,7-hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]sulfane-1,1-dioxide and 2,2,3,3,4,6-hexafluoro-5,7-dichloro-2,3-dihydrobenzo[*b*]sulfane-1,1-dioxide.

Keywords: 2,5-difluoro-3,4,6-trichlorobenzenethiol, tetrafluoroethylene, pyrolysis, 2,2,3,3,4,7-hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene, 2,2,3,3,4,7-hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]sulfane-1,1-dioxide

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Among the reactions of simultaneous pyrolysis of polyfluoroaromatic compounds and tetrafluoroethylene in a continuous flow system, the transformations of polyfluorochlorarenethiols bearing chlorine atoms in the *ortho*- and *para*-positions relative to the thiol group have been described [1]. The main direction of pyrolysis of a mixture of polyfluoro-*o*-chloroarethiols with tetrafluoroethylene is the unexpected formation of polyfluoro-2,3-dihydrobenzo[*b*]thiophene derivatives through the migration of a sulfur atom. Small amounts of polyfluoroindanes and isomeric products were also obtained in which the sulfur atom was in the initial position. The reactions of 2,3,6-trifluoro-5-chloropyridine-4-thiol with tetrafluoroethylene at 410–620°C in a continuous flow system proceeded similarly with the formation of nitrogen-containing analogs. The pyrolysis products are apparently formed through the formation of intermediate radicals, including radical σ-complexes, as well as radical σ-spirocomplexes [1]. The formation of two isomeric compounds complicates the isolation of the major isomer with a migrated sulfur atom. Individual polyfluoro-2,3-dihydrobenzo[*b*]thiophenes are difficult to obtain. The preparation of perfluoro-2,3-dihydrobenzo[*b*]thiophene and some of its transformations have been reported earlier [2]. Pyrolysis of a mixture of 6-(methylsulfanyl)-octafluoroindane-5-thiol with tetrafluoroethylene at 420°C afforded individual dodecafluoro-3,5,6,7-tetrahydro-2*H*-indene[5,6-*b*]thiophene [3].

Due to the possibility of rearrangement during the formation of a polyfluorinated thienyl ring in the synthesis of polyfluorodihydrobenzo[*b*]thiophenes, pyrolysis of a mixture of tetrafluoroethylene and 2,5-difluorinated *o*-chlorobenzenethiols bearing the same substituents at positions 3 and 4 is appropriate. 2,5-difluoro-3,4,6-trichlorobenzenethiol **1** complies with these requirements. Therefore, we performed the simultaneous pyrolysis of thiol **1** with tetrafluoroethylene at different temperatures in order to obtain 2,2,3,3,4,7-hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene **2**.

The starting thiol **1** was obtained in high yield by reacting available 1,2,4-trifluorotrichlorobenzene [4] with KSH [5]. Pyrolysis of a mixture of thiol **1** with tetrafluoroethylene at 600–620°C in a continuous flow reactor resulted in the formation of compound **2**. However, the formation of another isomer (2,2,3,3,4,6-hexafluoro-5,7-dichloro-2,3-dihydrobenzo[*b*]thiophene **3**) was unexpectedly observed. In addition, trace amounts of 1,1,2,2,3,3,4,7-octafluoro-5,6-dichloro-indane **4** were found in the reaction mixture along with a noticeable amount of 1,4-difluorotetrachlorobenzene **5** (21%, see Table 1, entry 1). Among these compounds, 2,2,3,3,4,7-

Table 1. Pyrolysis of a mixture of 2,5-difluoro-3,4,6-trichlorobenzenethiol with tetrafluoroethylene

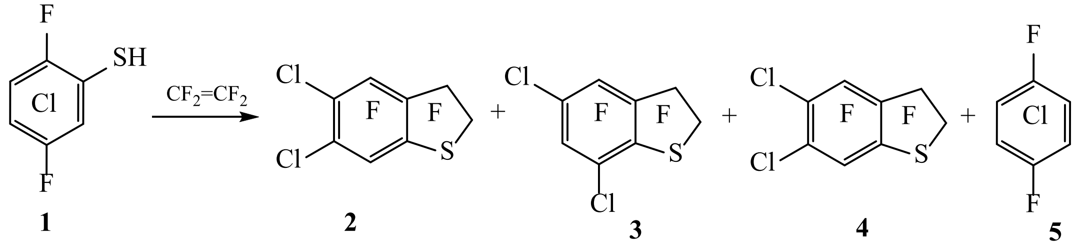
Entry no.	**1**, g	τ, min	*T*, °C	Yield, g	Composition of the reaction mixture according to GLC, % (isolated yield, %)			
					2	**3**	**4**	**5**
1	2.60	3.7	600–620	0.68	46.1 (10)	15.7 (3.5)	2.6 (0.5)	21.3 (4)
2	40.30	33.7	510–530	28.52	56.7 (32)	20.5 (11.5)	4.7 (2.5)	5.1 (2)
3	2.59	4.5	400–420	1.15	50 (18)	16.1 (6)	2.2 (1)	0.3 (~0.1)

hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene **2** predominates (yield 10%, 46% in the mixture). A decrease in the reaction temperature to 510–530 and 400–420°C leads to an increase in the yield of compound **2** (32 and 18%) (see Table 1, entries 2, 3) (Scheme 1).

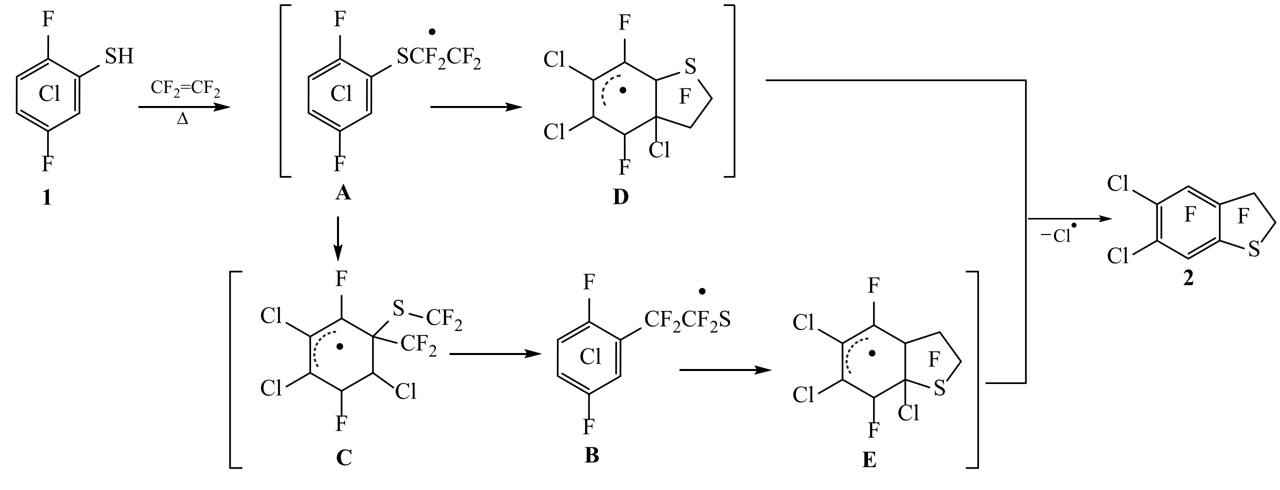
Pyrolysis of a mixture of thiol **1** with tetrafluoroethylene at 600–620°C was accompanied by strong resinification, which apparently explains the low yield of compound **2** and other reaction products. The strong resinification is possibly due to a decrease in the thermal stability of thiol **1** due to the presence of three chlorine atoms. This assumption is supported by a comparison with the result of the reaction of 2,4,5-trifluoro-3,6-dichlorobenzenethiol with tetrafluoroethylene under similar conditions, which leads to the formation of isomeric polyfluorochlorodihydrobenzo[*b*]thiophenes in higher yields [1].

It can be assumed (cf. [1]) that the formation of compound **2** occurs through the 2-(2,5-difluoro-3,4,6-trichlorophenylsulfanyl)tetrafluoroethyl radical **A** (Scheme 2) derived from a 2,5-difluoro-3,4,6-trichlorobenzenethiyl radical and tetrafluoroethylene. A thiyl radical can be generated by thermolysis of the S–H bond, as well as by the action of a chlorine atom, which is eliminated from radical σ-complexes. Probably, the formation of arene **2** also involves the intermediate [2-(2,5-difluoro-3,4,6-trichlorophenyl)tetrafluoroethane]-thiyl radical **B** generated from the σ-spiro complex **C**. The latter can be formed as a result of the transformation of radical **A**. Radicals **A** and **B** undergo intramolecular cyclization to give radical σ-complexes **D** and **E** followed

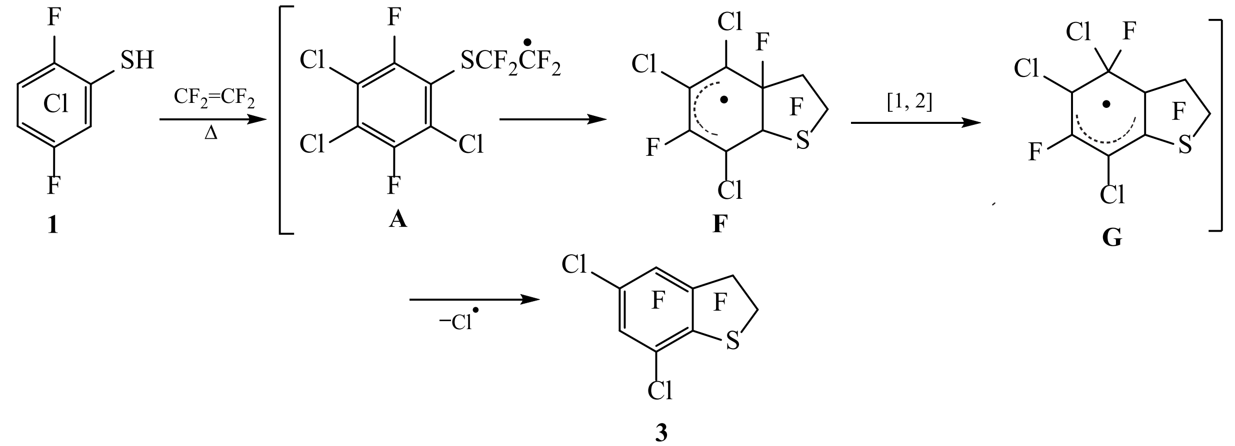
Scheme 1.



Scheme 2.

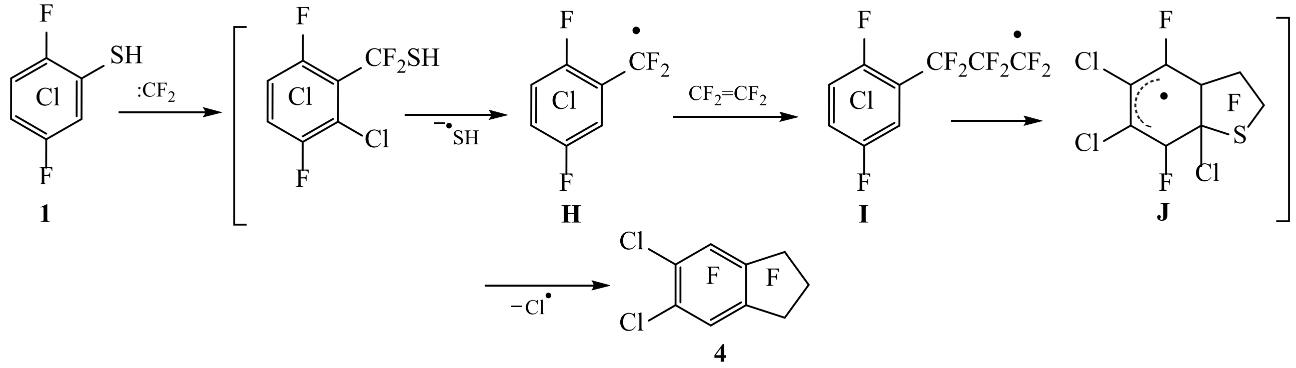


Scheme 3.



Scheme 4.

$CF_2{=}CF_2 \rightleftharpoons 2{:}CF_2$



by elimination of the chlorine atom to form compound **2** (Scheme 2).

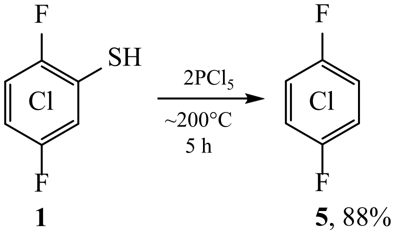
Presumably, compound **3** is obtained due to the ring closure in radical **A** and generation of radical σ-complex **E**. Further migration of the fluorine atom leads to the formation of radical σ-complex **G** (Scheme 3). A similar mechanism with the migration of a fluorine atom has been previously proposed in the case of the reaction of pentafluorobenzoyl peroxide with hexafluorobenzene [6]. The ring- closure of the radical **A** through position 2 and the migration of the fluorine atom is facilitated by the participation of the vacant *d*-orbitals of chlorine and sulfur atoms in the stabilization of the radical σ-complexes **E** and **G**. Elimination of the chlorine atom from the σ-complex **G** leads to the formation of compound **3** (Scheme 3).

Probably, the formation of compound **4** includes the incorporation of difluorocarbene generated from tetrafluoroethylene [7] through the C–S bond of thiol **1** to yield tetrafluorotrichlorobenzyl radical **H**. The latter reacts with tetrafluoroethylene followed by cyclization of the polyfluorotrichlorophenylpropyl radical **I** and elimination of the chlorine atom from the radical σ-complex **K** (Scheme 4).

Taking into account the elimination of the chlorine atom during the aromatization of σ-complexes **D**–**G** and **K**, it can be assumed that compound **5** is formed as a result of the reaction of thiol **1** with chlorine atoms. Earlier, we have showed that in the reactions of polyfluoroarenethiols with PCl_5 at ~ 200°C, a substitution of the thiol group by a chlorine atom occurs readily [8] (Scheme 5).

In order to study the chemical properties and to confirm the structure of compounds **2** and **3**, a ~77:23 mixture of these compounds was oxidized with H_5IO_6 in the presence of CrO_3 in acetonitrile. As a result, a mixture of 2,2,3,3,4,7-hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]-thiophene-1,1-dioxide **6** and 2,2,3,3,4,6-hexafluoro-5,7-dichloro-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide **7** in approximately the same ratio was obtained (Scheme 6). Previously, decafluorodiphenylsulfide was oxidized in a

Scheme 5.



similar way, and decafluorodiphenylsulfone was obtained in high yield [9].

Composition and structure of compounds **2**, **3**, **6**, and **7** were established by means of elemental analysis data, high-resolution mass spectrometry, and NMR spectroscopy methods. The regularities observed in the ^{19}F NMR spectra of compounds **2**, **3**, **6**, and 7 are similar to those in polyfluoro-2,3-dihydrobenzo[*b*]thiophenes and their sulfoxides [2].

Chemical shifts of F^2 and F^3 atoms and spin-spin coupling constants $J(C^2F, C^3F)$, $J_{F^3F^4}$ in the spectra of compounds **2** and **3** are close to the corresponding values in the spectra of perfluoro-2,3-dihydrobenzo[*b*]thiophene and its 5- and 6-derivatives with *O*- and *S*-containing substituents [2]. Spin-spin coupling constants $J_{F^4F^7}$ in arene **2** and $J_{F^4F^6}$ in compound **3** coincide with those in perfluoro-2,3-dihydrobenzo[*b*]thiophene [2]. The signals at 46.8 ppm in the spectrum of compound **2** have only a doublet constant ($J_{F^7F^4}$) in the absence of a triplet constant, which allows us to assign them to the fluorine atom at position 7.

The assignment of signals of fluorine atoms in positions 4, 7 and 4, 6 in the spectra of compounds **2** and **3** is consistent with calculations using the additive scheme taking into account the corresponding shifts of fluorine atoms in perfluoro-2,3-dihydrobenzo[*b*]thiophene [2] and the effect of chlorine atoms in pentafluorochlorobenzene [10].

The chemical shifts of fluorine atoms F^2 and F^3 and their coupling constants in the spectra of compounds **6** and **7** are close to the corresponding values in the spectra of 2,2,3,3-tetrafluoro-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide and its 5-bromo derivative [11]. The values of $J_{F^4F^7}$ and $J_{F^3F^4}$ constants in the spectra of compounds **2** and **6** are comparable; the values of $J_{F^4F^6}$ constant in the spectra of compounds **3** and **7** are close. The chemical shifts of the F^4 atoms in the spectra of compounds **2**, **3**, **6**, **7** are close to each other.

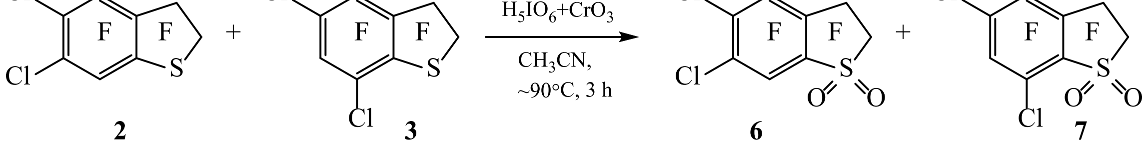
In conclusion, the thermal transformations of 2,5-difluoro-3,4,6-trichlorobenzenethiol in the presence of tetrafluoroethylene were studied. 2,2,3,3,4,7-Hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene and 2,2,3,3,4,6-hexafluoro-5,7-dichloro-2,3-dihydrobenzo[*b*]-thiophene were obtained, the oxidation of which leads to the formation of the corresponding 2,3-dihydrobenzo[*b*]-sulfane-1,1-dioxides.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Bruker AV-300 (282.4 MHz) instrument from solutions CCl_4–$CDCl_3$ relative to the internal standard—C_6F_6. Positive values of chemical shifts correspond to a downfield shift of the signal from C_6F_6. ^{13}C NMR spectra ($CDCl_3$) were recorded on a Bruker AV-300 (75.5 MHz) and Bruker AV-400 (100.6 MHz) instruments. IR and UV spectra were registered on a Bruker Vector 22 IR and Hewlett Packard 8453 UV instruments, respectively. Molecular masses and elemental composition were determined from mass spectra taken on a DFS instrument with an ionization energy of 70 eV. For gas chromatography-mass spectrometry (GC-MS), a Hewlett Packard HP 5890 chromatograph with an HP 5971 mass selective detector and an Agilent 6890N chromatograph with an Agilent 5973N gas chromatography–mass spectrometric system were used. The energy of ionizing electrons is 70 eV. Gas chromatographic analysis was performed on a Hewlett Packard HP 5980 instrument equipped with an HP-5 quartz capillary column (stationary phase—dimethyldiphenylpolysiloxane), 30 m×0.52 mm/2.6 μm, and a thermal conductivity detector. Melting points were determined on a Mettler Toledo FP900 apparatus.

Pyrolytic reactions of 2,5-difluoro-3,4,6-trichloro-benzenethiol 1 with tetrafluoroethylene were carried out in a reactor consisting of a quartz tube (400×20 mm) heated in an electric tube furnace. The starting compound **1** was placed into a dropping funnel attached to the quartz tube of the reactor and melted. Before the start of the

Scheme 6.



reaction, the system was purged with argon, then thiol was supplied simultaneously with a flow of tetrafluoroethylene (~ 15 L/h). Upon completion of the addition of compound **1** to the reactor, the supply of tetrafluoroethylene was stopped. The reaction products were collected in a flask cooled with ice water, then distilled with steam. The organic layer was separated, dried with $CaCl_2$ and analyzed by GC-MS, GC and ^{19}F NMR methods. The reaction conditions, compositions of the mixtures and the yields are given in Table. The ^{19}F NMR spectra of the mixtures were used to identify compounds **2**, **3**, **4**. For identification of arene **5** in the mixture, an authentic synthesis was performed.

Vacuum distillation (18–20 mmHg) of 26.14 g of the mixture obtained in entry 2 (see Table 1) yielded a fraction of 20.32 g of compounds **2** and **3** (bp ~ 105°C, purity of 91.9% by GC) in a ratio of ~77 : 23 (according to ^{19}F NMR). For a mixture, it was found *m/z* 311.8995 $[M]^+$ (calcd. for $C_8Cl_2F_6S$: 311.8997).

Data of the NMR spectra recorded for a mixture of compounds **2** and **3**. Are given below.

2,2,3,3,4,7-Hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene (2). ^{13}C NMR spectrum, δ_C, ppm: 14.3 t. d (C^{3a}, $^2J_{CF}$ = 25.0, $^2J_{CF}$ = 20.0 Hz), 117.7 t. t. d (C^3F_2, $^1J_{CF}$ = 265.0, $^2J_{CF}$ = 25.0, J_{CF} ~3.0 Hz), 121.2 d (C^5 or C^6, $^2J_{CF}$ = 20.0 Hz), 121.8 d. m (C^{7a}, $^2J_{CF}$ ~ 22.0 Hz), 127.9 d (C^5 or C^6, $^2J_{CF}$ = 20.0 Hz), 128.8 t. t (C^2F_2, $^1J_{CF}$ = 295.0, $^2J_{CF}$ = 28.0 Hz), 149.3 d. m (C^4 or C^7, $^1J_{CF}$ = 249.0 Hz), 152.2 d. m (C^4 or C^7, $^1J_{CF}$ = 262.0 Hz). ^{19}F NMR spectrum, δ_F, ppm: 45.6 d. t (F^4, $J_{F^4F^7}$ = 15.5, J_{F^4F} = 10.5 Hz), 46.8 d (F^7, $J_{F^7F^4}$ = 15.5 Hz), 51.2 d. t (C^3F_2, J_{FF^4} = 10.5, J_{FF} = 2.5 Hz), 68.2 t (C^2F_2, J_{FF} = 2.5 Hz).

2,2,3,3,4,6-Hexafluoro-5,7-dichlorop-2,3-dihydrobenzo[*b*]thiophene (3). ^{19}F NMR spectrum, δ_F, ppm: 47.4 t. d (F^4, J_{F^4F} = 10.0, $J_{F^4F^6}$ = 8.0 Hz), 52.7 d. q (C^3F_2, J_{FF^4} = 10.0, J_{FF^2} ~ J_{FF^6} ~2.0 Hz), 59.8 d. t (F^6, $J_{F^6F^4}$ = 8.0, J_{F^6F} ~2.0 Hz), 67.7 t (C^2F_2, J_{FF} ~2.0 Hz).

1,1,2,2,3,3,4,7-Octafluoro-5,6-dichloroindane (4). ^{19}F NMR spectrum, δ_F, ppm: 31.8 quintet (C^2F_2, J_{FF} ~ 4.0 Hz), 47.6 br. s (F^4, F^7), 54.1 br. s $[C^{1(3)}F_2]$ [12]. Mass-spectrum, *m/z*: 330 $[M]^+$ (calcd. $C_9Cl_2F_8$: 330).

1,4-Difluoro-2,3,5,6-tetrachlorobenzene (5). Thiol **1** (3.33 g, 13.35 mmol) was placed into an ampoule, then 5.68 g of PCl_5 (27.60 mmol) was added. The resulting mixture was slowly heated until boiling. Upon completion of gas evolution, the ampoule was sealed, placed into a metal casing, and heated at 200–202°C for 5 h. After the reaction completed, the ampoule was cooled. The mixture was transferred into the flask under a layer of ice water (80–100 g). The mixture was stirred for 2 h with the aim of hydrolysis of phosphorus compounds, then 12.31 g of Na_2CO_3 (116.83 mmol) was added. The resulting mixture was stirred for another 2 h, then distilled with steam. The organic layer was separated, dried with $CaCl_2$, and analyzed by GC and ^{19}F NMR. By GC data, content of compound 5 in the mixture was ~ 98.9%, yield 2.98 g (88%), mp 74.9–75.3°C (mp 76.5°C [13]). IR spectrum (KBr), cm^{-1}: 1632, 1487, 1444, 1394, 1346, 1296, 1252, 1180, 1130, 1117, 912, 879, 729, 633. UV spectrum (hexane), λ_{max}, нм (ε, L mol^{-1} cm^{-1}): 207 (2.032), 227 (1.250), 282 (0.162), 290 (0.185). ^{13}C NMR spectrum, δ_C, ppm: 119.5 m ($C^{2,3,5,6}$), 151.9 d. d ($C^{1,4}$, $^1J_{CF}$ = 251.0, $^4J_{CF}$ = 5.0 Hz). ^{19}F NMR spectrum: δ_F 51.2 ppm [14, 15]. Found, %: C 28.64; Cl 56.15; F 15.51. $C_6Cl_2F_4$. Calculated, %: C 28.61; Cl 56.30; F 15.09.

Synthesis of compounds 6 and 7. Oxidation of a mixture of compounds **2** and **3** (see Table 1, entry 2, distillation) was carried out according to a known procedure [9]. To 9.76 g of H_5IO_6 (42.82 mmol) in 35 mL of anhydrous CH_3CN was added 0.37 g of CrO_3 (1.05 mmol). The mixture was stirred for 30 min at room temperature, then 1.40 g of a mixture of compounds **2** and **3** in 15 mL of anhydrous CH_3CN was added. The resulting mixture was stirred for 3 h under reflux. After removal of acetonitrile, ~5 mL of water and 0.57 g of Na_2CO_3 (5.38 mmol) were added, and the mixture was extracted with DCM (3 × 5 mL). The extract was purified by passing it through silica gel, DCM was distilled off. A mixture of compounds **6** and **7** (1.18 g, 93.1%, GC) in a ratio of ~ 75 : 25 (^{19}F NMR) was obtained. 1.01 g of the mixture was sublimated in a static vacuum (~2 mmHg) at 150–160°C to give 0.89 g of a mixture of compounds **6** and **7** of 98.0% purity (GC). 0.68 g of the mixture was recrystallized from ~1.5 mL of hexane at –30°C, and then washed with ~1.5 mL of cold hexane to yield 0.58 g of a mixture of compounds **6** and **7** (98.4% purity, GC). Mass spectrum, *m/z*: 343.8896 $[M]^+$ (calcd for $C_8Cl_2F_6O_2S$: 343.8895). Found, %: C 27.75; Cl 20.46; F 33.30; S 9.35. $C_8Cl_2F_6O_2S$. Calculated, %: C 27.85; Cl 20.55; F 33.04; S 9.29. The NMR spectra recorded for a mixture of compounds **6** and **7** are given below.

2,2,3,3,4,7-Hexafluoro-5,6-dichloro-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (**6**). ^{13}C NMR spectrum, δ_C, ppm: 108.9 t. t. d (C^3F_2, $^1J_{CF}$ = 266.0, $^2J_{CF}$ = 23.0, J_{CF} ~2.0 Hz), 113.1 t. t (C^2F_2, $^1J_{CF}$ = 305.0, $^2J_{CF}$ = 25.0 Hz), 113.9 t. d (C^{3a}, $^2J_{CF}$ = 27.0, $^2J_{CF}$ = 18.0 Hz), 123.5 d. m (C^{7a}, $^{2}J_{CF}$ ~22.0 Hz), 130.4 d. t (C^5 or C^6, $^{2}J_{CF} = 19.0$, $J_{CF} = 1.5$ Hz), 131.5 d. t (C^5 or C^6, $^{2}J_{CF} = 19.0$, $J_{CF} = 1.5$ Hz), 149.6 d. d (C^4 or C^7, $^{1}J_{CF} = 263.0$, $J_{CF} = 4.0$ Hz), 151.9 d. d (C^4 or C^7, $^{1}J_{CF} = 267.0$, $J_{CF} = 4.0$ Hz). ^{19}F NMR spectrum, δ_F, ppm: 42.4 t (C^2F_2, $J_{FF} = 5.0$ Hz), 49.9 d (F^7, $J_{F^7F^4} = 17.5$ Hz), 51.3 d. t (F^4, $J_{F^4F^7} = 17.5$, $J_{F^4F} = 12.5$ Hz), 55.8 d. t. d (C^3F_2, $J_{FF^4} = 12.5$, $J_{FF^2} = 5.0$, $J_{FF^7} = 1.0$ Hz).

2,2,3,3,4,6-Hexafluoro-5,7-dichloro-2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide (7). ^{19}F NMR spectrum, δ_F, ppm: 42.6 t (C^2F_2, $J_{FF} = 5.0$ Hz), 53.3 t. d (F^4, $J_{F^4F} = 12.0$, $J_{F^4F^6} = 10.0$ Hz), 56.0 d. t. d (C^3F_2, $J_{FF^4} = 12.0$, $J_{FF^2} = 5.0$, $J_{FF^6} = 2.0$ Hz), 64.1 d. t (F^6, $J_{F^6F^4} = 10.0$, $J_{F^6F} = 2.0$ Hz).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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