

## Synthesis of Polychlorofluoroarenes from Polyfluoroarenethiols, $\text{SOCl}_2$ and $\text{SO}_2\text{Cl}_2$

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**Abstract.** *The thiol group in polyfluoroarenethiols was replaced by the chlorine atom, using  $\text{SOCl}_2$  and  $\text{SO}_2\text{Cl}_2$  as chlorinating reagents. By heating in ampules at 200–220°C polyfluoro- and polychlorofluoroarenethiols with  $\text{SO}_2\text{Cl}_2$  monochloro- and dichloropolyfluoroarenes and also 1,2,4-trichlorotrifluorobenzene were synthesized. Dichloropolyfluoroarenes contain chlorine atoms in ortho- and para-positions.*

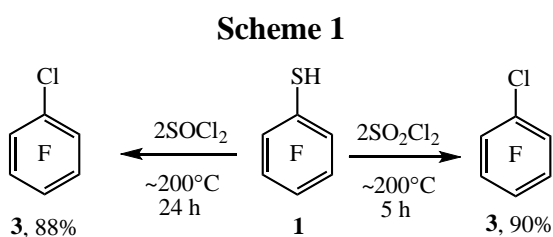
**Keywords:** Thionyl chloride, sulfuryl chloride, thiol group, polyfluoroarenethiols, polychlorofluoroarenes

Polychlorofluoroarenes are important products for the synthesis of a large number of polyfluoroaromatic compounds with various functional groups. Selective participation of the  $\text{C}_{\text{Ar}}\text{-Cl}$  bond in the metallation reactions is one of the directions of transformation of chloropolyfluoroarenes. The Grignard reagents [1], polyfluoroaryl lithiums [1] and polyfluoroarylzinc compounds [2] formed from chloropolyfluoroarenes are versatile and convenient to use for the synthesis of a large number of functional derivatives of polyfluoroaromatic compounds. In this connection, in recent years, we have been developing a method of synthesis of chloropolyfluoroarenes consisting in substitution of the thiol group in polyfluoroarenethiols by chlorine atom. By this method a series of chloropolyfluoroaromatic compounds was synthesized in high yields [3, 4]. The process was realized at high temperature ( $\sim 400^\circ\text{C}$ ) in a flow reactor as joint pyrolysis of polyfluoroarenethiols with  $\text{Cl}_2$  as well as with  $\text{SOCl}_2$  and  $\text{SO}_2\text{Cl}_2$  as chlorine sources [3]. In addition to the reactions in the flow system, we studied the conversion of polyfluoroarenethiols with  $\text{PCl}_5$  in ampoules at  $\sim 200^\circ\text{C}$ , which also led to the preparation of chloropolyfluoroarenes [4]. On the example of the reaction of pentafluorobenzenethiol **1** with  $\text{Cl}_2$  and  $\text{PCl}_5$ , carried out under different conditions, the scheme for the replacement of the thiol group by the chlorine atom was suggested. This scheme includes the

intermediate formation of pentafluorobenzenesulfonyl chloride **2** and its conversion under the action of Cl<sub>2</sub> and PCl<sub>5</sub> to chloropentafluorobenzene **3** with the participation of an intermediate radical σ- complex [3, 4].

Use in the gas phase process, along with Cl<sub>2</sub>, thionyl chloride and sulfuryl chloride as chlorine sources, characterizes the reaction of substitution of the thiol group in polyfluoroarenethiols by the chlorine atom in the methodical and practical sense as a rather general way of synthesis of chloropolyfluoroarenes. The reactions of polyfluoroarenethiols with PCl<sub>5</sub>, carried out in ampoules at a lower temperature (~200°C) [4], are additional evidence in favor of such conclusion. We have also studied the conversion of polyfluoroarenethiols with SOCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub> in ampoules under similar conditions to increase the possibilities of this type of reactions.

We have shown that when thiol **1** was heated with SOCl<sub>2</sub> or SO<sub>2</sub>Cl<sub>2</sub> in ampoules at ~200°C, arene **3** was obtained with high yields. It was found that the reaction of thiol **1** with SOCl<sub>2</sub> requires a longer time to achieve a good yield of arene **3** than in the case of using SO<sub>2</sub>Cl<sub>2</sub> at the same temperature of process (Scheme 1).



When the reaction time of thiol **1** with SOCl<sub>2</sub> was reduced from 24 h to 5 h at ~200°C, the reaction mixture contained arene **3**, the supposed decafluorodiphenylpolysulfanes and sulfonyl chloride **2** in a ratio of ~ 55: 34: 11, respectively (according to NMR <sup>19</sup>F).

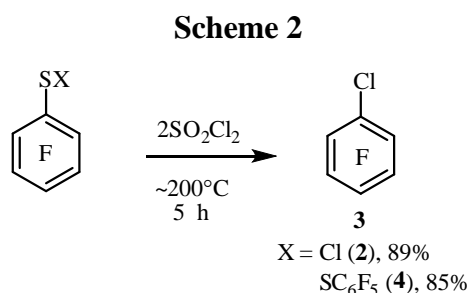
In the reaction of thiol **1** with SO<sub>2</sub>Cl<sub>2</sub> at ~200 ° C for 2.5 h, the reaction mixture contained arene **3** in a larger amount than in the case of the reaction of thiol **1** with SOCl<sub>2</sub> for 5 h. In addition to arene **3**, the supposed decafluorodiphenylpolysulfanes and sulfonyl chloride **2** were also present in the mixture. The ratio of these products was ~ 79: 18: 3, respectively (according to NMR <sup>19</sup>F). However, a comparison of the results of the reactions of thiol **1** with SOCl<sub>2</sub> (5 h) and SO<sub>2</sub>Cl<sub>2</sub> (2.5 h) is relative, since the mass yields of the reaction mixtures have not been evaluated.

The above results of the reactions of thiol **1** with SOCl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub> may indicate that the process involving SO<sub>2</sub>Cl<sub>2</sub> takes less time than using SOCl<sub>2</sub>. Therefore, we further carried out the reactions of polyfluoroarenethiols with SO<sub>2</sub>Cl<sub>2</sub>.

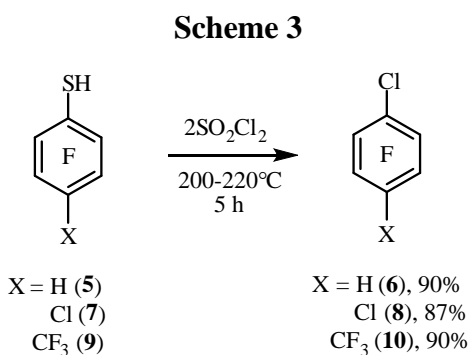
Sulfonyl chloride **2** and decafluorodiphenylpolysulfanes formed in the reaction of thiol **1** with SO<sub>2</sub>Cl<sub>2</sub> at ~ 200°C for 2.5 hours can be of interest to obtain arene **3** from them under the action of SO<sub>2</sub>Cl<sub>2</sub>. In this connection, the reaction of sulfonyl chloride **2** with SO<sub>2</sub>Cl<sub>2</sub> (~ 200 ° C, 5 h) was carried out. As a representative of these polysulfanes, it seemed reasonable to carry out the

reaction of decafluorodiphenyldisulfane **4** with  $\text{SO}_2\text{Cl}_2$  in the reaction conditions of thiol **1** with  $\text{SO}_2\text{Cl}_2$  ( $\sim 200^\circ\text{C}$ , 5 h).

As it turned out, when sulfenyl chloride **2** and disulfane **4** were heated with  $\text{SO}_2\text{Cl}_2$ , compound **3** was also obtained in high yields (Scheme 2).

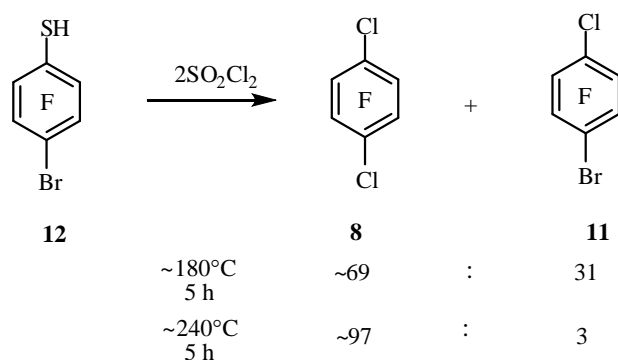


A similar process occurs in the case of *para*-substituted derivatives of thiol **1**. Thus, when 2,3,5,6-tetrafluorobenzenethiol **5** was heated with  $\text{SO}_2\text{Cl}_2$ , 1-chloro-2,3,5,6-tetrafluorobenzene **6** was obtained. The reaction of 4-chloro-2,3,5,6-tetrafluorobenzenethiol **7** with  $\text{SO}_2\text{Cl}_2$  gave 1,4-dichloro-2,3,5,6-tetrafluorobenzene **8**. When 4-trifluoromethyl-2,3,5,6-tetrafluorobenzenethiol **9** was reacted with  $\text{SO}_2\text{Cl}_2$ , 4-chloroheptafluorotoluene **10** was obtained in a high yield (Scheme 3).



At the same time, the attempt to obtain 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene **11** by chlorination of 4-bromo-2,3,5,6-tetrafluorobenzenethiol **12** at  $\sim 180^\circ\text{C}$  showed that in this reaction the replacement of the bromine atom by chlorine occurs also to a large extent. With an increase in the reaction temperature to  $\sim 240^\circ\text{C}$ , compound **8** was obtained with a small admixture of arene **11** (Scheme 4). We have previously shown that a similar process occurred in the reaction of thiol **12** with  $\text{PCl}_5$  under similar conditions [4].

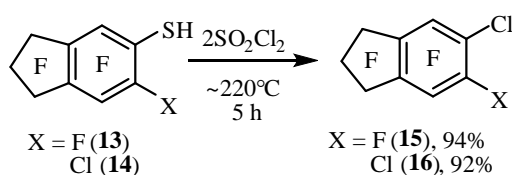
**Scheme 4**



Ratio according to the  $^{19}\text{F}$  NMR spectrum

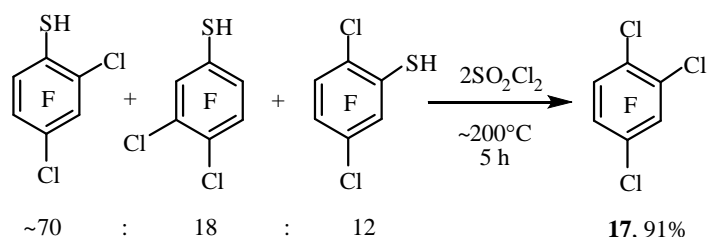
5-Chlorononafluorindan **15** and 5,6-dichlorooctafluorindan **16** were obtained from 5-nonafluorindanthiol **13** and 6-chlorooctafluorindan-5-thiol **14**, respectively (Scheme 5).

#### Scheme 5



Heating of a mixture of dichlorotrifluorobenzenethiols with  $\text{SO}_2\text{Cl}_2$  in an ampoule was used to synthesize practically individual 1,2,4-trichlorotrifluorobenzene **17** (Scheme 6)..

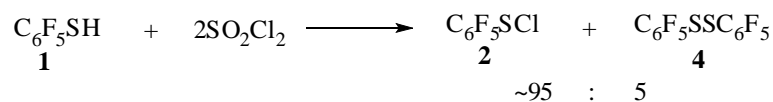
#### Scheme 6



Ratio according to the  $^{19}\text{F}$  NMR spectrum

The isomeric mixture of dichlorotrifluorobenzenethiols was prepared from a technical mixture of *o*-, *m*-, *p*- $\text{C}_6\text{Cl}_2\text{F}_4$  and KSH (90% yield) [5]. When thiol **1** is mixed with  $\text{SO}_2\text{Cl}_2$  at room temperature, mainly sulfenyl chloride **2** is formed, along with a small amount of disulfane **4** (according to NMR  $^{19}\text{F}$ , Scheme 7).

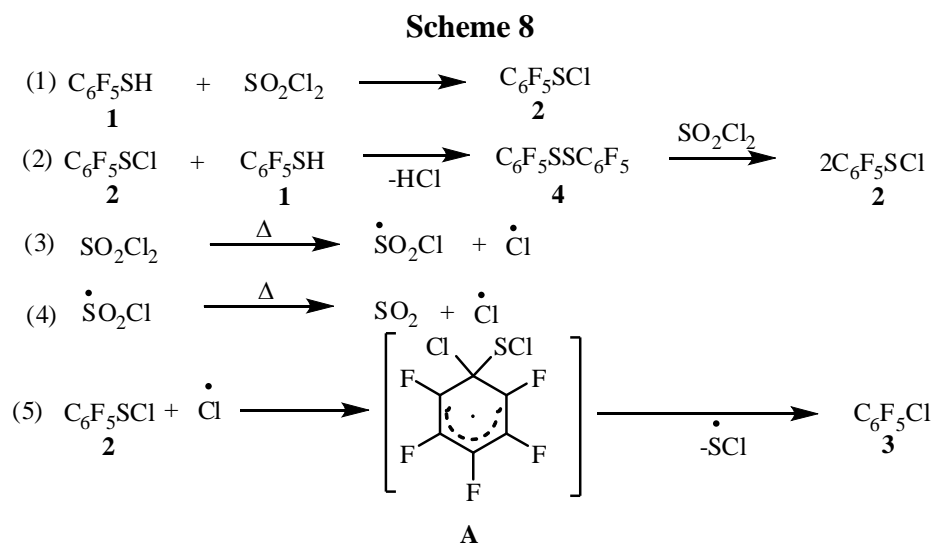
#### Scheme 7



Ratio according to the  $^{19}\text{F}$  NMR spectrum

It is possible that compound **4** in the reaction with  $\text{SO}_2\text{Cl}_2$  is converted to sulfenyl chloride **2** [6]. The latter, under the action of the chlorine atom formed from  $\text{SO}_2\text{Cl}_2$  [7-9] (Equations 3 and 4, Scheme 8), is converted to arene **3**, including the intermediate formation of the radical  $\sigma$ -complex **A**

[4]. Probably, the reaction of thiol **1** with  $\text{SO}_2\text{Cl}_2$  in the flow system at  $\sim 400^\circ\text{C}$ , described by us earlier [3], proceeds in a similar manner.



## EXPERIMENTAL

Authors would like to acknowledge the Multi-Access Chemical Service Center SB RAS for spectral and analytical measurements.

The  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were recorded on a Bruker AV-300 [282.4 ( $^{19}\text{F}$ ) and 300 ( $^1\text{H}$ ) MHz] spectrometer in  $\text{CCl}_4$  with added  $(\text{CD}_3)_2\text{CO}$ , internal reference  $\text{C}_6\text{F}_6$  and HMDS (0.04 ppm from TMS). Positive values of chemical shifts correspond to the signal downfield shift.

GC analysis was carried out on gas chromatograph LKhM-72 with a detector of thermal conductivity (TDC) and packed (stuffed) columns 2 m long and 4 mm inside diameter, which were filled with a solid inert carrier of Chromosorb W-AW-DMCS, impregnated with a liquid stationary phase (dimethyl polysiloxane BC-1 or dimethyltrifluoropropyl polysiloxane SCTF-50) in an amount of 15% of the mass of the carrier. The flow rate of helium through each of the columns is 60 ml/min. The temperature of the evaporator is  $280^\circ\text{C}$ , the initial temperature of the column is  $50^\circ\text{C}$  -1 min, 10 deg/min to  $280^\circ\text{C}$ , the isotherm at  $280^\circ\text{C}$  before the exit of all components of the sample, the temperature of TDC  $280^\circ\text{C}$ .

Initial polyfluoroarenethiols were obtained by the method [10].

The formation of compounds **2** and **4** and the final products by reactions of the polyfluoroarenethiols chlorination was confirmed by comparing the chemical shifts and spin-spin coupling constants of the  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra of these compounds with the literature data [3, 5, 11].

**Method 1.** Polyfluoroarenethiol was placed in an ampoule and  $\text{SOCl}_2$  or  $\text{SO}_2\text{Cl}_2$  was added by portions. After the end of the visible gas evolution, the ampoule was sealed, placed into a metal case, and heated. After the reaction completed, the ampoule was cooled, opened, its content was placed into a flask under a layer of water with ice (80–100 g), and subjected to steam distillation.

The reaction product was separated, dried with CaCl<sub>2</sub>, and analyzed by GC, <sup>19</sup>F and <sup>1</sup>H NMR methods.

Similarly, the reactions of sulfenyl chloride **2** and disulfane **4** with SO<sub>2</sub>Cl<sub>2</sub> were carried out. In this case, the ampoule was sealed immediately after the reagents were placed in it.

**Reactions of pentafluorobenzenethiol 1 with SOCl<sub>2</sub>.** From 2.77 g (13.84 mmol) of compound **1** and 3.30 g (27.74 mmol) of SOCl<sub>2</sub> (200–202°C, 24 h), 2.52 g of compound **3** were obtained (GC content: 97.3%), yield: 88%.

The results of the reactions of polyfluoroarenethioles (**1**, **5**, **7**, **9**, **13**, **14**, a mixture of C<sub>6</sub>Cl<sub>2</sub>F<sub>3</sub>SH, and also compounds **2** and **4**) with SO<sub>2</sub>Cl<sub>2</sub> are given in Table 1.

**Table 1**  
**Synthesis of chloropolyfluoroarenes**

Run No.	Substrate, g (mmol)	SO <sub>2</sub> Cl <sub>2</sub> , g (mmol)	The molar ratio of the substrate to SO <sub>2</sub> Cl <sub>2</sub>	Temp. (°C)	Time (h)	Yield of mixture (g)	The content (yield) of the product by GC (%)
1	<b>1</b> , 2.76 (13.79)	4.01 (29.95)	2.17	203-205	5	2.55	<b>3</b> , 98.3 (90)
2	<b>2</b> , 3.01 (12.83)	3.76 (21.21)	2.19	200-202	5	2.37	<b>3</b> , 98.0 (89)
3	<b>4</b> , 3.05 (7.66)	2.08 (15.53)	2.03	203-205	5	2.67	<b>3</b> , 91.2 (85)
4	<b>5</b> , 2.24 (12.30)	3.40 (25.39)	2.06	200-202	5	2.07	<b>6</b> , 99.0 (90)
5	<b>7</b> , 3.29 (15.19)	4.21 (31.41)	2.07	203-205	5	2.91	<b>8</b> , 99.1 (87)
6	<b>9</b> , 2.39 (9.55)	2.88 (21.51)	2.25	218-220	5	2.17	<b>10</b> , ~100 (90)
7	<b>13</b> , 1.98 (6.34)	1.79 (13.37)	2.11	220-222	5	1.89	<b>15</b> , 99.4 (94)
8	<b>14</b> , 3.00 (9.13)	2.54 (18.97)	2.08	218-220	5	2.80	<b>16</b> , 99.3 (92)
9	a mixture of C <sub>6</sub> Cl <sub>2</sub> F <sub>3</sub> SH, 3.04 (13.37)	3.87 (28.90)	2.22	203-205	5	2.82	<b>17</b> , 99.4 (91)

0.15 g (0.75 mmol) of compound **1** was mixed in a flask with 0.21 g (1.57 mmol) of SO<sub>2</sub>Cl<sub>2</sub> at room temperature. At the end of the gas evolution, the resulting mixture was compounds **2** and **4** in a ratio of ~ 95: 5, respectively (<sup>19</sup>F NMR data).

**Method 2.** Compound **1** was placed in an ampoule and SOCl<sub>2</sub> or SO<sub>2</sub>Cl<sub>2</sub> was added by portions. After the end of the visible gas evolution, the ampoule was sealed, placed into a metal case, and heated. After the reaction completed, the ampoule was cooled, opened, its content was dissolved in ~ 2 ml of methylene chloride and analyzed by <sup>19</sup>F NMR.

Heating of 0.12 g (0.60 mmol) of compound **1** with 0.16 g (1.35 mmol) of SOCl<sub>2</sub> at 202–204°C for 5 h gave a mixture of compounds **2**, **3**, **4** (NMR <sup>19</sup>F) and also probably decafluorodiphenyltrisulfane (δ, ppm: 13.5 (F-4 and F- 4') [12]) and decafluorodiphenyltetrasulfane

( $\delta$ , ppm: 13.4 (F-4 and F-4') ( [12]) contained in the methylene chloride solution. In these two polysulfanes, chemical shifts of *meta*-atoms of fluorine are in the region of 2.1÷2.6 ppm [12], *ortho*- atoms of fluorine are in the region of 31÷32 ppm [12]. The ratio of compounds **2**, **3**, **4** and a mixture of decafluorodiphenyltri- and -tetrasulfane was ~ 11: 55: 10: 24, respectively ( $^{19}\text{F}$  NMR data).

Similarly, heating of 0.20 g (1.00 mmol) of thiol **1** with 0.27 g (2.02 mmol) of  $\text{SO}_2\text{Cl}_2$  at 200-202°C for 2.5 h gave compounds **2**, **3**, **4** and a mixture of decafluorodiphenyltri- and -tetrasulfane in a ratio of ~ 3: 79: 3: 15, respectively ( $^{19}\text{F}$  NMR data).

**Reactions of 4-bromo-2,3,5,6-tetrafluorobenzenethiol (12) with  $\text{SO}_2\text{Cl}_2$ .** From 0.32 g (1.23 mmol) of compound **12** and 0.34 g (2.54 mmol) of  $\text{SO}_2\text{Cl}_2$  (180-182°C, 5 h), a mixture containing compounds **8** and **11** in a ratio of 69: 31, respectively,) was obtained (NMR  $^{19}\text{F}$  data). When the reaction temperature was increased to 238-240°C (5 h), heating of 0.27 g (1.03 mmol) of compound **12** and 0.30 g (2.24 mmol) of  $\text{SO}_2\text{Cl}_2$  gave a mixture containing compounds **8** and **11** in a ratio of 97: 3, respectively ( $^{19}\text{F}$  NMR data).

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