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Synthesis of bromopolyfluoroarenes from polyfluoroarenethiols with PBr₅ and Br₂

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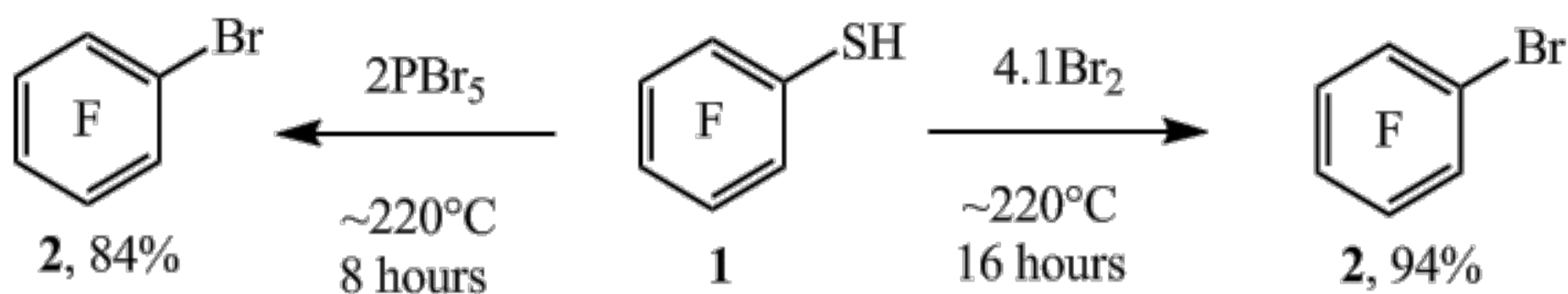
Abstract: Using the reactions of the polyfluoroarenethiols with PBr₅ and Br₂ at 150-240°C in ampules and with Br₂ in a flow system at 350-650°C, there were made the substitute reactions of thiol group by bromine atom and there was synthesized a variety of bromopolyfluoroarenes, among which there are also bromopolyfluoroarenes that at the same time contain chlorine and bromine atoms in ortho – and para-positions.

Keywords: Bromine, bromopolyfluoroarenes, polyfluoroarenethiols, thiol group

The thiol function is easily and selectively introduced into polyfluoroarenes by reaction of nucleophilic substitution [1]. Earlier we developed a method of introducing bromine and chlorine atoms into polyfluoroarenes by thermal replacement of a thiol group into polyfluoroarenethiols for chlorine and bromine atoms [2,3]. This process occurs at high temperature (400-500°C) in a flow system and leads to a variety of chloro – and bromopolyfluoroaromatic compounds with the high yield of compounds [2,3]. When using PCl₅ as the source for chlorine, the substitute reaction of thiol group was made at lower temperature (200-220°C, reactions in ampules) [4]. In that context it is of interest to make such transformations of the polyfluoroarenethiols with PBr₅ and Br₂.

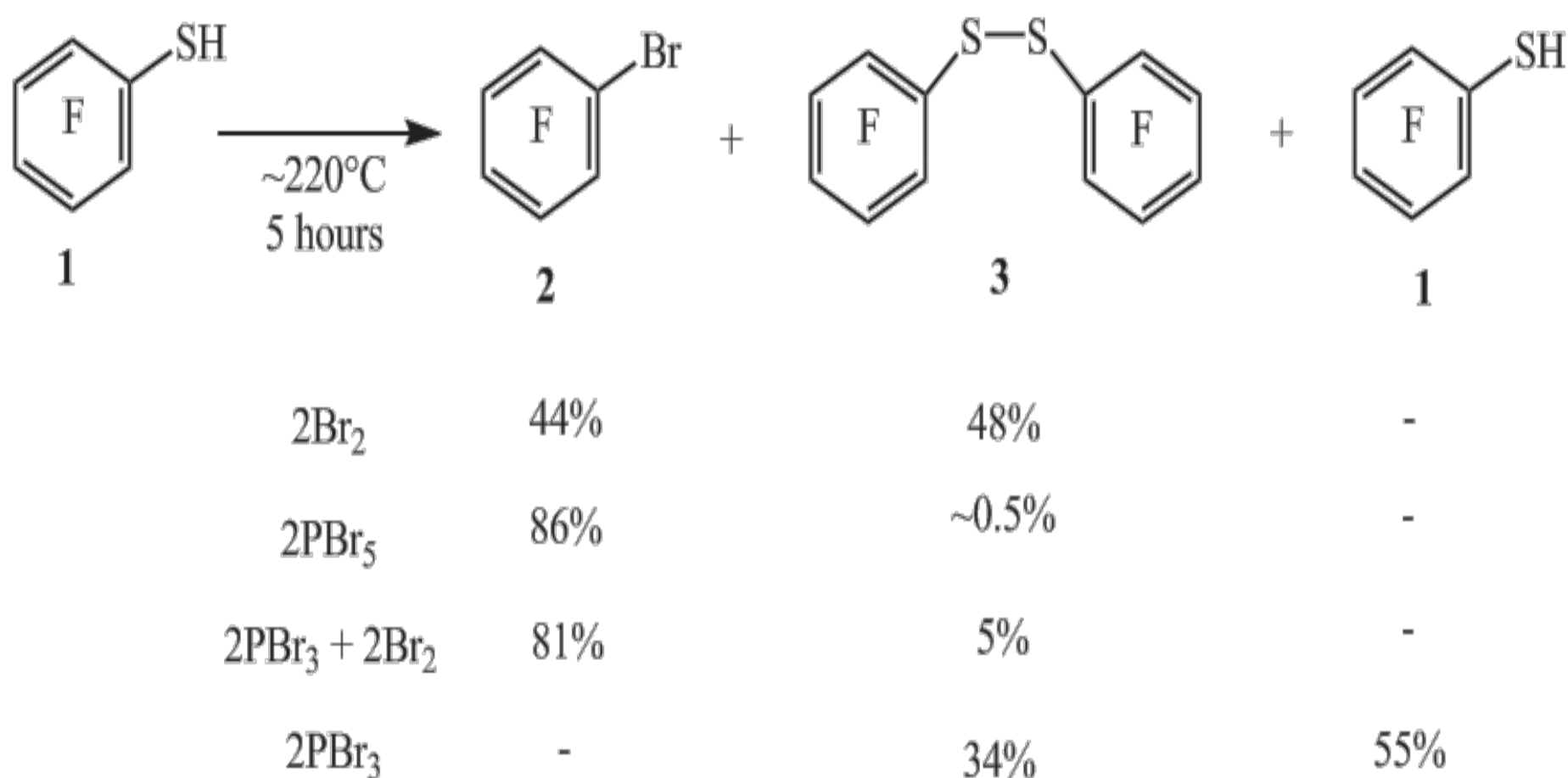
We have shown that the thiol group in polyfluoroarenethiols when heated at ~220°C in ampules with PBr₅ or Br₂ converts to bromine atom. In that way from the pentafluorobenzenethiol **1** and PBr₅ (in the molar ratio of 1:2) at ~220°C during 8 hours bromopentafluorobenzene (**2**) with high yield was prepared (scheme 1). In the pentafluorobenzenethiol (**1**) reaction, there can be used Br₂ instead of PBr₅. Thiol (**1**) when heated with Br₂ (in the molar ratio of ~1:4.5) at ~220°C during 8 hours in this case arene **2** and decafluorodiphenyl disulfide (**3**) are formed (in the molar ratio of ~84 : 16 according to ¹⁹F NMR data). By increasing the time of the reaction till 16 hours the compound **2** was obtained with high yield (scheme 1).

Scheme 1



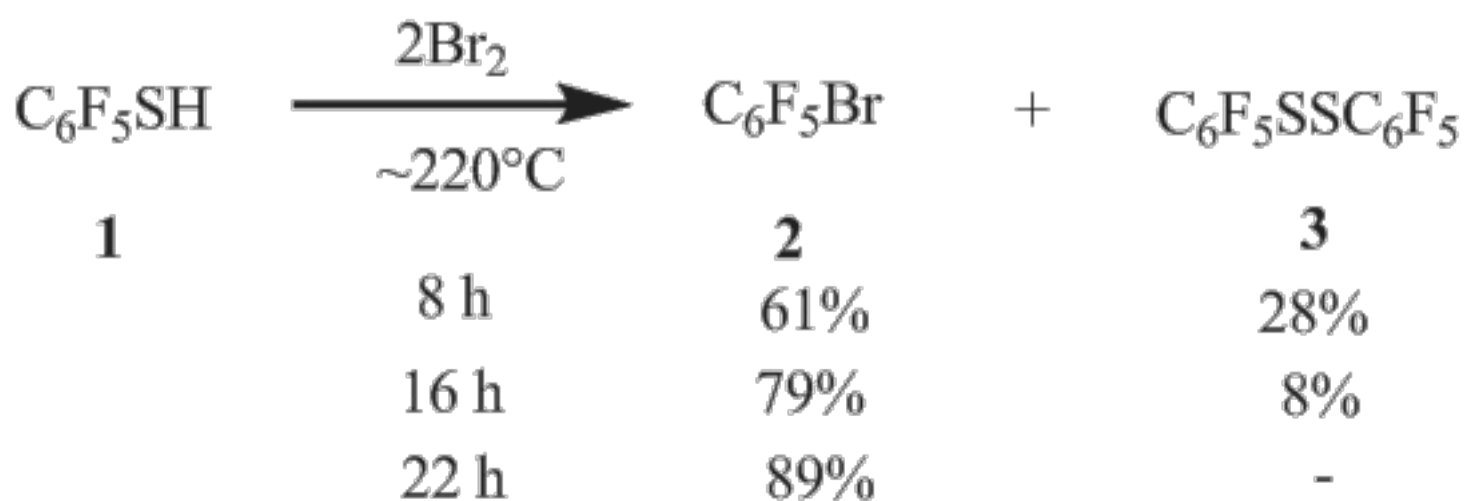
Reducing the amount of Br_2 to 2 moles, and reaction time to 5 hours resulted in the formation of arene **2** and disulfide **3** with the yields 44% and 48% respectively (according to GLC, scheme 2). Under similar conditions reactions of thiol **1** with Br_5 (in the molar ratio of $\sim 1:2$) or $\text{PBr}_3 + \text{Br}_2$ (in the molar ratio of $\sim 1:2:2$) the compound **2** is formed and this compound contains small amounts of disulfide **3** (^{19}F NMR and GLC). In the reactions of the thiol **1** with PBr_3 (in the molar ratio of $\sim 1:2$) only the compound **3** is formed.

Scheme2



In case of increasing the reaction of **1** time with Br_2 (in the molar ratio of $\sim 1:2$) to 8 and 16 hours, the reaction didn't proceed fully and the reaction mixtures contained the disulfide **3** (scheme 3). By increasing the time of the reaction to 22 hours the arene **2** was obtained with the yield of 89%.

Scheme3

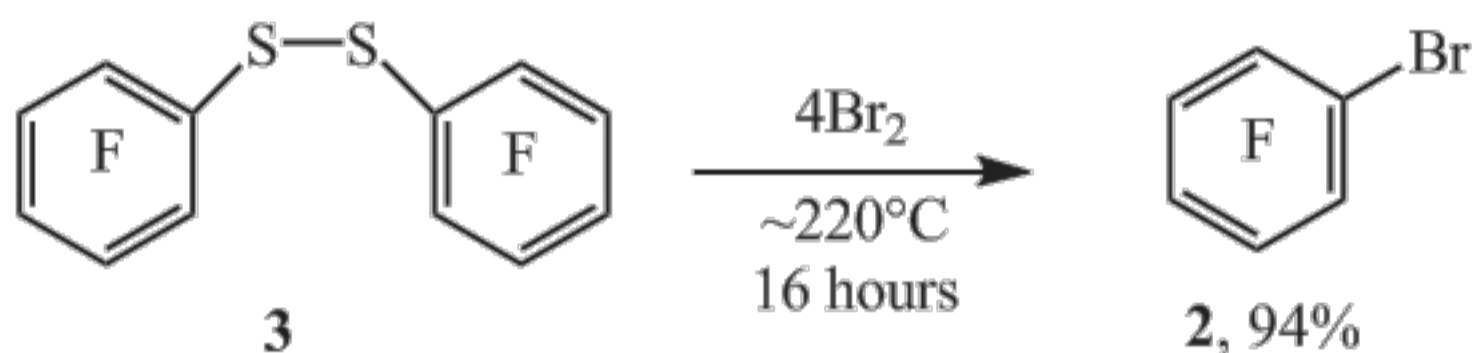


In the reaction of thiol **1** with Br₂ in the molar ratio of ~1:3 at 220°C reaction during 16 hours, the yield of the compound **2** was 91%. As stated above, in the similar conditions, from thiol **1** and Br₂ (in the molar ratio of ~1:4.1) there was obtained the compound **2** with the yield of 94%. Although there isn't much difference between the yields of the target products in these reactions, in order to get the maximum yields of the final products, for further transformations of polyfluoroarenethiols with bromine, we chose their molar ratio of ~1:4-4.3.

In case of increasing temperature of the reaction of the compound **1** with Br₂ (in the molar ratio of ~1:4.1) to 250°C (16 hours) an arene **2** is obtained with small impurity of polybromopolyfluorobenzenes, according to ¹⁹F NMR, GC-MS and GLC (table 1, entry 7). Earlier in co-pyrolysis of C₆F₆ with Br₂ at ~770°C arene **2** and polybromopolyfluorobenzenes [5] were formed. In this regard, the temperature ~220°C is acceptable for bromination of the compound **1** and its derivatives.

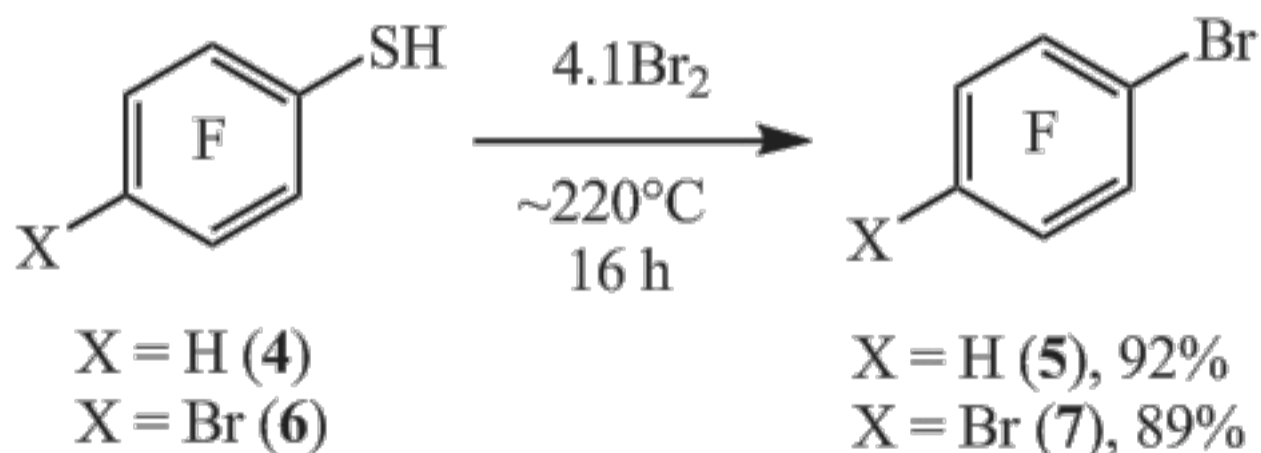
When heated disulfide **3** with bromine at ~220°C also arene **2** with high yield is obtained (scheme 4).

Scheme4



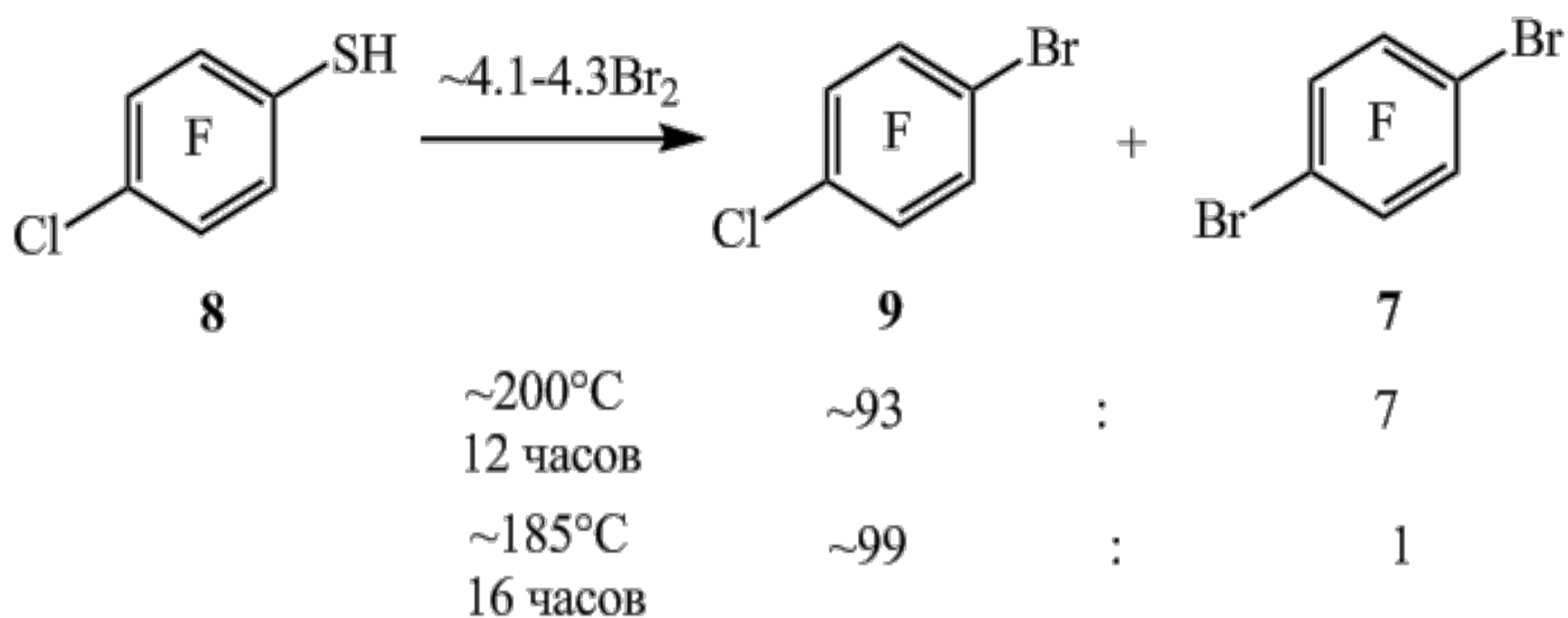
In case of thiol's **1** para-substituted, the thiol group is also smoothly substituted by bromine. In such way 1-bromo-2,3,5,6-tetrafluorobenzene (**5**) is obtained by heating 2,3,5,6-tetrafluorobenzenethiol (**4**) with bromine at ~220°C. In this case, the C-H bond remains unreacted. Much the same there was 1,4-dibromotetrafluorobenzene (**7**) obtained from 4-bromotetrafluorobenzenethiol (**6**) (scheme5).

Scheme5



4-Chloro-2,3,5,6-tetrafluorobenzenethiol (**8**) when heated with bromine at ~220°C, than apart from 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene (**9**) arene **7** (scheme 6) is formed as a co-product in virtue of the part substitution of chlorine atom by the bromine. A decrease of temperature in the reaction to ~180°C allowed to decrease the content of the compound **7** (scheme6).

Scheme 6

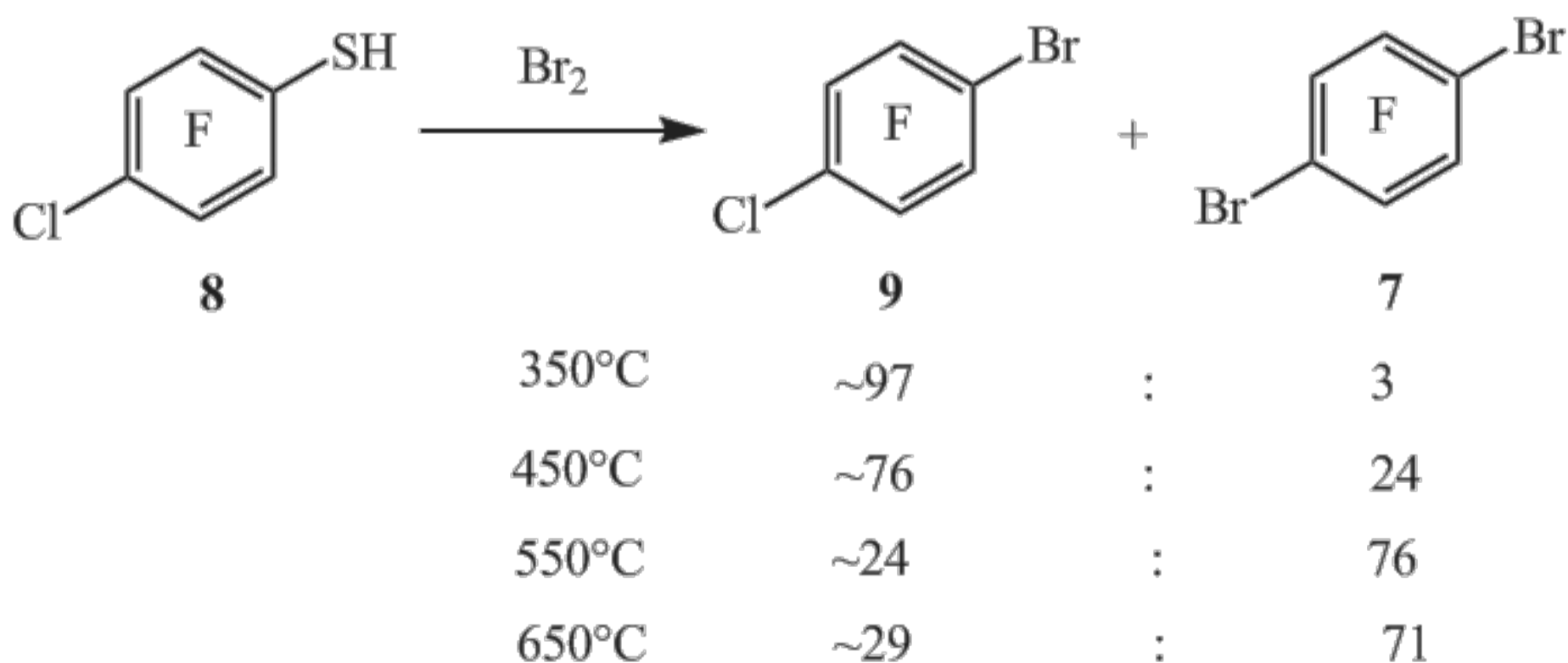


mole ratio of reaction products in reacting masses calculated from GLC data

The were made co-pyrolysis reactions of thiol **8** with Br_2 in a flow system at different temperatures. At 350°C from thiol **8** and Br_2 there was got arene **9** with the smaller yield and with an impurity of the compound **7**.

In this case not full thiol's **8** conversion ($\sim 60\%$) appeared (scheme 7) (table 2, entry 1). With increasing the co-pyrolysis temperature to 450°C the formation of compound **7** increases, while at 550°C the compound **7** becomes the main product of the reaction (table 2, entry 3). Raising of co-pyrolysis temperature to 650°C leads to resinification and a decrease in yield of the reaction mixture (table 2, entry 4).

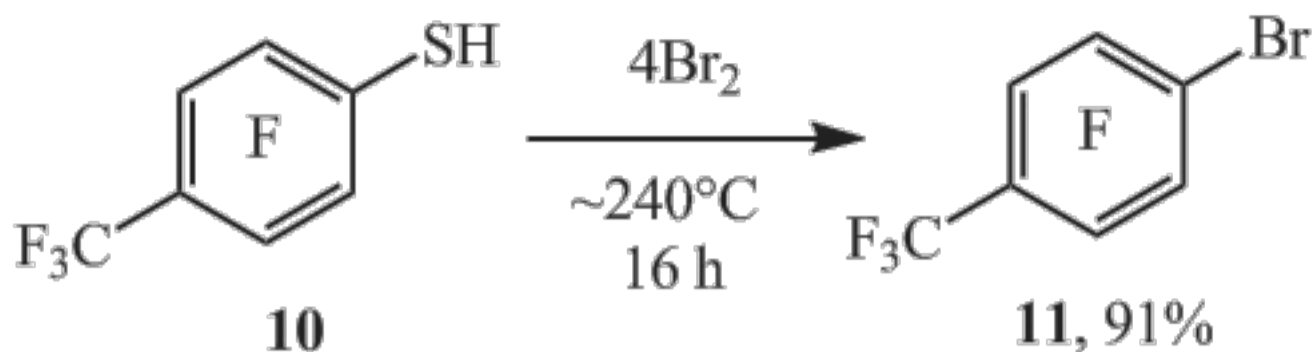
Scheme 7



mole ratio of reaction products in reacting masses calculated from GLC data

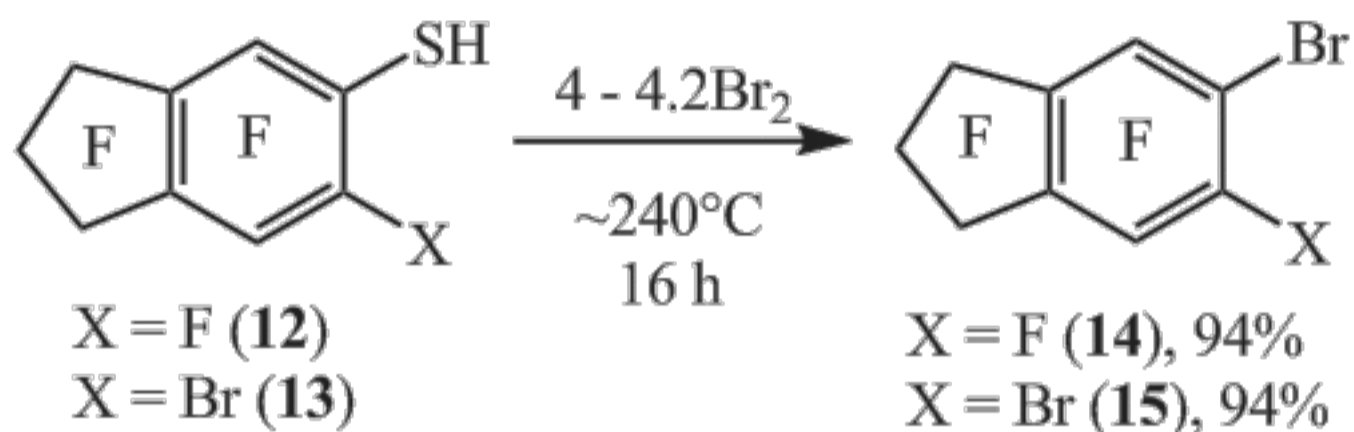
The 4-bromoheptafluorotoluene (**11**) with the high yield was prepared from the 4-trifluoromethyl-2,3,5,6-tetrafluorobenzenethiol (**10**) and bromine in an ampule (scheme 8).

Scheme 8



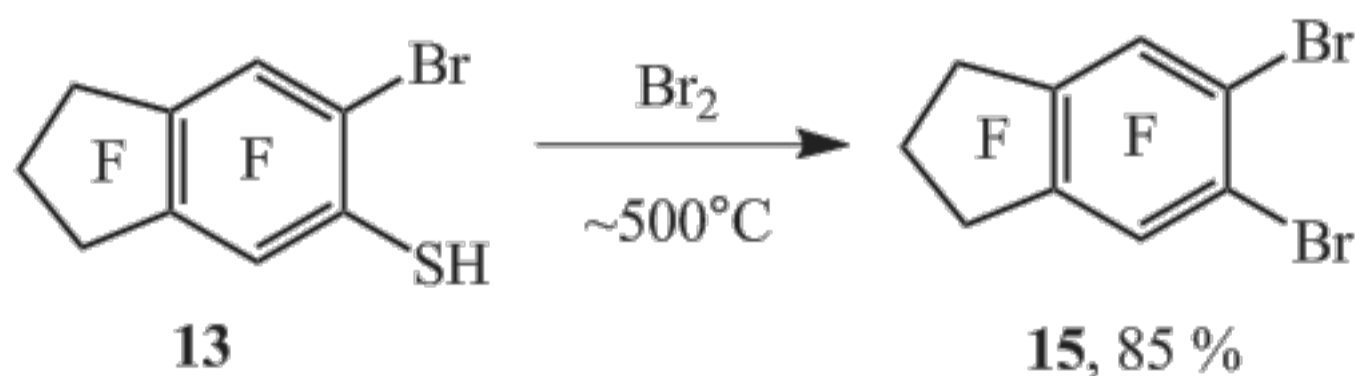
Similar from 5-nonafluoroindanethiol (**12**) and 6-bromooctafluoroindane-5-thiol (**13**) with the high yields there were synthesized 5-bromononafluoroindane (**14**) and 5,6-dibromooctafluoroindane (**15**) respectively (scheme 9).

Scheme 9



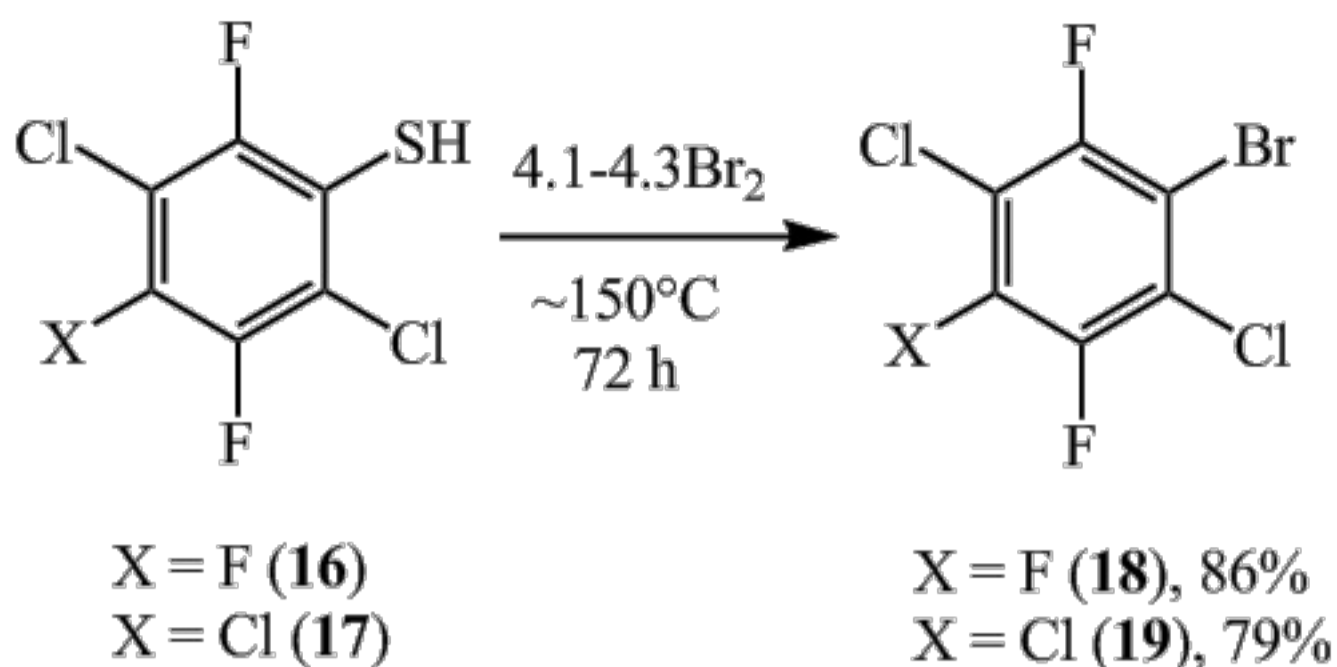
It also should be underlined that the compound **15** can be produced in a flowing reactor from the thiol **13** and Br_2 with the yield of 85% (scheme 10).

Scheme 10



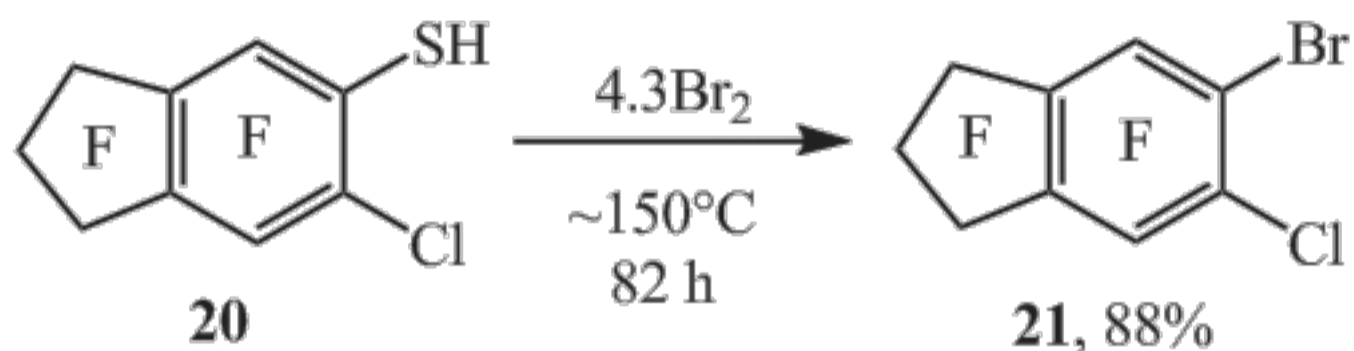
Varying the reaction time and temperature in ampules makes it possible to synthesize polyfluoroarenes, that at ortho-position contain chlorine and bromine atoms. In such a way, 1-bromo-2,5-dichloro-3,4,6-trifluorobenzene (**18**) and 1-bromo-2,4,5-trichloro-3,6-difluorobenzene (**19**) were produced by heating with bromine 2,5-dichloro-3,4,6-trifluorobenzenethiol (**16**) and 2,4,5-trichloro-3,6-difluorobenzenethiol (**17**) (scheme 11). By doing so, according to ^{19}F NMR, GC-MS and GLC data, difluoro-derivants in small amounts appeared as co-products.

Scheme 11



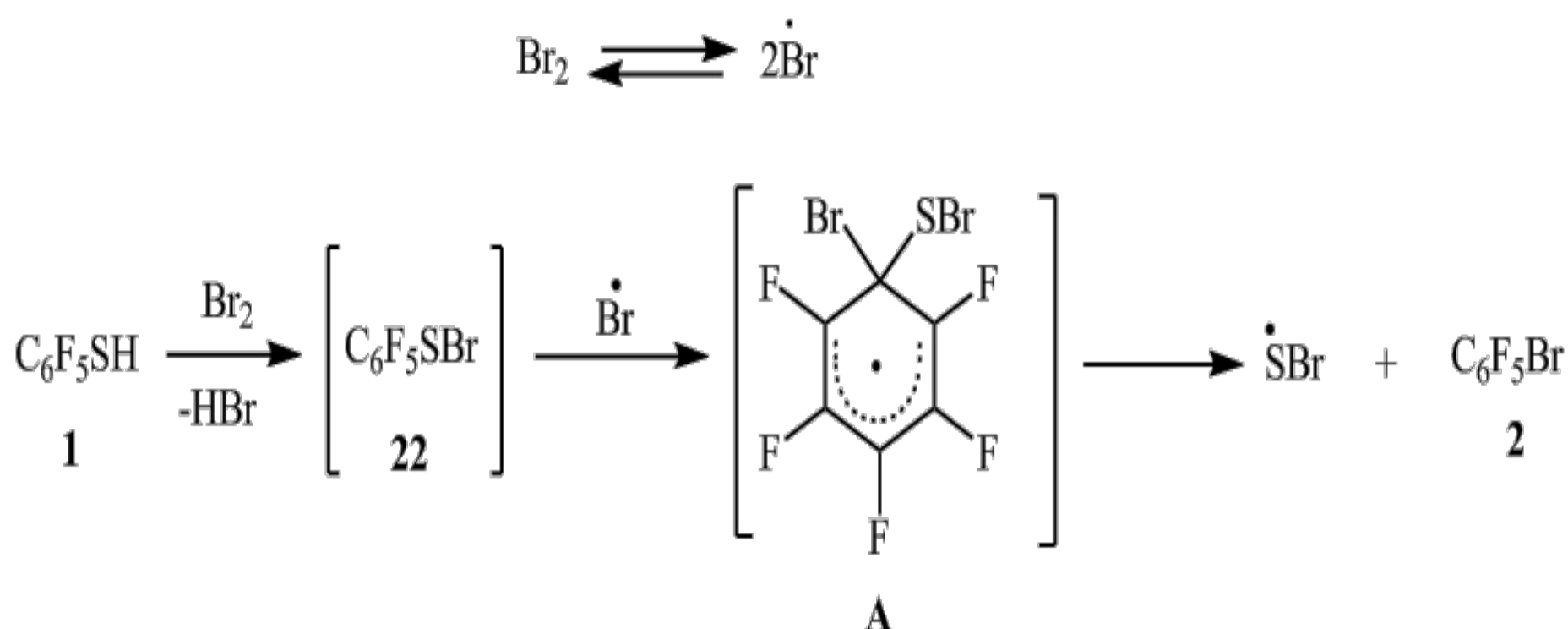
Similar when by brominating 6-chlorooctafluoroindane-5-thiol (**20**) 5-bromo-6-chlorooctafluoroindane (**21**) was produced (scheme 12), at the same time the formation of the compound **15**, according to ^{19}F NMR, GC-MS and GLC data, was practically not observed.

Scheme12



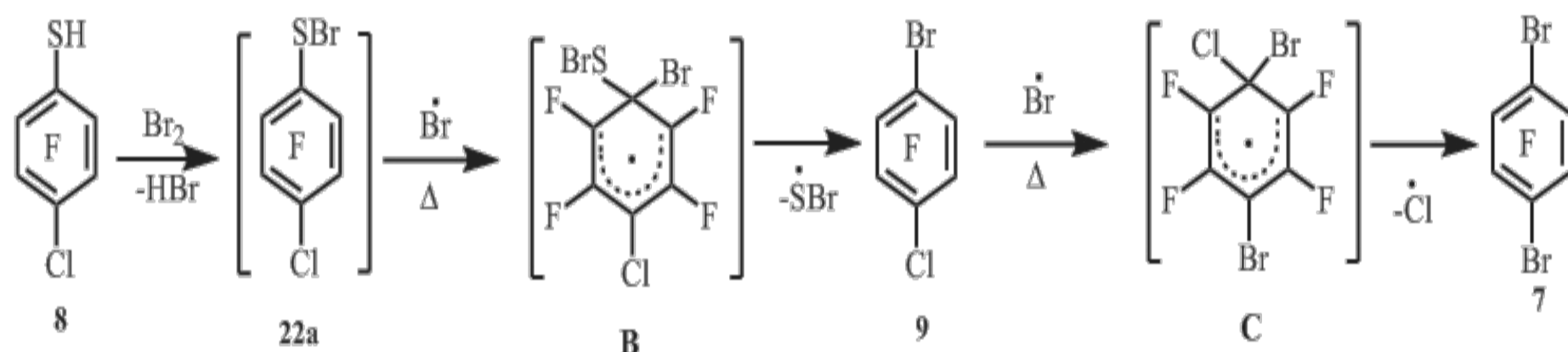
The substitution of the thiol group by bromine atom in polyfluoroarenethiols probably proceeds via homolytic mechanism similar to the substitution of the thiol group by chlorine atom in the co-pyrolysis of polyfluoroarenethiols with chlorine [2]. Polyfluorosulfenylbromides [6] and bis(polyfluoroarene)disulfides might appear as the intermediate products in the reaction of polyfluoroarenethiols with bromine. By analogy with the transformation of disulfide **3** under the action of Cl_2 into pentafluorobenzosulfenylchloride [2], probably the transformation of bis(polyfluoroarene)disulfides under the action of bromine into the intermediate products (polyfluoroarenesulfenylbromides) on the way to bromopolyfluoroarene is possible. For example: the interaction of pentafluorobenzesulfenylbromide (**22**) with the bromine atom with the formation of intermediate radical σ -complex (**A**) and following elimination of sulfur-containing function probably leads to the arene **2** appearance (scheme 13).

Scheme13



In the chloropolyfluoroarenethiols with Br_2 reactions the substitution of the chlorine atoms by bromine seems to proceed via homolytic mechanism (scheme 14). When this happens, the substitution of the thiol group by bromine proceeds easier than substitution of chlorine by bromine.

Scheme 14

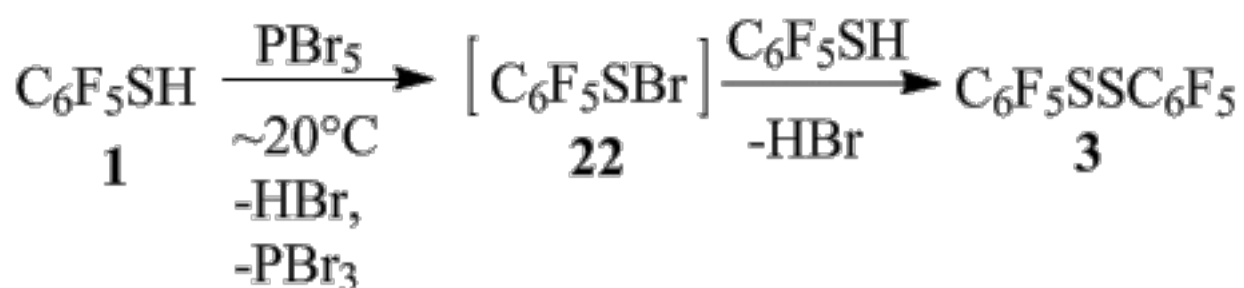


Probably, in the radical σ -complex (**B**) C-S bond is weaker than C-Br (bond energies C-S, $E=52$ kcal/mole, C-Br, $E=58$ kcal/mole [7]) that leads to elimination of the sulfur-containing function. In case of radical σ -complex (**C**) formation, for stronger C-Cl bond ($E=93,8$ kcal/mole [7]) substitution, the higher temperature ($450-550^\circ\text{C}$) is required. Probably, in the compound **8** with bromine reaction the radical σ -complex (**B**) step formation is the rate-limiting step for sulfenyl bromide **22a** into the compound **9** transformation under the bromine atom action, while in case of radical σ -complex (**C**) formation, the rate-limiting step will be the second with chlorine atom elimination (scheme 14).

To some extent, probably, the substitution of chlorine atom by bromine in the compound **8**, followed by substitution of the thiol group by bromine atom in the intermediate thiol **6**, can't be excluded.

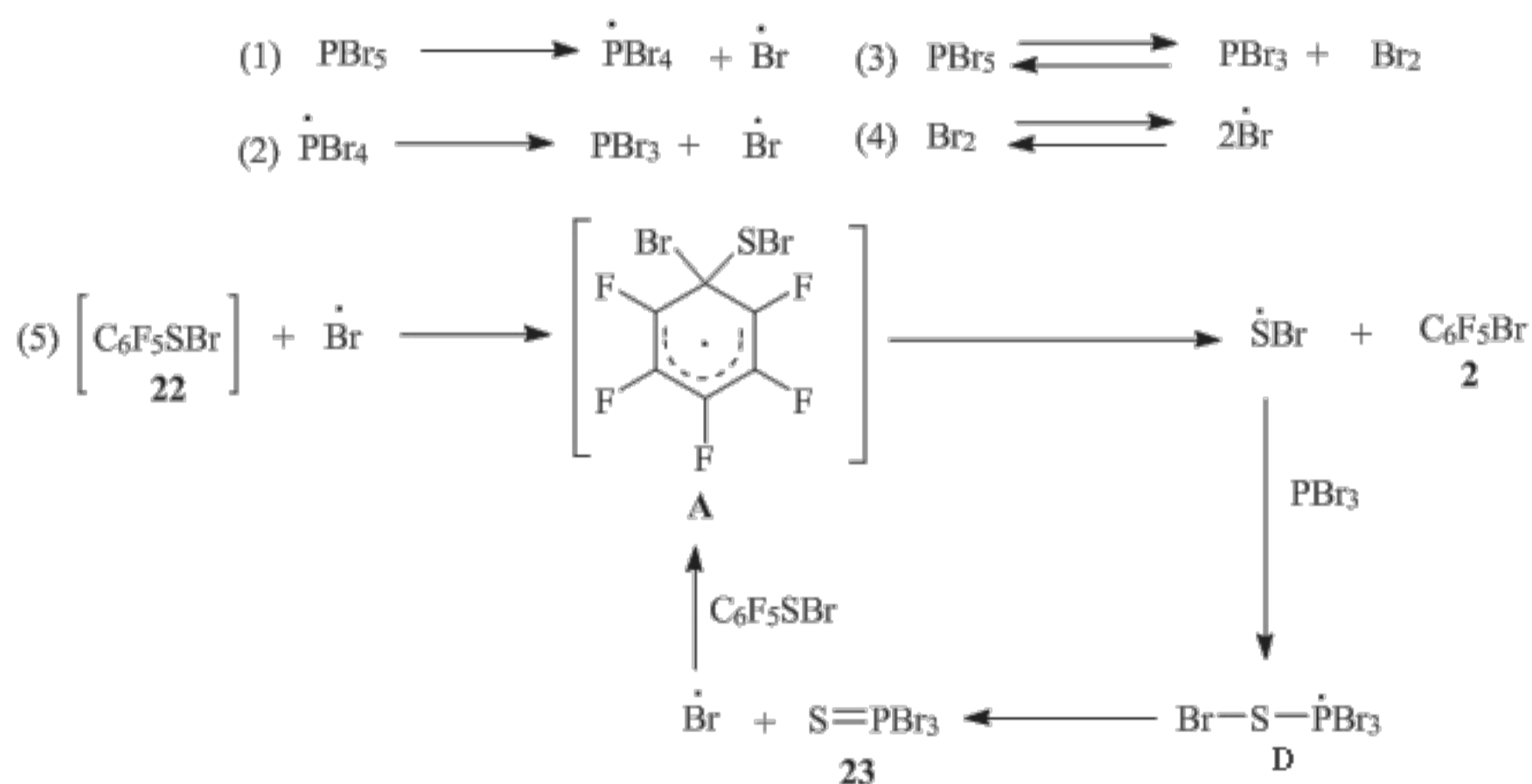
For the thiol **1** with PBr_5 reaction, taking into account that in crystalline state PBr_5 has an ion structure $[\text{PBr}_4]^+\text{Br}^-$ [8], then when involving cation $[\text{PBr}_4]^+$, sulfenyl bromide **22** might be formed, which when interacts with thiol **1** transforms into disulfide **3** (scheme 15). Also, the formation of disulfide **3** from thiol **1** and PBr_5 without sulfenyl bromide **22** participation probably can't be excluded. Disulfide **3** under the PBr_5 action could give sulfenyl bromide **22** similar to the conversion of this disulfide **3** into pentafluorosulfenylchloride in the reaction with PCl_5 [4].

Scheme 15



It is known that PBr_5 boils and decomposes at 106°C [9] and in this way it is a bromine source. According to the assessment, that we have made by analogy with the same for PCl_5 [10], the axial bond P-Br energy in the trigonal bipyramidal structure of PBr_5 [11] is equal to 28 kcal/mole [10], whereas Br-Br bond energy is a higher measure (45.4 kcal/mole [7]). According to this, it's possible to assume that initially PBr_5 is decomposed with formation of bromine atom and $\cdot\text{PBr}_4$ radical (scheme 16, formula 1). $\cdot\text{PBr}_4$ radical also can be decomposed with the formation of PBr_3 and $\cdot\text{Br}$ (formula 2). Further reactions, sulfenyl bromide **22** with bromine atom for example, probably gives radical σ -complex (**A**) [2], and at its decomposition the compound **2** appears (formula 5). $\cdot\text{SBr}$ radical that is eliminated at σ -complex (**A**) decomposition, if reacting with PBr_3 , then the phosphoranyl radical (**D**) might appear. The latter at β -decomposition gives thiophosphoryl bromide **23**, that was fixed by us using ^{31}P NMR spectrum and GC-MS. It's known that the phosphoranyl radicals, despite their relative stability, may undergo β -decomposition, including the one with generation of S=P bond [12].

Scheme 16



As far as the P-Br axial bond energy in PBr_5 is less than Br-Br bond energy, it is possible to presume that PBr_5 is a better source of atomic bromine than Br_2 . This fact probably explains why the thiol **1** with PBr_5 reaction needs less time than with Br_2 .

Besides the formulas 1 and 2, on the scheme 16 there is shown the Br_2 formation from PBr_5 and the Br_2 dissociation on the bromine atoms (formulas 3,4) by analogy with PCl_5 transformation [4]. Such type of PBr_5 decomposition shouldn't be excluded.

P-Cl axial bond energy in trigonal bipyramid PCl_5 [11] is equal to 34 kcal/mole [10], whereas Cl-Cl bond energy is a higher measure (57.2 kcal/mole [7]). According to this, there might take place the

change of the compound **1** reactivity with respect to PCl_5 [4] and Cl_2 in favor of the process with PCl_5 . However, we did not study this question experimentally.

Experimental

The analytical and spectral studies were performed at the Joint Chemical Service Center, Siberian Branch, Russian Academy of Sciences.

^{31}P , ^{19}F and ^1H NMR spectra were recorded on a Bruker AV-300 spectrometer (121 MHz for ^{31}P , 282 MHz for ^{19}F , 300 MHz for ^1H) in CCl_4 with CDCl_3 additive. External standard for ^{31}P NMR – H_3PO_4 . For ^{19}F and ^1H NMR spectra internal standards – C_6F_6 and HMDS (0.04 ppm from TMS) respectively. The positive values of chemical shifts correspond to the signals downfield shift. IR - spectra were prepared on a Bruker Vector 22 IR. UV - spectra were recorded on a Hewlett Packard 8453 UV and Cary 5000. Molecular weights and elemental compositions were determined from the high-resolution mass spectra which were obtained using a DFS instrument (electron impact, 70 eV). A chromatograph HP 5890 with a mass-selective detector HP 5971 and a chromatograph Agilent 6890N with a system Agilent 5973N were used for GC-MS. The ionizing electron energy was 70 eV. Separation of substances was carried out on a column HP-5, 30 m x 0.25 mm x 0.25 μm , helium was used as a carrier gas with flow rate 1 mL/min, column temperature 50 - 280°C, ion source temperature 173°C. GLC-analysis was carried out on a chromatograph HP 5890 with a column HP-5, 30 m x 0.52 mm/2.6 μm and a thermal conductivity detector.

The starting thiols were prepared using a procedure given in [13].

A solution of KSH in ethylene glycol (~4.1 mol/l) was prepared by blowing hydrogen sulphide in the solution 2 mole KOH in 330 ml of in ethylene glycol till the mass increased on 64gr.

6-bromooctafluoroindan-5-thiol (13) preparation. Indan (**14**) solution 50.35 g. (140.26 mmole) in 100 ml of dimethyl carbinol on cooling by water with ice and while mixing during 1.5 hours was being added 71 ml of KSH solution in ethylene glycol, at no more than 5°C. Further, the reaction mixture was being stirred during 2.5 hours at 0-1°C. Then the reaction mixture was poured into a mixture of concentrated hydrochloric acid (350 ml) and ice (500 g). The residuum was separated, dried over CaCl_2 . The dry product mass – 48.95g. This was analyzed by ^{19}F , ^1H NMR and GLC methods. The content of the compound **13** by GLC – 98% (the yield – 91%). M.p. - 32-33.5°C (pentan). ^{19}F NMR spectrum (δ , ppm): 31.9 quintet (2- CF_2 , $J_{2-\text{CF}_2-1,3-\text{CF}_2}$ 4.5 Hz), 51.2 dt (F^4 , $J_{\text{F}^4-\text{F}^7}$ 21 Hz, $J_{\text{F}^4-3-\text{CF}_2}$ 7.5 Hz), 53.7 broad multiplet (1(3)- CF_2), 53.9 dt (F^7 , $J_{\text{F}^7-\text{F}^4}$ 21 Hz, $J_{\text{F}^7-1-\text{CF}_2}$ 7.5 Hz), 54.7 broad multiplet (1(3)- CF_2). ^1H NMR (δ , ppm): 4.56 s. UV-spectrum (hexane), λ_{max} , nm ($\lg \epsilon$): 223 (4.19), 262 (3.82), 288 (3.18), 297 (3.21). IR- spectrum (KBr), ν , cm^{-1} : 2587, 2568, 1627, 1455, 1298, 1247, 1204, 1154, 1096, 1060, 955, 944, 869, 804, 576, 543. Found, %: C 28.84; H 0.24; F 40.71; S 8.76; Br 21.25. M^+ 371.8854. $\text{C}_9\text{HBrF}_8\text{S}$. Calculated, %: C, 28.98; H, 0.27; F, 40.74; S, 8.60; Br, 21.42. M^+ 371.8849.

Reactions of thiol 1 with PBr_5 . 2.27 g. (11.34 mmole) of thiol **1** was placed into an ampoule and there was portioned added 10.13 g. (23.53 mmole) of PBr_5 . When gas isolation finished the ampoule was sealed up. Then the ampoule was placed in a metal sheath and was being heated at 218-220°C during 5 hours. Following of the end of the reaction the ampoule was being cooled with liquid nitrogen and opened. There was obtained 11.49 g of reacting masses, that according to GC-MS contains 46% of the compound **2** and 50% of Br_3PS **23**. Then content was transferred under water with ice (~60g) sheet into a flask. The mixture was being mixed by magnetic stir bar during 2 hours for the purpose of phosphorus compounds hydrolysis, then it was alkalized by Na_2CO_3 and was being mixed for 2 hours and it was steam distilled. The product (2.44g.) was separated, dried over CaCl_2 and analyzed by ^{19}F NMR and GLC methods. This product contents compound **2** - 98.3 % (according to GLC) and disulfide **3** – 0.5% (according to GLC).

Identification of compound **23** was carried out using ^{31}P NMR (δ , ppm: - 115.3 p [14]) and GC-MS. The total mass-spectrum of the compound **23** is: 306 (15.1), 304 (42.3), 302 (42.2), 300 (14.6; Br_3PS), 225 (52.8), 223 (100), 221 (51.0; Br_2PS), 193 (3.7), 191 (7.4), 189 (3.7; Br_2P), 112 (6.4), 110 (6.5; BrP), 81 (6.6), 79 (6.7; Br), 63 (26.0; PS), 32 (1.5; S), 31 (3.0; P).

By analogy, from the 2.12 g. (10.59 mmole) of thiol **1** and 89.14 g. (21.23 mmole) of PBr_5 (at 218-220°C, 8 hours) this was prepared 2.21 of reacting mass with 99.1% content of compound **2** according to GLC, yield 84%.

The compound **3** (according to ^{19}F NMR) without the formation of other polyfluoroarenes was prepared when 0.09 g. (0.45 mmole) of the compound **1** was mixed with 0.39 g. (0.91 mmole) PBr_5 at room temperature.

Reaction of thiol 1 with $\text{PBr}_3 + \text{Br}_2$. From the 2.09 g. (10.44 mmole) of the compound **1**, 5.68 g. (20.98 mmole) of PBr_3 and 3.45 g. (21.59 mmole) of Br_2 (at 218-220°C, 5 hours) this was prepared 2.25 g of reacting mass with 93.1% content of compound **2** (according to GLC) and with 4.4 % content of disulfide **3** (according to GLC).

Reaction of thiol 1 with PBr_3 . By heating 2.09 g. (10.44 mmole) of the thiol **1** and 5.77 g. (21.32 mmole) of PBr_3 (at 218-220°C, 5 hours) this was prepared 1.91 of reacting mass, that contains the starting thiol **1** (60.1% according to GLC) and disulfide **3** (37.0% according to GLC).

Reaction of thiol 1 with Br_2 . 0.17 g. (0.85 mmole) of the compound **1** was placed into an ampoule and there were portioned added 0.61 g. (3.80 mmole) of bromine. When gas isolation finished the ampoule was sealed up. Then the ampoule was placed in a metal sheath and was being heated at ~220°C during 8 hours. Following of the end of the reaction the ampoule was being cooled, opened and the content of ampoule poured into water. Surplus of bromine was deleted using sodium sulphite, then it was extracted using ~2 ml of dichloromethane and analyzed by ^{19}F NMR (**2:3** ~84:16 according to ^{19}F NMR data).

The general procedure for bromofluoroarenes synthesis. Polyfluoroarenethiol was placed into an ampoule and there were portioned added bromine. When gas isolation finished the ampoule was sealed up and was placed in a metal sheath and then was being heated. Following of the end of the reaction the ampoule was being cooled with liquid nitrogen, opened and then content was transferred into a flask under the water sheet (80-100 ml). Surplus of bromine was deleted using sodium sulphite, then the reacting mass was steam distilled. Surplus of bromine was deleted using sodium sulphite, then the reacting mass was steam distilled. The product was separated, dried over CaCl_2 and analyzed by ^{19}F NMR and GLC methods. By analogy the reaction of disulfide **3** with bromine was made. The results are shown in the Table 1.

The formation of the compounds **2,3,4,5,7,11** and **14** is proved by ^{19}F NMR spectra [2,3,15].

Table 1.

# Entry	Compound, g (mmole)	Bromine, g (mmole)	Molar ratio of thiol to Br_2	Temperature, °C	Time, hours	Mix yield,
1	1 , (10.04) 2.01	3.31 (20.71)	2.06	218-220	5	2.0
2	1 , 2.05	3.39	2.07	218-220	8	2.1

	(10.24)		(21.21)				
3	1, (10.09)	2.02	3.32 (20.77)	2.06	218-220	16	2.1
4	1, (10.49)	2.10	3.46 (21.65)	2.06	218-220	22	2.3
5	1, 2.08(10.39)		5.10 (31.91)	3.07	218-220	16	2.3
6	1, (14.44)	2.89	9.51 (59.51)	4.12	220-222	16	3.3
7	1, (13.79)	2.76	9.08 (56.82)	4.12	250-255	16	3.1
8	3, 3.11(7.81)		5.11 (31.98)	4.09	219-221	16	3.6
9	4, (15.15)	2.76	9.91 (62.01)	4.09	218-220	16	3.2
10	6, 2.52 (9.65)		6.30 (39.42)	4.08	220-222	16	2.6
11	8, (16.11)	3.49	11.2 (69.83)	4.33	201-203	12	4.0
12	8, (15.98)	3.46	10.4 (65.02)	4.07	185-187	16	3.4
13	10, (13.31)	3.33	8.53 (53.38)	4.01	238-240	16	3.6
14	12, (8.94)	2.79	6.02 (37.67)	4.21	238-240	16	3.0
15	13, (7.32)	2.73	4.73 (29.60)	4.04	238-240	16	2.9

16	16 , (31.37)	7.31	20.09 (125.71)	4.29	149-151	72	8.0
17	17 , (14.19)	3.54	9.23 (57.57)	4.07	149-151	72	3.6
18	20 , (11.38)	3.74	7.79 (48.75)	4.28	150-152	82	3.8

^aThe content of disulfide 3 in the reaction mixture is equal to 46.7% according to GLC.

^bThe content of disulfide 3 in the reaction mixture is equal to 27.0% according to GLC.

^cThe content of disulfide 3 in the reaction mixture is equal to 7.9% according to GLC.

^dAccording to GC-MS the reaction mixture contents 3.4% of polybromopolyfluorobenzenes (GLC).

^eAccording to GC-MS the reaction mixture contents 8% of an arene 8 (GLC).

^fAccording to GC-MS the reaction mixture contents 1.4% of arene 8 (GLC).

^jAccording to GC-MS the reaction mixture contents 2.5% of dibromotrifluorochlorobenzenes (GLC).

^hAccording to GC-MS the reaction mixture contents 6.9% of dibromodifluorodichlorobenzenes (GLC).

ⁱAccording to GC-MS the reaction mixture contents 0.3% of indane 15 (GLC).

1-Bromo-4-chloro-2,3,5,6-tetrafluorobenzene (9) (98.3% according to GLC data). M.p. 55-57°C. ¹⁹F NMR spectrum, δ , ppm: 22.6 m (F^{3,5}), 30.3 m (F^{2,6}). UV- spectrum (hexane), λ_{\max} , nm (lg ϵ ,): 222 (4.00). IR- spectrum (KBr), ν , cm⁻¹: 1742, 1634, 1493, 1462, 995, 964, 808, 594. Found, %: C 27.20; Br 30.50; Cl 13.30; F 29.17. M^+ 261.8801 C₆BrClF₄. Calculated, %: C 27.36; Br 30.33; Cl 13.46; F 28.85. M^+ 261.8803.

5,6 - Dibromooctafluoroindane (15). (99.7% according to GLC data). M.p. 37.5-38.5°C (pentan). ¹⁹F NMR spectrum, δ , ppm: 31.7 quintet (2-CF₂, $J_{2-CF_2-1,3-CF_2} \sim 4$ Hz), 53.7 m (1(3)-CF₂), 57.9 m (F^{4,7}). UV- spectrum (hexane), λ_{\max} , nm (lg ϵ ,): 221 (3.79), 238 (3.64), 243 (3.57, shoulder), 280 (3.03), 288 (3.14). IR- spectrum (KBr), ν , cm⁻¹: 1724, 1624, 1607, 1460, 1439, 1398, 1331, 1290, 1246, 1221, 1205, 1159, 1096, 1051, 949, 874, 800, 689, 671, 575, 536. Found, %: C 26.09; F 36.37; Br 38.08. M^+ 417.8230. C₉Br₂F₈. Calculated, %:C, 25.74; F, 36.20; Br 38.06. M^+ 417.8234.

1-Bromo-2,5-dichloro-3,4,6-trifluorobenzene (18). (98.3% according to GLC data). Distillation under vacuum (~12 mm Hg) of 4.74 g. of the mixture there were prepared 2.64 g. fraction with b.p. 94-95°C and purity 98.3% and 1.27 g. fraction with b.p. ~95°C and purity 95.1% according to GLC data. ¹⁹F NMR spectrum, δ , ppm: 27.6 dd (F³, $J_{F_3-F_4} 21$, $J_{F_3-F_6} 9.5$ Hz), 28.9 d (F⁴, $J_{F_4-F_3} 21$ Hz), 57.0 d (F⁶, $J_{F_6-F_3} 9.5$ Hz).. UV- spectrum (hexane), λ_{\max} , nm (lg ϵ ,): 225 (4.06), 280 (2.85). IR- spectrum (film), ν , cm⁻¹: 1597, 1468, 1441, 1354, 1308, 1076, 964, 874, 748, 700, 638. Found, %: C 25.91; Br 28.50; Cl 25.17; F 20.26. M^+ 277.8508 C₆Cl₂BrF₃. Calculated, %: C 25.75; Br 28.55; Cl 25.34; F 20.36. M^+ 277.8507.

1-Bromo-2,4,5-trichloro-3,6-difluorobenzene (19). (96.9% according to GLC data). Distillation under vacuum (~12 mm Hg.) of 2.69 g. of the mixture there were prepared 1.20 g. fraction with b.p. ~127°C and purity 96.9% and 0.94 g. fraction with b.p. 127-128°C and purity 96.5% according to GLC data. M.p. 94-96°C. ¹⁹F NMR spectrum, δ , ppm: 52.5 d (F³, $J_{F_3-F_6} 11$ Hz), 60.4 d (F⁶, $J_{F_6-F_3} 11$ Hz). UV- spectrum (hexane). λ_{\max} , nm (lg ϵ ,): 229 (4.12), 232 (4.13), 282 (3.26, shoulder), 290 (3.35). IR-

spectrum (KBr), ν , cm^{-1} 1435, 1387, 1287, 1252, 901, 881, 860, 698, 677, 631. Found, %: C 24.50; Br 27.00; Cl 35.90; F 13.03. M^+ 293.8210 $\text{C}_6\text{Cl}_3\text{BrF}_2$. Calculated, %: C 24.32; Br 26.97; Cl 35.89; F 12.82. M^+ 293.8212.

5-Bromo-6-chlorooctafluoroindan (21). (98.3% according to GLC data). ^{19}F NMR spectrum, δ , ppm: 31.8 quintet (2- CF_2 , $J_{2-\text{CF}_2-(1)3-\text{CF}_2} \sim 4.5$ Hz), 48.5 dt (F^7 , $J_{\text{F}^7-\text{F}^4} 19.5$ Hz, $J_{\text{F}^7-1-\text{CF}_2} 7.5$ Hz), 53.8 and 54.6 broad multiplets (1(3)- CF_2), 56.7 dt (F^4 , $J_{\text{F}^4-\text{F}^7} 19.5$ Hz, $J_{\text{F}^4-3-\text{CF}_2} 7.5$ Hz). UV- spectrum (hexane), λ_{max} , nm (lg ϵ ,): 234 (3.93), 279 (3.34), 287 (3.42). IR- spectrum (film), ν , cm^{-1} ., 1612, 1464, 1441, 1408, 1315, 1302, 1248, 1207, 1157, 1099, 1059, 966, 949, 880, 818, 702, 673, 592, 579, 546. Found, %: C 28.36; Br 21.50; Cl 9.90; F 40.44. M^+ 373.8732. C_9BrClF_8 . Calculated, %: C 28.79; Br 21.28; Cl 9.44; F 40.48. M^+ 373.8739.

The co-pyrolysis reactions of polyfluoroarenethiols in a flow system

The co-pyrolysis reaction of thiol **8** with Br_2 was made in a quartz tube (reactor with the sizes 400x20mm), that was being heated in a electric tube heater. Before starting, the system was blowed off with argon. The supplement of bromine and thiol **8** into the reactor was carried out synchronously from the separate dropping funnels in the flowing argon (~ 3 l/hour). Before starting the thiol **8** was melt. The products of bromination were collected in a receiving flask cooled with ice water. Afterwards the temperature of the reaction mixture was adjusted to room temperature, and the reaction mixture was treated with a sodium sulphite solution to remove the bromine and then it was steam distilled. The resulting solid product was separated from the water and dried over CaCl_2 and analyzed by ^{19}F NMR and GLC methods. The results are shown in the table 2.

Table 2.

# Entry	Compound 8 , g (mmole)	Bromine, g (mmole)	Molar ratio of thiol to Br_2	T, °C	The yield of mixture, g	Co (yield prodt GLC,
1	43.50 (200.85)	88.10 (551.54)	2.75	350	22.83 ^A	92.
2	4.07 (18.79)	8.77 (54.81)	2.92	450	4.24	71.
3	2.75 (12.70)	9.36 (58.50)	4.61	550	2.95	21.
4	3.04 (14.04)	13.80 (86.60)	6.17	650	2.94	22.

^A The distillation residue was extracted with CHCl_3 3x20 ml, and after boiling – down on a rotary evaporator there was prepared 31.14 g. with 56% content of thiol **8** (according to GLC data).

5,6 - Dibromooctafluoroindane (15). The reaction was made in a flow reactor by analogy with copyrolysis of thiol **8** with bromine. From 9.70 g. (26.00 mmole) of thiol **13** and 18.38g. (114.88 mmole) of Br₂ at ~500°C there was prepared 9.90 g. of product. This product content 98% of the compound **15** according to GLC, with the yield – 85%.

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