

## SUBSTITUTION OF THIOL GROUPS IN POLYFLUOROARENETHIOLS FOR CHLORINE AND BROMINE ATOMS. PRODUCTION OF CHLORO- AND BROMOPOLYFLUOROARENES

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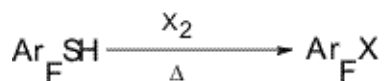
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Chlorine-containing and bromine-containing polyfluoroarenes are major raw materials used in the production of a broad spectrum of polyfluoroaromatic substances with various functional groups [1]. Yet, only the most simple chloro- and bromopolyfluorobenzenes are rather easily accessible (chloro- and bromopentafluorobenzene, dibromotetrafluorobenzenes).

It is well known that chloropentafluorobenzene (**1**) is formed (with yield 20%), along with hexafluorobenzene (21%), and polychlorofluorobenzenes, when hexachlorobenzene is heated with potassium fluoride at 450-500°C [2]. In order to produce (**1**) it also was proposed to chlorinate pentafluorobenzene with the help of Cl<sub>2</sub> [3], HCl or NaCl [4] in the presence of SbF<sub>5</sub> or using a complex of chlorofluorosulfate with SbF<sub>5</sub> [5]. Through the action of bromine on pentafluorobenzene in 65% oleum [6] or in 20% oleum in the presence of AlBr<sub>3</sub> bromopentafluorobenzene (**2**) was produced (yield 81%) [7]. Under similar conditions tetrafluorobenzenes are brominated to their dibromo-derivatives (yield 38-78%) [8, 9]. However, the attempts to chlorinate 1,2,4,5-tetrafluorobenzene through the action of SO<sub>2</sub>Cl<sub>2</sub> in 65% oleum did not meet success [10].

Having in mind to develop a general method for the production of chloro- and bromopolyfluoroarenes and their heteroanalogues, we investigated the possibilities for easy and sufficiently selective nucleophilic substitution of thiol groups in polyfluoroarenes [11] for chlorines or bromines.

We have shown that during the co-pyrolysis of polyfluoroarenethiols with chlorine or bromine in a flow-through system at 300-650°C the substitution of thiol groups for chlorines or bromines occurs resulting in the formation of related halogen-containing polyfluoroarenes (diagram 1) [12].

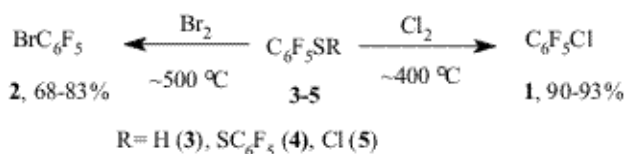


X = Cl, Br

### Diagram 1

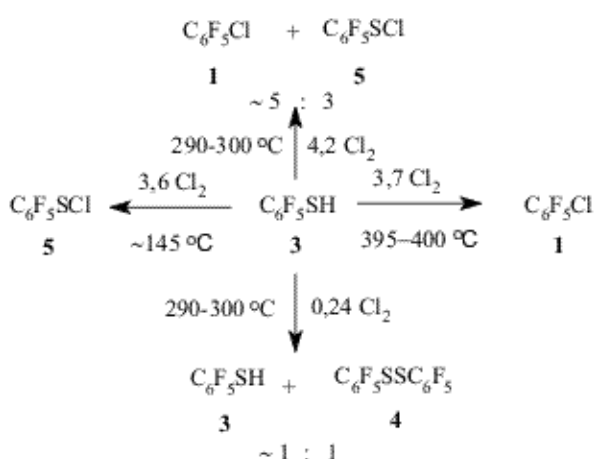
The method provides with good yields a simple route to a wide spectrum of various chloro- and bromopolyfluoroarenes. While so doing the process occurs with high selectivity making it possible to synthesize individual isomeric substances.

The co-pyrolysis of pentafluorobenzenethiol (**3**) with chlorine or bromine results in the formation of substances (**1**) or (**2**). Decafluorodiphenyldisulphide (**4**) and pentafluorobenzenesulphenylchloride (**5**) also undergo similar conversions under the action of Cl<sub>2</sub> (diagram 2) [12].



### Diagram 2

At lower temperatures ~145°C the reaction between thiol (**3**) and Cl<sub>2</sub> results in high yield of sulphenylchloride (**5**) with only small admixture of substance (**1**), while at 290-300°C and decreased chlorine consumption ((**3**):Cl<sub>2</sub> ~ 4:1) the reaction mixture contains non-reacted thiol (**3**) and disulphide (**4**), their mole ratio being ~1:1, and trace amounts of substance (**1**). If at 290-300°C the mole ratio of thiol (**3**) to Cl<sub>2</sub> is ~ 2:1 the process results in substances (**3**), (**4**) and (**5**) produced with mole ratio ~1:4:17 [12]. The further rise in Cl<sub>2</sub> consumption ((**3**):Cl<sub>2</sub> ~ 1:4) brings about to formation a blend of substance (**1**) (major product) and sulphenylchloride (**5**) ((**1**):(**5**) ~ 5:3) (diagram 3) [12].



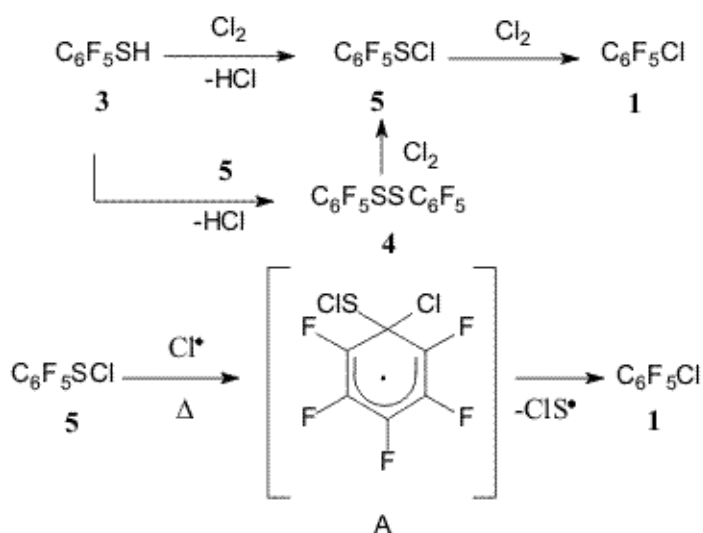
### Diagram 3

Judging by the data of chromato-mass-spectrometry the pyrolysis of sulphenylchloride (**5**) (at 395°C) results in the formation of substance (**1**) and disulphide (**4**), and, to a lesser extent, in that of decafluorodiphenylsulphide and decafluorodiphenyltrisulphide [12]. Recently the formation of substance (**1**) with quantitative elimination of elemental sulfur from substance (**5**) at 700-750°C (10-13

Pa, 3.5 h) was reported [13]. At 405-410°C disulphide (**4**) reacts with Cl<sub>2</sub> to give substance (**1**) with high yield [12].

The maximal yield of substance (**2**) in co-pyrolysis of thiol (**3**) with Br<sub>2</sub> (1:2,7) is achieved at temperatures higher (500°C) than that of substance (**1**) formation when thiol (**3**) reacts with Cl<sub>2</sub> (400°C). Either drop or rise in the reaction temperature results in lower yields of the target product in the reaction between thiol (**3**) and Br<sub>2</sub>. The yield of substance (**1**) decreases with the amount of Br<sub>2</sub> taken for the reaction. Disulphide (**4**) and Br<sub>2</sub> at 500°C produce substance (**2**) as well [12].

Reasoning from the above data on the co-pyrolysis of thiol (**3**) with Cl<sub>2</sub> at various conditions a mechanism of the substance (**1**) formation was suggested that involved initial conversion of thiol (**3**) under the action of Cl<sub>2</sub> to give sulphenylchloride (**5**). The latter reacts with Cl<sub>2</sub> to form substance (**1**). Sulphenylchloride (**5**) in the presence of thiol (**3**) may form disulphide (**4**) [14], the latter is then converted to substance (**1**) under the action of Cl<sub>2</sub>. According to [15] at first disulphide (**4**) reacts with Cl<sub>2</sub> giving sulphenylchloride (**5**). The latter therefore may perform as an intermediate product on the way from thiol (**3**) and disulphide (**4**) to substance (**1**) (diagram 4). However, one must not rule out the possibility of direct substitution of HS or C<sub>6</sub>F<sub>5</sub>SH groups for chlorines in substances (**3**) and (**4**).



**Diagram 4**

The replacement of sulfur-containing functional groups by chlorines or bromines at high temperature apparently involves the formation of an intermediate radical -complex (**A**) followed by delimitation of the sulfur-containing functional group. The conversion of disulphide (**4**) to pentafluorobenzene sulphenylbromide under the action of hydrogen bromide [16] may serve as a guide for predicting similar conversions of substances (**3**) and (**4**) to pentafluorobenzene sulphenylbromide, and its further conversion to substance (**2**) under the action of Br<sub>2</sub> at the conditions of reaction between thiol (**3**) with Br<sub>2</sub>. One may also assume the existence of similar mechanisms of the substitution of sulfur-containing functional groups for chlorines or bromines in the process of other polyfluoroarenethiols conversion.

The substitution of RS groups by chlorines are not in conflict with the data on C-X binding energies in  $C_6H_5X$  molecules, here X = SH (355.5 kJ/mole), F (510.8 kJ/mole), Cl (396.9 kJ/mole), H (457.6 kJ/mole),  $CF_3$  (448.8 kJ/mole) [17], C-S bond being the less strong. The results of the comparison with C-Br binding energies (328.7 kJ/mole) in  $C_6H_5Br$  are not so obvious [17].

It is conceivable that in the formation of polyfluorobromoarenes the substitution of BrS (and ArFSH) groups for bromines acts its part, if we assume downtrend in CArF-SX (X = Br, S-ArF) binding energy depending on the nature of X as to compare with the binding energy of ArF-SH. Thus, when passing from benzenethiol to methylthiobenzene and diphenylsulphide the CAr-S binding energy tends to go down [17].

The co-pyrolysis of 2,3,5,6-tetrafluorobenzenethiol with  $Cl_2$  or  $Br_2$  occurs smoothly resulting in 1-chloro-2,3,5,6-tetrafluorobenzene (**6**) and 1-bromo-2,3,5,6-tetrafluorobenzene (**7**) (diagram 5). When so doing, the replacement of hydrogens by halogens in the ring was never observed in fact [12].

Similar process has place as well for other thiol (**3**) derivatives that contain chlorines, bromines or trifluoromethyl groups in para-position in their tetrafluorobenzene rings. The co-pyrolysis of 4-chlorotetrafluorobenzenethiol with chlorine at 400<sup>o</sup>C resulted in 1,4-dichlorotetrafluorobenzene (**8**), and that of 4-bromotetrafluorobenzenethiol with bromine at 500<sup>o</sup>C gave 1,4-dibromotetrafluorobenzene (**9**). Both *p*-chloro- and *p*-bromoheptafluorotoluenes (**10**) and (**11**) were also synthesized from 4-trifluoromethyl 2,3,5,6 tetrafluorobenzenethiol (diagram 5) [12].

In the reaction of 4-trifluoromethyl-3,5,6-trifluoro-2-chlorobenzenethiol with  $Cl_2$  (400<sup>o</sup>C) the yield of 1,2-dichloro-4-trifluoromethyl-3,5,6-trifluorobenzene (**12**) was 94% (diagram 5).

It was shown that the co-pyrolysis of 2,4-bis(trifluoromethyl)-3,5,6-trifluorobenzenethiol with  $Cl_2$  at 400<sup>o</sup>C or with  $Br_2$  at 500<sup>o</sup>C results in 1-chloro-2,4-bis(trifluoromethyl)-3,5,6-trifluorobenzene (**13**) [18] and 1-bromo-2,4-bis(trifluoromethyl)-3,5,6-trifluorobenzene (**14**) relatively (diagram 5) [12].

In the similar manner 2,5-bis(trifluoromethyl)-3,4,6-trifluorobenzenethiol was used in the synthesis of 1-chloro-2,5-bis(trifluoromethyl)-3,4,6-trifluorobenzene (**15**) [18] and 1-bromo-2,5-bis(trifluoromethyl)-3,4,6-trifluorobenzene (**16**) (diagram 5) [12]. The presence of  $CF_3$  group in ortho-position to SH-group does not rule out its substitution for chlorines or bromines.

Co-pyrolysis of 5-nonafluoroindanthiol with  $Cl_2$  (at 400<sup>o</sup>C) or with  $Br_2$  (at 500<sup>o</sup>C) results in 5-chlorononafluoroindan (**17**) [18] and in 5-bromononafluoroindan (**18**) accordingly (diagram 5) [12].

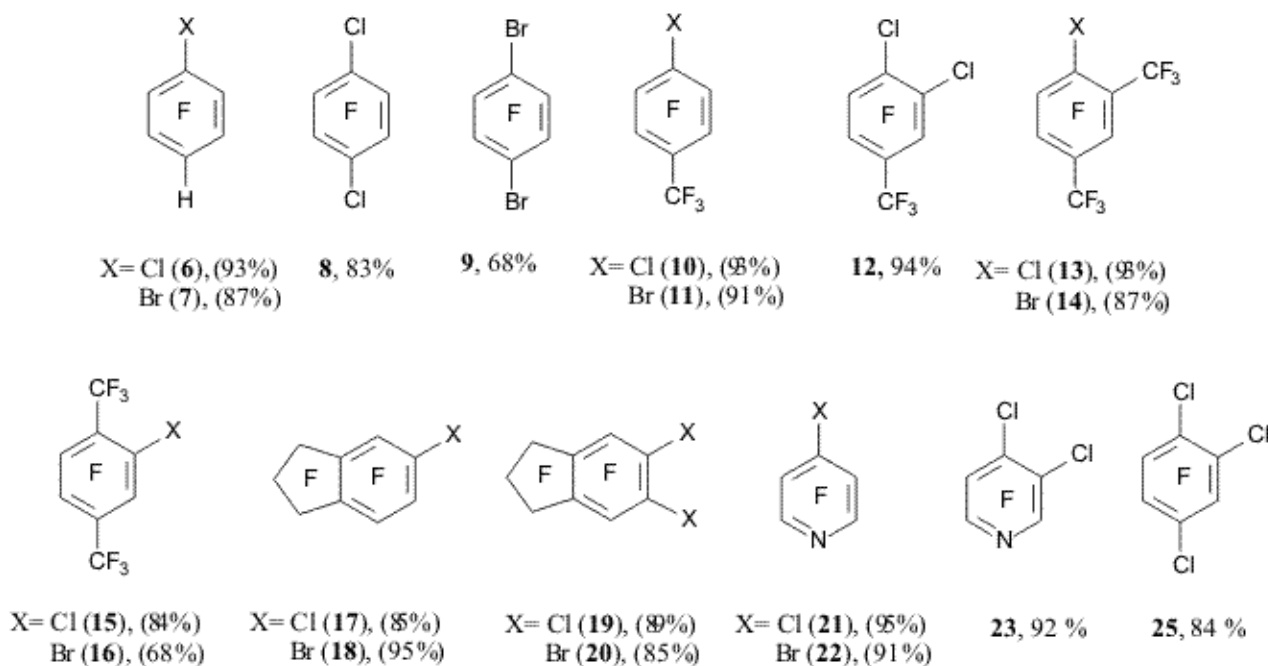
Through the action of KSH substances (**17**) and (**18**) are converted to 6-chlorooctafluoroindan-5-thiol and 6-bromo-octafluoroindan-5-thiol, those two react with  $Cl_2$  (400<sup>o</sup>C) or  $Br_2$  (500<sup>o</sup>C) giving 5,6-dichloro-octafluoroindan (**19**) and 5,6-dibromo-octafluoroindan (**20**) [19] relatively (diagram 5).

This type of hetarene conversion is exemplified by the reaction of 4-tetrafluoropyridothiol with  $Cl_2$  (400<sup>o</sup>C) or  $Br_2$  (500<sup>o</sup>C) resulting in the formation of 4-chlorotetrafluoropyridine (**21**) and 4-bromotetrafluoropyridine (**22**) respectively [12] (diagram 5). 3-chlorotrifluoropyrido-4 thiol is also smoothly chlorinated at 400<sup>o</sup>C resulting in 3,4-dichloro-2,5,6 trifluoropyridine (**23**) (diagram 5).

It was shown that 2,5-dichloro-3,4,6-trifluorobenzenethiol (**24**) reacts with Cl<sub>2</sub> (400°C) to form 1,2,4-trifluorotrichlorobenzene (**25**) (diagram 5) [20]. Thiol (**24**) was synthesized from substance (**8**) through the action of KSH [20].

Substance (**8**) being not easily available from technical standpoint, a more practicable method for the product (**25**) manufacture was developed. The method makes use of easily available technical-grade mixture of isomeric dichlorotetrafluorobenzenes that is produced through the reaction of hexachlorobenzene with KF. The mixture consists mainly of *m*-dichlorotetrafluorobenzene besides of *o*- and *p*-isomers [2].

By the action of KSH on the dichlorotetrafluorobenzene mixture (with ratio *m*: *o*: *p* = 44: 10: 10) 2,4-, 2,5- and 3,4-dichlorotrifluorobenzenethiols were produced, their ratio being ~43: 10: 10, judging by their NMR<sup>19</sup>F spectra. The latter is close to the initial ratio of isomeric dichlorotetrafluorobenzenes. Orientation of *m*- and *o*-dichlorotetrafluorobenzenes in their reaction with KSH is in good conformity with literature data on those substances nucleophilic substitution when reacted with sodium methylate [21]. The co-pyrolysis of thus produced dichlorotrifluorobenzenethiol mixture with Cl<sub>2</sub> at 400°C results in 1,2,4-trifluorotrichlorobenzene (**25**) with good yield (diagram 5) [20].



### Diagram 5

Therefore, various chloro- and bromopolyfluoroarenes were produced through the co-pyrolysis of polyfluoroarenethiols with chlorine and bromine. A number of novel chlorine- or bromine-containing derivatives of perfluoroarenes are synthesized. Some of thus produced substances are practically inaccessible when using any other methods. It also should be marked that the method developed by us is well applicable in the synthesis of hardly accessible *o*-dichloroderivatives of perfluoroarenes and trifluorotrichlorobenzene (**25**).

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