

Dedicated to Professor H.-J Frohn (University of Duisburg, BRD)
on occasion of his 60th anniversary

Organofluorine Sulfur-containing Compounds: V.* Joint Pyrolysis with Chlorine or Bromine of Polyfluoroarenethioles, Polyfluorohetarenethioles, and Their Derivatives

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Abstract—Joint pyrolysis with chlorine and bromine of polyfluoroarenethiols, -hetarenethiols, and their derivatives at 300–650°C furnished polyfluorocompounds containing chlorine and bromine.

Polyfluoroarenes containing chlorine and bromine are important material for preparation of versatile polyfluoroaromatic compounds with various functional groups [2]. At the same time only the simplest representatives of chloro- and bromopolyfluoroarenes are relatively accessible compounds (chloro- and bromopentafluorobenzenes, dibromotetrafluorobenzenes).

It is known that chloropentafluorobenzene (**I**) (yield 20%) is obtained alongside the hexafluorobenzene (21%) and polychlorofluorobenzenes from the hexachlorobenzene by heating with potassium fluoride at 450–500°C [3]. Recently the use of the phase-transfer catalysts was suggested for reducing the process temperature [4]. In reaction of the hexabromobenzene with the potassium fluoride bromopentafluorobenzene (**II**) (yield 6%) formed alongside the isomers of dibromotetrafluorobenzene (yield 8–9%) and tribromotrifluorobenzene (yield 4–5%) [5].

The replacement of hydrogen by chlorine in the pentafluorobenzene was studied effected by Cl_2 [6], HCl , or NaCl [7] in the presence of SbF_5 or SbF_5 complex with sulfur chloride fluoride [8]. The reaction resulted in compound **I**. The preparation of compound **II** was performed by treating the pentafluorobenzene with bromine in 65% [9] or 20% oleum in the presence of AlBr_3 (yield 81%) [10]. Under similar conditions the tetrafluorobenzenes were brominated into dibromo derivatives (yield 38–78%) [11, 12]. At the same time the attempt to chlorinate the 1,2,4,5-tetrafluorobenzene using SO_2Cl_2 in 65% oleum was unsuccessful [13]. The preparation of 1,2,4-tribromotrifluorobenzene from 1,2,4-trifluorobenzene was performed by action of Br_2 in the presence of aluminum [14].

* For communications IV, see [1].

The substitution of a hydrogen by bromine in 3-*H*-heptafluorotoluene was described performed in 60% oleum to obtain 3-bromoheptafluorotoluene [15]. However the use of oleum as the medium may cause difficulties in halogenation with the goal of replacing the hydrogen in the *para*-position in polyfluorobenzenes having trifluoromethyl substituents since the latter exert a destabilizing effect on the carbocation center [16, 17] and are prone to hydrolysis under the action of oleum [18, 19]. In turn at the use of the system Al^+Br_2 it is presumable that the bromine would substitute the fluorine atoms in the side chain as is the case in the reaction of the octafluorotoluene with AlBr_3 [17].

Another approach to the synthesis of chloro- and bromopolyfluoroarenes consisted in replacement of the fluorine atom by chlorine or bromine in the hexafluorobenzene at its joint pyrolysis with Cl_2 or Br_2 or with their sources at 650–740°C. The maximum yield of compound **I** was 60%, and of compound **II** 27% [20]. Also a substitution of iodine by chlorine or bromine was described occurring at heating iodopentafluorobenzene with Cl_2 or Br_2 at 120–150°C [21].

Taking into account the cited data we regarded as feasible to study an opportunity of replacing by chlorine or bromine other functional groups, in particular, thiol groups which were introduced into polyfluoroarenes easily and relatively selectively by the nucleophilic substitution [22].

It was formerly mentioned that a small amount of 4-chlorotetrafluoroacetanilide formed at treating with chlorine 4-acetamidotetrafluorothiophenol in the glacial acetic acid in the presence of water or hydrogen perox-

Table 1. Joint pyrolysis of sulfur-containing polyfluoroarenes and -hetarenes with Cl₂

Run no.	Compound (mmol; molar ratio to Cl ₂)	T, °C	Duration (min) of reagents input	Reaction products (content in mixture, %), yield, %
1	III (47.40; 3.7)	395–400	17.2	I (99.1) 90
2	III (41.90; 3.5)	290–300	14.2	I (72.4) 47 IV (5.6) 3.7 IV (54.4) 13 ^a
3	III (62.50; 4.2)	290–295	25.7	I (49.3) 58 ^b V (34.3) 35 ^b
4	III (46.60; 3.6)	~145	16.3	I (1.5) 1.8 ^b V (97.9) 98 ^b
5	III (50.30; 0.5)	290–300	1.2	I (<1) 6 ^b III (35.7) 35 ^b IV (60.7) 56 ^b
6	III (54.70; 0.5)	295–300	2.8	I (2.5) 2.5 ^b IV (84.9) 86 ^b V (11.8) 10 ^b
7	IV (20.03; 9.1)	405–410	17.7	I (99.2) 90
8	V (45.33; 4.0)	395–405	17.7	I (97.8) 93
9	VI (45.27; 4.2)	-400	18.3	VII (99.1) 93
10	X (37.00; 4.5)	390–395	16.0	XII (99.1) 93
11	IX (39.17; 3.9)	395–405	14.8	XI (100) 83
12	XX (48.47; 4.1)	400–405	19.0	XXI (99.9)

^a Still residue. ^b According to the data of ¹⁹F NMR spectroscopy.

Table 2. Joint pyrolysis of sulfur-containing polyfluoroarenes and -hetarenes with Br₂

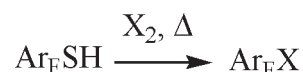
Run no.	Compound, mmol	Bromine, mmol	T, °C	Reaction product (content in mixture, %), yield, %
1	III, 5.00	5.63	500	II (94) 65
2	III, 36.90	103.19	400	II (77) 42 IV (15) 10
3	III, 36.55	99.19	500	II (97) 83
4	III, 5.00	16.88	650	II (97) 72
5	VI ^a , 36.26	120.38	500–510	VIII (97) ^b 87
6	X, 326.00	567.50	500	XIII (98) 91
7	XIV, 102.67	281.25	500–510	XV (98) 87
8	XVI, 13.33	26.88	500	XVII (97) 68
9	XVIII, 2.05	112.50	500	XIX (98) 95
10	XX, 26.56	75.19	500	XXII (96) 91
11	IV, 2.51	9.38	500	II (98) 68

^a The compound contains 0.84% of benzenethiol III as impurity.

^b In the reaction product is present 0.9% of compound II.

ide. The main reaction product was the corresponding sulfochloride [23].

We demonstrated that at the joint pyrolysis of polyfluoroarene thiols with chlorine, its sources, or with bromine in a flow system at 300–650°C the thiol group was replaced by chlorine or bromine atoms furnishing the corresponding haloderivatives of the polyfluoroarenes (Tables 1 and 2, Scheme 1). As chlorine sources SO₂Cl₂ and SOCl₂ were applied (Table 3).

Scheme 1.

This method makes it possible to obtain in an easy way a wide range of various chloro- and bromopolyfluoroarenes. Therewith the process is characterized by a high selectivity, and the yields of the target products in reactions with chlorine (400°C) or bromine (500°C) reach 68–95%; the crude reaction product obtained in this process is of 96–99% purity. The high selectivity of the process provides a possibility to synthesize isomer compounds in individual state. It should be emphasized that the use of Cl₂ is preferred as opposed to SO₂Cl₂ and especially to SOCl₂ for in reactions with Cl₂ the products were obtained in higher yields and purity (cf. data in Tables 1 and 3).

The joint pyrolysis of pentafluorobenzenethiol (III) with Cl₂ or Br₂ gave rise to compounds I and II respec-

Table 3. Joint pyrolysis of polyfluorobenzenethiols with SO₂Cl₂ and SOCl₂

Compound, mmol	SO ₂ Cl ₂ , mmol	T, °C	Reaction product (content in mixture, %), yield, %
III, 29.10	83.33	395–400	I (95) 90
VI, 33.02	101.78	395–400	VII (94) 75
X, 2 16.00	562.96	400	XII (97) 86
III, 26.75	93.03 ^a	395–405	I (82) 41 IV (11) 5.9 ^b
VI, 27.66 ^c	69.24 ^a	400–405	VII (97) 52 ^d

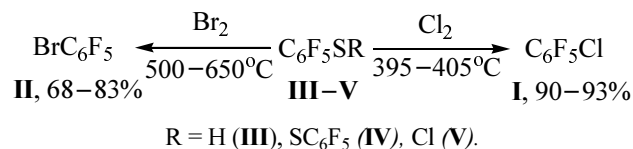
^a SOCl₂.

^b In the still residue (1.7 g) was identified disulfide IV (content 35%) by comparing the ¹⁹F NMR spectrum with that of an authentic sample.

^c The compound contains as impurity 0.8% of benzenethiol III.

^d The product contained 0.9% of compound I. In the still residue (1.7 g) was identified disulfide XXIII (content 30%) by comparing the ¹⁹F NMR spectrum with that of an authentic sample. Same as in case (b) the rest of the still residue contains presumably compounds with two polyfluorinated benzene rings.

Scheme 2.



tively. Analogous transformations occurred under the effect of Cl_2 also with decafluorodiphenyl disulfide (IV) and pentafluorobenzenesulfonyl chloride (V) (Tables 1 and 2, Scheme 2).

At decreasing the temperature of reaction between thiol III and Cl_2 to $\sim 145^\circ\text{C}$ (Table 1, run no. 4) sulfonyl chloride V was obtained in a high yield with a small impurity of compound I. Formerly sulfonyl chloride V was obtained in reaction of Cl_2 with thiol III and disulfide IV under mild conditions (-10 and 20°C respectively) [24].

In reaction of thiol III with Cl_2 at $290-300^\circ\text{C}$ and with reduced chlorine supply (III: $\text{Cl}_2 \sim 4:1$) (Table 1, run no. 5) the final reaction mixture contained unreacted thiol III and disulfide IV in a molar ratio $\sim 1:1$ alongside traces of compound I. Under similar conditions but at the ratio of thiol III to $\text{Cl}_2 \sim 2:1$ (Table 1, run no. 6) was obtained additionally sulfonyl chloride V [molar ratio (I):(V):(IV) $\sim 1:4:17$]. At further growing Cl_2 supply (III: $\text{Cl}_2 \sim 1:4$) (Table 1, run no. 3) the resulting mixture contains compound I as the main reaction product alongside sulfonyl chloride V [(I):(V) $\sim 5:3$] (Scheme 3).

On pyrolysis (395°C) sulfonyl chloride V was converted into compound I and disulfide IV, and also to a lesser degree into decafluorodiphenyl sulfide and decafluorodiphenyl trisulfide as revealed the GC-MS analysis. The formation of compound I at $700-750^\circ\text{C}$ ($10-13$ Pa, 3.5 h) with quantitative elimination of sulfur

from compound V was observed previously in [24]. Compound I was obtained in high yield from disulfide IV and Cl_2 at $405-410^\circ\text{C}$ (Table 1, run no. 7).

The maximum yield of compound II at the joint pyrolysis of thiol III with Br_2 is attained at higher temperature (500°C) (Table 2, run no. 3) than in preparation of compound I by reaction of thiol III with Cl_2 (400°C). The raising or reducing the reaction temperature of thiol III with Br_2 diminished the yield of the target product (Table 2, runs nos. 2 and 4). At the decrease in the amount of Br_2 used in the process the yield of compound II also decreases (Table 2, run no. 7). Compound II also forms from disulfide IV and Br_2 at 500°C (Table 2, run no. 11).

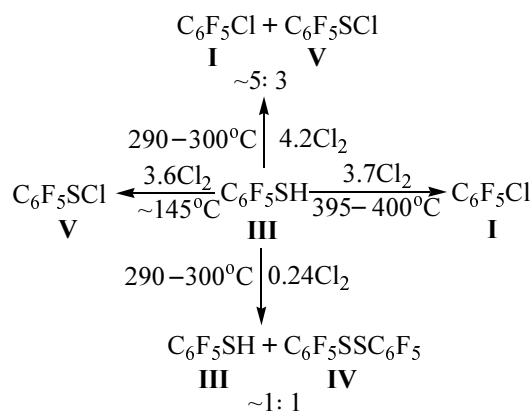
The joint pyrolysis of 2,3,5,6-tetrafluorothiophenol (VI) with Cl_2 or Br_2 cleanly afforded 1-chloro-2,3,5,6-tetra-fluorobenzene (VII) and 1-bromo-2,3,5,6-tetrafluoroben-zene (VIII) respectively. Therewith the hydrogen in the ring virtually does not suffer replacement by halogen atom (Scheme 4).

Similar processes occur with the other derivatives of benzenethiol III containing in the *para*-position a chlorine atom or a trifluoromethyl group. Thus were obtained 1,4-dichlorotetrafluorobenzene (XI), *p*-chloro- and *p*-bromoheptafluorotoluenes (XII) and (XIII) (Scheme 5).

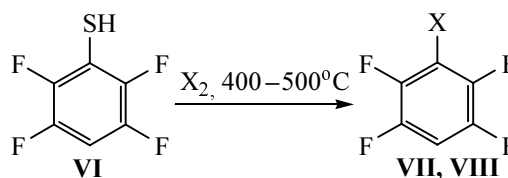
The presence of a CF_3 group in the *ortho*-position with respect to SH does not hamper the substitution of the latter by bromine (Scheme 6). In the same way from 5-nonafluoroindanethiol (XVIII) was obtained 5-bromo-nonafluoroindane (XIX).

The joint pyrolysis of 4-tetrafluoropyridinethiol (XX) with Cl_2 or Br_2 to form 4-chloro- (XXI) and 4-bromo-tetrafluoropyridine (XXII) is an example of the same

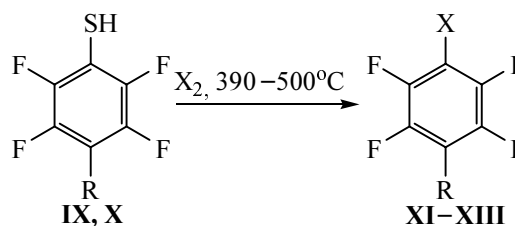
Scheme 3.



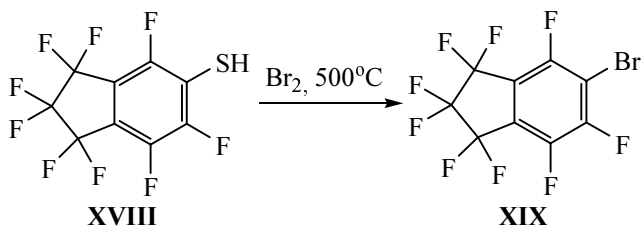
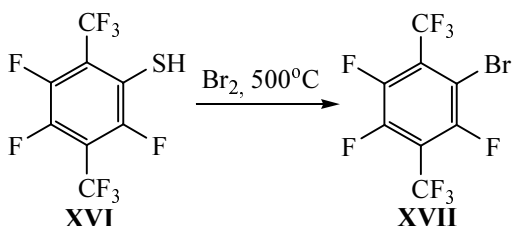
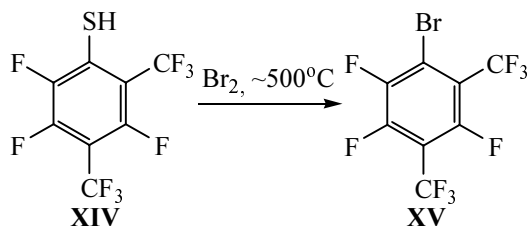
Scheme 4.



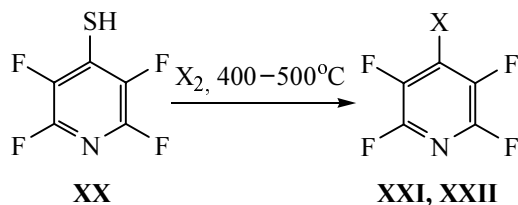
Scheme 5.



Scheme 6.



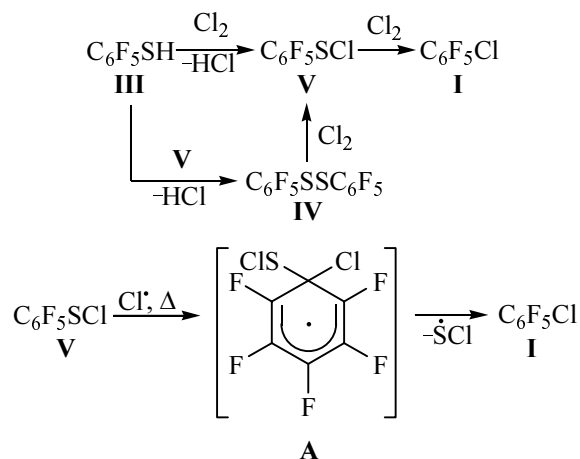
Scheme 7.



The data cited above on the joint pyrolysis of thiol **III** with Cl_2 under various conditions make it possible to suggest a scheme of compound **I** formation involving primary conversion of thiol **III** under the action of Cl_2 into sulfenyl chloride **V**. The latter then reacting with Cl_2 furnished compound **I**. In the presence of thiol **III** sulfenyl chloride **V** can give disulfide **IV** [25] which treated with Cl_2 also is converted into compound **I**. Therewith according to [23] it is presumable that disulfide **IV** with chlorine first transforms into sulfenyl chloride **V**. Thus the latter might be an intermediate on the route to compound **I** from thiol **III** and disulfide **IV** (Scheme 8). However the direct replacement of SH and $\text{C}_6\text{F}_5\text{SS}$ groups with chlorine in compounds **III** and **IV** cannot be completely disregarded.

Similar schemes were earlier suggested for formation of RSCl and RSSR from RSH and Cl_2 [26]. The replacement of the sulfur-containing function with chlorine and bromine atoms at the high temperature involves appar-

Scheme 8.



ently an intermediate formation of a radical σ -complex **A** followed by elimination of the sulfur-containing function. The known example of conversion of decafluorodiphenyl disulfide at treatment with hydrogen bromide into pentafluorobenzene sulfenyl bromide [27] may underlie the suggestion of analogous conversion of polyfluorodiaryl disulfides into polyfluoroarenesulfenyl bromides effected by HBr under the conditions of joint pyrolysis. Poly-fluoroarenesulfenyl bromides may also arise alongside polyfluorodiaryl disulfides under the action of bromine on the polyfluoroarene thiols.

Analogous schemes of replacement of the sulfur-containing function by chlorine and bromine may be assumed for conversions observed with the other polyfluoroarene thiols under the action of Cl_2 or Br_2 . The processes where chlorine sources are applied are apparently more complex.

The substitution of RS groups by chlorine atom does not contradict the data on the bond energy of the C-X bonds for compounds $\text{C}_6\text{H}_5\text{X}$ where $\text{X} = \text{SH}$ (355.5 kJ/mol), F (510.8 kJ/mol), Cl (396.9 kJ/mol), H (457.6 kJ/mol), CF (448.8 kJ/mol) [28]. The weakest bond is C-S . The comparison with the bond energy of C-Br in $\text{C}_6\text{H}_5\text{Br}$ (328.7 kJ/mol) is less obvious [28].

Presumably, in formation of polyfluorobromoarenes is involved the substitution with bromine of groups BrS (and also $\text{Ar}_\text{F}-\text{SS}$) if it is possible to suggest the decreased bond energy $\text{C}_{\text{Ar}}-\text{SX}$ ($\text{X} = \text{Br}, \text{S}-\text{Ar}_\text{F}$) caused by X as compared to the energy of the $\text{C}_{\text{Ar}}-\text{SH}$ bond. For instance, a trend to decreasing bond energy of $\text{C}_{\text{Ar}}-\text{S}$ is observed in going from benzenethiol to methylthiobenzene and to diphenyl sulfide [28]. The methyl disulfide radical (MeSS) was described as more resonance-stabilized than

methylthiyl one (MeS), and also was mentioned the higher reactivity of SH radical compared to that of SSH [29].

EXPERIMENTAL

^{19}F and ^1H NMR spectra were registered on spectrometer Bruker WP-200SY (at 188 and 200 MHz respectively) from solutions in CCl_4 . The chemical shifts are reported downfield from C_6F_6 and TMS; internal references are C_6F_6 and HMDS (0.04 ppm from TMS) respectively. IR spectra were recorded on spectrophotometer Vector-22 from thin film or pellets with KBr. Mass spectra were measured on Finnigan MAT-8200 instrument, temperature at sample admission 70–110°C, nominal energy of ionizing electrons 70 eV; mass spectra were used for evaluation of the precise molecular mass and of the composition of compounds synthesized.

GLC analysis was carried out on chromatographs LKhM-72 and HP-5820 equipped with katharometer. LKhM-72: columns 4000×4 mm, solid carrier Chromosorb W, liquid stationary phases: silicone SKTFT-50, silicone SKTFV-803, methylsilicone SE-30, and fluorosilicone QF-1 (the ratio of liquid phase to solid carrier 15:100, oven temperature 50–250°C, detector temperature 250°C, helium flow rate 10 ml/min). HP-5820: column 30000×0.5 mm coated with copolymer HP-5, oven temperature 40–280°C, detector temperature 280°C, helium flow rate 5 ml/min.

GC-MS procedure was performed on an instrument equipped with a mass-selective detector HP G1801A. Ionizing electrons energy was 70 eV. The separation of compounds was performed on a column 30 m long with the internal diameter of 0.25 mm, coated with a film of copolymer HP-5 0.25 μm thick, carrier gas helium at a flow rate 1 ml/min, oven temperature 50–280°C, temperature of the ion source 173°C.

Benzenethiols III and VI. To a solution of 1 mol of hexafluorobenzene or pentafluorobenzene in 1000 ml of DMF was added at stirring within 7–10 min at room temperature a solution of KSH prepared by passing hydrogen sulfide through a solution of 2 mol of KOH in 350 ml of ethylene glycol till gain in weight of 64 g. At the addition of the KSH solution the reactor was cooled with water to maintain the temperature of the reaction mixture below 45–55°C. Then the reaction mixture was stirred for 4–5 h till it cooled to 25–28°C, and then it was poured into 3000 ml of ~10% hydrochloric acid. The organic layer was separated, dried over CaCl_2 , and analyzed by GLC. The reaction products were subjected to a vacuum distillation at 12–14 mm Hg, yield 85–90%.

The synthesis of compound **XIV** is described in [30]. The other sulfur-containing compounds (**IX**, **X**, **XVI**, **XVIII**, **XX**) were prepared as in [31].

2,5-Bis(trifluoromethyl)-3,4,6-trifluorobenzenethiol (XVI). ^1H NMR spectrum, δ , ppm: 4.12 quintet [$J(\text{H-F}^6)$ 8.5, $J(\text{H-2-CF})$ 8.5 Hz]. ^{19}F , δ , ppm: 25.5 m ($2\text{F}^{3,4}$), 55.2 d.d [F^6 , $J(\text{F}^6\text{-5-CF})$ 24, $J(\text{F}^6\text{-H})$ 8.5 Hz], 105.1 t [5-CF , $J(5\text{-CF-F}^4)$ 24, $J(5\text{-CF-F}^6)$ 24 Hz], 105.3 d.d (2-CF , $J(2\text{-CF-F}^5)$ 28, $J(2\text{-CF-H})$ 8.5 Hz). Found: $[M]^+$ 299.9646. $\text{C}_8\text{HF}_9\text{S}$. Calculated: M299.9655.

Joint pyrolysis of sulfur-containing arenes and hetarenes with halogens and their sources. The process was carried out in a quartz pipe (400×20 mm) heated in an electric pipe oven. The initial compound was charged into a dropping funnel (the compound was melted if necessary) connected to the reactor. Before the experiment the system was flushed with argon. The liquid compounds were supplied simultaneously with the flow of Cl_2 . The rate of the chlorine flow was ~44 g/h; the duration of reagents input was mentioned in Table 1. In experiments with chlorine sources and also with Br_2 the reagents were charged into the reactor from separate dropping funnels in an argon flow (~5 l/h); in this case the rate of polyfluoroarene (hetarene) input was 20–25 g/h (Tables 2 and 3). On completion of initial compound input into the reactor the supply of Cl_2 , Br_2 , or SO_2Cl_2 and SOCl_2 was also finished. In some runs of joint pyrolysis with chlorine the reaction products were collected under a layer of ice water (Table 1, runs nos. 1, 2, 7–12), then the collected mixture was warmed to room temperature, separated, and subjected to steam distillation. The distillate obtained was separated from water, dried over CaCl_2 , and analyzed by GLC, GC-MS, and NMR methods. In other cases the products were collected in a receiver cooled with liquid nitrogen (Table 1, run no. 3–6). Then the products were slowly defrosted and analyzed by NMR spectroscopy.

In the runs of the joint pyrolysis with bromine or the chlorine sources the reaction products were collected in a receiver cooled with ice water. Then the reaction mixture was warmed to room temperature and subjected to steam distillation. In the experiments with bromine the reaction mixture was preliminary treated with a solution of sodium sulfite to remove the excess bromine. After distillation the distillate obtained was separated from water, dried with CaCl_2 , and analyzed by GLC and NMR methods.

The results of joint pyrolysis are presented in Tables 1–3.

The formation of compounds **I**, **IV**, and **V** was confirmed by ^{19}F NMR spectra, by GC-MS data, and by comparison with the published data on chemical shifts and coupling constants in the ^{19}F NMR spectra [25, 32].

1-Chloro-2,3,5,6-tetrafluorobenzene (VII). IR spectrum, cm^{-1} : 715, 846, 920, 937, 1136, 1178, 1248, 1455, 1515, 1635, 3093. ^1H NMR spectrum, δ , ppm: 7.05 t.t [$J(\text{H}-\text{F}^{3,5})$ 9.9, $J(\text{H}-\text{F}^{2,6})$ 7.2 Hz]. ^{19}F NMR spectrum, δ , ppm: 21.7 m ($\text{F}^{2,6}$), 24.9 m ($\text{F}^{3,5}$) [33]. Found $[M]$ 183.9708. C_6HClF_4 . Calculated M 183.9703.

1-Bromo-2,3,5,6-tetrafluorobenzene (VIII). IR spectrum, cm^{-1} : 699, 847, 863, 913, 929, 1132, 1176, 1237, 1445, 1501, 1626, 3085. ^1H NMR spectrum, δ , ppm: 7.10 t.t [$J(\text{H}-\text{F}^{3,5})$ 9.5, $J(\text{H}-\text{F}^{2,6})$ 7.0 Hz]. ^{19}F NMR spectrum, δ , ppm: 24.8 m ($\text{F}^{3,5}$), 29.1 m ($\text{F}^{2,6}$). Found $[M]$ 227.9205. C_6HBrF_4 . Calculated M 227.9198.

1,4-Dichlorotetrafluorobenzene (XI). mp 48.5–51°C (publ.: mp 50.5–51.5°C [34]). ^{19}F NMR spectrum, δ , ppm: 22.4 s [35].

4-Chloroheptafluorotoluene (XII). IR spectrum, cm^{-1} : 717, 845, 988, 1156, 1188, 1334, 1496, 1646. ^{19}F NMR spectrum, δ , ppm: 23.4 m ($\text{F}^{2,6}$), 24.1 m ($\text{F}^{3,5}$), 106.6 t [CF , $J(\text{F}^5-\text{F}^a)$ 22 Hz] (av. 22.6, 23.7, and 105.3 respectively [36]). Found $[M]$ 251.9600. C_7ClF_7 . Calculated M 251.9577.

4-Bromoheptafluorotoluene (XIII). IR spectrum, cm^{-1} : 716, 818, 984, 1155, 1183, 1331, 1499, 1645. ^{19}F NMR spectrum, δ , ppm: 23.1 m ($\text{F}^{2,6}$), 31.7 m ($\text{F}^{3,5}$), 105.5 t [CF , $J(\text{F}^5-\text{F}^a)$ 22 Hz] [37]. Found $[M]$ 295.9096. C_7BrF_7 . Calculated M 295.9072.

1-Bromo-2,4-bis(trifluoromethyl)-3,5,6-trifluorobenzene (XV). IR spectrum, cm^{-1} : 870, 946, 1165, 1200, 1240, 1340, 1370, 1455, 1490, 1610, 1635. ^{19}F NMR spectrum, δ , ppm: 37.1 quintet, all lines broadened (F^5), 37.9 d.d [F^6 , $J(\text{F}^6-\text{F}^5)$ 22, $J(\text{F}^6-\text{F}^5)$ 12.5 Hz], 49.8 q.q.d.d [F^5 , $J(\text{F}^5-2-\text{CF})$ 34.5, $J(\text{F}^5-4-\text{CF})$ 23, $J(\text{F}^5-\text{F}^6)$ 12.5, $J(\text{F}^5-\text{F}^5)$ 1.5 Hz], 105.5 d.d [4-CF, $J(4-\text{CF}-\text{F}^3)$ 24, $J(4-\text{CF}-\text{F}^5)$ 23 Hz], 105.9 d [2-CF, $J(2-\text{CF}-\text{F}^5)$ 34.5 Hz]. Found, %: C 27.54, 27.72; Br 22.60, 22.90; F 48.86, 49.18. $[M]$ 345.9038. C_8BrF_9 . Calculated, %: C 27.67; Br 23.05; F 49.28. M 345.9040.

1-Bromo-2,5-bis(trifluoromethyl)-3,4,6-trifluorobenzene (XVII). IR spectrum, cm^{-1} : 875, 955, 1075, 1155, 1170, 1190, 1310, 1375, 1450, 1475. ^{19}F NMR spectrum, δ , ppm: 26.9 q.d.d [F^3 , $J(\text{F}^3-2-\text{CF})$ 33, $J(\text{F}^3-\text{F})$ 19, $J(\text{F}^5-\text{F})$ 13.5 Hz], 31.3 q.d [F , $J(\text{F}-5-\text{CF})$ 23.5, $J(\text{F}-\text{F}^3)$ 19 Hz], 61.1 q.d [F , $J(\text{F}-5-\text{CF})$ 22, $J(\text{F}-\text{F}^3)$ 13.5 Hz], 104.8 d [2-CF₃, $J(2-\text{CF}_3-\text{F}^3)$ 33 Hz], 104.9 d.d [5-CF₃, $J(5-\text{CF}_3-\text{F})$ 23.5, $J(5-\text{CF}_3-\text{F})$ 22 Hz]. Found, %: C 27.77, 27.99;

Br 22.82, 22.90; F 49.08, 49.32. $[M]$ 345.9048. C_8BrF_9 . Calculated, %: C 27.67; Br 23.05; F 49.28. M 345.9040.

5-Bromononafluoroindane (XIX). ^{19}F NMR spectrum, δ , ppm: 23.1 d.d.t [F^7 , $J(\text{F}^7-\text{F})$ 21, $J(\text{F}^7-\text{F}^4)$ 19, $J(\text{F}^7-1-\text{CF}_2)$ 7 Hz], 32.1 quintet [F , $J(\text{F}-1,3-\text{CF}_2)$ 4 Hz], 48.9 d, components broadened [F , $J(\text{F}-\text{F}^7)$ 21 Hz], 54.0 d.t.d [F^4 , $J(\text{F}^4-\text{F}^7)$ 19, $J(\text{F}^4-3-\text{CF}_2)$ 7, $J(\text{F}^4-\text{F})$ 5 Hz], 54.6 br.s [1(3)-CF₂], 55.0 br.s [1(3)-CF₂] [38].

4-Chlorotetrafluoropyridine (XXI). IR spectrum, cm^{-1} : 579, 698, 915, 956, 1241, 1474, 1498, 1633. ^{19}F NMR spectrum, δ , ppm: 21.0 m (F^3), 74.0 m (F) [39]. Found $[M]$ 184.9653. $\text{C}_5\text{ClF}_4\text{N}$. Calculated M 184.9655.

4-Bromotetrafluoropyridine (XXII). IR spectrum, cm^{-1} : 565, 697, 864, 950, 1232, 1463, 1481, 1622. ^{19}F NMR spectrum, δ , ppm: 27.6 m (F^3) 74.4 m (F). Found $[M]$ 228.9146. $\text{C}_5\text{BrF}_4\text{N}$. Calculated M 228.9150.

2,2',3,3',5,5',6,6'-Octafluorodiphenyl disulfide (XXIII). ^1H NMR spectrum, δ , ppm: 7.15 t.t [$J(\text{H}-\text{F}^3)$ 9.2, $J(\text{H}-\text{F}^{2,6})$ 7.2 Hz] [40]. ^{19}F NMR spectrum, δ , ppm: 25.0 m (F^3), 29.5 m (F).

Thermolysis of sulfonyl chloride (V) was carried out in a quartz pipe (400 × 20 mm) heated in an electric pipe oven. From a dropping funnel was uniformly supplied into the reactor 30.1 mmol of compound **V** within 11 min in an argon flow (5–6 l/h) at ~395°C. We obtained 6.4 g of reaction products that according to NMR spectra contained no initial compound **V**. From 5.8 g of the crude product by steam distillation we obtained 3.4 g of a mixture containing according GC-MS data 66.7% of compound **I**, 27.9% of disulfide **IV**, and also 2.0% of decafluorodiphenyl sulfide, and 0.3% of decafluorodiphenyl trisulfide. The estimated percent content of compounds **I** and **IV** in this mixture is consistent with the ^{19}F NMR spectrum. The composition of the still residue was not analyzed.

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