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Fluoro-organic sulphur-containing compounds. IV. Haloalkylation reactions of polyfluorinated thiophenols with $CHal_3R$ compounds in the presence of $AlCl_3$ Synthesis and some reactions of polyfluorophenylthio derivatives of halomethanes[1]

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Abstract

The haloalkylation of polyfluorothiophenols with $CHal_3R$ compounds (Hal=Cl, F; R=Cl, H, C_6H_5, C_6F_5) in the presence of $AlCl_3$ has been investigated. The reactions of polyfluorothiophenols 4-XC_6F_4SH (X=F, H, CH_3) with CCl_4 and $AlCl_3$ lead to dichloromethane derivatives (4-$XC_6F_4S)_2CCl_2$. The reaction of pentafluorothiophenol with $CHCl_3$ in the presence of $AlCl_3$ gave $(C_6F_5S)_2CHCl$ and $(C_6F_5S)_3CH$ (ratio by GLC 8:1). In the reaction of pentafluorothiophenol with $ArCX_3$ (Ar=C_6H_5, C_6F_5; X=Cl, F) compounds $(C_6F_5S)_2CClAr$ (Ar=C_6H_5, C_6F_5) together with $C_6F_5SCCl_2Ar$ (Ar=C_6H_5, C_6F_5) are formed. Peculiarities of these processes are considered. The hydrolysis of $(C_6F_5S)_2CCl_2$ and $C_6F_5SCCl_2C_6H_5$ leads to bis(pentafluorophenyl)dithiocarbonate and the *S*-(pentafluorophenyl) ester of thiobenzoic acid, respectively. Compounds $(C_6F_5S)_2CF_2$ and $(C_6F_5S)_2CClF$ were obtained from $(C_6F_5S)_2CCl_2$ by the action of caesium fluoride. An attempt to produce these compounds through the action of antimony fluorides was unsuccessful. The compounds $(C_6F_5S)_2CCl_2$, $(C_6F_5S)_2CClF$ and $(C_6F_5S)_2CF_2$ are stable to oxidation. The reactions of $(C_6F_5S)_2CF_2$ and $(C_6F_5S)_2CClF$ with CrO_3 in acetic acid proceeded only with the formation of mono-sulphoxide. The conversion is low in the former case. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polyfluorothiophenols; Haloalkylation reaction; $AlCl_3$; Polyfluorophenylthiohalomethanes

1. Introduction

We have previously described the haloalkylation reaction of polyfluoroaromatic amino and hydroxy derivatives with compounds of the formula $CHal_3R$ (Hal=Cl, F; R=Cl, C_6H_5, C_6F_5) in the presence of $AlCl_3$. The reaction proceeds at the heteroatom and leads to compounds of various classes. The products of the reactions of polyfluoroaromatic amines with $CCl_4/AlCl_3$ have been shown to be polyfluoroaromatic carbonimidoyl dichlorides [1]. The products of the reactions with $CHal_3Ar(Ar_f)/AlCl_3$ are polyfluoroaromatic imidoyl chlorides [1,2]. The reaction of pentafluorophenol with $CCl_4/AlCl_3$ under similar conditions leads to the formation of bis(pentafluorophenyl)carbonate as the main product along with trichloromethyl pentafluorophenyl ether and tris(pentafluorophenoxy)chloromethane. The ratio of these compounds depends on the reaction conditions. The reaction of aliphatic polyfluorinated alcohols leads only to carbonates [3].

It was of interest to study the possibility of a haloalkylation reaction of polyfluoroaromatic thio derivatives with compounds of the formula $CHal_3R$ in the presence of $AlCl_3$. The alkylation or arylation of thiols with RHal is usually accomplished in the presence of a strong base, e.g. NaOH, tertiary amines, etc., in order to promote the nucleophilicity of the sulphur atom and to remove the halide ion as it is released. In the case of pentafluorothiophenol (**1**) the presence of an inorganic or even weak organic base causes extensive polymerization as a result of repeated nucleophilic substitution of the *p*-fluorine atoms by the thiolate anion. Alkylation or arylation of (**1**) therefore presents problems

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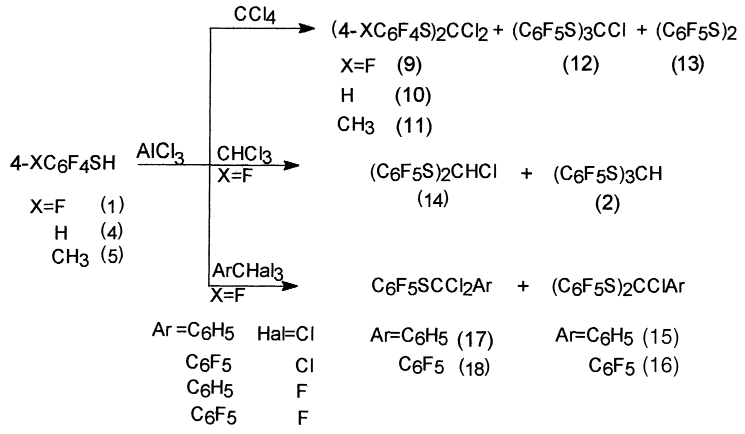


Scheme 1.

[4]. However, compounds containing activated halide atoms combined with (**1**) in DMF without the necessity of adding a base. The reaction of (**1**) with iodoform in DMF occurs to afford tris(pentafluorophenylthio)methane (**2**) and a higher molecular weight material as a result of further reactions of (**1**) at the para position of the former product. Octafluorotoluene (**3**) reacts with (**1**) in DMF at room temperature to give the product which resulted from reaction of (**1**) at the para position of (**3**) [4].

In the present paper we describe the reactions of pentafluorothiophenol (**1**), 2,3,5,6-tetrafluorothiophenol (**4**) and 4-methyl-2,3,5,6-tetrafluorothiophenol (**5**) with CCl_4, $CHCl_3$, benzotrichloride (**6**) and pentafluorobenzotrichloride (**7**) or benzotrifluoride (**8**) and octafluorotoluene (**3**) in the presence of $AlCl_3$.[2] The reactions of hydrolysis, replacement of chlorine by fluorine, using antimony fluorides and caesium fluoride, and the oxidation of the compounds obtained have been studied.

2. Results and discussion

2.1. *Reactions of polyfluorinated thiophenols with $CHal_3R/AlCl_3$*

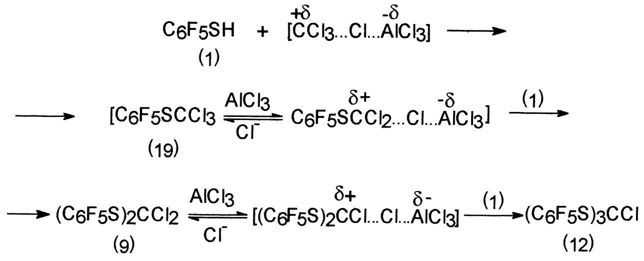
The results obtained in the reactions of compounds (**1**, **4**, **5**) with CCl_4, $CHCl_3$ and $ArCHal_3$ in the presence of $AlCl_3$ are shown in Scheme 1 and Table 1.

2.1.1. *Reactions with CCl_4 and $AlCl_3$*

Polyfluorinated thiophenols, like pentafluorophenol, undergo polychloroalkylation at the heteroatom in reaction with CCl_4 in the presence of $AlCl_3$. However, as opposed to pentafluorophenol, the reactions of pentafluorothiophenol (**1**) and para-substituted tetrafluorothiophenols (**4**, **5**) lead to bis(polyfluoroarylthio)dichloromethanes (**9**–**11**) in high yields. At times the formation of tris(pentafluorophenylthio)chloromethane (**12**) was observed in the reactions of (**1**), but only as an impurity, in very small amounts. Compounds (**9**–**11**) are stable to hydrolysis under the reaction conditions.

We have studied the interaction of compound (**1**) and CCl_4 in the presence of $AlCl_3$ under various conditions. We tried to produce mainly pentafluorophenylthiotrichloromethane (**19**) or tris(pentafluorophenylthio)chloromethane (**12**) by varying the amounts of CCl_4 and $AlCl_3$ or temperature, but these attempts failed. Dichloromethane derivative (**9**) was formed as the main product irrespective of the amount of CCl_4 and $AlCl_3$ at 60°C and at room temperature, but much decafluorodiphenyl disulphide (**13**) was formed in the latter case probably as a result of competitive transformation of (**1**) under the action of $AlCl_3$. A mixture consisting of unreacted starting material (**1**), disulphide (**13**) and derivative (**9**) (5:3:1 according to ^{19}F NMR data) was formed at 0°C. Hence, lowering the temperature of the reaction favours only the formation of disulphide (**13**). A temperature rise up to 80°C also leads to compound (**9**) as a main product. According to MS and ^{19}F NMR data, one fraction after column chromatography of the reaction mixture on silica gel contained (**12**), but in very small amounts.

The suggested reaction Scheme 2 can explain a formation of observed products and can help an understanding of the difference in the end products formation in the reactions of polyfluoroaromatic hydroxy and thio derivatives with CCl_4 and $AlCl_3$. The scheme involves a primary attack on (**1**) by CCl_4 activated by $AlCl_3$ to form trichloromethylthio derivative (**19**) which is then further converted to the compound



Scheme 2.

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[2] Preliminary communications [5,6].

Table 1
Interaction of polyfluorothiophenols with compounds of the $CHal_3R$ type in the presence of $AlCl_3$

Experiment	Thiocompound g (mmol)	$CHal_3R$ g (mmol)	$AlCl_3$ g (mmol)	$CHCl_3$ (ml)	Reaction temperature °C (time, h)	Weight of residue after reaction (g)	Content of main products in residue after reaction		
							Compound	% by GLC	Ratio by ^{19}F NMR
Reaction with CCl_4 (ml)									
1	(**1**) 1.52 (7.6)	10	3.04 (22.8)		60–70 (6)	2.0	(**9**)	90	
2	(**1**) 1.21 (6)	85	2.42 (18)		60–70 (6)	1.52	(**9**)	90	
							(**13**)	4	
3	(**1**) 1.0 (5)	10	0.67 (5)		60–70 (6)	1.17	(**9**)	91	
							(**13**)	4	
4	(**1**) 20 (100)	120	26.6 (100)		60–70 (9)	23.56	(**9**)	90	
							(**13**)	3	
5	(**1**) 0.73 (3.65)	10	1.46 (10.1)		20 (6)	0.7	(**9**)	82	
							(**13**)	10	
6	(**1**) 1.9 (9)	80	1.27 (9)		20 (6)		(**9**)		8
							(**13**)		1
7	(**1**) 1.3 (65)	80	0.87 (6.5)		0 (6)		(**1**)		5
							(**9**)		1
							(**13**)		3
8	(**1**) 1.05 (5.25)	10	2.10 (15.7)		80 (6)	1.45[a]	(**9**)		Main
							(**12**)		traces
9	(**4**) 1.89 (10)	100	4 (30)		60–70 (6)	2.3	(**10**)		
10	(**5**) 1.57 (5)	80	2.9 (15)		60–70 (6)	1.7	(**11**)		
Reaction with $CHCl_3$									
11	(**1**) 3.72 (18.6)		7 (55.8)	20	60–70 (7)	3.89	(**2**)[b]	9	
							(**13**)	2	
							(**14**)[c]	82	
12	(**1**) 0.96 (4.8)		–	10	60–70 (6)	1.05	(**1**)		12
							(**13**)		1
Reaction with $Ar(Ar_f)CF_3$									
13	(**1**) 1.98 (10)	(**8**) 1.45 (10)	3.96 (30)	80	60–70 (6)	3.25	(**15**)[d]		3
							(**20**)		1
14	(**1**) 1.83 (9)	(**3**) 2.12 (9)	3.5 (27)	80	60–70 (6)	2.77	(**16**)		
Reaction with $Ar(Ar_f)CCl_3$									
15	(**1**) 2.33 (11.6)	(**6**) 2.28 (11.6)	4.67 (34.9)	80	60–70 (**6**)	3.8	(**15**)		1
							(**17**)		2
16	(**1**) 2.08 (10.4)	(**6**) 2.01 (10.3)	4.1 (31)	45	60–70 (6)	4.3	(**15**)		2.25
							(**17**)		39
							(**20**)		1
17	(**1**) 2.22 (11)	(**6**) 2.17 (11)	4.44 (33)	80	20 (6)	3.6	(**13**)		0.5
							(**15**)		2.7
							(**20**)		1
							(**17**)		1
18	(**1**) 1.5 (7.5)	(**6**) 1.52 (7.7)	1.04 (7.7)	60	20 (6)	2.75	(**1**)		1
							(**15**)		19
							(**17**)		3.5
							(**20**)		3.5
19	(**1**) 1.6 (8)	(**7**) 2.26 (8)	3.2 (24)	80	60–70 (6)	3.5	(**7**)		1
							(**16**)		1.5
							(**18**)		1.5
20	(**1**) 1.0 (5)	(**7**) 1.42 (5)	0.67 (5)	10	20 (6)	2	(**7**)		1.5
							(**16**)		1
							(**18**)		1.3
21	(**1**) 1.05 (5)	(**7**) 3.76 (12)	2.1 (15)		20 (6)	3.10	(**7**)		7.5
							(**16**)		1
							(**18**)		2.6
22	(**1**) 5 ml	(**7**) 1.48 (5)	2.1 (15)	2	60–70 (6)	8	(**13**)		1
							(**14**)		1.5
							(**16**)		1

Table 1 (*continued*)

Experiment	Thiocompound g (mmol)	$CHal_3R$ g (mmol)	$AlCl_3$ g (mmol)	$CHCl_3$ (ml)	Reaction temperature °C (time, h)	Weight of residue after reaction (g)	Content of main products in residue after reaction		
							Compound	% by GLC	Ratio by ^{19}F NMR
23	(**1**) 1 (5)	(**7**) 1.42 (5)	2 (15)	80	5–10 (6)	2.07	(**7**)		16
							(**13**)		1.5
							(**16**)		16
							(**18**)		1

[a] Compound (**9**) (0.9 g), the mixture of compounds (**9**) and (**21**) (0.09 g), compound (**21**) (0.15 g) and the mixture of compounds (**21**) and (**12**) (0.3 g, ratio by ^{19}F NMR 1:1.3) were obtained from the residue by column chromatography (eluent hexane).

[b] 0.2 g of (**2**) was isolated from 1.35 g residue by column chromatography (eluent hexane).

[c] 1.4 g of (**15**) was isolated from 2.5 g residue by distillation at 165–167°C/10 mm Hg.

[d] 1.38 g of (**16**) was isolated from 2.5 g residue by filtration and washing with small amount of hexane.

(**9**). In the thiophenols series the conversion to dichloromethane derivatives seems to be easier due to higher nucleophility of thiophenols as compared to phenols, and the trichloromethylthio derivative may not be detected. The different behaviour of derivative (**9**) in a further reaction with (**1**) or in hydrolysis as compared to the oxygen analogue may be explained by the different ability of oxygen and sulphur atoms to stabilize the adjacent carbocationic centre [7]. The sulphur atom is less effective and this could explain the stability of (**9**) towards hydrolysis or further reaction with (**1**) to (**12**).

2.1.2. Reaction with $CHCl_3$ and $AlCl_3$

Pentafluorothiophenol (**1**) did not react with $CHCl_3$ at 60°C in the absence of $AlCl_3$. The reaction mixture contained only disulphide (**13**) together with unreacted starting material (1) (ratio of (**1**) and (**13**) 16:1 deduced from ^{19}F NMR data). In the presence of $AlCl_3$ reaction of (**1**) and $CHCl_3$ gave bis(pentafluorophenylthio)chloromethane (**14**) as main product and tris(pentafluorophenylthio)-methane (**2**) (ratio by GLC 8:1).

2.1.3. Reaction with $ArCHal_3$ and $AlCl_3$

Reactions of (**1**) with aryltrihalomethanes and $AlCl_3$ proceeded similarly. Bis(pentafluorophenylthio)arylchloromethanes were formed, but, in contrast, in these reactions the primary dichloromethane derivatives have also been isolated and characterized (see Table 1). Reaction of (**1**) with benzotrifluorides (**8**, **3**) and $AlCl_3$ at 60°C gave as the main products bis(pentafluorophenylthio)arylchloromethanes (**15**, **16**). In the reaction mixture with (**8**) a small amount of *S*-pentafluorophenyl thiobenzoate (**20**) was identified which probably forms as a result of a side reaction involving hydrolysis of the primary product (**17**). Reactions of (**1**) with benzotrichlorides (**6**, **7**) gave (**15**, **16**) and pentafluorophenylthioaryldichloromethanes (**17**, **18**). Product ratios depended on the temperature and amount of reagents. Reactions of (**1**), $ArCHal_3$ and $AlCl_3$ proceeded in excess of $ArCHal_3$ as well as with equimolar amounts of (**1**) and $ArCHal_3$ in $CHCl_3$. It should be noted that compound (**1**) and $CHCl_3$ reacted with no or low conversion in the presence of more reactive compounds of the $ArCHal_3$ type. Therefore, it was possible to use $CHCl_3$ as a solvent. Attempts to use excess of (**1**) in the reaction of (**1**) with (**7**) in $CHCl_3$ (exp. 22) gave compound (**16**), but the reaction is complicated due to the formation of by-products (**13**) and (**14**).

2.2. Hydrolysis of dichloromethane derivatives (**9**, **17**)

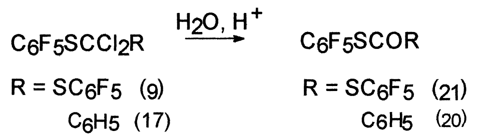
The dichloromethane derivatives formed in the polyhaloalkylation reactions of (**1**) are stable to hydrolysis but they react with water when an excess of 10% HCl in dioxane (100°C) was used (Scheme 3). Thus, bis(pentafluorophenyl)dithiocarbonate (**21**) and compound (**20**) were obtained from compounds (**9**) and (**17**) under these conditions. The derivative (**20**) was identical with that described in the literature [8].

2.3. Reactions of halogen exchange

It is known [9] that the fluorinated sulphides of the $(4\text{-}FC_6H_4S)_2(CF_2)_n$ type are starting compounds to bis-sulphone monomers which react with bis-phenols to give fluorinated poly-(ether sulphone)s as new polymers. In this respect it was of interest to study bis(pentafluorophenylthio)difluoromethane (**22**) as the simplest compound of the perfluorinated series. For this reason chlorine atoms exchange with fluorine under the action of the antimony fluorides and caesium fluoride has been studied for chloro compound (**9**). The main results of this investigation are shown in Scheme 4 and Tables 2 and 3.

2.3.1. Reactions with antimony fluorides

It is known that $RSCCl_3$ compounds transform into $RSCF_3$ derivatives with SbF_3 [10] or SbF_3+$SbCl_5$ [11].

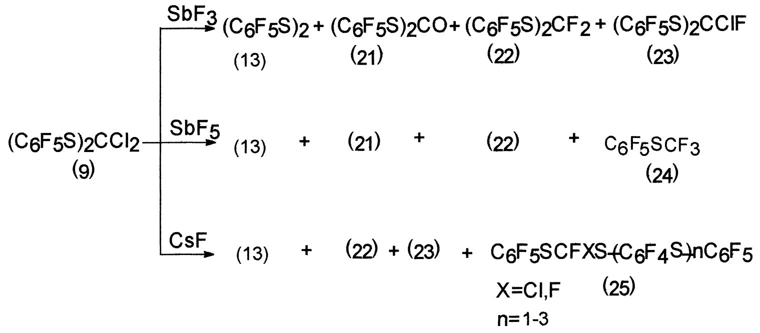


$$C_6F_5SCCl_2R \xrightarrow{H_2O,\ H^+} C_6F_5SCOR$$

$R = SC_6F_5$ (9) $R = SC_6F_5$ (21)

C_6H_5 (17) C_6H_5 (20)

Scheme 3.



Scheme 4.

The reaction is usually realized by heating with simultaneous distillation of reaction products.

Reaction of (**9**) with an excess of SbF_3 similar to the transformation of $PhSCCl_3$ to $PhSCF_3$ [10] at 150°C (exp. 1, Table 2) gave dithiocarbonate (**21**) as the main product, small amounts of difluoromethane derivative (**22**) and disulphide (**13**) (75%, 16% and 6%, GLC data). Lowering of the temperature of the reaction to 110°C did not change the result. Compound (**9**) did not react with SbF_3 at 45°C. Disulphide (**13**) was the main product in the reaction of compound (**9**) with $SbF_3/SbCl_5$ at 120–140°C/25 mm Hg. Derivative (**22**) and dithiocarbonate (**21**) were among the reaction products, but in small amounts. Unreacted starting compound (**9**) remained in the mixture (exp. 5, Table 2). The use of SbF_5 favours the exchange process. The reaction of (**9**) with SbF_5 at 90°C (exp. 6, Table 2) resulted in an increase in formation of difluoromethane derivative (**22**) but the main product was disulphide (**13**). Chlorofluoromethane derivative (**23**) and dithiocarbonate (**21**) were also identified among the reaction products. Pentafluorophenylthiotrifluoromethane (**24**) previously described in [12] is likely formed in this reaction according to ^{19}F NMR and GC–MS data.

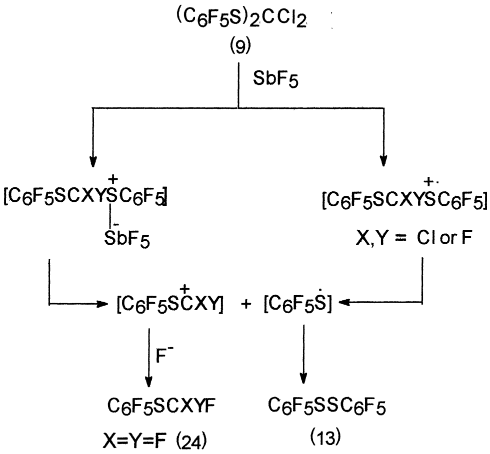
The formation of compound (**21**) in the reactions with antimony fluorides is presumably a result of partial hydrolysis of the dihalomethanes in the presence of traces of moisture. This hydrolysis occurs most easily for starting material (**9**) and is more favourable than the exchange process. Difluoromethane derivative (**22**) and chlorofluoromethane derivative (**23**) are stable to the action of SbF_3 and traces of moisture to 160°C (exp. 7 and 8, Table 2). The transformation of dihalomethane derivatives by SbF_5 with a rupture of the C–S bond and formation of a pentafluorophenylthiodihalomethyl cation and a pentafluorophenylthio radical as intermediates could be the explanation of the reaction pathway into trifluoromethane derivative (**24**) and disulphide (**13**) (Scheme 5, compare [13]).

Disulphide (**13**) could be also formed from dithiocarbonate (**21**) under the reaction conditions (exp. 9, Table 2).

2.3.2. *Reactions with caesium fluoride*

The results obtained in the reactions of compound (**9**) with caesium fluoride are shown in Scheme 4.

Dichloromethane derivative (**9**) reacts with a threefold molar excess of anhydrous caesium fluoride without solvent at 180°C to give chlorofluoromethane derivative (**23**) as main product. Difluoromethane derivative (**22**), disulphide (**13**) and polysulphides of the (**25**) type were also identified among the reaction products (see Table 3). An increase of reaction temperature favours the formation of compound (**22**) and polysulphides. At 225°C (exp. 4) from GLC data the reaction mixture not only contained ~5% chlorofluoromethane derivative (**23**) and 43% difluoromethane derivative (**22**) but also 34% polysulphides (**25**) and 8% disulphide (**13**). Compound (**22**) was not obtained pure and was identified according to ^{19}F NMR , GC–MC and GLC data. Separation of a mixture of (**22**), (**23**) and (**13**) was difficult. The compounds show close chromatographic retention times. An unseparated mixture of these compounds was isolated by column chromatography. An attempt to distil off compound (**22**) from the reaction mixture was also unsuccessful. An unseparated mixture of polysulphides (**25**) was identified by ^{19}F NMR data. The determination of the amount of each component was difficult. The compounds show coincident ^{19}F NMR signals. The ^{19}F NMR signals at 115.5–117 ppm were attributed to the fluorine atoms of CF_2 and CFCl groups, the signals at 30–34 ppm to the *ortho*-fluorine atoms, the signals at 2.3–2.7 ppm to the *meta*-fluorine atoms and the signals at 12.6–12.9 ppm to the



Scheme 5.

Table 2
Interaction of dihalomethanes with antimony fluorides

Experiment	Starting compound		Antimony fluoride g (mmol)	Reaction temperature °C (time, h)	Method	Weight of product after reaction (g)	Reaction products	
	g (mmol)	Content in mixture					Compound	Ratio by ^{19}F NMR
1	(**9**) 0.48 (1)		SbF_3 0.16 (0.85)	150 (2)	A	0.41	(**9**)	0.3
							(**13**)	1
							(**21**)	9.3
							(**22**)	2
2	(**9**) 0.15 (0.31)		SbF_3 0.05 (0.28)	110 (3)	C	0.1	(**9**)	0.5
							(**13**)	0.75
							(**21**)	13.2
							(**22**)	3
3	(**9**) 0.15 (0.31)		SbF_3 0.05 (0.28)	45 (1.5)	C	0.1	(**9**)	
4	(**9**) 0.48 (1)		SbF_3 0.17 (0.8), $SbCl_5$ (5 drops)	120–140/15 mm Hg (45 min)	B	0.1[a]	(**13**)	41
							(**21**)	2.4
							(**22**)	1
						0.05	(**13**)	19
							(**21**)	1
5	(**9**) 0.15 (0.31)		SbF_3 0.05 (0.28), $SbCl_5$ (2 drops)	55 (4)	C		(**9**)	1.5
							(**13**)	1.5
							(**21**)	1
							(**22**)	[b]
							(**23**)	[b]
6	(**9**) 0.15 (0.31)		SbF_5 0.03 (0.14)	90 (**4**)	C	0.11	(**9**)	1.5
							(**13**)	6
							(**21**)	1.5
							(**22**)	3
							(**23**)	1
							(**24**)	4
7	(**22**)	1	SbF_3	110 (4)	C	0.06	(**22**)	1
	(**23**)	5	0.06				(**23**)	8
		0.1 (^{19}F NMR)						
8	(**13**)	2	SbF_3	160 (6)	C	0.08	(**13**)	2.5
	(**22**)	10	0.06				(**21**)	2
	(**23**)	81					(**22**)	14
		0.08 (% GLC)					(**23**)	77 (% GLC)
9	(**21**) 0.08 (0.19)		SbF_3 0.03 (0.17), $SbCl_5$ (2 drops)	140 (1.5)	C	0.05	(**13**)	93 (% GLC)

[a] A solid which sublimed on the condenser.

[b] Traces, the ratio of (**22**) and (**23**) is approximately 1:2.

Table 3
Interaction of dihalomethanes with caesium fluoride

Experiment	Substrate g (mmol)	Caesium fluoride, g (mmol)	Reaction temperature, °C (time, h)	Weight of residue after reaction (g)	Reaction products	
					Compound	Ratio by ^{19}F NMR
1	(**9**) 0.96 (2)	1.92 (12)	180 (19)	0.85[a]	(**13**)	1.5
					(**22**)	7
					(**23**)	18
					(**25**)	6
2[b]	(**9**) 8 (17)	16 (100)	180 (27)	3.2[c]	(**9**)	1
					(**13**)	1.1
					(**22**)	1
					(**23**)	11
				1.65	(**13**)	1
					(**23**)	19
					(**25**)	63 (% GLC)
3	(**9**) 1.2 (2.5)	2.28 (15)	210 (19)	1.05[d]	(**13**)	1
					(**22**)	2
					(**23**)	3
					(**25**)	1.8
4	(**9**) 1.2 (2.5)	2.28 (15)	225 (22)	1.06[e]	(**13**)	1
					(**22**)	4
					(**23**)	1
					(**25**)	6
5	(**23**) 0.93 (2)	1 (6)	220 (18)	0.8	(**13**)	1.5
					(**22**)	19.5
					(**23**)	55.5
					(**25**)	20 (% GLC)

[a] A mixture (0.38 g) of 2% of (**13**), 10% of (**22**) and 84% of (**23**) (GLC) was obtained from residue by sublimation at 110°C/15 mm Hg.

[b] Carried out in argon.

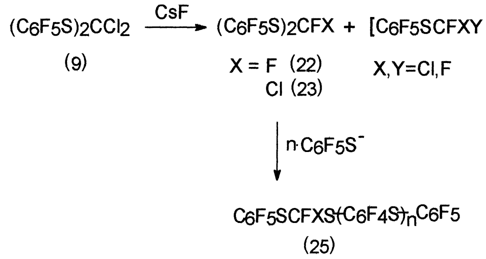
[c] The solid product sublimed on the flask from which compound (**23**) was separated and purified.

[d] A mixture (0.35 g) of 10% of (**13**), 33.5% of (**22**) and 50% of (**23**) (GLC) was obtained from products after reaction by sublimation at 105–110°C/15 mm Hg.

[e] This mixture was treated with petroleum ether (70–100°C), organic layer was filtered, solvent distilled off. From 0.72 g of solid residue by column chromatography (eluent hexane) a mixture (0.21 g) of 15% of (**13**), 70% of (**22**) and 7% of (**23**) (GLC) was isolated.

para-fluorine atoms. The signals coincide with those for similar polysulphide fragments in the compounds described previously [14]. Polysulphides (**25**) probably result from a side reaction involving *para*-fluorine atom displacement by the pentafluorophenylthio group. Formation of compounds (**25**) may be represented in Scheme 6.

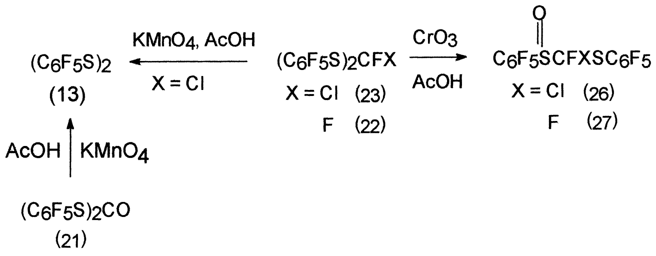
The scheme involves an attack by fluoride anion at aliphatic carbon atom with substitution of chlorine by fluorine and a rupture of C–S bond and further transformations by the pentafluorophenylthio anion. An attempt to obtain pure difluoromethane derivative (**22**) from chlorofluoromethane derivative (**23**) by heating with caesium fluoride at 220°C did not gave a positive result (exp. 5, Table 3).



Scheme 6.

2.4. Reactions with oxidants

Dihalomethane derivatives (**9**, **23**) did not react with potassium permanganate in acetone. Treatment of (**23**) with potassium permanganate in boiling acetic acid resulted in formation of disulphide (**13**) (see 1 of Section 3.5). Disulphide (**13**) probably results from dithiocarbonate (**21**) formed by hydrolysis of starting material (**23**). Such a pathway was confirmed by the transformation of (**21**) into (**13**) on heating with potassium permanganate in acetic acid (2 of Section 3.5). Compound (**22**) did not react with potassium permanganate under these conditions. Chromium trioxide/acetic acid as oxidant was more effective, but insufficient. Previously, this oxidant was used for oxidation of the fluoro-containing sulphides to sulphones [9,15]. By boiling fluorochloromethane derivative (**23**) with threefold molar excess of chromium trioxide in acetic acid, only mono-sulphoxide (**26**) was obtained (Scheme 7). The ^{19}F NMR spectrum of (**26**) shows two different C_6F_5-groups, and changes with the CFCl-group and aromatic fluorine atoms on going from sulphide to sulphoxide. In the



Scheme 7.

MS spectra of this compound fragment ions with structure of sulphide (C_6F_5SCFCl, C_6F_5S) and sulphoxide (C_6F_5SO) were observed. The ions containing sulphone groups and the molecular ion were not observed. Unfortunately, we have not managed to obtain single crystals of compound (**26**) suitable for X-ray structure analysis.

Difluoromethane derivative (**22**) is the least reactive substrate in the reactions with oxidants.

Only a small amount of derivative (**22**) reacted with chromium trioxide in acetic acid to give compound (**27**) which was identified spectroscopically in the reaction mixture. GC–MS and ^{19}F NMR data for (**27**) are similar to those for (**26**). Increasing amounts of chromium trioxide gave a mixture of two main products – unreacted starting compound (**22**) and a polyfluoroaromatic compound which probably results from a reaction with acetic acid and containing one pentafluorophenyl group (exp. 3, Table 4).

3. Experimental

^{19}F and ^{1}H NMR spectra were recorded on a Bruker WP-200SY instrument in CCl_4 solution. The internal standards were hexafluorobenzene and hexamethyldisiloxane. IR spectra were measured on a Specord M-80 instrument for a 5% CCl_4 solution. GLC analyses were carried out on a LHM-7a instrument with a thermal conductivity detector and a linear temperature programme of 10°C min^{-1}, using internal normalization (80–270°C, a 4000×4 mm column packed with methylsilicon E-30, fluorosilicon QF-1/Chromosorb W, silicon SKTFT-50 and SKTFV-803/Celite, 5:100 and 15:100 with He carrier at 60 ml min^{-1}). Column chromatography was carried out on silica gel 100–160 mesh. GC–MS analysis of the reaction mixtures was carried out on a GCHP 5890 with an HP 5971 mass spectrometer, ionization potential 70 eV. Molecular weights and molecular formulae were determined mass spectrometrically on a GC–MS Finnigan MAT-8200 instrument. The nominal energy of the ionizing electrons was 70 eV. Newly synthesized compounds were purified by recrystallization from petroleum ether (b.p. 70–100°C) and hexane or by sublimation in a vacuum, or by column chromatography. All these compounds have correct analytical data. The reaction conditions and the results of experiments are presented in Tables 1, 2–4. Spectroscopic and analytical data for new synthesized compounds are presented in Table 5.

3.1. Reactions with $RCHal_3$ and $AlCl_3$

Corresponding thiophenol was added to a vigorously stirred suspension of $AlCl_3$ in $RCHal_3$. The reaction mixture was stirred at the temperature indicated in Table 1, poured into cold water and extracted with ether. The ether layer was dried over $CaCl_2$, the solvents distilled off and the residue analysed by ^{19}F and ^{1}H NMR spectroscopy, GC–MS, IR spectroscopy and GLC. Compounds (9–11, 15, 16, 17, 18) were purified by recrystallization from CCl_4 or hexane and sublimed at 100–140°C/10 mm Hg. Compound (**15**) was purified by distillation at 164–166°C/13 mm Hg. Compound (**2**) was separated by column chromatography on

Table 4
Reactions with chromium trioxide in acetic acid

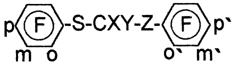
Experiment	Starting compound		Chromium trioxide (g)	AcOH (ml)	Reaction time (h)	Reaction products		
	g	Content in mixture (% GLC)				Compound	Content in mixture	
							g	(% GLC)
1	(**13**)	10	0.4	4	6.5	(**13**)		2
	(**22**)	33				(**22**)		20
	(**23**)	50				(**26**)		44
	0.22					(**27**)		25
							0.09[a]	
2	(**23**) 0.72		0.9	5	6	(**26**)	0.31[b]	
3	(**13**)	15	0.71	4	15		0.05[c]	
	(**22**)	70						
	(**23**)	7						
	0.19							

[a] A mixture (0.02 g) of (**26**) and (**27**) (76% and 21% by GLC) was obtained from the solid residue after washing with petroleum ether (70–100°C).

[b] The compound was purified by recrystalization from petroleum ether (70–100°C).

[c] A mixture of two main products: compound (**22**) and compound with unknown structure (1.5:1 from ^{19}F NMR data).

Table 5
Analytical data and spectroscopic characteristics of new compounds



Compound	M.p. (°C)	C	H	Cl Found (%) Calculated	F	S	M–Cl (^{35}Cl) Found Calculated	Composition	^{19}F NMR spectrum, δ, ppm (solvent)	^{1}H NMR spectrum δ, ppm (solvent)	IR spectrum ν (cm^{-1})
(**2**)	120–122 (134–135 [4])	37.84; 37.84 37.38	0.16; 0.46 0.16		46.50; 47.12 46.72	15.42; 15.30 15.74	608.88942[a] 608.89225	$C_{19}HF_{15}S_3$	30.67 ($6F_o$) 13.92 ($3F_p$) 2.55 ($6F_m$) ($CHCl_3$)	5.51 (H) (CCl_4)	855(vs) 980(vs) 1080(vs) 1490–1510(vs) 1630(m) 2900(w)
(**9**)	120–122.5[b]	32.96; 32.64 32.43		15.21; 15.40 14.76	39.91; 40.00 39.50	13.14; 13.46 13.30	444.8976 444.8970	$C_{13}Cl_2F_{10}S_2$	35.8 ($4F_o$) 17.75 ($2F_p$) 3.05 ($4F_m$) (Ether+CCl_4)		870(s) 995(vs) 1100(vs) 1500–1515(vs) 1630(m)
(**10**)	141.5–143.5[b]	34.98; 34.59 35.05	0.49; 0.48 0.45	16.29; 16.36 15.95	34.21; 34.48 34.16	14.82; 15.10 14.38	408.9160 408.9159	$C_{13}H_2Cl_2F_8S_2$	34.6 ($4F_o$) 25.6 ($4F_m$) (Ether+CCl_4)	7.4 (H_{Ar}) (Ether+CCl_4)	870(s) 920(vs) 1190(s) 1235(s) 1390(s) 1500(vs) 1610(w) 3090(w)
(**11**)	135–137	38.10; 38.25 38.13	1.14; 1.20 1.14	14.25; 14.51 15.04	31.65; 31.80 32.20	13.64 13.56	436.9466 436.9471	$C_{15}H_6Cl_2F_8S_2$	33.51 ($4F_o$) 21.10 ($4F_m$) (CCl_4)	2.37 (6H, $2CH_3$) (CCl_4)	920(vs) 1080(vs) 1280(vs) 1490(vs) 1630(w) 2880(w) 2935(w)
(**12**)[c]							608.89007 608.89223	$C_{19}ClF_{15}S_3$	36.79 ($6F_o$) 16.88 ($3F_p$) 2.39 ($6F_m$) (CCl_4)		
(**14**)	[d]	35.48; 35.61 35.0	0.50; 0.57 0.22	7.90; 8.20 7.82	42.77; 42.83 42.82	14.10; 14.40 14.35	410.93485 410.93595	$C_{13}HClF_{10}S_2$	31.92 ($4F_o$) 14.38 ($2F_p$) 2.45 ($4F_m$) (CCl_4)	6.25 (H) (CCl_4)	835(s) 975(vs) 1100(s) 1490–1540(vs) 1640(m) 3000(w)
(**15**)	94–96	43.19; 42.93 43.68	1.31; 1.17 0.96	6.56; 6.53 6.80	36.17 36.40	12.33; 12.50 12.26	486.9673 486.9673	$C_{19}H_5ClF_{10}S_2$	35.09 ($4F_o$) 15.34 ($2F_p$) 1.80 ($4F_m$)	7.9 ($2H_{Ar}$) 7.3 ($3H_{Ar}$) (CCl_4)	875(m) 995(vs) 1100(vs)

Table 5 (*continued*)

Compound	M.p. (°C)	C	H	Cl Found (%) Calculated	F	S	M–Cl (^{35}Cl) Found Calculated	Composition	^{19}F NMR spectrum, δ, ppm (solvent)	^{1}H NMR spectrum δ, ppm (solvent)	IR spectrum ν (cm^{-1})
									($CHCl_3$)		1495–1520(vs) 1630(m) 3075(w)
(**16**)	59–60	37.36; 37.40 37.20		6.34; 6.30 6.04	46.74; 46.57 46.56	10.51; 10.42 10.46	576.9241 576.9202	$C_{19}ClF_{15}S_2$	34.75 ($4F_o$) 32.27 ($2F_o$) 17.02 ($2F_p$) 12.41 (F'_p) 2.57 ($4F_m$) 1.77 ($2F'_m$) (CCl_4)		880(m) 995(vs) 1010(m) 1100(vs) 1125(m) 1495–1520(vs) 1635(m)
(**17**)	101–102	44.15; 43.88 43.57	1.71; 1.67 1.40	19.77; 20.06 19.55	26.02; 25.82 26.54	9.10; 9.30 8.94	322.97157 322.97206	$C_{13}H_5Cl_2F_5S$	34.28 ($2F_o$) 15.84 (F_p) 1.95 ($2F_m$) (CCl_4)	7.89 ($2H_{Ar}$) 7.40 ($3H_{Ar}$) (CCl_4)	980(vs) 1095(vs) 1175(m) 1400(m) 1445(m) 1488(vs) 1512(vs) 1630(m) 3040(w)
(**18**)	67–68							412.92328 412.92495	$C_{13}Cl_2F_{10}S$	34.50 ($2F_o$) 17.59 (F_p) 2.74 ($2F_m$) ($S–C_6F_5$) 30.96 ($2F'_o$) 12.68 (F'_p) 1.76 ($2F'_m$) ($C–C_6F_5$) (CCl_4)	990–1020(vs) 1100(vs) 1135(vs) 1310(m) 1490–1520(vs) 1640(m) 1650(m)
(**20**)	34–37 (34–37) [8]						[e]	$C_{13}H_5F_5OS$	31.51 ($2F_o$) 12.60 (F_p) 1.30 ($2F_m$) (CCl_4)	7.99 ($2H_{Ar}$) 7.55 ($3H_{Ar}$) (CCl_4)	960(vs) 1075(vs) 1490–1500(vs) 1650(vs) 1690(vs) 2915–2925(w)
(**21**)	50–52	36.17; 35.92 36.62			44.69; 44.86 44.60	15.60; 15.90 15.02	425.92428[f] 425.92308	$C_{13}F_{10}OS_2$	32.50 ($4F_o$) 15.48 ($2F_p$) 2.59 ($4F_m$) (CCl_4)		990(vs) 1100(vs) 1495–1520(vs) 1640(m) 1730(m)
(**22**)[g]							448[h] 448	$C_{13}F_{12}S_2$	114.78 (2F, CF_2) 33.39 ($4F_o$)		

Table 5 (*continued*)

Compound	M.p. (°C)	C	H	Cl Found (%) Calculated	F	S	M–Cl (^{35}Cl) Found Calculated	Composition	^{19}F NMR spectrum, δ, ppm (solvent)	^{1}H NMR spectrum δ, ppm (solvent)	IR spectrum ν (cm^{-1})
									16.41 ($2F_p$) 2.66 ($4F_m$) (CH_2Cl_2)		
(**23**)	80–84	33.26 33.62		8.30; 8.00 8.64	45.29; 45.53 44.99	14.00; 14.28 13.78	428.92600 428.92657	$C_{13}ClF_{11}S_2$	116.65 (1F, CFCl) 33.90 ($4F_o$) 16.91 ($2F_p$) 2.78 ($4F_m$) (CH_2Cl_2)		975(vs) 1100(vs) 1175(vs) 1375(m) 1500–1525(vs) 1640(m)
(**24**)[i]									120.27 (3F, CF_3) 33.39 ($2F_o$) 16.83 (F_p) 2.76 ($2F_m$) (CH_2Cl_2)		
(**26**)	120–121	32.55; 32.75 32.47		8.00; 8.19 7.39	43.0; 42.70 43.5	13.56; 13.76 13.3	535; 539[e,j] 480.5	$C_{13}ClF_{11}OS_2$	74.60 (1F, CFCl) 35.50 ($2F_o$, SC_6F_5) 18.05 (F_p) 2.94 ($2F_m$) 32.66 ($2F_o$, SOC_6F_5) 24.39 (F_p) 5.25 ($2F_m$) (CH_2Cl_2)		965(s) 970(vs) 1100(vs) 1175(s) 1375(m) 1500–1525(vs) 1640(m)
(**27**)									82.34 (2F, CF_2) 35.46 ($2F_o$, SC_6F_5) 18.05 (F_p) 2.92 ($2F_m$) 31.79 ($2F_o$, SOC_6F_5) 24.81 (F_p) 5.21 ($2F_m$) (CH_2Cl_2)		

[a] The ion M–H.

[b] In a sealed capillary.

[c] This compound was identified in the mixture with (**9**) from GC–MS and ^{19}F NMR data.

[d] B.p. 164–166°C/13 mm Hg.

[e] The molecular ion was absent.

[f] The molecular ion.

[g] A mixture of 15% of (**13**), 70% of (**22**) and 7% of (**23**) (GLC).

[h] The molecular ion with low intensity. Found composition was determined for the fragment ion C_7F_7S (M–SC_6F_5) (found 248.96080; calculated 248.96089).

[i] This compound was previously described in [12]. The literature chemical shifts for the signals corresponding to aromatic fluorines ($2F_o$ 54.6, F_p 72.6, $2F_m$ 86.5 ppm with external trifluoroacetic acid as the reference) and our data for this signals are different, but this difference could be attributed to the use of external and internal references.

[j] Molecular weights was determined by the vapour-phase osmometry in acetone.

silica gel (eluent hexane) and then recrystallized from petroleum ether (70–100°C).

3.2. Hydrolysis of compounds (**9**, **17**)

To a solution of 1.1 g of compound (**9**) in 20 ml dioxane, 35 ml of 10% HCl was added. A mixture was refluxed for 7 h. After reaction the mixture was extracted with ether, the organic layer was washed with water and dried over $CaCl_2$, the solvents were distilled off. The solid residue was filtered, washed with small amount of petroleum ether (70–100°C) and 0.31 g of compound (**21**) was obtained which was purified by sublimation at 110°C/15 mm Hg.

The reaction with (**19**) was carried out by a procedure similar to that for (**9**) (0.34 g of (**19**), 4 ml of dioxane and 6 ml of 10% HCl were used). 0.16 g of compound (**18**) was obtained which was purified by sublimation at 70°C/15 mm Hg.

3.3. Reactions with antimony fluorides – see Table 2

Antimony trifluoride was dried at 210–220°C.

Method A. The reaction was carried out in a flask connected via a condenser to a trap immersed in a cooling bath. Antimony halogenide was added to corresponding substrate. The reaction mixture was further heated. Products did not distil off during the reaction. After reaction, the mixture was cooled to room temperature, extracted with methylene chloride, the precipitate was filtered off. Then a solution was washed with water, organic layer was dried over $CaCl_2$, the solvent distilled off and a residue analysed by ^{19}F NMR spectroscopy, GLC and GC–MS.

Method B. The reaction was carried out by a procedure similar to that for A, but in vacuo.

Method C. The reaction was carried out in the closed steel vessel. After reaction, the mixture was worked up as in A.

3.4. Reactions with caesium fluoride

Caesium fluoride was dried at 270°C. The reactions were carried out in the closed steel vessel or in the flask. The reaction conditions are indicated in Table 3.

A substrate was added to a caesium fluoride and the mixture was heated. Work-up of the reaction mixture by a procedure similar to that for Method A for antimony fluorides afforded a residue which was purified by column chromatography or sublimation and recrystallization.

3.5. Reaction with oxidants

1. To a suspension of 0.26 g potassium permanganate in 3 ml of acetic acid, 0.12 g of the mixture of compounds (**13**, **22**, **23**) (2%, 10.5% and 84% according to GLC data) was added. The mixture was refluxed for 6 h, then 0.04 g potassium permanganate was added and the mixture was refluxed for a further 3 h. After reaction, the mixture was poured into water and extracted with ether. The ether layer was washed with water, dried over $CaCl_2$, the solvents distilled off and the residue (0.09 g) was analysed by ^{19}F NMR spectroscopy and GLC. The residue contained (**13**), (**22**) and (**23**) in the ratio 6:4.7:1 according to ^{19}F NMR data or 30%, 38% and 7%, respectively, by GLC.
2. Boiling of 0.04 g of (**21**) with 0.06 g of $KMnO_4$ and 1.5 ml AcOH (3.5 h) gave 0.11 g of the reaction mixture containing AcOH and disulphide (**13**).
3. To a suspension of chromium trioxide in acetic acid, a dihalomethane was added. The mixture was refluxed, then acetic acid distilled off, the residue was poured into water and extracted with methylene chloride. The organic layer was washed with water, dried over $CaCl_2$, the solvents distilled off, the residue analysed by ^{19}F NMR spectroscopy, GC–MS, GLC and purified by recrystallization. The conditions and results are shown in Table 4.

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