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Reactions of polyfluoroaromatic imidoyl chloride derivatives with S-nucleophilic reagents

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Abstract

The interactions of *N*-pentafluorophenylcarbonimidoyl dichloride, *N*-pentafluorophenylbenzimidoyl chloride and *N*-pentafluorophenyl (*C*-pentafluorophenyl) imidoyl chloride with the S-nucleophilic reagents thiourea, sodium *N,N*-diethyldithiocarbamate, thiocarbonyl difluoride and bis(trifluoromethyl)trithiocarbonate in the presence of CsF or $AgSCF_3$, or thiophenol and polyfluorinated thiophenols in the presence of anhydrous K_2CO_3, were studied. Reactions with charged S-nucleophiles and with S-nucleophiles in the presence of a base proceeded with preservation of the N=C multiple bond in the reaction products. By varying the reaction conditions in the case of *N*-pentafluorophenylcarbonimidoyl dichloride it was possible to substitute one or two chlorines and obtain mono- or di-thioimidates. When C_6F_5 or SC_6F_5 groups were present at the C atom of the N=C multiple bond, preferential substitution of the *para*-fluorine atom occurred. Semiempirical PM3 calculation data were used to explain the direction of these reactions. *N*-Pentafluorophenylcarbonimidoyl dichloride reacted with sodium *N,N*-diethyldithiocarbamate or thiourea to give pentafluorophenylisothiocyanate. Depending on the conditions of the reactions of polyfluorinated benzimidoyl chlorides with thiourea, *N*-pentafluorophenylthioamides and 2-aryl-4,5,6,7-tetrafluorobenzothiazoles were formed. An attempt to produce SCF_3 derivatives from $AgSCF_3$ was unsuccessful.

Keywords: Reactions; Polyfluoroaromatic imidoyl chloride derivatives; S-nucleophilic reagents; NMR spectroscopy; IR spectroscopy; Semiempirical calculations

1. Introduction

We have previously described methods for synthesizing polyfluoroaromatic imidoyl chloride derivatives [1,2] and have studied their reactions with N- and O-nucleophilic reagents [3–5]. Such reactions proceeded with retention or transformation of the imidoyl N=C multiple bond and resulted in compounds of various types, including heterocyclic derivatives. It was of interest to study the reactions of polyfluorinated imidoyl chlorides with S-nucleophilic reagents, including those containing other heteroatomic reaction centres, and also with polyfluorinated S-nucleophiles. Reagents for the introduction of SCF_3 groups are of interest as a CF_3 group in a molecule is frequently responsible for physiological activity [6]. However, it should be noted that the introduction of a substituent containing the electron-attracting CF_3 group into electron-deficient polyfluoroaromatic imidoyl chloride derivatives by nucleophilic substitution can be difficult. In the present paper we describe the reactions of *N*-pentafluorophenylcarbonimidoyl dichloride (**1**), *N*-pentafluorophenylbenzimidoyl chloride (**2**) and *N*-pentafluorophenyl(*C*-pentafluorophenyl)imidoyl chloride (**3**) with various sulphur-containing nucleophiles.

2. Results and discussion

2.1. Reactions with thiourea

The results obtained in the reactions of compounds **1–3** with thiourea are shown in Scheme 1.

The carbonimidoyl dichloride **1** reacts with a twofold excess of thiourea in acetonitrile even at room temperature, to give pentafluorophenyl isothiocyanate (**4**) as the sole polyfluorinated product. Compound **4** was shown by spectroscopy and chromatography to be identical to the product described in Ref. [7]. The 1:1 reaction of the imidoyl chloride **2** and thiourea in acetonitrile at 80 °C gave *N*-pentafluorophenyl

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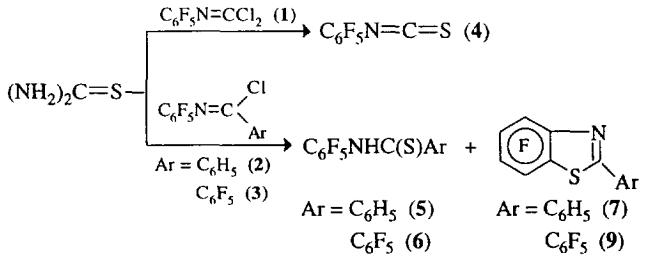
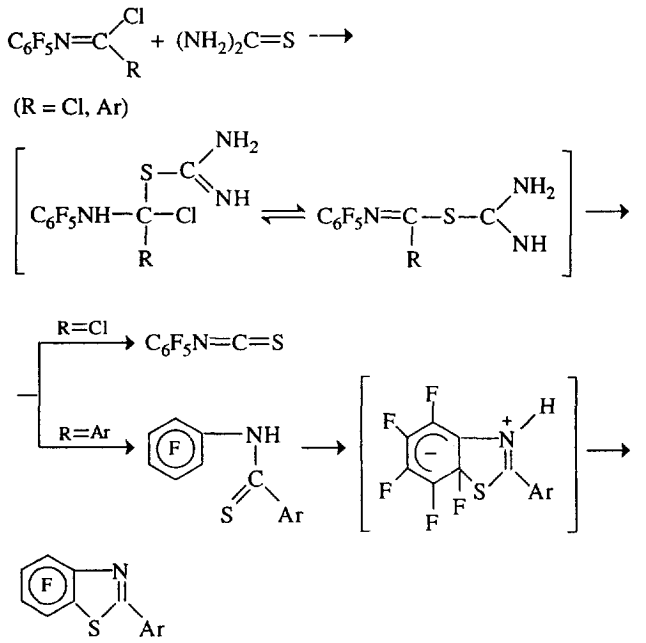


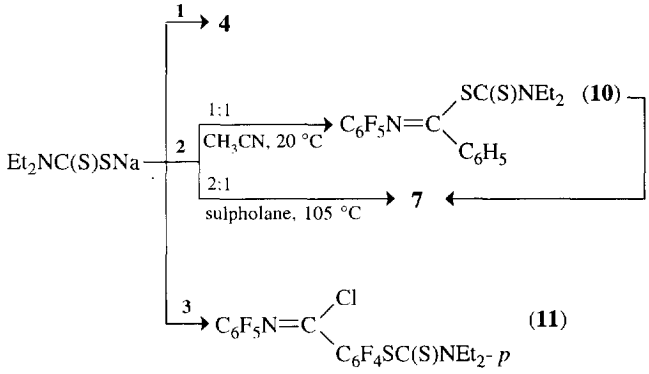
Scheme 1.



Scheme 2.

thioamide (**5**), but much unreacted starting compound **2** remained. When a twofold molar excess of thiourea was used (acetonitrile, 80 °C), a mixture consisting of equal amounts of thioamide **5** and 2-phenyl-4,5,6,7-tetrafluorobenzothiazole (**7**) was formed. This benzothiazole was previously [7,8] obtained from *N*-pentafluorophenylbenzamide (**8**) and P_2S_5 by the intramolecular thermal cyclization of the intermediate thioamide **5**. Imidoyl chloride **3** is the least reactive substrate in the reactions with thiourea. Only part of compound **3** reacted to give thioamide **6** even in the presence of a twofold molar excess of thiourea at 80 °C (acetonitrile). According to ^{19}F NMR data the reaction mixture contains 1:2 amounts of **3** and **6**. When the reaction with thiourea was carried out in sulpholane at 120 °C, both imidoyl chlorides **2** and **3** were transformed into the corresponding benzothiazoles **7** or **9**. According to ^{19}F NMR data, thioamides **5** and **6** are partially transformed into benzothiazoles **7** and **9** on standing. In the mass spectra of thioamides **5** and **6** only molecular ions of these benzothiazoles were observed. The transformation may be represented as in Scheme 2.

Addition of thiourea to a substrate N=C multiple bond seems to be the first reaction step by analogy with the reaction



Scheme 3.

of polyfluoroaromatic imidoyl chloride derivatives with O-nucleophiles in the absence of base [5].

2.2. Reactions with sodium N,N-diethyldithiocarbamate

The reaction of carbonimidoyl dichloride **1** with sodium *N,N*-diethyldithiocarbamate in acetonitrile at 20 °C was similar to the reaction with thiourea. Only isothiocyanate **4** was formed (see Scheme 3). A twofold molar excess of carbamate favours the formation of **4**. A similar transformation of the carbonimidoyl dichloride into isothiocyanate by the reaction of sodium *N,N*-dimethyldithiocarbamate with a non-fluorinated compound has been described for *p*-chlorophenylcarbonimidoyl dichloride [9].

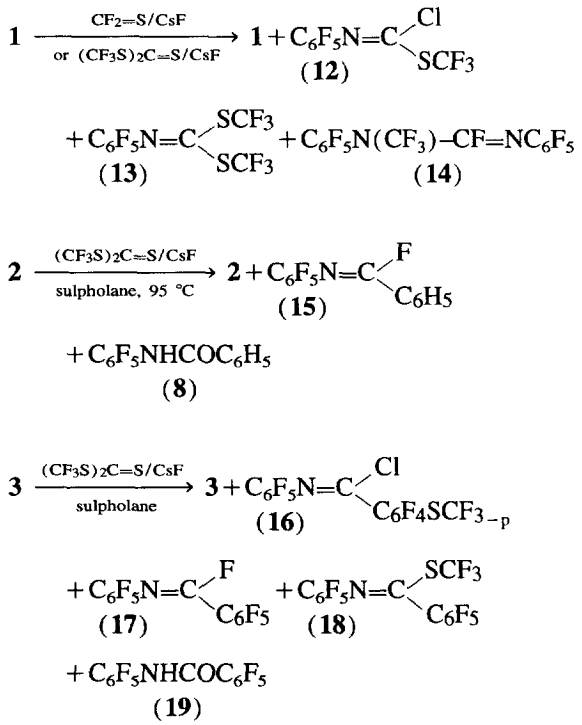
Imidoyl chloride **2** reacted with carbamate (molar ratio 1:1) at 20 °C in acetonitrile with substitution of the chlorine and the formation of compound **10**. The reaction mixture in this case contained ca. 15% of unreacted starting **2** according to GLC data. A temperature rise up to 80 °C did not change the result, but under more severe conditions (sulpholane, 105 °C, twofold molar excess of carbamate), benzothiazole **7** was the main reaction product. The mass spectrum of compounds **10** contained a molecular ion corresponding to benzothiazole **7**, which suggests benzothiazole formation through intramolecular cyclization of **10**. Such a pathway was confirmed by the transformation of **10** into **7** on heating at 105 °C in sulpholane.

Imidoyl chloride **3** behaves very differently from imidoyl chloride **2** in its reaction with carbamate, and the *p*-fluorine atom of the C-pentafluorophenyl group at the carbon N=C bond is substituted to form compound **11**.

2.3. Reactions with $^-SCF_3$ anion sources

It is known that the trifluoromethanethiolate ion $^-SCF_3$, generated by the reversible addition of a fluoride ion to the thiocarbonyl difluoride $CF_2=S$ monomer or its trimer bis(trifluoromethyl)trithiocarbonate in an aprotic solvent, reacts with electrophilic substrates such as pentafluoropyridine and tetrafluorodiazines [10,11]. Substitution of aromatic fluorines by the SCF_3 group proceeds under mild conditions. *N*-Phenylbenzimidoyl chloride is known to be

transformed into trifluoromethyl *N*-phenylthiobenzimidate under the action of $AgSCF_3$ in acetone [12]. In acetonitrile, the resulting thioimidate decomposes to give *N*-phenylbenzimidoyl fluoride [13]. We have therefore studied the interaction of compounds **1–3** with $^-SCF_3$ anion precursors under various conditions. The results are shown in Scheme 4.



Scheme 4.

It should be noted that compounds **1–3** reacted with no or low conversion. Thus, according to GC–MS and ^{19}F NMR data, in the reactions of **1** (Table 1), monothioimidate **12** and dithioimidate **13** as well as dimeric *N*-pentafluorophenylcarbonimidoyl difluoride (**14**) were among the reaction products. The latter is likely to be formed from **1** under the action of CsF as noted by us previously [14]. Separation of mixtures of **1**, **12** and **13**, as well as the determination of the amount of each component, was difficult. The compounds show very similar chromatographic retention times and coincident ^{19}F NMR signals. Column chromatography allowed only the isolation of an unseparated mixture of compounds **12** and **13**, identified by ^{19}F NMR, MS and GLC data. Attempts to produce SCF_3 derivatives from **1** with $AgSCF_3$ failed in acetone and acetonitrile. In both cases starting compound **1** did not undergo any transformation.

Imidoyl chloride **2** did not react with trimer both in acetonitrile at 20 °C or 80 °C, and in sulpholane at 20 °C. According to GC–MS and ^{19}F NMR data, the reaction mixture obtained in sulpholane at 95 °C contained unreacted **2** together with *N*-pentafluorophenylbenzimidoyl fluoride (**15**) and *N*-pentafluorophenyl benzamide (**8**). These compounds probably result from a side reaction involving chlorine atom exchange for fluorine under the action of CsF of partial hydrolysis of the fluoride in the presence of traces of moisture. An attempt to produce SCF_3 derivatives from **2** with $AgSCF_3$ in acetone, in a similar manner to the transformation in the non-fluorinated series, was unsuccessful.

Imidoyl chloride **3** did not react with monomer in acetonitrile at −5 °C. Reaction of **3** with trimer in sulpholane at 20 °C and 100 °C also resulted in large amounts of unreacted starting material. GC–MS data identified products of SCF_3 group substitution of the *p*-fluorine atom of the C–C_6F_5 group (**16**) and of the N=C chlorine atom (**18**) as well as *N*-pentafluorophenyl(*C*-pentafluorophenyl)imidoyl fluoride (**17**). At 100 °C, instead of imidoyl fluoride **17**, the pentafluorobenzamide of pentafluorobenzoic acid (**19**) was identified among the reaction products, presumably as a result of imidoyl fluoride hydrolysis. The same amide was obtained in the reaction of **3** with $AgSCF_3$ in acetonitrile at 20 °C together with unreacted **3**.

2.4. Reactions with thiophenols

Reactions of compounds **1–3** with thiophenol and polyfluorinated thiophenols (pentafluorothiophenol and 2,3,5,6-tetrafluorothiophenol) proceeded in acetonitrile at 20 °C in the presence of anhydrous K_2CO_3 as a base (see Scheme 5).

By varying the amounts of the corresponding thiophenol and K_2CO_3, it possible to substitute one or both chlorine atoms in **1** and obtain thioimidates **20** or dithioimidates **21**. The reactions of **1** with 2,3,5,6-tetrafluorothiophenol and K_2CO_3 proceeded readily. A molar ratio 1:1:0.5 gave both the monosubstituted product (**20c**) and the disubstituted one (**21c**), although unreacted starting **1** remained in the mixture (reaction time was 6 h), ratio of products was 2.5:1:1.75 according to ^{19}F NMR data). The use of 2,3,5,6-tetrafluorothiophenol (twofold molar excess) with 2 equiv. of K_2CO_3 gave dithioimidate (**21c**). Reaction of **1** with thiophenol (reagent ratio was 1:1:0.5) gave monosubstituted product **20a** together with unreacted starting compound (24 h, ratio of **20a** and **1** was 2:1 from ^{19}F NMR data). Approximately 12% of the non-fluorinated product of thiophenol transformation in this case could not be separated from the thioimidate **20a** and analytically pure **20a** was not obtained. In the reaction of **1** with 2 mol of thiophenol and 2 equiv. of K_2CO_3, a mixture of **20a** and **21a** (2:1 from ^{19}F NMR data) was formed. The reaction with pentafluorothiophenol is complicated due to the formation of byproducts unconnected with the main process [e.g. decafluorodiphenyl disulphide (**23**)]. With a reagent molar ratio of 1:1:0.5, dithioimidate **21b** was formed together with monothioimidate **20b** and unreacted starting compound **1**, but substitution of the *p*-fluorine atoms of the SC_6F_5 group in the initially formed compounds was also observed. This process proceeded more readily than substitution of the chlorine (Table 1). Compounds **21b** and **22** have been isolated and characterized completely, but compounds **24** and **25** were not obtained analytically pure and were only identified spectroscopically and by GLC. Mono-

Table 1
Interaction of polyfluoroaromatic imidoyl chlorides with S-nucleophilic reagents

Expt. No.	Substrate, g (mol)	Reagent, g (mol)	Solvent, ml	Reaction temperature, °C (time, h)	Weight of product after reaction, g	Reaction products				
						Compound	Quantity	M.p., °C	M.W. (^{35}Cl) Found Calc.	Composition found
Reactions with $(NH_2)_2C=S$										
1	**1** 0.26 (0.001)	0.15 (0.002)	CH_3CN 3	20 (3)	0.29	**4**				
2	**2** 0.3 (0.001)	0.08 (0.001)	CH_3CN 3	80 (3)	0.23	**2**	main			
						5				
3	**2** 0.3 (0.001)	0.15 (0.002)	CH_3CN 3	80 (13)	0.17	**5** (nc)	0.06 g	107–108		$C_{13}H_6F_5NS$
						7	0.05 g	133–135 (133–135 [8])		
4	**3** 0.3 (0.001)	0.15 (0.002)	sulpholane 5	120–130 (21)	0.3	**7**	0.17 g			
5	**3** 0.2 (0.0005)	0.08 (0.001)	CH_3CN 3	80 (24)	0.2	**3**				
						6 (nc)	0.17 g [a]	149–149.5		$C_{13}HF_{10}NS$
6	**3** 0.2 (0.0005)	0.08 (0.001)	sulpholane 3	120–130 (21)	0.23	**9** (nc)	0.15 g	87–88	372.962 20 372.960 77	$C_{13}F_9NS$
Reactions with $NaSC(S)NEt_2$										
7	**1** 0.26 (0.001)	0.17 (0.001)	CH_3CN 3	20 (1.5)	0.3	**1**, **4**	2: 1 } ^{19}F NMR			
8	**1** 0.26 (0.001)	0.34 (0.002)	CH_3CN 3	20 (1.5)	0.37	**1**, **4**	1: 14 } ^{19}F NMR			
9	**2** 0.3 (0.001)	0.17 (0.001)	CH_3CN 5	20 (22.5)	0.29	**2** [b],				
						10 (nc)		79.5–81		$C_{18}H_{15}F_5N_2S_2$
10	**2** 0.3 (0.001)	0.34 (0.002)	sulpholane 4	105–110 (26.5)	0.47	**7**				

11	**3** 0.2 (0.0005)	0.09 (0.0005)	CH_3CN 4	20 (23)	0.3	**11** (nc)	0.27 g	101–103		$C_{18}H_{10}ClF_9N_2S_2$
Reactions with $^-SCF_3$ anion sources										
12	**1** 0.52 (0.002)	CF_2=S 0.15 (0.002) CsF 0.22 (0.0014)	CH_3CN 4	−5 (4.5)	0.8	**1**, **12**, **13**, **14**	0.3 g			
13	**1** 0.26 (0.001)	$(CF_3S)_2C$=S 0.25 (0.001) CsF 0.11 (0.0007)	CH_3CN 3	70 (24.5)	0.28	**1**, **12** (nc), **13** (nc), **14**	0.24 g [c]		328.930 60 328.931 22 394.930 58 394.929 64	C_8ClF_8NS $C_9F_{11}NS_2$
14	**2** 0.3 (0.001)	$(CF_3S)_2C$=S 0.25 (0.001) CsF 0.11 (0.0007)	sulpholane 6	95 (90)	0.23	**2**, **15**, **8**	5 6 1 (ratio by ^{19}F NMR)			
15	**3** 0.2 (0.0005)	$(CF_3S)_2C$=S 0.12 (0.0005) CsF 0.06 (0.0005)	sulpholane 5	100 (89)	0.26	**3**, **16**, **17**, **18**, **19**				
Reactions with $ArSH/K_2CO_3$										
16	**1** 0.28 (0.0011)	Ar=4-HC_6F_4 0.19 (0.0011)/0.08 (0.0006)	CH_3CN 2	20 (55)	0.3	**1**, **20c** (nc), **21c**	0.12 g	47–48.5	408.937 91 408.937 44	$C_{13}HClF_9NS$
17	(1) 0.26 (0.001)	Ar=4-HC_6F_4 0.36 (0.002)/0.14 (0.001)	CH_3CN 2	20 (5)	0.47	**21c** (nc)		70–73	554.942 10 554.945 60	$C_{19}H_2F_{13}NS_2$
18	(2) 0.33 (0.0011)	Ar=4-HC_6F_4 0.21 (0.0011)/0.09 (0.0006)	CH_3CN 5	20 (22)	0.5	**26c** (nc)		91–93	451.006 70 451.007 71	$C_{19}H_6F_9NS$
19	**3** 0.2 (0.0005)	Ar=4-HC_6F_4 0.09 (0.0005)/0.04 (0.00025)	CH_3CN 4	20 (22)	0.22	**29c** (nc)		88–90	556.927 80 556.931 05	$C_{19}HClF_{13}NS$

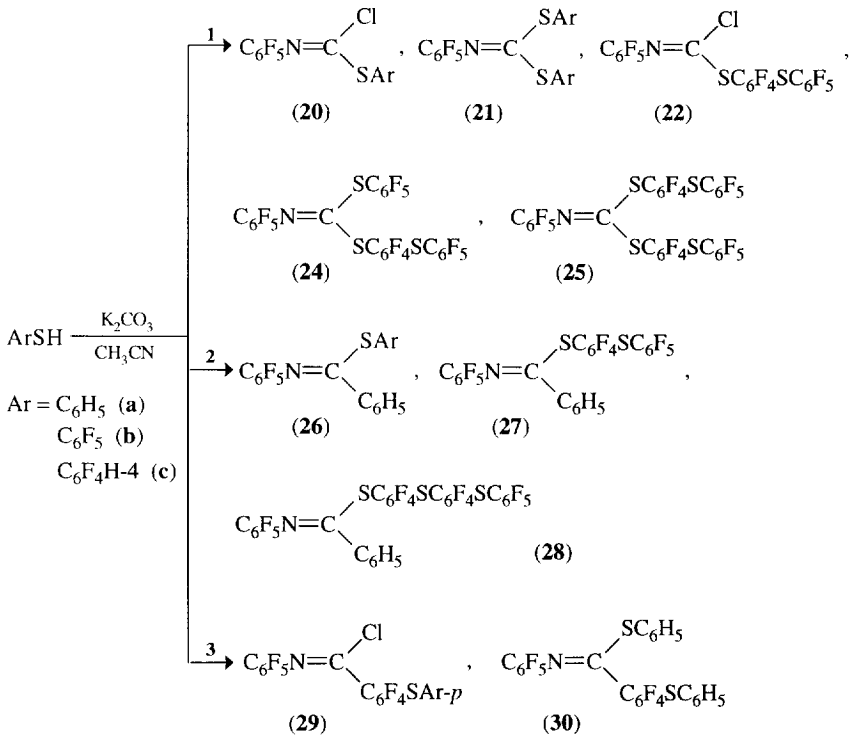
(continued)

Table 1 (*continued*)

Expt. No.	Substrate, g (mol)	Reagent, g (mol)	Solvent, ml	Reaction temperature, °C (time, h)	Weight of product after reaction, g	Reaction products				
						Compound	Quantity	M.p., °C	M.W. (^{35}Cl) Found Calc.	Composition found
20	**1** 0.38 (0.0014)	Ar = C_6H_5 0.16 (0.0014)/0.1 (0.0007)	CH_3CN 3.5	20 (140)	0.45	**20a** (nc)	0.23 g [d]		336.975 99 336.975 14	$C_{13}H_5ClF_5NS$
21	**1** 0.32 (0.0012)	Ar = C_6H_5 0.27 (0.0024)/0.17 (0.0012)	CH_3CN 3.5	20 (125)	0.44	**21a** (nc), **20a**	0.27 g	133–134	411.019 40 411.017 48	$C_{19}H_{10}F_5NS_2$
22	**2** 0.29 (0.00095)	Ar = C_6H_5 0.11 (0.001)/0.07 (0.0005)	CH_3CN 5	20 (47)	0.4	**26a** (nc)		86.5–88	379.046 68 379.045 41	$C_{19}H_{10}F_5NS$
23	**3** 0.2 (0.0005)	Ar = C_6H_5 0.06 (0.0005)/0.04 (0.00025)	CH_3CN 4	20 (23)	0.25	**29a** (nc), **30**	0.18 g 0.03 g [f]	47–50 [e]	484.966 49 484.968 73	$C_{19}H_5ClF_9NS$
24	**3** 0.2 (0.0005)	Ar = C_6H_5 0.11 (0.001)/0.14 (0.001)	CH_3CN 3	20 (48)	0.27	**29a**, **30** (nc)	0.08 g [g] 0.19 g	108.5–110.5	559 559	$C_{25}H_{10}F_9NS_2$
25	**1** 0.26 (0.001)	Ar = C_6F_5 0.2 (0.001)/0.07 (0.0005)	CH_3CN 3	20 (28)	0.4	**1**, **20b**, **21b**, **22**, **23**, **24**, **25**	35.5, 26, 8.5, 16.5, 5, 0.5, 5 GLC %			
26	**1** 0.26 (0.001)	Ar = C_6F_5 0.4 (0.002)/0.14 (0.001)	CH_3CN 3	20 (27)	0.29	**22** (nc), **1**, **20b**, **21b**, **22**, **23**, **24**, **25**	0.06 g [g] 22.5, 7, 3, 22, 5, 8, 8 GLC %	85.5–87.5	606.894 53 606.893 68	$C_{19}ClF_{14}NS_2$

27 [i]	**1** 0.26 (0.001)	Ar = C_6F_5 0.4 (0.002)/0.07 (0.0005)	CH_3CN 3	20 (94.5)	0.5	**20b** (nc) **1**, **21b**, **22**, **23**, **25**	0.43 g [a] 16.5 8.5 13 4.5 2.5 } GLC %	74.5–76.5	426.929 53 426.928 02	$C_{13}ClF_{10}NS$
28 [i]	**1** 0.26 (0.001)	Ar = C_6F_5 0.8 (0.004)/0.28 (0.002)	CH_3CN 4	20 (46.5)	0.7	**21b** (nc)	0.08 g 0.17 g [k]	87–89	[j]	$C_{19}F_{15}NS_2$
29	**2** 0.3 (0.001)	Ar = C_6F_5 0.2 (0.001)/0.07 (0.0005)	CH_3CN 5	20 (47)	0.45	**2**, **26b** (nc) [m]	55 GLC % 0.07 g	105–107	469 [l] 469	$C_{19}H_5F_{10}NS$
30 [i]	**2** 0.3 (0.001)	Ar = C_6F_5 0.4 (0.002)/0.14 (0.001)	CH_3CN 6	40–50(6) 20 (71)	0.52 [n]	**2**, **27**, **28**				
31	**3** 0.2 (0.0005)	Ar = C_6F_5 0.1 (0.0005)/0.04 (0.00025)	CH_3CN 4	20 (47)	0.32	**29b** (nc)	0.16 g	113–115.5	574.921 60 574.921 63	$C_{19}ClF_{14}NS$

[a] From two experiments.
[b] 15% (GLC) in the reaction mixture.
[c] From five experiments; the content of **12** and **13** were 43% and 35% (GLC).
[d] A mixture of 85.5% of **20a** and 13.5% of unidentified non-fluorinated compound (GLC).
[e] The content of **29a** was 97% (GLC).
[f] The content of **30** was 67% (GLC).
[g] The content of **29a** was 90.5% (GLC).
[h] The content of **22** was 97% (GLC).
[i] Carried out in argon.
[j] The intensity of the molecular ion was low. Found composition was determined for the fragment ion $M - SC_6F_5$, $C_{13}F_{10}NS$; 391.959 56, 391.959 17.
[k] A mixture of 4% of **23**, 2.5% of **20b**, 12% of **21b**, 14% of **22**, 33% of **24** and 31.5% of **25** (GLC).
[l] The intensity of the molecular ion was low.
[m] A mixture of 18% of **26b**, 68% of **27** and 13% of **28** (0.02 g, GLC), and 0.1 g of a mixture of 73% of **27** and 13% of **28** (GLC).
[n] 0.09 g of **27** and 0.04 g of **28** were obtained from 0.23 g of the filtered precipitate containing 50% of **2** and 40% of **27** (GLC). Compounds **27** and **28** could not be purified further. The mixture (0.18 g) of **27** and **28** (80% and 10% by GLC) was isolated from 0.29 g of solid residue containing 52% of **2**, 25% of **27** and 6% of **28** by column chromatography. This solid residue was obtained by evaporation of the filtrate.



Scheme 5.

thiomidate **20b** was isolated in the experiment in argon with a twofold excess of pentafluorothiophenol and 1 equiv. of K_2CO_3. Its content in the reaction mixture was 41% (GLC).

Preferential substitution of fluorine was observed in the reaction of pentafluorothiophenol with imidoyl chloride **2** (Table 1). Compounds **27** and **28** were difficult to purify and were not obtained as analytically pure samples. Molecular ions were absent in the mass spectra of these compounds, but fragmentation was consistent with the proposed structures. In contrast, reactions of **2** with tetrafluorothiophenol and thiophenol proceeded to give benzothioimidates **26c** and **26a** in good yield.

Substitution of the *p*-fluorine atom of the $N{=}CC_6F_5$ group with the formation of compounds of type **29** is the main reaction between all thiophenolic reagents and imidoyl chloride **3** as well as in the reactions with sodium *N,N*-diethyldithiocarbamate and $^-SCF_3$ anion sources. At twofold molar excess of thiophenolic reagent and 2 equiv. of K_2CO_3, substitution of the chlorine atom takes place to give compounds of type **30**.

Hence, the reactions of polyfluoroaromatic imidoyl chloride derivatives with charged S-nucleophiles and S-nucleophiles in the presence of a base proceeded with retention of the N=C multiple bond in the reaction products and substitution of chlorine by nucleophilic residues. On varying the conditions for carbonimidoyl dichloride **1**, it is possible to substitute one chlorine atom or both and obtain mono- or dithioimidates. The formation of isothiocyanate **4** in the reaction with sodium *N,N*-diethyldithiocarbamate may be explained in terms of successive transformations of the primary products of the substitution process. For those substrates where substitution of both chlorine atoms at the N=C multiple bond and aromatic fluorines of C_6F_5 or SC_6F_5 groups at the C atom of this multiple bond is possible, the latter reaction prevails although products of chlorine atom substitution are also formed if excess reagents were used.

In order to explain these results, we have performed semi-empirical PM3 calculations of the substrate molecules and their σ-complexes with the simplest $^-SCF_3$ anion and with the $^-SC_6H_5$ anion using the MNDO-90 program [15]. Some data obtained with full geometry optimizations are given in Table 2.

Charge distribution does not fully explain the experimental data since carbon atoms bearing the largest positive charges are at the *ortho* positions of the pentafluorophenyl rings. For all substrate molecules considered, the LUMO is of the π-type. The largest frontier densities ($C_{\mu\pi}{}^2$) are concentrated at the *para* positions of the pentafluorophenyl rings (C_{para} for **1** and **2**, C'_4 for **3**) and at the imidoyl carbon atom (C_{im}) (Table 2). This can explain the reaction pathway for compound **3** but not for **1** or **2**. At the same time the σ-complexes of **1** and **2**, formed by $^-SCF_3$ (or $^-SC_6H_5$) addition to C_{im} and to C_{para}, differ considerably in energy (ΔH_f). The former are more favourable by 14.0 (18.4) kcal mol^{-1} for compound **1** and by 6.6 (11.6) kcal mol^{-1} for compound **2**. This probably accounts for chlorine atom substitution. In the case of compound **3**, anion addition to C_{para} remains the least favourable, whereas the σ-complexes which form on addition of $^-SCF_3$ (or $^-SC_6H_5$) to C_{im} and to C'_4 are rather close in energy. Hence, for this compound, the frontier

Table 2
PM3 calculations for substrate molecules and σ-complexes with $^{-}SCF_3$ and $^{-}SC_6H_5$ anions

Substrate molecule					σ-Complexes, ΔH_f (kcal mol^{-1})					
Compound	ΔH_f (kcal mol^{-1})	$C_{\mu\pi}{}^2$			With $^{-}SCF_3$[a]			With $^{-}SC_6H_5$[a]		
		(C_{im})	(C_{para})	(C'_4)	(C_{im})	(C_{para})	(C'_4)	(C_{im})	(C_{para})	(C'_4)
1	−176.4	0.111	0.247	–	−380.3	−366.3	–	−209.4	−191.0	–
2	−145.9	0.112	0.230	0.019	−340.0	−333.4	–	−169.4	−157.8	–
3	−352.5	0.105	0.087	0.151	−550.1	−545.7	−549.4	−377.4	−371.4	−374.3

[a] The ΔH_f values for $^{-}SCF_3$ and $^{-}SC_6H_5$ anions are equal to −183.3 and −2.0 kcal mol^{-1}, respectively.

density distribution provides a possible explanation for favourable substitution at C'_4.

In the reaction with thiourea, addition of a molecule of thiourea to the N=C bond of the imidoyl chloride first takes place and the structure of the final products is determined by transformations of the primary intermediates.

The structures of compounds obtained in the reactions with S-nucleophiles were determined analytically and spectroscopically. According to these data all compounds except **26–28** and **30** are formed as single isomers. Compounds with a chlorine atom at the N=C bond are likely to have a Z-configuration by analogy with literature data and our data [16–18] for chloroformamidines and imidoyl chlorides. In the ^{19}F NMR spectra of dithioimidates, different signals are observed for the fluorine of fluoro groups in the *cis* and *trans* positions with respect to the *N*-pentafluorophenyl ring. Compounds **26–28** and **30** have two sets of signals for all fluoro groups in their ^{19}F NMR spectra. The multiplicity and integral intensity of the signals correspond to two isomers for each compound.

3. Experimental details

^{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 an LHM-7a instrument with a thermal conductivity detector having a linear temperature programme of 10 °C min^{-1}, using internal normalization (80–270 °C), a 4000×4 mm column packed with methylsilicon SE-30, fluorosilicon QF-1/Chromosorb W, silicon SKTFT-50 and SKTTV-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 5989A mass spectrometer, ionization potential 70 eV.

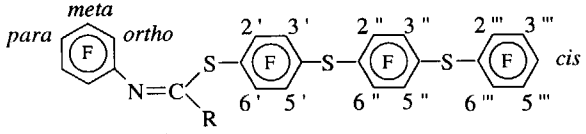
Molecular weights and molecular formulae were determined mass spectrometrically on a GC–MS Finnigan MAT-8200 instrument. The nominal energy of the ionizing electrons was 70 eV. Acetonitrile was purified by refluxing with P_2O_5, distillation, redistillation from anhydrous K_2CO_3 and standing over molecular sieves. Sulpholane was freshly distilled. Acetone was utilized after standing over molecular sieves.

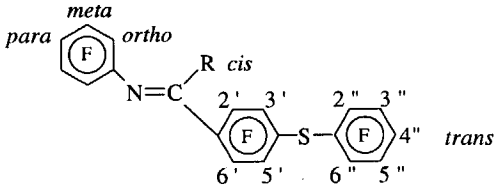
The reaction conditions and the results of experiments are presented in Table 1. Spectroscopic and analytical data for newly synthesized compounds are presented in Tables 3 and 4.

3.1. Reactions with $(NH_2)_2C{=}S$

To a vigorously stirred solution of dry thiourea in a solvent was added a solution of the imidoyl chloride derivative in the

Table 3
Spectroscopic characteristics of newly synthesized compounds (nc)





Compound	^{19}F NMR spectrum, δ, ppm (solvent)	^{1}H NMR spectrum, δ, ppm (solvent)	IR spectrum, cm^{-1} ($CHCl_3$)
5	0 ($2F_m$); 7.50 (F_p); 18.68 ($2F_o$)	7.47–8.05 (C_6H_5, NH)	985 (s); 1025 (w); 1445 (m); 1510 (vs); 3170 (br m); 3400 (br) (CCl_4)
6	0.91 ($2F_m$); 1.84 (F'_3, F'_5); 9.66 (F_p); 10.45 (F'_4); 19.61 ($2F_o$); 20.87 (F'_2, F'_6)	8.1 (s, NH)	1000 (vs); 1155 (m); 1190 (m); 1325 (vs); 1500 (vs); 3400 (s) (CCl_4)
9	1.84 ($2F_m$); 5.77, 6.32 (F_5, F_6); 13.78 (F_p); 17.12 (F_4); 23.97 (F_7); 24.62 ($2F_o$)		980 (vs); 1040 (m); 1090 (m); 1340 (m); 1460–1520 (vs); 1640 (w) (KBr)
10	−1.46 ($2F_m$); 0.24 (F_p); 12.58 ($2F_o$) ($CDCl_3$)	1.09 (t, CH_3); 1.29 (t, CH_3); 3.76 (m, $2CH_2$); 7.45, 8.07 (C_6H_5) ($CDCl_3$)	970–990 (vs); 1136 (m); 1260 (s); 1350 (m); 1412 (m); 1445 (m); 1480–1512 (vs); 1575 (m); 1606 (vs); 2888 (w); 2925 (m); 2994 (m); 3087 (w)
11	0 ($2F_m$); 3.75 (F_p); 13.09 ($2F_o$); 22.63 (F'_2, F'_6); 32.78 (F'_3, F'_5) ($CDCl_3$)	1.29 (t, CH_3); 1.45 (t, CH_3); 3.88 (q, CH_2); 3.99 (q, CH_2) ($CDCl_3$)	982–1005 (vs); 1272 (s); 1422 (s); 1482–1522 (vs); 1677 (s); 2877 (w); 2938 (m); 2988 (m) (CCl_4)
12	0.46 ($2F_m$); 4.37 (F_p); 12.90 ($2F_o$); 120.19–121.67 * (SCF_3) (hexane)		
13	0.10 ($2F_m$); 3.74 (F_p); 11.93 ($2F_o$); 120.19–126.57 * (SCF_3) (hexane)		
20a	−0.30 ($2F_m$); 1.80 (F_p); 11.75 ($2F_o$) (CH_3CN)	7.42, 7.57 (C_6H_5)	905 (vs); 995–1005 (vs); 1520 (vs); 1618–1645 (vs); 3070 (w)
20b	0.23 ($2F_m$); 2.82 (F'_3, F'_5); 3.23 (F_p); 12.37 ($2F_o$); 16.18 (F'_4); 31.97 (F'_2, F'_6) (CH_3CN)		855 (s); 900 (s); 975–990 (vs); 1000 (s); 1495–1510 (vs); 1640–1650 (s)
20c	−0.55 ($2F_m$); 2.55 (F_p); 12.34 ($2F_o$); 25.61 (F'_3, F'_5); 31.16 (F'_2, F'_6) ($CDCl_3$)	7.24 (H_{Ar}) ($CDCl_3$)	916–928 (s); 988–1005 (vs); 1244 (m); 1511 (vs); 1628 (m); 1655 (vs); 2982 (w) (CCl_4)
21a	−1.97 ($2F_m$); −1.20 (F_p); 10.50 ($2F_o$) ($CDCl_3$)	7.40, 7.54 (C_6H_5) ($CDCl_3$)	990 (vs); 1000 (vs); 1512 (vs); 1585–1590 (vs); 3070–3080 (w) (CCl_4)
21b	0.50 ($2F_m$); 2.65 (*cis*, *trans*-F'_3, F'_5); 3.65 (F_p); 11.51 ($2F_o$); 15.55 (br, *trans*-F'_4); 17.67 (br, *cis*-F'_4); 31.71 (br, *trans*-F'_2, F'_6); 33.30 (br, *cis*-F'_2, F'_6) (CH_3CN)		980–990 (vs); 1100 (s); 1495–1505 (vs); 1600 (m); 1630 (m) (CCl_4)

21c	0 (*cis, trans*-2F_m); 2.31 (*cis, trans*-F_p); 11.73 (*cis, trans*-2F_o); 25.73 (br, *trans*-F'_3, F'_5); 26.56 (br, *cis*-F'_3, F'_5); 31.08 (br, *trans*-F'_2, F'_6); 32.39 (br, *cis*-F'_2, F'_6) (CH_3CN)	7.56 (H_{Ar})	928 (s); 988–1005 (vs); 1244 (m); 1511 (vs); 1600 (vs); 2982 (w) (CCl_4)
22	−0.2 (2F_m); 2.34 (F''_3, F''_5); 3.11 (F_p); 12.67 (F''_4, 2F_o); 30.10, 31.08, 32.97 (F'_3, F'_5; F''_2, F''_6; F'_2, F'_6) (hexane)		907 (s); 970 (s); 985 (vs); 1000 (vs); 1100 (s); 1255 (m); 1475–1520 (vs); 1650 (s) (CCl_4)
25	0.08 (2F_m); 2.49 (*cis, trans*-F''_3, F''_5); 2.86 (F_p); 12.01 (2F_o); 13.01 (*cis, trans*-F''_4); 30.48–30.61, 32.59, 33.55 (*cis, trans*-F'_3, F'_5; F''_2, F''_6; F'_2, F'_6)		
26a	−2.29 to −1.80 (F_p, 2F_m); 10.58 (2F_o) } 4:1 −2.29 to −1.80 (F_p, 2F_m); 9.75 (2F_o)	7.16–7.81 (C_6H_5)	980 (vs); 1240 (m); 1500 (vs); 1575–1595 (m); 3075 (w)
26b	−0.78 to −0.33, 0.33 (4F_m, F_p); 1.50–2.50 (2F'_3, 2F'_5, F_p); 10.91 (4F_o); 13.57 (2F'_4); 31.40 (2F'_2, 2F'_6)	7.38, 7.71 (C_6H_5)	975–990 (vs); 1090 (s); 1490–1510 (vs); 1625–1640 (m); 2850 (w); 2915 (w)
26c	−1.52 to 0.87, 0.95 (4F_m, 2F_p); 10.64 (2F_o); 11.10 (2F_o); 24.45 (F'_3, F'_5); 25.00 (F'_3, F'_5); 30.25 (2F'_2, 2F'_6) ($CDCl_3$)	7.35–7.76 (H_{Ar}) ($CDCl_3$)	975 (vs); 988 (vs); 1175 (s); 1237 (s); 1500–1512 (vs); 1620 (vs); 3075 (w)
27	−1.13 to −0.69, 0.0 (4F_m, F_p); 1.23, 2.05 (F_p, 2F''_3, 2F''_5); 10.73 (4F_o); 12.29 (2F''_4); 28.91–31.76 (2F''_2, 2F''_6; 2F'_3, 2F'_5; 2F'_2, 2F'_6)	7.37–7.66 (C_6H_5)	
28	−0.53, −0.04, 0.65 (4F_m, F_p); 1.86, 2.97 (F_p, 2F'''_3, 2F'''_5); 11.34 (4F_o); 13.27 (2F'''_4); 30.16–32.65 (2F'''_2, 2F'''_6; 2F''_3, 2F''_5; 2F''_2, 2F''_6; 2F'_3, 2F'_5; 2F'_2, 2F'_6)	7.47–7.74 (C_6H_5)	
29a	0 (2F_m); 3.63 (F_p); 12.85 (2F_o); 22.79 (F'_2, F'_6); 30.76 (F'_3, F'_5)	7.30, 7.43 (C_6H_5)	980 (vs); 1005 (vs); 1295 (m); 1480 (vs); 1520 (vs); 1680 (vs); 3080 (w)
29b	0.54 (2F_m); 2.17 (F''_3, F''_5); 4.15 (F_p); 12.66 (F''_4); 13.26 (2F_o); 23.48 (F'_2, F'_6); 30.91, 31.19 (F'_3, F'_5; F''_2, F''_6) ($CCl_4+CH_3(CN)$)		965–987–1000 (vs); 1095 (s); 1287 (m); 1475–1495–1512 (vs); 1636 (m); 1675 (s) (CCl_4)
29c	0 (2F_m); 4.01 (F_p); 13.09 (2F_o); 23.46 (F''_3, F''_5); 25.18 (F'_2, F'_6); 29.30, 31.21 (F''_2, F''_6; F'_3, F'_5) ($CDCl_3$)	7.12–7.24 (H_{Ar}) ($CDCl_3$)	970 (s); 1005 (vs); 1480–1512 (vs); 1680 (m); 3080 (w)
30	0.38 (2F_m); 2.13 (F_p); 11.63 (2F_o); 22.96 (F'_2, F'_6); 30.81 (F'_3, F'_5) (CH_3CN)	7.10–7.56 (C_6H_5) (CH_3CN)	975 (vs); 990 (vs); 1275 (m); 1470 (vs); 1500 (vs); 1612 (s); 1635 (m); 3025 (w) (CCl_4)

* Signals for the fluorine atoms of the SCF_3 groups and impurities signals in **12** and **13**.

Table 4
Analytical data for newly synthesized compounds (nc)

Compound	Found (%) / Calculated (%)					
	C	H	Cl	F	N	S
5	51.8 / 51.2	1.4 / 1.9	–	31.43 / 31.35	4.3 / 4.6	10.2 / 10.5
6	39.4 / 39.7	0 / 0.25	–	47.35 / 48.34	3.6 / 3.6	8.5 / 8.1
9	41.4 / 41.8	–	–	45.45 / 45.84	3.9 / 3.7	8.8 / 8.6
10	51.3 / 51.7	3.28 / 3.59	–	22.70 / 22.73	6.9 / 6.7	15.4 / 15.3
11	41.3 / 41.2	1.80 / 1.91	7.1 / 6.8	33.27 / 32.60	5.2 / 5.3	12.2 / 12.2
20b	36.81 / 36.49	0.2 / –	8.30 / 8.30	44.47 / 44.44	3.42 / 3.27	8.52 / 7.48
20c	38.49 / 38.09	0.4 / 0.24	8.36 / 8.67	42.34 / 41.75	3.42 / 3.42	
21a	55.6 / 55.5	2.6 / 2.4	–	23.19 / 23.11	3.2 / 3.4	15.6 / 15.6
21b	38.71 / 38.58	0.3 / –	–	48.19 / 48.22	2.44 / 2.37	11.60 / 10.83
21c	40.64 / 41.08	0.53 / 0.3	–	43.72 / 44.50	2.54 / 2.52	11.56 / 11.53
22	/ 37.56	–	/ 5.85	/ 43.82	2.20 / 2.31	/ 10.54
26a	60.52 / 60.16	2.56 / 2.64	–	25.61 / 25.06	3.91 / 3.69	8.80 / 8.44
26c	50.56 / 50.55	1.27 / 1.33	–	38.08 / 37.91	3.15 / 3.10	7.3 / 7.1
29a			7.20 / 7.31	34.46 / 35.22	2.93 / 2.88	7.10 / 6.59
29b	/ 39.65	–	6.70 / 6.17	/ 46.26	2.20 / 2.43	/ 5.56
29c	41.2 / 40.9	0.2 / 0.2	6.4 / 6.4	44.5 / 44.3	2.4 / 2.5	6.2 / 5.7
30	53.50 / 53.67	1.88 / 1.79	–	30.94 / 30.59	2.54 / 2.50	11.96 / 11.45

same solvent and the reaction mixture stirred at the temperature indicated in Table 1. After reaction, the mixture was warmed up to room temperature, poured into water and extracted with ether. The ether layer was dried over $CaCl_2$, the solvents distilled off and the residue analyzed by ^{19}F and ^{1}H NMR spectroscopy, GC–MS and IR spectroscopy. The mixtures of compounds **5**, **7** and **3**, **6** were separated by column chromatography on silica gel, eluent $CHCl_3$. Compounds **5** and **6** were purified by recrystallization from hexane while compound **7** was sublimed at 125 °C/20 mmHg. Compound **9** was isolated from the reaction mixture by column chromatography (eluent $CHCl_3$) and sublimed at 120 °C/20 mmHg.

3.2. Reactions with $NaSC(S)NEt_2$

$NaSC(S)NEt_2$ was dried over P_2O_5 at 80 °C in a vacuum system. The reactions were carried out by a procedure similar to that for thiourea. Compounds **10** and **11** were purified by recrystallization from petroleum ether (b.p. 70–100 °C) and hexane.

3.3. Heterocyclization of 10

A stirred solution consisting of 0.02 g of **10** in 1.5 ml of dry sulpholane was heated at 105 °C for 26.5 h. From the ^{19}F NMR data, the reaction mixture contained starting **10** and benzothiazole **7**, ratio 1.2:1.

3.4. Reactions with $^{-}SCF_3$ anion sources

(a) Caesium fluoride was dried at 200 °C. The reaction with gaseous thiocarbonyl difluoride was carried out in a Carius tube as in Ref. [10]. The reactions with bis(trifluoromethyl)trithiocarbonate were carried out in argon. A

solution of the trimer in a solvent was added to a suspension of caesium fluoride in a vigorously stirred solution of the imidoyl chloride derivative in the same solvent. After completion of the reaction, the reaction mixture was poured into water. In the case of compound **1** the mixture obtained was worked-up as described for the reactions with thiourea. Unseparated mixtures of compounds **12** and **13** were separated by column chromatography (eluent hexane). For compounds **2** and **3**, after dilution of the reaction mixture with water the precipitate was filtered off and analyzed.

(b) To a vigorously stirred solution consisting of 0.001 mol of the imidoyl chloride derivative in 2 ml of solvent was added a solution of 0.001 mol or 0.002 mol of $AgSCF_3$ in 2 ml of the same solvent at room temperature and the mixture stirred for 20 h. The precipitate was filtered off and treated with petroleum ether (70–100 °C). After evaporation of the solvent from the filtrate, the residue was treated with petroleum ether (70–100 °C). Ether solutions were combined, the solvent distilled off and the residue analyzed.

3.5. Reactions with thiophenols/K_2CO_3

To a vigorously stirred suspension of freshly prepared anhydrous K_2CO_3 in acetonitrile were added solutions of the thio reagent and the imidoyl chloride derivative in acetonitrile. After completion of the reaction, the precipitate was filtered off and washed with water. Solvent was distilled off in vacuum without heating and the residue analyzed and purified. Compounds **21a**, **26a**, **26c** and **29c** were purified by recrystallization from petroleum ether (70–100 °C). Compound **26a** was also sublimed at 100 °C/5 mmHg. Compounds **20a–c**, **21b**, **21c**, **22**, **24**, **25**, **26b** and **27–30** were isolated and purified by column chromatography on silica gel and then recrystallized from petroleum ether (70–100 °C) or sublimed at 90–100 °C/5 mmHg. For compounds **20b**, **21b**, **22** and **29a**, the eluent was hexane; for compound **20c**, a mixture of hexane/chloroform, 10:1 by volume; for compounds **20a**, **26b** and **29b**, a mixture of hexane/CCl_4 (3:1 by volume); for compounds **24**, **25**, **28** and **30**, CCl_4; for **21c** and **27**, $CHCl_3$.

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