SOME REACTIONS OF PENTAFLUOROBENZENESULFENYL CHLORIDE AND PENTAFLUOROBENZENESULFENYL CYANATE

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SUMMARY

Some of the reactions of pentafluorobenzenesulfenyl chloride, C_6F_5SCl, have been studied. These show that the properties of the S–Cl bond are as expected in typical sulfenyl chlorides with bond polarity $\overset{+}{S}$–$\overset{-}{Cl}$.

Pentafluorobenzenesulfenyl cyanate, C_6F_5SNCO, has been prepared from C_6F_5SCl and AgNCO and is a polymeric solid. It reacts with compounds containing active hydrogen to give fracture of the S–N bond and formation of corresponding pentafluorobenzenesulfenyl derivative and cyanuric acid.

The infrared, Raman, mass and ^{19}F NMR spectra of the new compounds prepared are discussed.

INTRODUCTION

Pentafluorobenzenesulfenyl chloride, C_6F_5SCl, has recently been reported[1,2]. It can be prepared from pentafluorothiophenol or its lead salt, $(C_6F_5S)_2Pb$, and chlorine. In continuation of the study of the reactions of fully-halogenated aromatic thiols and their derivatives, some of the reactions of pentafluorobenzenesulfenyl chloride have been studied, and compared with those of trifluoromethanesulfenyl chloride, and non-halogenated thiol derivatives. It has recently been shown that the pentafluorophenyl group inductively withdraws electrons more strongly than a phenyl group, but much less than the trifluoromethyl group, so that the relative inductive effects are $CF_3 > C_6F_5 > C_6H_5$[3]. The electronegativity of the C_6F_5 group depends on its environment, but is generally intermediate between chlorine and bromine[4], while that of the CF_3 group is about the same as chlorine[5]. The reactions of CF_3SCl suggest that the bond polarity is $CF_3\overset{+}{S}$–$\overset{-}{Cl}$, so in C_6F_5SCl the bond

polarity would be $C_5F_6\overset{+}{S}-\overset{-}{Cl}$, and this is confirmed by its reactions. This paper describes some of the reactions of pentafluorobenzenesulfenyl chloride and cyanate. The physical properties of the products are reported.

RESULTS AND DISCUSSION

The reactions of sulfenyl chlorides may be divided into four categories.

1. Formation of disulfides, symmetrical or unsymmetrical, by reaction with a thiol, or a metal salt of a thiol.

$$RSCl + R'SH \rightarrow RSSR' + HCl$$
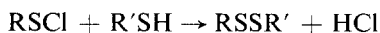
2. Thiolalkylation or thioarylation, resulting in the formation of C–S bonds, for instance with Grignard reagents

$$ArMgHal + CF_3SCl \rightarrow ArSCF_3 + MgHalCl$$
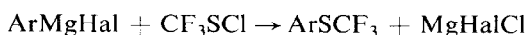
This reaction will depend upon the polarity of the molecule, in CF_3SCl the polarity would be $CF_3\overset{+}{S}-\overset{-}{Cl}$, but some displacement of $CF_3\overset{-}{S}$ is also observed [6]. Addition to olefins also gives C–S and C–Cl bonds [7].

$$CH_2 = CH_2 + C_6H_5SCl \rightarrow C_6H_5SCH_2CH_2Cl$$

3. Exchange reactions, such as

$$RSCl + MX \rightarrow RSX + MCl$$
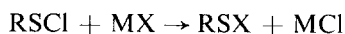
Reactions have been observed with C_6F_5SCl and MX, where MX = AgCN, AgSCN, AgNCO and AgSeCN [1].

4. Reactions involving the formation of sulfenamides. C_6F_5SCl has very recently been shown to react with ammonia and piperidine to form $C_6F_5SNH_2$, $(C_6F_5S)_2NH$ or $(C_6F_5S)_3N$, and $C_6F_5SNC_5H_{10}$ respectively, depending on the conditions, together with the base hydrochloride [2, 8].

$$RSHal + 2HNR'_2 \rightarrow RSNR'_2 + R'_2NH_2Hal$$

The reactions of C_6F_5SCl, shown diagrammatically in Figure 1, illustrate some of these reactions.

These reactions are completely characteristic of sulfenyl chlorides, and the presence of the C_6F_5 group does not appear to affect the properties of the S–Cl bond. The compounds C_6F_5SSCN and C_6F_5SSeCN were too unstable to be isolated pure at room temperature.

Trifluoromethanesulfenyl cyanate, CF_3SNCO, can exist in monomeric, dimeric, and trimeric forms, the dimeric and trimeric forms are cyclic with 4- and 6-membered rings respectively [9, 10]. The reaction of trifluoromethanesulfenyl

C_6F_5SCl

+ $CH_2 = CH_2 \rightarrow C_6F_5SCH_2CH_2Cl$
+ i-PrLi $\rightarrow C_6F_5S(i\text{-}Pr)$
+ t-BuLi $\rightarrow C_6F_5S(t\text{-}Bu)$
+ MeMgCl $\rightarrow C_6F_5SMe$
+ EtMgCl $\rightarrow C_6F_5SEt$
+ PhMgCl $\rightarrow C_6H_5SC_6H_5$
+ MeSH $\rightarrow C_6F_5SSMe$
+ n-BuSH $\rightarrow C_6F_5SS(n\text{-}Bu)$
+ C_6F_5SH $\rightarrow C_6F_5SSC_6F_5$
+ NH_3 $\rightarrow (C_6F_5S)_2NH$ (see also Ref. 2)
+ Me_2NH $\rightarrow C_6F_5SNMe_2$
+ $n\text{-}Bu_2NH$ $\rightarrow C_6F_5SN(n\text{-}Bu_2)$
+ Ph_2NH $\rightarrow C_6F_5SNPh_2$
+ AgCN $\rightarrow C_6F_5SCN$ (see Ref. 1)
+ KCN $\rightarrow C_6F_5SCN$ (see Ref. 2)
+ AgSeCN $\rightarrow C_6F_5SSeCN$ (see Ref. 1)
+ AgNCO $\rightarrow C_6F_5SNCO$ (see Ref. 1)
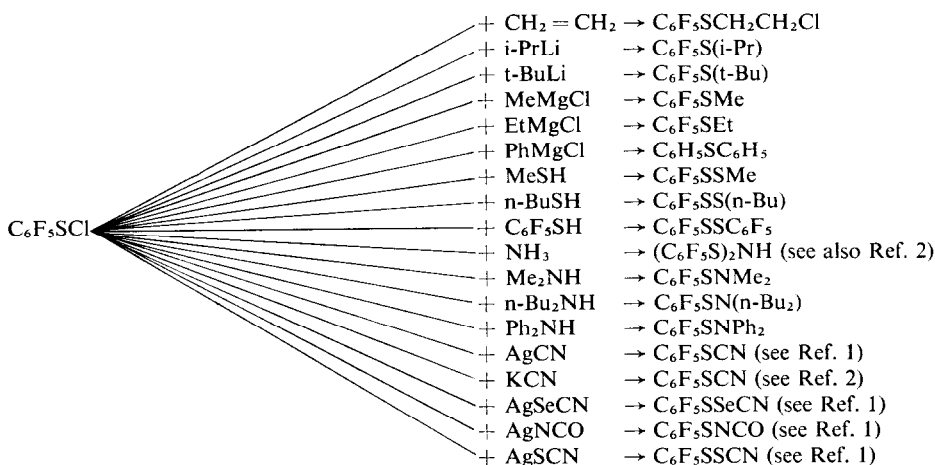+ AgSCN $\rightarrow C_6F_5SSCN$ (see Ref. 1)

Fig. 1. Some reactions of pentafluorobenzenesulfenyl chloride.

chloride with silver cyanate gave about 75% of monomeric and 25% of dimeric trifluoromethanesulfenyl cyanate. The trimeric form can be prepared from the monomer at 100° in the presence of sodium acetate[9]. Pentafluorobenzenesulfenyl cyanate, prepared from pentafluorobenzenesulfenyl chloride and silver cyanate, has a molecular weight, determined osmometrically in benzene, corresponding to a mixture of dimer and trimer, although the mass spectrum shows only a molecular ion corresponding to the monomer. The infrared spectrum shows $C = O$ frequencies at 1746 and 1735 cm^{-1}, similar to those observed in the polymeric forms of CF_3SNCO[11], but there are no coupled $N = C = O$ stretching frequencies at about 2270 cm^{-1} as observed in monomeric cyanates[12]. Most monomeric sulfenyl cyanates react with compounds containing active hydrogen, adding across the $-N = C =$ bond, reacting with hydrogen halides or amines as shown in the following equations,

$$RNCO + HHal \rightarrow RNHCOHal$$
$$RNCO + HNR'_2 \rightarrow RNHCONR'_2$$
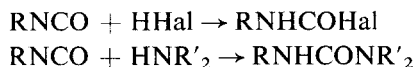
When $R = CF_3$ and $Hal = Cl$ and Br, the carbamyl halides are not very stable and readily decompose to the corresponding sulfenyl halide and cyanuric acid[13].

$$3CF_3SNHCOHal \rightarrow 3CF_3SHal + (HNCO)_3.$$
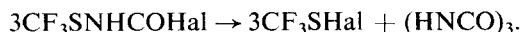
In the reactions of pentafluorobenzenesulfenyl cyanate no intermediate products were observed, and cyanuric acid and pentafluorobenzenesulfenyl derivatives were isolated (see Figure 2). These reactions suggest that the S–N in polymeric C_6F_5-

$$C_6F_5SNCO \begin{cases} + HCl & \rightarrow C_6F_5SCl \\ + MeSH & \rightarrow C_6F_5SSMe \\ + n\text{-}BuSH & \rightarrow C_6F_5S(n\text{-}Bu) \\ + C_6F_5SH & \rightarrow C_6F_5SSC_6F_5 \\ + NH_3 & \rightarrow (C_6F_5S)_2NH \\ + Me_2NH & \rightarrow C_6F_5SNMe_2 \\ + Ph_2NH & \rightarrow C_6F_5SNPh_2 \end{cases}$$
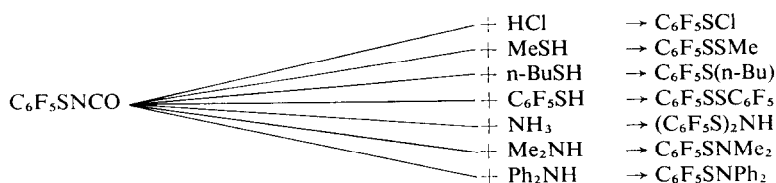
Fig. 2. Some reactions of pentafluorobenzenesulfenyl cyanate.

SNCO and any intermediate product is very labile. The mass spectrum of C_6F_5SNCO is that of the monomer, showing that it readily depolymerises and that the monomeric species has a labile S–N bond, as a peak of high relative abundance corresponds to the $C_6F_5S\overset{+}{\bullet}$ ion.

The vibrational spectra, infrared and Raman, of C_6F_5SCl, C_6F_5SMe, C_6F_5SEt, $C_6F_5S(i\text{-}Pr)$, $C_6F_5S(n\text{-}Bu)$, C_6F_5SSMe have been examined, and a correlation of observed vibrations and assignments is shown in Table 1, together with some of the fundamentals of C_6F_5Br[14] for comparison. The spectra can be divided into three parts, the C_6F_5 group, the R–S group, and the C–S–C group. A detailed study of the fundamental frequencies of C_6F_5Hal (Hal = Cl, Br and I) shows that they are relatively insensitive to the mass of Hal[14]. Using these assignments the frequencies due to the C_6F_5 group can be readily assigned. The assignment of the R–S frequencies is more difficult, but various correlations are known. The C–S frequency decreases as the mass of the group R increases. Correlation can be made using the C–S values found in MeSH (705 cm^{-1}, IR; 702 (p) cm^{-1}, Raman)[15] PhSMe (722 (p) cm^{-1}, Raman)[16], EtSSEt (640 cm^{-1}, IR)[17], and n-BuSS(n-Bu) (633 cm^{-1}, IR; 636 (p) cm^{-1}, Raman)[18].

In C_6F_5SSMe, the polarised Raman line at 694 cm^{-1} may be assigned to the H_3C–S stretching frequency, and the Raman line of unknown polarity at 512 cm^{-1}, with the corresponding infrared absorption at 515 cm^{-1}, may be assigned to the S–S stretching frequency. In MeSSMe, the S–S stretching frequency is observed at 517 cm^{-1} (IR) and 512 cm^{-1} (Raman)[15]. The polarised Raman line at 505 cm^{-1} (vs) in the spectrum of C_6F_5SCl may be assigned to the C_6F_5–S stretching frequency, and the bands at 521 (w) cm^{-1} (IR) and 516 cm^{-1} (Raman) may be assigned to the S–Cl modes. The S–Cl frequency in CF_3SCl has been assigned at 535 cm^{-1} [19].

The ^{19}F NMR spectra of various of the compounds prepared have been studied. The spectra were recorded in benzene solution with hexafluorobenzene as an internal standard, although the results (see Table 2) are reported with respect to $CFCl_3$ as internal standard. Exact comparison with previous data is difficult as most spectra were recorded using CCl_4 as a solvent and $CFCl_3$ as internal standard[20], and the chemical shifts may vary by 2–3 ppm depending on the choice of solvent, as has recently been shown in the ^{19}F NMR spectrum of pentafluorophenol[21]. For a variety of pentafluorophenyl derivatives, there is a linear relation-

ship between the *ortho–para* coupling constant ($J(24)$) and the chemical shift of the *para* fluorine (δ_p), as defined by the equation $J((24)) = -0.453\delta_p + 71.98$[22]. This relationship has been derived from the Hammett–Taft functions σ_R^0 and the resonance and inductive parameters respectively, and it has been assumed that δ_p is determined largely by σ_R^0 alone, and therefore to a first approximation δ_p is a measure of the π-interaction between the pentafluorophenyl ring and its substituent. In the numerous compounds studied, phosphorus substituents were found to be more electron-withdrawing than sulfur substituents. The data presented show that methyl, ethyl and n-butyl pentafluorophenyl sulfides are weak acceptors, suggesting that the alkyl group has only a small inductive effect on the electrons of the sulfur.

The mass spectra of several of the compounds prepared have been examined; the sulfides C_6F_5SR (R = Et, i-Pr, n-Bu, Ph, CH_2CH_2Cl), the disulfides C_6F_5SSR (R = Me, n-Bu), the sulfenamides $C_6F_5SNR_2$ (R = Me, Et, Ph), $(C_6F_5S)_2NH$ and C_6F_5SNCO. The spectra can be correlated with those observed for a series of pentafluorophenylthio derivatives[23]. In all cases where the $C_6F_5S^+$ ion is formed, particularly in the disulfides and sulfenamides with labile S–S and S–N bonds, the spectra below m/e 199 are very characteristic. Other features of the spectra include rearrangement with loss of sulfur from the parent ion in C_6F_5SCN, C_6F_5SSMe, $C_6F_5SS(n\text{-Bu})$, and $C_6F_5SC_6H_5$, and rearrangement with formation of the $C_6F_5SH^+\cdot$ ion from the hydrogen-containing compounds, except $C_6F_5SC_6H_5$. Other fragments include ions of general formulae $C_xF_yS^+\cdot$ and $C_xF_y^+\cdot$, where x = 5–0 and y = 5–0. Some of the ions have very low relative intensity.

Various alkyl sulfides fragment upon electron impact with the cleavage of the R–S and α-C–β-C bonds[24]. Both of these modes were observed for the sulfides studied here, except that $C_6F_5SC_6H_5$ decayed initially by fracture of the aromatic ring to sulfur bonds, and fracture of the C–C bond was also observed in C_6F_5-SCH_2CH_2Cl. In $C_6F_5SCH_2CH_2Cl$, some rearrangement occurred as a peak characteristic of the $C_6F_5SCl^+\cdot$ ion was found.

Initial modes of decay may be postulated for the disulfides studied.

$$C_6F_5SSR^+\cdot$$

$-SR$	$-(SR-H)$	$-R$	$-(R-H)$

$$C_6F_5S^+ \qquad C_6F_5SH^+\cdot \qquad C_6F_5SS^+ \qquad C_6F_5SSH^+\cdot$$

TABLE 1

VIBRATIONAL FREQUENCIES (CM⁻¹) AND ASSIGNMENTS

$C_6F_5SCH_3$		$C_6F_5SC_2H_5$		$C_6F_5SCH(CH_3)_2$		$C_6F_5S(CH_2)_3CH_3$		$C_6F_5SSCH_3$		C_6F_5SCl		$C_6F_5Br^*$		Assignments
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
							137 (p)				148 (p)			
	250 (p)				230 (p)		229 (p)		231 (p)		235 (p)			
									268 (p)					
									279 (p)					
312 (w)	313 (p)			310 (w)		311 (w)	315 (dp)	312 (w)	314 (p)	316 (w)	317 (p)			
		338 (w)	340 (dp)	336 (w)	340 (dp)									
368 (w)														
378 (w)	383 (dp)	380 (w)	382 (dp)	381 (w)	384 (dp)		384 (dp)		384 (dp)		384 (dp)			
403 (w)								407 (w)		410 (w)	410 (p)			
	444 (dp)	444 (vw)	443 (dp)	440 (w)	443 (dp)		443 (dp)		444 (dp)		444		443 (mdp)	ring def.
512 (vw)	510 (sp)	515 (vw)	513 (sp)	519 (w)	517 (sp)		501 (sp)		502 (sp)	508 (w)	505 (sp)	498 (s)	497 (sp)	ν(C–S) ring
							511 (sh)	512 (w)	512	521 (w)	516 (sh)			ν(S–S)
539														
	588 (p)	576 (w)	585 (p)	572 (w)	588 (p)		587 (p)		588 (p)	594 (vw)	590 (p)	595 (w)	585 (sp)	ring def.
				614 (w)	618 (p)									
631 (w)		630 (w)				630 (w)	635 (p)	633 (w)		639 (w)				
		645 (p)	648 (p)	645 (w)	648 (p)									
698 (w)	698 (p)							690 (vw)	694 (p)					
721 (w)		722 (w)		725		720 (w)		724 (w)		728 (w)				ν(S–CH₂R)
						743 (w)								
862 (s)	864 (p)	862 (s)	864 (p)	862 (s)	865 (p)	862 (s)	855 (p)	852 (s)	855 (p)	865 (m)	865 (m)			
970 (s)								955 (m)						
985 (s)		980 (vs)		987 (s)		980 (s)		980 (s)		984 (s)		979 (vvs)		ν(C–F)
1015 (m)		1015 (w)		1054 (m)		1015 (w)		1019 (w)		1023 (s)		1007 (vvs)		ν(C–F)
1090 (s)		1090 (vs)		1092 (s)		1091 (s)		1090 (s)		1099 (s)		1093 (vvs)		
				1145 (sh)										
				1154 (m)										
						1225 (w)								
		1262 (m)		1245 (m)		1272 (w)								

							Assignment
1288(vw)1292 (p)	1292 (w)	1290 (w)	1292 (w)	1289 (w)	1295 (m) 1296 (p)		
				1312 (w)			
		1370 (m)					
		1385 (m)	1380 (w)	1378 (w)			
1405 (p)	1403 (p)	1404 (p)	1400 (p)	1399 (w) 1401 (p)	1402 (m) 1402 (p)	1429 (p)	ν(C–F) sym.
				1417 (w)			
		1485 (vs)	1484 (vs)	1486 (vs)			
1511 (vs)	1510 (vs)	1510 (vs)	1515 (vs)	1513 (vs)	1514 (vs)	1510(vvs) 1511 (w)	ν(C–C) ring
1640 (m) 1642 (p)	1639 (m) 1638 (p)	1638 (m) 1639 (p)	1639 (m) 1638 (p)	1638 (m) 1639 (p)	1638 (m) 1636 (p)	1639(vvs) 1635(sdp)	ring def.
	2880 (w) 2880 (p)	2870 (w) 2872 (p)	2880 (m) 2880 (p)				
	2905 (sh)		2910 (p)	2925 (w) 2926 (p)			
2938 (p)	2938 (w) 2937 (p)	2930 (w) 2935 (p)	2938 (m) 2940 (p)				ν(C–H) sym.
	2975 (w) 2972 (p)	2970 (m) 2975 (p)	2965 (m)				

Intensities: w = weak, m = medium, s = strong, vs = very strong, p = polarised, dp = depolarised.
* see Reference 14, fundamentals only reported.

TABLE 2

^{19}F CHEMICAL SHIFTS RELATIVE TO CFCl$_3$ AS INTERNAL STANDARD IN BENZENE SOLUTION AND COUPLING CONSTANTS

Compound	Chemical shifts (ppm)			Coupling constants (Hz)					
	δ_m	δ_p	δ_o	$^3J(34)$	$^3J(23)$	$^4J(35)$	$^4J(26)$	$^4J(24)$	$^5J(25)$
C$_6$F$_5$SH	162.3	159.1	137.5	20.2	$\pm$22.2	0.0	3.0	0.0	$\mp$7.6
C$_6$F$_5$SCH$_3$	162.52	155.19	134.23	19.6	$\pm$22.0	2.8	1.8	1.9	$\mp$8.0
C$_6$F$_5$SCH$_2$CH$_3$	162.32	154.35	133.24	20.5	$+$24.0	2.0	2.7	2.1	$\mp$8.3
C$_6$F$_5$SCH(CH$_3$)$_2$	162.41	153.9	132.10	19.6	$\pm$23.7	2.4	2.0	2.1	$\mp$8.3
C$_6$F$_5$SCH$_2$(CH$_2$)$_2$CH$_3$	162.24	154.42	133.37	21.0	$\pm$24.4	2.7	1.9	2.1	$\mp$8.1
C$_6$F$_5$SC$_6$H$_5$	161.32	152.20	132.50	20.8	$\pm$24.4	3.6	1.7	2.8	$\mp$8.1
C$_6$F$_5$SSCH$_3$	161.27	151.64	131.87	19.4	$+$24.9	3.6	1.8	3.3	$\mp$7.4
C$_6$F$_5$SS(CH$_2$)$_3$CH$_3$	161.48	152.05	131.85	19.5	$\pm$23.7	3.5	1.9	3.1	$\mp$8.5
(C$_6$F$_5$S)$_2$*	160.4	150.4	132.4	19.8	$\pm$23.4	0.3	3.3	4.0	$\mp$7.9
C$_6$F$_5$SN(C$_6$H$_5$)$_2$	161.24	152.75	133.10	20.7	$\pm$24.7	3.9	1.6	2.9	$+$7.9
C$_6$F$_5$SCN*	158.8	146.3	130.2	20.4				5.1	
C$_6$F$_5$SCl*	160.1	145.0	128.0	20.0	$\pm$18.4	1.3	5.8	5.9	$\mp$4.7

* Sample dissolved in CCl$_4$. All other samples measured with C$_6$F$_6$ as internal standard and corrected to CFCl$_3$ as internal standard.

The ions C$_6$F$_5$SS$^+$ and C$_6$F$_5$SSH$\bullet^+$ are of relatively low intensity. In (C$_6$F$_5$S)$_2$NH, rearrangement with loss of NH must be among the initial modes of decay, which include

$$C_6F_5SNHSC_6F_5 \bullet^+$$

C$_6$F$_5$SSC$_6$F$_5\bullet^+$ $-NH$ $-SC_6F_5$ C$_6$F$_5$SNH$^+$ $-H$ (C$_6$F$_5$S)$_2$N$^+$
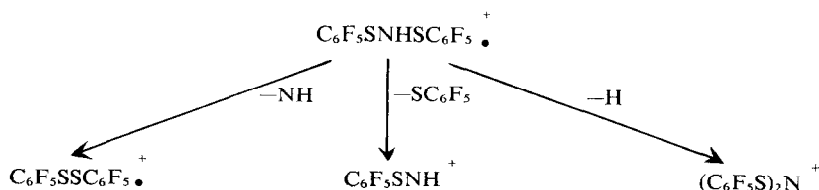
The interesting feature of the spectrum of C$_6$F$_5$SNCO is that although the molecular weight in benzene shows it to be a mixture of dimer and trimer the parent ion in the mass spectrum corresponds to the monomer. The source temperature may be sufficiently high to pyrolyse the polymer to the monomer.

EXPERIMENTAL

Most reagents were available commercially. Pentafluorobenzenesulfenyl chloride was prepared by a literature method[1]. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Western Germany. The

TABLE 3

PRODUCTS AND ANALYSES*

Compound	Color	m.p./b.p. (°C)	n_D^{23}	Density	Method: Solvent: Purification	Found (%) C	H	N	S	Calculated (%) C	H	N	S
C_6F_5SEt	Colorless	72/2 mm	1.4648	1.4065	B:THF:3	42.1	2.5		14.2	42.1	2.2		14.1
$C_6F_5S(i-Pr)$	Colorless	62/4.2 mm	1.4610		B:pentane:3	44.8	3.1		13.2	44.6	2.9		13.2
$C_6F_5S(n-Bu)$	Colorless	82.5/48 mm	1.4686		B:hexane:3	46.8	3.5		13.1	46.8	3.5		12.5
C_6F_5SSMe	Light yellow	97/12 mm	1.5140		A:benzene:3	34.4	1.4		26.0	34.1	1.2		26.0
$C_6F_5SS(n-Bu)$	Light yellow	69-73/0.2 mm	1.5002		B:benzene:3	42.2	3.3		22.0	41.6	3.2		22.2
$C_6F_5SNMe_2$	Colorless	85-89/11 mm	1.4742	1.4096	A:benzene:3	39.9	2.7	5.7		39.5	2.5	5.8	
$C_6F_5SNEt_2$	Colorless	93/8 mm	1.4730	1.3296	B:benzene:3	44.3	3.6	5.4	11.9	44.3	3.7	5.2	11.8
$C_6F_5SN(n-Bu)_2$	Colorless	84-86/0.25 mm	1.4702		B:benzene:3	50.9	5.2	4.1		51.3	5.5	4.3	
$C_6F_5SNPh_2$	White	78.5-79			B:benzene:1,2	58.8	2.8	3.9		58.8	2.8	3.8	
$(C_6F_5S)_2NH$	Light brown	83.5-84.5			A:benzene:4	35.0	0.2	3.2		34.9	0.2	3.4	
C_6F_5SCN	Colorless	63-66/1-3 mm	1.4839		B:benzene:3	37.3	0.0	6.2		37.5	0.0	6.0	
C_6F_5SNCO	White	149 (decomp.)			$B:C_6H_6, CCl_4:5$	35.2	0.0	5.9		34.9	0.0	5.8	
C_6F_5SSeCN	White	50 (decomp.)			B:benzene:-	28.8	0.0	3.9		27.7	0.0	4.6	
$C_6F_5SCH_2CH_2Cl$	White	35-35.5			B:benzene:2,4	36.5	1.2		12.2	36.6	1.5		12.2

* Methods of purification: 1 = recrystallization, 2 = sublimation, 3 = vacuum distillation, 4 = TLC, 5 = washing.

infrared spectra were recorded on a Perkin–Elmer 457 spectrophotometer as mulls with Nujol or hexachlorobutadiene, or as thin films. The NMR spectra were recorded on a Varian A56/60 instrument. The mass spectra were recorded on a Du Pont (CEC) 21–110B high-resolution mass spectrograph. The Raman spectra were recorded on a Coderg PHO Raman spectrograph using a Coherent Radiation M.G. 52 ion laser. The analytical data and physical properties of the new compounds prepared are shown in Table 3. All experiments were performed using about 10 mmoles of reagents.

Method A

Stoichiometric amounts of pentafluorobenzenesulfenyl chloride and a volatile reagent, such as NH_3, were allowed to react in a sealed tube, to which 10 ml of benzene had also been added. The tube was opened after 12–24 h and the products purified by standard techniques.

Method B

Stoichiometric amounts of the reactants were stirred in dry benzene. The desired product was isolated from the benzene solution, and purified by standard techniques.

Known products were obtained from the following reactions: C_6F_5SCl + $C_6F_5SH \rightarrow C_6F_5SSC_6F_5$ [25]; $C_6F_5SCl + NH_3 \rightarrow (C_6F_5S)_2NH$ [26]; C_6F_5SNCO + $HCl \rightarrow C_6F_5SCl$ [1]; $C_6F_5SCl + C_6H_5MgCl \rightarrow C_6F_5SC_6H_5$ [27]. These products and cyanuric acid were identified by standard techniques, including melting points, boiling points, infrared spectra and refractive indices. The yields of crude products in most reactions were high, but this decreased on purification. In the reactions involving the formation of cyanuric acid there was almost 100% recovery of the cyanuric acid.

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