Preparation and Properties of some Non-Metallic Derivatives of Pentafluorothiophenol

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Various non-metallic derivatives of pentafluorothiophenol, containing sulfur bonded to boron, carbon, silicon, germanium, phosphorus, arsenic, antimony, sulfur, and chlorine, have been prepared, mainly from the reaction of $Pb(SC_6F_5)_2$ with a non-metallic halide, and characterized. The ^{19}F n.m.r. spectra have been examined. The coordinating power of sulfur attached to a C_6F_5 group is minimal.

Divers dérivés non-métalliques du pentafluorothiophénol contenant du soufre lié au bore, au carbone, au silicium, au germanium, au phosphore, à l'arsenic, à l'antimoine, au soufre, et au chlore ont été préparés, principalement par réaction de $Pb(SC_6F_5)_2$ avec des halogénures non-métalliques et caractérisés. Les spectres r.m.n. de ^{19}F ont été examinés. Le pouvoir de coordination du soufre attaché à un groupe C_6F_5 est minimal.

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The metallic derivatives of pentafluorothiophenol, $M(SC_6F_5)_x$ (1) and complex ions of the types $M(SC_6F_5)_x^{n-}$, where M is a metal, have been investigated (2, 3). Few non-metallic derivatives have been reported; this paper describes the preparation of some pentafluorophenylthio derivatives of B, C, Si, Ge, P, As, Sb, S, and Cl. The aims of this study were to examine the effects, if any, of the relatively electronegative C_6F_5 group, on the ease of preparation of these derivatives and its effect on the coordinating ability of the sulfur. The electronegativity of the C_6F_5 group depends on its interaction with the rest of the molecule, and has been estimated to be between that of chlorine and bromine to less than that of iodine in various organotin compounds (4). The C_6F_5 group could be classified as a pseudohalide group.

Non-metallic derivatives of thiols may be prepared by two general methods, starting with the non-metallic halide (5).

(*a*) The reaction of a thiol with the non-metallic halide in a suitable solvent; when the product is susceptible to attack by the hydrogen halide generated, a hydrogen halide acceptor, such as triethylamine is added. Similar products may be obtained from the reaction of a sulfenyl chloride with some non-metallic hydrides.

(*b*) The reaction of a thiol salt, such as a lead salt, with the non-metallic halide.

The compounds $C_6F_5SMR_3$, where $MR_3 = SiMe_3$, $SiPh_3$, $GeMe_3$, and $GePh_3$ (6), have been prepared using method *a*. Pentafluorothiophenol slowly polymerizes in air in the presence of a base (1), including triethylamine which was used as a hydrogen chloride acceptor in method *a*. Exclusion of air, either by working in a nitrogen atmosphere or using vacuum line techniques has enabled simple salts of pentafluorothiophenol with bases such as diethylamine, which would cause polymerization in air, to be prepared. Method *b*, which was used with the majority of compounds described in this paper, can be used in air without polymerization occurring.

The compounds $(C_6F_5S)_xY$, where Y = B, Me, CPh_3, CH_2, CH_2CH_2, MeCO, PhCO, C_6F_5CO, Me_3Si, Ph_3Ge, Ph_2Ge, Ge, P, PO, Ph_2P, As, PhAs, Sb, MeHg, and PhHg, were prepared from the corresponding chloride or iodide and bis(pentafluoro-phenylthio) lead, $Pb(SC_6F_5)_2$, subsequently referred to as the lead salt, in an inert solvent such as carbon tetrachloride or benzene. The products containing B—S, Si—S, and P—S bonds were somewhat hydrolytically sensitive.

No reaction was observed with $Me_{4-x}SiCl_x$, $x = 2, 3,$ or 4, and the lead salt although this is a standard method for preparation of this type of mercapto silicon derivative (7). Trimethyl(pentafluorophenylthio) silane was also prepared from pentafluorothiophenol and hexamethyldisilazane in benzene, eq. 1. A similar reaction occurs with allylthiol(8).

$$[1] \quad (Me_3Si)_2NH + 2C_6F_5SH \rightarrow 2Me_3SiSC_6F_5 + NH_3\uparrow$$

Phosphorus and arsenic trichlorides react with bis(trifluoromethylthio) mercury to give the compounds $(CF_3S)_xMCl_{3-x}$, $x = 1, 2,$ or 3, depending on the stoichiometry of the reactants (9). No mixed pentafluorophenylthio chloro derivatives of phosphorus or arsenic,

TABLE 1. The ^{19}F chemical shifts relative to $CFCl_3$ as internal standard (p.p.m.) and coupling constants (Hz)

Compound	Solvent	$\delta_{2,6}$	δ_4	$\delta_{3,5}$	$\pm J_{3,4}$	$\pm J_{2,4}$
$(C_6F_5)_2S$	CCl_4	132.4	150.4	160.4	20.6	3.5
$(C_6F_5S)_2$	Acetone	134.1	151.3	162.9	19.8	4.0
$(C_6F_5S)_2$	CCl_4	131.6	148.4	160.1	—	—
$(C_6F_5SCH_2)_2$	CCl_4	132.7	152.2	161.0	20.0	2.0
C_6F_5SCl	CCl_4	128.0	145.6	160.1	20.0	5.9
$C_6F_5SCPh_3$	CCl_4	126.8	151.4	162.6	20.5	3.7
$(C_6F_5S)_3P$	CCl_4	130.2	149.2	163.1	~20	—
C_6F_5SCN*	CCl_4	130.2	146.3	158.8	20.4	5.1

*See ref. 18.

$(C_6F_5S)_xMCl_{3-x}$, $x = 1$ or 2, were obtained in the present work even if a considerable excess of the trichloride was present, the products being always the fully substituted derivative, $(C_6F_5S)_3M$, and the unreacted trichloride.

Bis(pentafluorophenyl) disulfide is readily obtained by oxidation of pentafluorothiophenol (1) and reacts with ammonia breaking the S—S bond according to eq. 2. Initial cleavage of the

$$[2] \quad 2(C_6F_5S)_2 + 3NH_3 \rightarrow (C_6F_5S)_2NH + 2NH_4SC_6F_5$$

S—S bond would form C_6F_5SH and $C_6F_5SNH_2$. The thiol forms the ammonium salt with excess ammonia, and the sulfenamide decomposes to the sulfenimide on purification by sublimation (10). A similar reaction of ammonia and $C_6F_5SSCF_3$ is observed, but the thiol formed, CF_3SH, reacts with the excess ammonia forming ammonium fluoride and thiocyanate (10). Attempted preparations of $(C_6F_5)_2S_x$, $x = 3$ or 4, from the lead salt and sulfur dichloride or sulfur monochloride, gave products whose mass spectra indicated that they were primarily mixtures of the disulfide and sulfur, although some of the desired product was present, but this may have been formed by recombination in the source. It was not possible to prepare $C_6F_5S—SO_x$ bonds. Thionyl and sulfuryl chlorides reacted with the lead salt yielding the disulfide, sulfur dioxide, and sulfur (thionyl chloride only) and benzene- and *p*-toluenesulfonyl chlorides did not react with the lead salt. The same types of reaction were observed with bis(trifluoromethylthio) mercury and thionyl and sulfuryl chlorides (11).

Attempts were made to prepare compounds containing S—Se—S and S—Te—S bridges. The compound $C_6F_5SSeC_6F_5$ has been prepared by heating bis(pentafluorophenyl) disulfide and bis(pentafluorophenyl) diselenide (12). Compounds of the type $(RS)_2M$, M = Se, Te, are known, but are relatively unstable (13), decomposing to the disulfide and selenium or tellurium; analogous results were obtained in the present work when R = C_6F_5. The reactions of R_2MCl_2 (R = Me, M = Se, Te: R = Ph, M = Se) with the lead salt yielded R_2M and the disulfide, the reaction probably proceeding through the formation of $R_2M(SC_6F_5)_2$ as an intermediate.

Sulfur compounds should theoretically be able to act as donors or acceptors. Sulfur acts as a donor in complexes such as $Me_2S.BCl_3$ (14), but examples where sulfur is an acceptor are rarer and usually occur with S(IV), as in liquid sulfur dioxide solution (15). The presence of the relatively electronegative C_6F_5 group attached to the sulfur would be expected to weaken its donor properties and enhance its acceptor properties, although the ^{19}F n.m.r. indicates π electron donation from the C_6F_5 ring to the sulfur. Sulfur complexes with the class B metals undoubtedly involve metal to ligand as well as ligand to metal bonding; the π electron donation from the C_6F_5 ring to the sulfur would impede the metal to ligand bonding, and complexes with the class B metals if formed, would not be expected to be particularly stable. Bis(pentafluorophenyl) sulfide formed no adducts with various donors or acceptors, such as the boron trihalides, various amines, metal ions, etc. The disulfide did not form complexes with Pd^{2+} or Ag^+ ions. The coordinating properties of both these potential ligands can be classified as minimal. The coordinating ability of the metal derivative, $Hg(SC_6F_5)_2$ has been studied; it formed an adduct with PPh_3, and an unstable adduct with $Ph_2P(SC_6F_5)$ but no adduct with triethylamine or ammonia.

The ^{19}F n.m.r. spectra of some of the products have been examined and the results are shown in Table 1. Similar spectra have been obtained for various other C_6F_5S derivatives (1). Using the derivations of Hogben *et al.* (16), it can be seen that the coupling constant $J_{2,4}$ varies regularly

TABLE 2. Product and analyses

Product (ref.)	Color	Melting point (°C)	n_D^{23}	Method: solvent: time: purification*	Found (%)			Calculated (%)		
					C	H	S	C	H	S
$B(SC_6F_5)_3$	White	135–139	—	D′: CCl_4: 1 day: 2	35.6	0.6	16.0	35.6	0.0	15.8
$C_6F_5SCPh_3$	Light yellow	120–122	—	A: acetone: 5 min: 2	68.1	3.4	7.2	67.9	3.4	7.3
$(C_6F_5S)_2CH_2$	White	65	—	A′: CH_2Br_2: 1 week: 2	37.8	0.7	16.2	37.9	0.5	15.6
$(C_6F_5SCH_2)_2$	White	139–140	—	A′: $(CH_2Br)_2$: 1h: 2	39.4	1.1	15.4	39.5	1.0	15.1
C_6F_5SCOMe	Colorless	b.p. 92/17 mm	1.4770	A: MeCOCl: 5 min: 1 B: CCl_4: 5 min: 1	39.7	1.8	—	39.7	1.3	—
C_6F_5SCOPh	Yellow	34–37 b.p. 76/0.02 mm	1.5578	A′: CCl_4: 1 h: 1	51.6	—	11.3	51.3	—	10.6
$C_6F_5SCOC_6F_5$	White	57–59	—	A′: CCl_4: 12 h: 2	39.6	0.0	8.2	39.6	0.0	8.1
$Me_3SiSC_6F_5$ (6)	Colorless	b.p. 76/15 mm	1.4676	A′: C_6H_6: 5 h: 1 B: C_6H_6: 3 day: 1 C′: C_6H_6: 3 day: 1	40.1	3.0	—	39.7	3.3	—
$Ph_3GeSC_6F_5$ (6)	White	87–90	—	A: Et_2O: 5 min: 2	57.9	3.1	6.1	57.3	3.0	6.4
$Ph_2Ge(SC_6F_5)_2$	White	62–66	—	A: Et_2O: 15 min: 3	46.9	0.9	10.5	46.1	1.6	10.3
$Ge(SC_6F_5)_4$	White	115	—	A′: Et_2O: 10 min: 3	32.6	0.0	—	33.2	0.0	—
$PO(SC_6F_5)_3$	White	145–146	—	A′: CCl_4: 12 h: 3	33.3	0.2	15.2	33.6	0.0	14.9
$P(SC_6F_5)_3$	White	63–64	—	A: C_6H_6: 5 min: 1	34.6	0.0	15.2	34.4	0.0	15.3
$Ph_2PSC_6F_5$	White	61–63	—	A: CCl_4: 1 h: 3	56.3	2.6	8.2	56.3	2.6	8.3
$PhP(SC_6F_5)_2$	White	63–65	—	A: C_6H_6: 10 min: 3	43.2	1.1	12.8	42.7	1.0	12.6
$As(SC_6F_5)_3$ (1)	White	76–77	—	A: Et_2O: 1 min: 2	32.5	0.0	14.3	32.2	0.0	14.3
$PhAs(SC_6F_5)_2$	White	74–76	—	A: Et_2O: 1 min: 3	38.9	0.6	12.1	39.3	0.9	11.7
$Sb(SC_6F_5)_3$	White	softens 80	—	A: C_6H_6: 1 h: 3	29.9	0.0	13.3	30.1	0.0	13.4
C_6F_5SCl†	Yellow	b.p. 89/0.1 mm	1.4993	D: — : 1 min: 1	31.0	0.0	13.3	30.7	0.0	13.7
$MeHgSC_6F_5$	White	95–97	—	A: Et_2O: 5 min: 2	20.7	0.7	7.6	20.3	0.7	7.7
$PhHgSC_6F_5$	White	148–149	—	A′: Et_2O: 40 h: 2	30.9	1.1	6.5	30.2	1.1	6.7
$Ph_3PHg(SC_6F_5)_2$	White	155–157	—	E: C_6H_6: 8 h: 4	42.3	2.0	7.4	41.8	1.8	7.5
$C_6F_5SH{\cdot}NH_3$	Yellow	296 dec.	—	D: — : 2 h: —	32.9	2.2	14.7	33.2	1.9	14.8
$C_6F_5SH{\cdot}HNEt_2$	White	> 300	—	C: CCl_4: 1 h: 4	43.8	4.5	4.8‡	43.9	4.4	5.1‡
$(C_6F_5SH)_2{\cdot}(H_2NCH_2)_2$	White	170 dec.	—	C: CCl_4: 1 h: 4	36.6	2.3	6.0‡	36.5	2.5	6.1‡
$C_6F_5SH{\cdot}H_2NPh$	White	121–122	—	C: CCl_4: 20 min: 4	48.3	2.7	4.9‡	48.5	2.7	4.7‡

*Methods of purification: 1 = distillation; 2 = recrystallization; 3 = vacuum sublimation; 4 = precipitation from reaction solvent.
†Percentage Cl: Found, 14.9; Calcd., 15.1.
‡Percentage N.

with the chemical shift δ_4 in a particular solvent. The values of $J_{2,4}$ suggest π electron withdrawal from the C_6F_5 nucleus due to the vacant d orbitals on the sulfur, and the magnitude of the withdrawal increases $CH_2CH_2SC_6F_5 < C_6F_5 < CPh_3 < SCN < SCl$. The i.r. spectra are analogous to those expected for compounds containing the C_6F_5S group and the requisite functional group (17).

Experimental

Most reagents were available commercially. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Western Germany. The i.r. spectra were recorded on a Perkin–Elmer 457 spectrophotometer as mulls with Nujol or hexachlorobutadiene or as liquid films. The n.m.r. spectra were recorded on a Varian A60 instrument. The new, and some known, compounds prepared are shown in Table 2, together with some physical properties and analytical data. All experiments were performed using 1–2 mmol of reagents.

On refluxing a benzene solution of pentafluorothiophenol and triethylamine in air for 18 h a yellow precipitate formed; further precipitation occurred on standing at room temperature. Analysis showed it to be somewhat impure perfluoropoly(phenylene sulfide), and the reaction is similar to that of other nitrogenous bases with the thiol (1).

Methods A and B

The lead and silver salts of pentafluorothiophenol (used in methods A and B respectively) were prepared by literature methods (1). The requisite amount of a nonmetallic chloride or iodide was added to a suspension of the lead or silver salt in a suitable solvent and the mixture was stirred at room temperature (A or B) or refluxed (A′ lead salt only). The extent of the reaction was estimated qualitatively by the disappearance of the yellow lead salt and the appearance of white plumbous chloride, and quantitatively by weighing the plumbous halide formed; all reactions proceeded in greater than 80% yield. Products were purified by standard techniques, recrystallizations being from EtOH or CCl_4.

Known products were obtained with the following reagents (products shown after reagents): MeI - C_6F_5SMe (19); PCl_5 - $(C_6F_5S)_3P$ and $(C_6F_5S)_2$ (19); $SOCl_2$ - $(C_6F_5S)_2$, SO_2, and S; SO_2Cl_2 - $(C_6F_5S)_2$ and SO_2; Se_2Cl_2 - $(C_6F_5S)_2$ and Se; Me_2SeCl_2 (preparation (20)) - $MeSe_2$ and $(C_6F_5S)_2$; Ph_2SeCl_2 - Ph_2Se and $(C_6F_5S)_2$; $SeOCl_2$ - $(C_6F_5S)_2$, SeO_2, and Se; $TeCl_2$ - $(C_6F_5S)_2$ and Te; Me_2TeCl_2 (preparation (20)) - Me_2Te and $(C_6F_5S)_2$; Br_2 - $(C_6F_5S)_2$. The products were identified by standard techniques, including melting points, boiling points, i.r. spectra, and molecular weights (mass spectroscopically).

The lead salt did not react appreciably (less than 10%) with $SiCl_4$, $MeSiCl_3$, Me_2SiCl_2 (anhydrous CCl_4 as solvent) $PhSO_2Cl$ (CCl_4), or *p*-$TolSO_2Cl$ (toluene); the latter two did not react with the silver salt.

Method C

Stoichiometric amounts of C_6F_5SH were allowed to react in an N_2 atmosphere with the appropriate amine by shaking at room temperature in CCl_4. The product precipitated in high yield from solution. In method C′ C_6F_5SH was refluxed with $(Me_3Si)_2NH$ in C_6H_6.

Method D

Stoichiometric amounts of C_6F_5SH and NH_3 or Cl_2 were allowed to react in a sealed tube. Method D′ used the lead salt in place of C_6F_5SH. Quantitative yields were obtained.

Method E

Equimolar amounts of $Hg(SC_6F_5)_2$ (1) and PPh_3 or $Ph_2PSC_6F_5$ were refluxed in C_6H_6 and the product precipitated. No reactions were observed between $(C_6F_5)_2S$ (preparation (21)) and BCl_3 (sealed tube), BBr_3 (CCl_4), BI_3(C_6H_6), NH_3 (sealed tube), MeI(Et_2O), $Hg(SC_6F_5)_2$(C_6H_6), Et_3N(C_6H_6), Hg^{2+}(H_2O,C_6H_6), Pd^{2+}(2NHCl,C_6H_6), Ag^+(H_2O,C_6H_6); $(C_6F_5S)_2$ and Pd^{2+}(2NHCl, C_6H_6), Ag^+(H_2O,C_6H_6); $(C_6F_5SCH_2)_2$ and Hg^{2+}(H_2O,C_6H_6), Pd^{2+}(2MHCl,C_6H_6); $Hg(SC_6F_5)_2$ and Et_3N(C_6H_6), NH_3 (sealed tube); $PhHgSC_6F_5$ and PPh_3(C_6H_6). The reactants were recovered unchanged after refluxing or allowing the sealed tube reactions to stand at room temperature for up to 5 days.

$(C_6F_5S)_2$ and NH_3

After allowing 10.0 mmol of $(C_6F_5S)_2$ and 30.0 mmol of NH_3 to stand at room temperature in a sealed tube for 6 days, 10.4 mmol of NH_3 were recovered on opening the tube. The increase in weight of the solid product recovered corresponded to 18.4 mmol of NH_3 having reacted. On vacuum sublimation of the solid product $(C_6F_5S)_2NH$, m.p. 80–82° (lit. 80–82° (10)) sublimed, which is formed by decomposition of $C_6F_5SNH_2$ on vacuum sublimation (10), leaving $C_6F_5SH.NH_3$, identified by its i.r. spectrum. The stoichiometry of the reaction is,

$$\begin{array}{r} 2(C_6F_5S)_2 + 4NH_3 \rightarrow 2C_6F_5SNH_2 + 2C_6F_5SH.NH_3 \\ \downarrow \text{ Vacuum sublimation} \\ (C_6F_5S)_2NH + NH_3 \end{array}$$

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