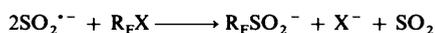
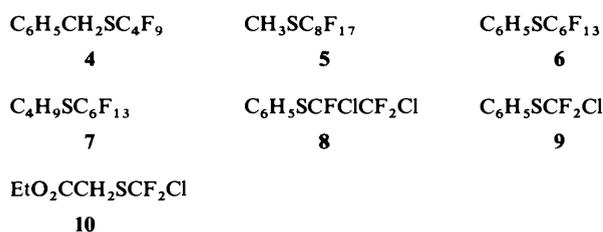


transformation of the two R groups of the disulfide. The major by-product was the perfluoroalkanesulfinate salt resulting from the direct reaction of the halide with the sulfoxylate anion radical³²⁻³⁴ (Scheme 3). The importance of this side-reaction was dependent on the reactivity of the fluorinated halide 2. Perfluoroalkyl iodides $\text{CF}_3(\text{CF}_2)_n\text{I}$ ($n = 1, 3, 5$) and 1,1,2-trichlorotrifluoroethane were more reactive than bromotrifluoromethane and bromochlorodifluoromethane.



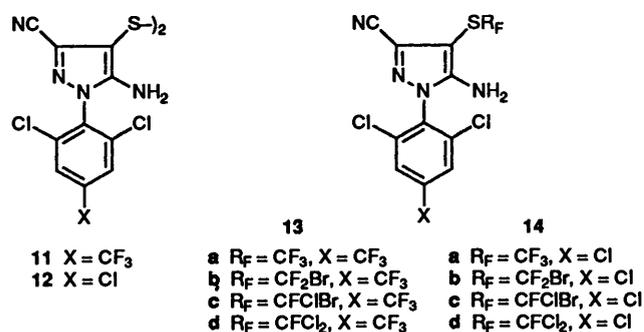
Scheme 3

Initially, simple aromatic and aliphatic disulfides 1 ($\text{R} = \text{Ph}, \text{Me}, \text{Bu}, \text{PhCH}_2$) were examined. Various fluoroalkyl sulfides 4-10 were obtained from $\text{C}_4\text{F}_9\text{I}$, $\text{C}_8\text{F}_{17}\text{I}$, $\text{C}_6\text{F}_{13}\text{I}$, $\text{CCl}_2\text{FCClF}_2$ and CF_2BrCl (see Scheme 4).



Scheme 4

The example 10 showed that the reaction was compatible with the presence of an ester group. The synthesis of substituted pyrazoles 13 and 14, from disulfides 11 and 12 respectively, extended the scope of this method to heterocyclic derivatives bearing cyano and amino groups (see Scheme 5; Table 1).

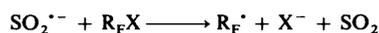


Scheme 5

Various perhalogenomethanes (CF_2Br_2 , CFBr_2Cl , CFCl_3 , CF_3Br) were used for the synthesis of these fluorinated pyrazoles, showing the versatility of the method.

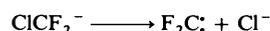
Discussion

Evidence for the presence of an intermediate perfluoroalkyl radical in the reactions of perfluoroalkyl halides with sulfoxylate anion radical precursors was provided by alkylation of aromatic substrates introduced into the reaction medium.^{27,28} The present synthesis can be considered as an attack on disulfides by these perhalogenoalkyl radicals (see Scheme 6).



Scheme 6

However, the ready reduction of disulfides to thiolates ions is well-known and the formation of trifluoromethyl sulfides from thiolates and CF_3Br by an $\text{S}_{\text{RN}}1$ pathway has already been observed.²¹ Some light was shed on the process by the reaction of bromochlorodifluoromethane and sodium benzenethiolate to give, by an ionic pathway, bromodifluoromethyl phenyl sulfide (see Scheme 7).³⁵ From the same halide and diphenyl disulfide, we have now obtained the chloro analogue 9. Formation of this compound agreed with a direct radical attack on the sulfur-sulfur bond (Scheme 8) and not with the ionic pathway (Scheme 7) resulting from initial reductive cleavage of this bond by the reductant.



Scheme 7

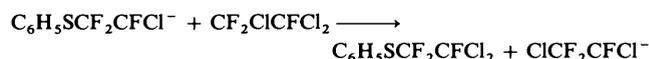
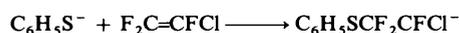


Scheme 8

The reaction of 1,1,2-trichlorotrifluoroethane with diphenyl disulfide gave compound 8 having two vicinal chlorine atoms (see Scheme 9), cleavage of the carbon-chlorine bond having occurred on one of the two geminal chlorine atoms, in agreement with the known homolysis of 1,1,2-trichlorotrifluoroethane.³⁶ In contrast, we had earlier observed the formation, by an ionic pathway from a reaction with benzenethiolate,²¹ of an isomer having two geminal chlorine atoms (Scheme 10).



Scheme 9



Scheme 10

Thus, the structures of the products formed from these two halides were in favour of a radical pathway (see Scheme 6). The existence of the sulfoxylate anion radical in the mixture of formic acid (or its sodium salt) with sulfur dioxide (or one of its associate base) in DMF was checked by the direct formation of perfluoroalkanesulfinate salts (in the absence of a disulfide) (Scheme 3; Table 2). Formation of trifluoromethanesulfinate from bromotrifluoromethane, sodium formate and sulfur dioxide has also been observed.³⁷

In the reaction with aromatic disulfides, no perfluoroalkylation of the nucleus was detected. However, perfluoroalkyl radical attack on anilines and phenols has been observed.^{28,29} The weak sulfur-sulfur bond is the most reactive site in these disulfides.

Table 1 Pyrazoles

Compd.	Yield (%)	M.p. (°C)	δ_F^a	Formula	Analyses: % Found (% Required)		
					C	H	N
13a	75	169.5–170.5	–44.9 (–63.8)	C ₁₂ H ₄ Cl ₂ F ₆ N ₄ S	34.6 (34.22)	1.05 (0.96)	13.2 (13.30)
13b	90	162.5–163.5	–24.3 (–63.8)	C ₁₂ H ₄ BrCl ₂ F ₅ N ₄ S	30.0 (29.90)	0.75 (0.84)	11.4 (11.62)
13c	24	191.5–193	–18 (–63.8)	C ₁₂ H ₄ BrCl ₃ F ₄ N ₄ S	29.4 (28.91)	0.75 (0.81)	11.0 (11.24)
13d	84	190–193	–21.4 (–63.8)	C ₁₂ H ₄ Cl ₄ F ₄ N ₄ S	31.6 (31.74)	0.85 (0.89)	12.4 (12.40)
14a	72 ^b	192–194	–45	C ₁₁ H ₄ Cl ₃ F ₃ N ₄ S	34.0 (34.08)	1.0 (1.04)	14.4 (14.45)
14b	53	163.5–165	–24.3	C ₁₁ H ₄ BrCl ₃ F ₂ N ₄ S	29.5 (29.46)	0.9 (0.90)	11.9 (12.49)
14c	71	192–193	–17.9	C ₁₁ H ₄ BrCl ₄ FN ₄ S	28.6 (28.42)	0.9 (0.87)	11.9 (12.05)
14d	64	189–191	–21.4	C ₁₁ H ₄ Cl ₅ FN ₄ S	31.65 (31.42)	0.9 (0.96)	13.1 (13.31)

^a SR_F and if necessary C₆H₂Cl₂CF₃ in parentheses. ^b Prepared by a classical method.⁸

Table 2

R _F X	Reductor	Precursor	Sulfinate	TP (%) ^a
C ₈ F ₁₇ I	HCO ₂ Na	SO ₂	C ₈ F ₁₇ SO ₂ Na 15	83 ^b
C ₄ F ₉ I	HCO ₂ Na	NaHSO ₃	C ₄ F ₉ SO ₂ Na 16	55
C ₄ F ₉ I	HCO ₂ H	NaHSO ₃	16	55
C ₄ F ₉ I	HCO ₂ H	Na ₂ S ₂ O ₅	16	53
C ₄ F ₉ I	HCO ₂ H	Na ₂ SO ₃	16	29
CFCl ₃	HCO ₂ Na	SO ₂	CFCl ₂ SO ₂ Na 17	44
CF ₂ BrCl	HCO ₂ H	NaHSO ₃	CF ₂ ClSO ₂ Na 18	38

^a TP transformation percentage of the perhalogenoalkane. ^b Isolated yield, transformation percentage 100%.

Conclusion

Introduction of disulfides into the reaction medium used for the preparation of perfluoroalkanesulfinate salts (from perfluoroalkyl halides and sulfoxylate anion radical precursors) gives perfluoroalkylsulfides, by a mild and safe method with wide scope using inexpensive reagents.

Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker AM 300 or AC 200 spectrometers in ppm downfield from tetramethylsilane. ¹⁹F NMR were obtained on Varian EM360L or AC 200 spectrometers and were recorded in ppm downfield from trichlorofluoromethane (solvent: CDCl₃). *J* values are recorded in Hz. Bromotrifluoromethane was purchased from Setic Labo, iodotrifluoromethane from Fluorochem Ltd., dimethylformamide, pyridine and organic reactants from Aldrich (and distilled before use), zinc, sodium hydrogen phosphate from Prolabo, sodium hydroxymethanesulfinate and sodium dithionite from Fluka. Iodoperfluoroalkanes were generous gifts of ATO-CHEM. Pyrazolyl disulfides were prepared by a literature method,³⁸ and diethyl dithioacetate by esterification of the corresponding acid.

Benzyl Perfluorobutyl Sulfide 4.—A mixture of perfluorobutyl iodide (3.5 g, 10 mmol), sodium hydroxymethanesulfinate (4 g, 26 mmol), dibenzyl disulfide (2.5 g, 10 mmol) in DMF (10 cm³) and water (0.5 cm³) was stirred at room temp. for 6 h. The mixture was diluted with water (100 cm³) and extracted with ether. The extract was washed with 5% aqueous hydrochloric

acid (2 × 20 cm³) and 10% aqueous sodium carbonate, dried (MgSO₄) and evaporated to give the title compound (0.6 g, 17%);²² b.p. 92 °C/17 Torr*; δ_H 7.3 (3 H, s) and 4.2 (2 H, s); δ_F –82.5 (3 F), –88.8 (2 F), –121.5 (2 F) and –126.5 (2 F).

Methyl Perfluorooctyl Sulfide 5.—A mixture of perfluoro-octyl iodide (5.5 g, 10 mmol), sodium dithionite (3 g, 17 mmol), sodium hydrogen phosphate (3 g, 21 mmol) and dimethyl disulfide (1 g, 10.6 mmol) was stirred in DMF (10 cm³) and water (5 cm³) for 6 h to give after work-up the title compound (0.9 g, 20%);²² b.p. 44 °C/10 Torr; δ_H 2.4; δ_F (SCF₂) –92.3.

Perfluorohexyl Phenyl Sulfide 6.—A mixture of perfluoro-hexyl iodide (4.5 g, 10 mmol), sodium hydroxymethanesulfinate (4 g, 26 mmol) and diphenyl disulfide (2.2 g, 10 mmol) in DMF (10 cm³) and water (0.5 cm³) was stirred for 12 h to give after work-up perfluorohexyl phenyl sulfide (1.7 g, 40%);²¹ b.p. 99 °C/18 Torr; δ_F (SCF₂) –87.2.

Butyl Perfluorohexyl Sulfide 7.—The preceding experiment was repeated with dibutyl disulfide (1.5 g, 10 mmol) to give the title compound (0.9 g, 22%); b.p. 65 °C/19 Torr; δ_H (SCH₂) 2.7 (m); δ_F (SCF₂) –92.3.

1,2-Dichloro-1,2,2-trifluoroethyl Phenyl Sulfide 8.—A mixture of 1,1,2-trichlorotrifluoroethane (3.8 g, 20 mmol), diphenyl disulfide (4.4 g, 20 mmol), sodium dithionite (7 g, 40 mmol) and disodium hydrogen phosphate (6 g, 40 mmol) was stirred in DMF (20 cm³) and water (10 cm³) for 6 h to give after steam distillation and work-up the title compound (2.7 g, 52%);³⁹ b.p. 55 °C/0.4 Torr; δ_F –63.3 (2 F, d, *J* 14.2), –89 (t, 1 F).

Chlorodifluoromethyl Phenyl Sulfide 9.—A thick glass flask containing a mixture of sodium hydroxymethanesulfinate (Rongalite®) (15.5 g, 100 mmol) and diphenyl disulfide (5.5 g, 25 mmol) in DMF (30 cm³) and water (2 cm³) was evacuated and thermostatted at 20 °C. The mixture was then stirred under a pressure (1.7 bar) of bromochlorodifluoromethane for 6 h. After this the mixture was diluted with water (100 cm³) and extracted with ether. The extract was washed with 5% hydrochloric acid (2 × 20 cm³) and 10% aqueous sodium carbonate, dried

* 1 Torr ≈ 133 Pa.

(MgSO₄) and evaporated to give the title compound (3.5 g, 72%); ²¹ b.p. 71 °C/25 Torr; δ_F(SCF₂) -27.

Ethyl (Chlorodifluoromethylthio)acetate 10.—The preceding experiment was repeated with diethyl 2,2'-dithiodiacetate (5.9 g, 25 mmol) to give the title compound (3.3 g, 65%); b.p. 81 °C/25 Torr; δ_H 4.23 (2 H, q, *J* 10.5), 3.75 (2 H, s) and 1.3 (3 H, t); δ_F(SCF₂) -27; ν_{max}/cm⁻¹ 1718; *m/z* 204, 206 (M⁺), 169 and 119.

5-Amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthio-1H-pyrazole 13a.—*Method 1.* To a solution of bis-5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazol-4-yl disulfide **11** (2 g, 2.9 mmol) in DMF (120 cm³) in a Teflon-coated autoclave (500 cm³) was added a solution of disodium hydrogen phosphate · 12H₂O (3.05 g, 9 mmol), in distilled water (60 cm³) followed, with stirring, by sodium dithionite (1.48 g, 9.5 mmol). Following closure, the autoclave was pressurized with bromotrifluoromethane (12–13 bar). After being stirred (1000 rpm Rushton turbine) at this pressure for 2 h at 25 °C, the autoclave was opened and the stirred reaction mixture diluted with water (500 cm³) and ether (500 cm³). The ethereal phase was separated, dried (MgSO₄) and filtered. Removal of ether under reduced pressure gave a yellow oil which was subjected to a vacuum pump at 100 °C to remove further volatile substances. The residue was passed through a lightning chromatography column containing silica gel (320 g), eluting with dichloromethane, to give the title compound (1.8 g, 75%); m.p. 169.5–170.5 °C.

Method 2. The disulfide (4 g, 5.9 mmol), sodium formate (1.16 g, 17.1 mmol), DMF (20 cm³) and sulfur dioxide (1.45 g, 22.8 mmol) were successively introduced into an autoclave and the mixture was stirred and heated at 60 °C. Bromotrifluoromethane (12–13 bar) was introduced and the mixture stirred for 4 h at this pressure to give the title compound (4.1 g, 85%).

5-Amino-4-bromodifluoromethylthio-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-1H-pyrazole 13b.—A solution of sodium dithionite (0.78 g, 4.5 mmol) and disodium hydrogen phosphate (0.64 g, 4.5 mmol) in water (20 cm³) was added to a stirred solution of the disulfide **11** (1.94 g, 3 mmol) in DMF (75 cm³) and water (5 cm³). After addition of dibromodifluoromethane (1.89 g, 9 mmol) the reaction mixture was stirred at ambient temperature for 17 h and then poured onto water (185 cm³). Work-up as described for **13a**, gave the title compound (1.31 g, 90%); m.p. 162.5–163.5 °C; *m/z* (IE) mode: 482 (parent with ³⁵Cl³⁷Cl⁷⁹Br and ³⁵Cl₂⁸¹Br) and 351 (parent ³⁵Cl₂⁸¹Br).

5-Amino-4-bromochlorofluoromethylthio-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-1H-pyrazole 13c.—Sodium dithionite (1.92 g, 11 mmol) and disodium hydrogen phosphate (1.56 g, 11 mmol) followed by water (45 cm³) were added to a stirred solution of bis-5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazol-4-yl disulfide **11** (5.11 g, 7.3 mmol) in DMF (115 cm³). Partial solubilization of the inorganic reactants occurred. Chlorodibromofluoromethane (4.96 g, 21.9 mmol) was then added in one portion, followed by an additional quantity of DMF (75 cm³) to give a homogeneous mixture. This was stirred at ambient temperature for 1.6 h and then poured onto water (450 cm³). Work-up as described for **13a** gave the title compound (1.76 g, 24%), m.p. 191.5–193 °C; *m/z* 498 (IE) (parent with ³⁵Cl₂³⁷Cl⁷⁹Br and ³⁵Cl₃⁸¹Br) and 351 (parent ³⁵Cl₂³⁷Cl⁷⁹Br minus CF⁷⁹Br³⁷Cl).

5-Amino-3-cyano-4-dichlorofluoromethylthio-1-(2,6-dichloro-4-trifluoromethylphenyl)-1H-pyrazole 13d.—Sodium dithionite (3.96 g, 23 mmol), disodium hydrogen phosphate (3.23 g, 22 mmol) and fluorotrichloromethane (3.9 g, 28 mmol) were added

with stirring to the disulfide **11** (4 g, 5.7 mmol) in DMF (178 cm³) and water (89 cm³). This mixture was stirred at 15–17 °C for 1 h and then poured into ice-water (1600 cm³) and stirred for a further 30 min. The white solid was filtered off, washed with water (800 cm³) and dried to give the title compound (4.34 g, 84%), m.p. 190–193 °C.

5-Amino-4-bromodifluoromethylthio-3-cyano-1-(2,4,6-trichlorophenyl)-1H-pyrazole 14b.—Sodium dithionite (0.42 g, 2.4 mmol) and disodium hydrogen phosphate (0.34 g, 2.4 mmol), followed by water (5 cm³) and dibromodifluoromethane (1.01 g, 4.8 mmol) were added with stirring to a solution of disulfide **12** (1.0 g, 1.6 mmol) in DMF (10 cm³). Since the stirred mixture remained heterogeneous, further DMF (15 cm³) and water (5 cm³) were added. The resulting solution, containing a small quantity of semisolid was then stirred at ambient temperature for 2.7 h. Work-up as described for **13a** gave the title compound as a pale-yellow solid (0.76 g, 53%); m.p. 163.5–165 °C; *m/z* (IE) 448 (parent with ³⁵Cl₂³⁷Cl⁷⁹Br and ³⁵Cl₃⁸¹Br) and 319 (parent ³⁵Cl₂³⁷Cl⁷⁹Br minus CF₂⁷⁹Br).

5-Amino-4-bromochlorofluoromethylthio-3-cyano-1-(2,4,6-trichlorophenyl)-1H-pyrazole 14c.—Sodium dithionite (1.23 g, 7 mmol) and disodium hydrogen phosphate (1 g, 7 mmol) followed by water (30 cm³) and chlorodibromofluoromethane (3.19 g, 14.1 mmol) were added with stirring to a solution of the disulfide **12** (3.0 g, 4.7 mmol) in DMF (75 cm³). The resulting mixture was stirred at ambient temperature for 40 min after which it was poured into water (300 cm³). Initially the mixture was extracted with diethyl ether (300 cm³) and then with dichloromethane. Lightning chromatography on a silica gel column of the material obtained by evaporation under reduced pressure of the ethereal extract gave a relatively impure product. The dichloromethane extract gave a product containing DMF which was removed by rotary evaporation at a temperature of 90–100 °C *in vacuo*. The resulting residue was dissolved in dichloromethane and extracted with water. Concentration of dried organic phase and lightning chromatography on a silica gel column gave the bright yellow title compound (0.5 g), m.p. 192–193 °C; total product yield, including the first fraction was 71%; *m/z* (IE) 464 (parent with ³⁵Cl₃³⁷Cl⁷⁹Br and ³⁵Cl₄⁸¹Br), 319 (parent ³⁵Cl₃³⁷Cl⁷⁹Br minus CF⁷⁹Br³⁵Cl).

5-Amino-3-cyano-4-dichlorofluoromethylthio-1-(2,4,6-trichlorophenyl)-1H-pyrazole 14d.—Zinc powder (60 g, 0.92 mol) was added to a stirred solution of the disulfide **12** (150 g, 0.2 mol) in DMF (1125 cm³) at ambient temp. To this mixture, was added a solution containing sulfur dioxide (60.6 g, 0.95 mol) in DMF (160 cm³), followed by fluorotrichloromethane (290 g, 2.1 mol) After *ca.* 30 min a slight exotherm was noted (maximum temp. 30 °C). The reaction mixture was stirred at ambient temperature overnight and then filtered and added dropwise over 2 h to ice-water (14 dm³). The resulting solid was collected, washed thoroughly with water and dried to yield a yellow–orange solid (185 g) which after recrystallization from toluene–hexane gave the title compound (123 g, 64%), m.p. 187–189 °C.

Sodium Perfluorooctanesulfinate 15.—Sodium formate (2 g, 29 mmol) was added to stirred DMF (50 cm³) containing sulfur dioxide (2 g, 31 mmol) to give a blue mixture. Iodoperfluorooctane (5.5 g, 10 mmol) was then added to the mixture which became yellow–orange with gas evolution. After 3 h, the mixture was analysed by ¹⁹F NMR. The iodide was almost completely transformed into the sulfinate salt **15** (δ_F CF₂SO₂⁻ -132). After filtration, DMF was removed under reduced pressure and the residue diluted with water (20 cm³). The solids were filtered off and chlorine (1 dm³, 44 mmol) was bubbled through the

filtrate to give perfluorooctane sulfonyl chloride (4.3 g, 83%)⁴⁰ after decantation.

Sodium Perfluorobutanesulfinate 16.—Sodium formate (1.2 g, 18 mmol), sodium hydrogen sulfite (2.1 g, 20 mmol) and iodoperfluorobutane (3.5 g, 10 mmol) were stirred in DMF (20 cm³) for 10 h when ¹⁹F NMR analysis showed a 55% transformation percentage of the iodide into the sulfinate salt (δ_F CF₂SO₂⁻ -131). After the usual treatment (see 15), perfluorobutanesulfonyl chloride⁴¹ (1.3 g) was obtained by decantation (yield 78%). The experiment was repeated with various mixtures: formic acid (1.2 g, 26 mmol) and sodium hydrogen sulfite (2.1 g, 20 mmol) (transformation percentage 55%); formic acid (1 g, 22 mmol) and sodium metabisulfite (1.9 g, 10 mmol) (transformation percentage 53%); formic acid (1 g, 22 mmol) and sodium sulfite (2.5 g, 20 mmol) (transformation percentage 29%).

Sodium Dichlorodifluoromethanesulfinate 17.—Sodium formate (1.4 g, 21 mmol) followed by fluorotrichloromethane (2.7 g, 20 mmol) were added to DMF (20 cm³) containing sulfur dioxide (2 g, 31 mmol) with stirring. After 3 h, the mixture was analysed by ¹⁹F NMR: the transformation percentage of the chloride into the sulfinate salt (δ_F CF₂SO₂⁻ -66) was 44%.⁴¹

Sodium Chlorodifluoromethanesulfinate 18.—Bromochlorodifluoromethane (1.65 g, 10 mmol) was condensed into DMF (20 cm³) after which formic acid (1.2 g, 26 mmol) and sodium hydrogenosulfite (2.1 g, 20 mmol) were added to it. After 14 h of stirring, the mixture was analysed by ¹⁹F NMR: the transformation percentage of the bromide into the sulfinate salt (δ_F CF₂SO₂⁻ -69) was 38%.³³

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