chiral α-alkyl α-hydroxy esters or acids with high optical purity were determined. This reaction has been now extended, with good results, to other substrates.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Perkin-Elmer (90 MHz) spectrometer using tetramethylsilane as an internal standard. Optical rotations were taken on a Perkin-Elmer 241 polarimeter using a 1-dm cell.

Chiral Lithium Alkoxytrialkylaluminates. LiAl-*i*-Bu_3OR*. This reagent can be prepared in stock quantities in the following manner: to 0.05 mol (14.17 g) of (+)-Darvon alcohol recovered with 20 mL of hexane is added 0.05 mol (31.25 mL) of *n*-BuLi (1.6 M solution in hexane) under argon at −78 °C. The mixture is allowed to warm to room temperature and 0.05 mol (55.5 mL) of a solution (0.9 M) of *i*-Bu_3Al in hexane is added. The concentration of the solution is brought to 0.5 M by adding hexane until the total volume reaches 100 mL. This solution can be stored during several months without modification of the reactivity or of the asymmetric induction.

LiAl-*n*-Bu_3OR* and $LiAlEt_3OR$* are prepared by the same procedure. Owing to its lower solubility in hexane, $LiAlMe_3OR$* is prepared directly in the reaction flask, under argon, before use.

Typical Procedure. Reaction of LiAl-*i*-Bu_3OR* (R*OH = (+)-Darvon alcohol) with methyl phenylglyoxylate (Table I, expt 5). Hexane (100 mL) was added to 0.005 mol (10 mL) of LiAl-*i*-Bu_3OR* (0.5 M in hexane). The solution was cooled to 0 °C and 0.0045 mol (0.738 g) of methyl phenylglyoxylate and 10 mL of hexane were added dropwise. The mixture was stirred 4 h at 0 °C and then hydrolized with 5 N HCl (5 equiv). Internal standard (tetradecane) was added, and the aqueous layer was extracted twice with 10 mL of 2 N HCl to remove the amino alcohol, washed with water saturated with NaCl, and dried over $MgSO_4$. Yield of **1a**, 2-hydroxy-2-phenyl-4-methylpentanoic acid methyl ester, determined by GC, is 95% with less than 5% of reduced alcohol.

After evaporation of the solvent, the α-hydroxy ester **1a** is purified by preparative GC (SE 30, 150 °C): $[\alpha]^{22}_D$ +22.8° (*c* 1.9, $CHCl_3$); NMR ($CDCl_3$) δ 0.9 (6 H, m), 1.6–2.3 (3 H, m), 3.72 (3 H, s), 3.82 (1 H, s, OH) 7.5 (5 H, m).

Saponification of the α-hydroxy ester **1a** was effected with 4 equiv of KOH in 20 mL of methanol and 2 mL of water, refluxing the mixture for 2 h. After the solvent was evaporated, the residue was acidified and extracted with diethyl ether to give **2a**, (2*S*)-2-hydroxy-2-phenyl-4-methylpentanoic acid: $[\alpha]^{22}_D$ +17° (*c* 1.8, ethanol); NMR ($CDCl_3$, Me_2SO-d_6) δ 0.87 (6 H, m), 2 (3 H, m), 7.1–7.9 (7 H, m, phenyl and 2 OH).

The above reaction was effected in a preparative way, using 5 g (30 mmol) of methyl phenylglyoxylate. After saponification of the α-hydroxy ester **1a**, 5.5 g (25 mmol) of crude acid (**2a** was obtained. Recrystallization in hexane–ethanol (94/6 by volume) gives 3.24 g (52% yield) of pure chiral α-hydroxy acid **2a** with 98% ee: $[\alpha]^{20}_D$ +19.6° (*c* 2.1, ethanol); mp 131 °C. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69; O, 23.07. Found: C, 69.21; H, 7.80; O, 22.85.

Registry No. (*S*)-**1a**, 97690-15-8; (+)-**1d**, 97690-16-9; (*S*)-**2a**, 73698-06-3; (*R*)-**2a**, 97690-17-0; (*S*)-**2b**, 13113-71-8; (*R*)-**2c**, 3966-31-2; (*S*)-**2c**, 24256-91-5; LiAl-*i*-Bu_3R*, 97690-11-4; LiAl-*n*-Bu_3OR*, 97690-12-5; $LiAlEt_3OR$*, 97690-13-6; $LiAlMe_3OR$*, 97690-14-7; methyl phenylglyoxylate, 15206-55-0.

Chemistry of Halogenoperfluoroalkanes. Synthesis of Fluorinated Ethers and Thioethers via Radical or Anionic Intermediates

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Condensation of bromotrifluoromethane with potassium thiophenoxides in DMF is performed under pressure (2–3 atm) in a glass apparatus. Inhibition by nitrobenzene shows that a $S_{RN}1$ mechanism is involved in the formation of aryl trifluoromethyl sulfides. Dichlorodifluoromethane itself reacts through a similar process to give aryl chlorodifluoromethyl sulfides. Condensation of 1,1,2-trichlorotrifluoroethane with potassium thiophenoxide or phenoxide occurs even in the presence of nitrobenzene. The formation of aryl 2,2-dichloro-1,1,2-trifluoroethyl sulfides or ethers can be explained by a chain carbanionic mechanism.

The reactivity of perhaloalkanes is known to decrease when the number of fluorine atoms increases. "Chlorofluorocarbons" are usually inert, which justifies their use as refrigerants, gas propellants, and solvents.[1] They are decomposed sometimes by powerful nucleophiles.[2] Bromofluorocarbons behave in such a way. A nucleophile attacks the heavy halogen (Br or Cl) with subsequent formation of an unstable carbanionic species which decomposes in the reaction medium. Iodoperfluoroalkanes are more reactive, and nucleophilic attack on iodine usually occurs.[3] However, $S_{RN}1$ substitutions have also been observed.[4–6] The two processes coexist in the reaction of $BrCF_2Cl$ with thiophenoxides.[7] We describe here the condensation of C_2F_5Br, $C_6F_{13}Br$, and $ClCF_2CFCl_2$ (F113) as well as that of the poorly reactive Freons CF_2Cl_2 (F12) and $BrCF_3$ (F13B1) with thiophenoxides and phenoxides.

$$\underset{1}{ArS^-} + \underset{2}{XCF_2X'} \rightarrow \underset{3}{ArSCF_2X'}$$

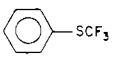
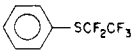
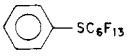
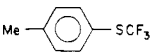
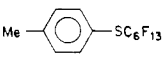
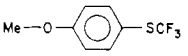
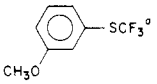
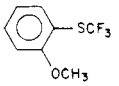
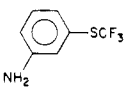
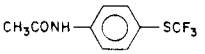
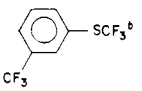
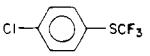
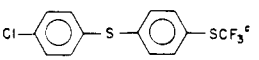
X = Br, Cl X′ = F, Cl, $CFCl_2$, CF_3, C_5F_{11}

We show that the monosubstitution observed involves radical (preliminary note[8]) or carbanionic intermediates.

(1) Banks, R. E. "Organofluorine Chemicals and Their Industrial Applications"; Society of Chemical Industry: London, 1979.
(2) Franzen, V.; Fikentscher, L. *Chem. Ber.* **1962**, *95*, 1958. Schlosser, M.; Le Van, C.; Spahic, B. *Helv. Chim. Acta* **1975**, *58*, 2575.
(3) Banks, R. E. "Fluorocarbons and Their Derivatives", 2nd ed.; McDonald: London, 1970.
(4) Cantacuzene, D.; Wakselman, C.; Dorme, R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1365.
(5) Boiko, V. N; Shchupak, G. M.; Yagupolskii, L. M. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *13*, 972. Popov, V. I.; Boiko, V. N.; Yagupolskii, L. M. *J. Fluorine Chem.* **1982**, *21*, 365.
(6) Feiring, A. E. *J. Org. Chem.* **1983**, *48*, 347.
(7) Rico, I.; Cantacuzene, D.; Wakselman, C. *J. Org. Chem.* **1983**, *48*, 1979.

0022-3263/85/1950-4047$01.50/0

Table I. Reactions of Bromoperfluoroalkanes

substrate	RFBr	product	bp, °C (mmHg)	^{19}F NMR, δ	yield, %
thiophenoxide	CF_3Br		77–78 (754)	−42	62
thiophenol, KOH (50%)	CF_3Br				45
thiophenoxide	C_2F_5Br		53 (28)	−83 (3 F), −92 (2 F, J_{FF} = 3.0 Hz)	33
thiophenoxide	$C_6F_{13}Br$		54 (0.4)	−87 (SCF_2)	72
4-methylthiophenoxide	CF_3Br		70 (20)	−43	75
4-methylthiophenoxide	$C_6F_{13}Br$		69 (0.4)	−87 (SCF_2)	77
4-methoxythiophenoxide	CF_3Br		90 (19)	−44	83
3-methoxythiophenoxide	CF_3Br		87 (20)	−43	40
2-methoxythiophenoxide	CF_3Br		89 (20)	−42	7
3-aminothiophenoxide	CF_3Br		112 (32)	−42	23
4-acetamidothiophenoxide	CF_3Br		183[d]	−44	9
3-(trifluoromethyl)thiophenoxide	CF_3Br		65 (17)	−42, −63	13
4-chlorothiophenoxide	CF_3Br		74 (19)	−42	34
			170 (19)	−42	20

[a] Anal. Calcd for $C_8H_7F_3OS$: C, 46.15; H, 3.39. Found: C, 46.21; H, 3.51. [b] Anal. Calcd for $C_8H_4F_6S$: C, 39.03; H, 1.64. Found: C, 39.31; H, 1.80. [c] Anal. Calcd for $C_{13}H_8ClF_3S_2$: C, 48.67; H, 2.51. Found: C, 48.76; H, 2.71. [d] Melting point.

Results

Reactivity of Bromoperfluoroalkanes. In the condensation of potassium thiophenoxide with perfluorohexyl iodide **5a** in DMF no clear inhibition by nitrobenzene was observed.[9] A $S_{RN}1$ mechanism could not be demonstrated.

$$\underset{4}{C_6H_5SK} + \underset{\substack{\mathbf{5a},\ X = I\\ \mathbf{5b},\ X = Br}}{XCF_2C_5F_{11}} \rightarrow \underset{6}{C_6H_5SCF_2C_5F_{11}}$$

Formation of the perfluoroalkyl sulfide **6** could be explained by an ionic mechanism as proposed by Haszeldine in the condensation of perfluoropropyl iodide with sodium thiomethoxide in Me_2SO.[10] However, recently, Feiring[11] showed that styrene inhibits the reaction between perfluorohexyl iodide and thiophenoxide. We used previously the less reactive perfluorohexyl bromide **5b** to see if inhibition by nitrobenzene could be observed. In fact inhibition occurs, which is in favor of a $S_{RN}1$ process.

Perfluoroalkyl bromides are more expensive than their iodide counterparts, and it is not advantageous to use them for perfluoroalkylation. However, bromotrifluoromethane (**7**), used as gas extinguisher, is much cheaper than iodotrifluoromethane. Furthermore aryl trifluoromethylsulfides **8** are useful in agrochemistry.[12]

Bromotrifluoromethane (**7**) was reacted with dry potassium thiophenoxide. No reaction occurs if the gas CF_3Br is bubbled through a solution of thiophenoxide in DMF at room temperature. If $C_6F_{13}Br$ is added to the

$$\underset{1}{ArSK} + \underset{7}{BrCF_3} \rightarrow \underset{8}{ArSCF_3}$$

same solution, condensation takes place. This liquid remains at the interphase with the DMF solution, whereas CF_3Br escapes from this solution. It appeared to us that if the reaction was of a $S_{RN}1$ type a minimal concentration of CF_3Br was necessary to maintain the chain process. In order to increase the amount of CF_3Br in solution the reaction was performed under pressure. No success was met if the reaction is run in a steel autoclave at 80 °C. However, condensation takes place at room temperature in a glass apparatus (Parr apparatus) under 2–3 atm (Table I).

Inhibition by nitrobenzene is clearly observed. The influence of substituents on the aromatic ring has been studied. The best yields are obtained with electron-donating substituents. In the case of *p*-chlorothiophenoxide a side reaction is observed.

An independant experiment shows that substitution of chlorine in compound **10** is easy and takes place even in the presence of nitrobenzene. This side reaction is a

$$\underset{\mathbf{9}}{p\text{-}ClC_6H_4SK} + \underset{7}{BrCF_3} \rightarrow \underset{\mathbf{10}}{ClC_6H_4SCF_3}$$

$$\mathbf{9} + \mathbf{10} \rightarrow \underset{\mathbf{11}}{ClC_6H_4SC_6H_4SCF_3}$$

classical S_N Ar substitution. The thiophenoxide can be

(8) Wakselman, C.; Tordeux, M. *J. Chem. Soc., Chem. Commun.* **1984**, 793.
(9) Wakselman, C.; Rico, I.; Tordeux, M., paper presented at the 8th European Symposium on Fluorine Chemistry, Jerusalem, July 22, 1983.
(10) Haley, B.; Haszeldine, R. N.; Hewitson, B.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1976**, 525.
(11) Feiring, A. E. *J. Fluorine Chem.* **1984**, *24*, 191.
(12) Kuhle, E.; Klauke, E. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 735.

$$\underset{\text{4, Z = H or 13, Z = p-CH}_3}{ZC_6H_4SK} + \underset{14}{ClCF_2Cl} \rightarrow \underset{15}{ZC_6H_4SCF_2Cl} + \underset{16}{ZC_6H_4SCF_2H} + \underset{17}{ZC_6H_4SCF_2SC_6H_4Z}$$

	15	16	17
a, Z = H	62%	8%	7%
b, Z = p-CH_3	44%	8%	6%

prepared in situ from the appropriate thiophenol in a mixture of DMF and 50% potassium hydroxide. The yield is lower than from dry thiophenoxide dissolved in DMF (Table I). The reaction of perfluoroalkyl bromides is quite general as shown by the example with C_2F_5Br (**12**) (Table I).

Reactivity of Dichlorodifluoromethane. The condensation of thiophenoxides with CF_2Cl_2 (**14**) have been performed in the same conditions as with CF_3Br. Several products are obtained.

The expected sulfide **15** is the major product. A previous experiment with potassium thiophenoxide and CF_2Cl_2 at normal pressure under UV irradiation (−40 °C) had given the same mixture, but the relative proportions of the products were quite different: **15a** (6%), **16a** (6%), and **17a** (22%), respectively.[7] In the present case total inhibition by nitrobenzene is observed: none of the three compounds could be detected. A $S_{RN}1$ process similar to the one postulated for CF_3Br is probably involved.

Reactivity of 1,1,2-Trichlorotrifluoroethane. Since 1,1,2-trichlorotrifluoroethane (**18**) is a liquid soluble in DMF the condensations with thiophenoxides have been performed at normal pressure. Monosubstituted sulfides **19** are obtained (Table II).[13] No additional products were detected by NMR of the crude reaction medium.

$$\underset{1}{ArS^-} + \underset{18}{ClCF_2CFCl_2} \rightarrow \underset{19}{ArSCF_2CFCl_2}$$

NMR data are in agreement with the proposed structure. Only a slight decrease in yield is observed when nitrobenzene is added. Recently Li Xing-Ya[14] described this reaction but in diglyme: in these conditions compound **19** and different other products are formed. If phenoxides are used the condensations in Me_2SO give two fluoroaryl ethers **21** and **22** (Table II).

$$\underset{20}{ArO^-} + \underset{18}{ClCF_2CFCl_2} \rightarrow \underset{21}{ArOCF_2CFCl_2} + \underset{22}{ArOCF_2CFClH}$$

Protonation of carbanionic intermediate is probably involved in the formation of the side product **22**. $ClCF_2CFCl_2$ behaves as described earlier for $BrCF_2CF_2Br$.[15]

Discussion

In the condensations of thiophenoxides with CF_3Br inhibition by nitrobenzene is observed which is good evidence for $S_{RN}1$ mechanism as described (Scheme I). Radical

Scheme I

$$ArS^- + CF_3Br \rightarrow ArS\cdot + CF_3Br^-\cdot$$

$$CF_3Br^-\cdot \rightarrow CF_3\cdot + Br^-$$

$$ArS^- + CF_3\cdot \rightarrow ArSCF_3^-\cdot$$

$$ArSCF_3^-\cdot + CF_3Br \rightarrow ArSCF_3 + CF_3Br^-\cdot$$

anions $CF_3X^-\cdot$ (X = Cl, Br, I) have been detected by ESR at low temperature. Their decomposition to $CF_3\cdot$ and X^- has been observed.[16]

A similar process takes places in the condensations of thiophenoxides with CF_2Cl_2. However radical anion $ArSCF_2Cl^-\cdot$ decomposes more readily than $ArSCF_3^-\cdot$, which explains the formation of a disubstituted product[7] (Scheme II).

Scheme II

$$ArSCF_2Cl^-\cdot \rightarrow ArSCF_2\cdot + Cl^-$$

$$ArS^- + ArSCF_2\cdot \rightarrow ArSCF_2SAr^-\cdot$$

$$ArSCF_2SAr^-\cdot + CF_2Cl_2 \rightarrow ArSCF_2SAr + CF_2Cl_2^-\cdot$$

This side reaction predominates under UV irradiation at −40 °C under normal pressure. Excess of energy of the anion radical might be involved or a slow competitive electron transfer due to a low concentration of CF_2Cl_2.

$$ArSCF_2Cl^-\cdot + CF_2Cl_2 \rightarrow ArSCF_2Cl + CF_2Cl_2^-\cdot$$

A minimal concentration of CF_2Cl_2 (or CF_3Br) is necessary to maintain the radical chain reaction. A pressure of 2–3 atm is sufficient to reach this concentration. The reaction takes place in a glass apparatus and not in a steel autoclave probably because of reductions by the metallic surface.

The behavior of $ClCF_2CFCl_2$ with thiophenoxides is very different from the one observed with CF_3Br or CF_2Cl_2. No inhibition by nitrobenzene is observed. The formation of the products can be explained by a series of reactions involving fluorocarbanions as described in (Scheme III).

Scheme III

$$ArS^- + ClCF_2CFCl_2 \rightarrow ArSCl + ClCF_2CFCl^-$$

$$ClCF_2CFCl^- \rightarrow CF_2{=}CFCl$$

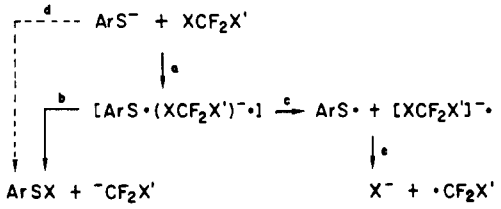
$$ArS^- + CF_2{=}CFCl \rightarrow ArSCF_2CFCl^-$$

$$ArSCF_2CFCl^- + ClCF_2CFCl_2 \rightarrow ArSCF_2CFCl_2 + ClCF_2CFCl^-$$

This mechanism is similar to the one proposed for $BrCF_2CF_2Br$[15] and also explains the results observed with phenoxides, particularly the formation of the side product **22**.

$$ArOCF_2CFCl^- + \text{"H" solvent} \rightarrow ArOCF_2CHFCl$$

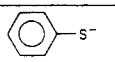
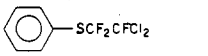
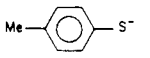
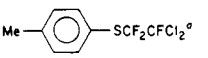
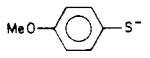
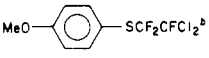
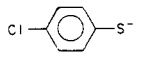
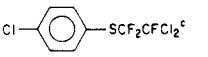
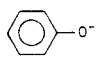
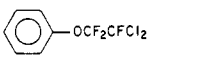
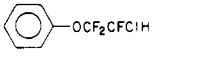
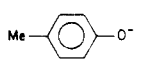
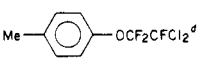
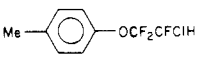
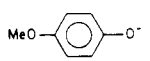
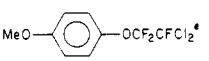
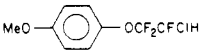
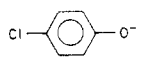
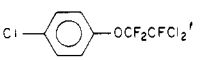
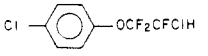
Scheme IV



Furthermore if a radical mechanism was involved the structure of the fluorinated sulfide would be ArSCFClC-

(13) Tordeux, M.; Wakselman, C. Fr. Demande FR 2 540 108; *Chem. Abstr.* **1985**, *102*, 45480x.
(14) Xing-Ya, L.; He-Qi, P.; Xi-Kui, J *Acta Chim. Sin.* **1984**, *42*, 297.
(15) Rico, I.; Wakselman, C. *J. Fluorine Chem.* **1982**, *20*, 759. We have observed recently that the condensation of phenoxides with $BrCF_2CF_2Br$ occurs even in the absence of thiol.
(16) Hasegawa, A.; Shiotani, M.; Williams, F. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 157.

Table II. Reactions of 1,1,2-Trichlorotrifluoroethane

substrate	solvent	product	bp, °C (mmHg)	NMR,[h] δ	yield, %
	DMF		56 (0.5)	−68 (1 F), −82 (2 F, J_{FF} = 13.4 Hz)	55
	DMF + $C_6H_5NO_2$				47
	Me_2SO				40
	DMF		81 (0.4)	−68 (1 F), −82 (2 F, J_{FF} = 13.2 Hz)	34
	DMF + $C_6H_5NO_2$				27
	Me_2SO				45
	Me_2SO		87 (0.4)	−68 (1 F), −84 (2 F, J_{FF} = 13.2 Hz)	45
	Me_2SO		oil[g]	−68 (1 F), −83 (2 F, J_{FF} = 13.2 Hz)	15
	Me_2SO		48 (0.7)	−74 (1 F), −84 (2 F, J_{FF} = 8.5 Hz), −83 (2 F), −153 (1 F)	37
				6.23 (J_{2HF} = 48 Hz, J_{3HF} = 4.9 Hz, J_{FF} = 12.9 Hz)	9
	Me_2SO		57 (0.4)	−75 (1 F), −83 (2 F, J_{FF} = 8.5 Hz), −84 (2 F), −153 (1 F)	35
				6.26 (J_{FF} = 12.8 Hz, J_{2FH} = 48 Hz, J_{3HF} = 4.8 Hz)	9
	Me_2SO		64 (0.4)	−74 (1 F), −84 (2 F, J_{FF} = 8.5 Hz), −83 (2 F), −153 (1 F)	31
				6.65 (J_{FF} = 12.8 Hz, J_{2FH} = 49 Hz, J_{3HF} = 4.5 Hz)	10
	Me_2SO		oil[g]	−74 (1 F), −84 (2 F, J_{FF} = 8.5 Hz), −83 (2 F), −154 (1 F)	8
				6.66 (J_{FF} = 12.8 Hz, J_{2FH} = 48 Hz, J_{3HF} = 4.5 Hz)	3

[a] Anal. Calcd for $C_9H_7Cl_2F_3S$: C, 39.29; H, 2.56. Found: C, 39.40; H, 2.80. [b] Anal. Calcd for $C_9H_7Cl_2F_3OS$: C, 37.13; H, 2.42. Found: C, 36.97; H, 2.22. [c] Anal. Calcd for $C_8H_4Cl_3F_3S$: C, 32.51; H, 1.36. Found: C, 32.67; H, 1.15. [d] Anal. Calcd for $C_9H_7Cl_2F_3O$: C, 41.72; H, 2.72. Found: C, 42.01; H, 2.75. [e] Anal. Calcd for $C_9H_7Cl_2F_3O_2$: C, 39.30; H, 2.56. Found: C, 39.37; H, 2.41. [f] Anal. Calcd for $C_8H_4Cl_3F_3O$: C, 34.38; H, 1.44. Found: C, 34.62; H, 1.48. [g] Purified by thin-layer chromatography on silica with pentane. [h] The multiplicities of the peaks in the ^{19}F NMR for compounds **19** and **21** are as follows: a triplet for the first peak and a doublet for the second one. In the case of compounds **22** the multiplicities are as follows: a doublet of a doublet for the first peak and a doublet of a triplet for the second one. In the ^1H NMR the multiplicity for **22** is a doublet of a triplet.

F_2Cl, since radical splitting of $ClCF_2CFCl_2$ is known to give $ClCF_2CFCl\cdot$.[17] Instead, NMR shows that sulfide $ArSCF_2CFCl_2$ is obtained: the formation of this product can only be explained by a carbanionic process (Scheme III). We observed the same structure in the condensations with phenoxides ($ArOCF_2CFCl_2$ and $ArOCF_2CFClH$).

The condensation of perfluorohaloalkanes with thiophenoxides show that two mechanisms are involved: a carbanionic process and a radical chain process. The first step can be explained[7] by a mechanism similar to the one proposed by Meyers for the reactions of CCl_4 and $BrCCl_3$[18] (Scheme IV).

In this hypothesis the monoelectronic transfer would be followed by competition between path c (radical process) and path b (carbanionic process). The abstraction of a "positive" halogen can also be explained[7] by a two-electron transfer reaction.[19] From this point of view the competition would be between path d (X-philic reaction) and path a, c, e, ($S_{RN}1$ reaction).

Whatever the process of positive X abstraction may be (path d or path a, b), the tendency for compounds of type XCF_2X' to be transformed into fluorinated carbanions seems higher when X' is a heavy halogen (or when X' is a trihalomethyl group that includes at least one voluminous halogen). On the contrary, the less reactive Freons having a relatively small molecular weight ($BrCF_3$, $ClCF_2Cl$) seem more prone to be transformed into fluorinated radicals according to a $S_{RN}1$ process. These observations, restricted to the peculiar case of thiophenoxides, can be drawn from the comparison of $BrCF_3$ and $BrCF_2Br$ reactions (or those of $BrCF_2CF_3$ and $BrCF_2CF_2Br$).

In the experiments that we described so far with halogenoperfluoroalkanes, phenoxides react by a carbanionic process[20] and enamines by a radical process. It appears that thiophenoxides are borderline and can distinguish fine variations of XCF_2X' reactivity depending on the nature of X and X'.

(17) Burton, D. J.; Kehoe, L. J. *Tetrahedron Lett.* **1966**, 5163.
(18) Meyers, C. Y.; Mattews, W. S.; Ho, L. C.; Kolm, W. H.; Parady, T. E. "Catalysis in Organic Synthesis"; Academic Press: New York, 1977.
(19) Zefirov, N. S.; Makhon'kov, D. I. *Chem. Rev.* **1982**, *82*, 615.

(20) After submission of this manuscript, a note describing spontaneous reactions of potassium phenoxide with dibromoperfluoroalkanes was published (Xingya, L.; Heqi, P.; Xikui, J. *Tetrahedron Lett.* **1984**, *25*, 4937). Similar spontaneous condensations were previously observed in some cases: CF_2Br_2 with 2-allylphenoxide (Rico, I.; Wakselman, C. *J. Fluorine Chem.* **1982**, *20*, 765) or *p*-nitrophenoxide (Jpn. Pat. 5 879 959; *Chem. Abstr.* **1983**, *99*, 87814*j*); $BrCF_2CF_2Br$ with ethoxide (Bagnall, R. D.; Bell, W.; Pearson, K.; Jeater, A. *J. Fluorine Chem.* **1979**, *13*, 123) and phenoxide (Angleton, W. P. C.; Ezzel, B. R. U.S. Pat. 4 423 249; *Chem. Abstr.* **1984**, *100*, 102755*a* and ref 15 of this manuscript). Acceleration of the condensation occurs in presence of a thiol or an enolizable ketone (Rico, I.; Wakselman, C. *Tetrahedron Lett.* **1981**, *22*, 323). However, we have not observed a spontaneous reaction between phenoxide and CF_2Br_2 in DMF. It seems that these condensations are very sensitive to the nature of the solvent and the purity of the reagents. The Chinese authors explain their results by a phenoxide attack on the bromine atom. This mechanism is exactly the same as one of the possible processes written in our previous publications (ref 15; ref 7, Scheme V, path c) or in this manuscript (Scheme IV, path d).

Conclusion. The condensation of thiophenoxides with the commercial Freons CF_3Br and CF_2Cl_2 is the first example of a $S_{RN}1$ type of monosubstitution of these poorly reactive haloalkanes. Furthermore this synthesis of the fluoro sulfides **3**[5,12,21] is very simple and inexpensive.

Experimental Section

Proton magnetic resonance spectra were recorded on a Varian EM360L spectrometer in parts per million (δ) downfield from tetramethylsilane. Fluorine magnetic resonance spectra were obtained on the same spectrometer (56.4 MHz) and are recorded in parts per million (δ_F) downfield from trichlorofluoromethane (solvent, $CDCl_3$). Phenols and benzenethiols were purchased from Aldrich and trifluorobromomethane and dichlorodifluoromethane from Setic-Labo; DMF (Aldrich) was distilled before use, and perfluorohexyl bromide was furnished by ATOCHEM.

The thiophenoxides (or phenoxides) were prepared by removing in vacuo water and methanol from a solution of thiophenol (or phenol) and potassium hydroxide in methanol. Spinning-band distillations were carried out with Perkin-Elmer NFT51 or MI3IT columns.

Preparation of [(Trifluoromethyl)thio]benzenes 8. General Methods. A pressure-safe glass bottle containing 0.05 mol of potassium thiophenoxide and 50 mL of dimethylformamide is placed under vacuum. Then the bottle is charged with 2.7 atm of bromotrifluoromethane and shaken for 3 h or until gas absorption ceases. The reaction is slightly exothermic. The mixture is poured in 100 mL of 17% hydrochloric acid. The aqueous phase is extracted with hexane. The organic layer is washed with water and dried over potassium carbonate. The solvent is evaporated, and the residue is distilled to give (trifluoromethylthio)benzene (**8**). The characteristics of the compounds are summarized in Table I.

When the reaction is performed with 5 mL of nitrobenzene added in the medium the substitution is obviously inhibited.

Preparation of [(Tridecafluorohexyl)thio]benzene (6). Potassium thiophenoxide (0.75 g, 0.005 mol) is dissolved in 4 mL of dimethylformamide. Then 2 g (0.005 mol) of bromotridecafluorohexane is added. The reaction is slightly exothermic. After 1 h, the conversion ratio of the bromotridecafluorohexane is estimated by NMR to be 85%. Then 10 mL of 17% hydrochloric acid is added, and the aqueous phase is extracted with ether. The organic layer is washed with aqueous solutions of sodium bicarbonate and sodium chloride, dried over magnesium sulfate, and evaporated. Distillation gives 1.7 g of [(tridecafluorohexyl)thio]benzene (**6**) (72% yield).

When the reaction is performed with 0.4 g (0.0032 mol) of nitrobenzene added in the medium the conversion ratio estimated by NMR falls to 30%.

The same product is obtained in 85% yield when bromotridecafluorohexane is replaced by iodotridecafluorohexane.

Preparation of [(Chlorodifluoromethyl)thio]benzenes 15. A pressure-safe bottle containing 0.05 mol of potassium thiophenoxide and 50 mL of dimethylformamide is placed under vacuum. Then the bottle is charged with 2.7 atm of dichlorodifluoromethane and shaken for 4 h or until gas absorption ceases. The reaction is slightly exothermic. The mixture is poured in 100 mL of 17% hydrochloric acid. The aqueous phase is extracted with hexane. The organic layer is washed with water, dried over potassium carbonate, and evaporated. The residue is distilled to give in the case of thiophenoxide itself several fractions. (1) [(Chlorodifluoromethyl)thio]benzene (**15a**) (62% yield): ^{19}F NMR δ_F −27; bp 75 °C (30 mmHg) [lit.[7] bp 82 °C (30 mmHg)]. (2) [(Difluoromethyl)thio]benzene (**16a**) (8% yield): ^{19}F NMR δ_F −91; ^1H NMR δ_H 6.76 (t, J_{HF} = 57 Hz). (3) Difluorodithiophenoxymethane (**17a**) (7% yield): ^{19}F NMR δ_F −48.

In the case of 4-methylthiophenoxide distillation of the residue gives the following fractions. (1) [(Chlorodifluoromethyl)thio]-4-methylbenzene (**15b**) (44% yield): ^{19}F NMR δ_F −27; bp 87 °C (18 mmHg). Anal. Calcd for $C_8H_7ClF_2S$: C, 46.05; H, 3.38. Found: C, 45.91; H, 3.21. (2) [(Difluoromethyl)thio]-4-methylbenzene (**16b**) (8% yield): ^{19}F NMR δ_F −90.5 (d); ^1H NMR δ_H 6.57 (t, J_{HF} = 57 Hz). (3) Difluorodi(4-methylthiophenoxy)methane (**17b**) (6% yield): ^{19}F NMR δ_F −49.

Preparation of [(2,2-Dichloro-1,1,2-trifluoroethyl)thio]benzene (19) or [(2,2-Dichloro-1,1,2-trifluoroethyl)oxy]benzene (21). Potassium thiophenoxide (or phenoxide) (0.05 mol) and 0.05 mol of 1,1,2-trichlorotrifluoroethane are stirred for 4 h in 50 mL of dimethylformamide or dimethyl sulfoxide. Hydrochloric acid (100 mL; 17%) is added, and the aqueous phase is extracted with hexane. The organic layer is washed with water, dried over potassium carbonate, and evaporated. The residue is distilled to give compounds **19** or **21**. Their characteristics are summarized in Table II. The unsuccessful attempts of inhibition were tried by addition of 5 mL of nitrobenzene in the medium.

Note Added in Proof: the condensation of thiols with perfluoroalkyl bromides in liquid ammonia under UV irradiation has been described recently: Ignatev, N. V.; Boiko, V. N.; Yagupolskii, L. M. *Zh. Org. Khim.* **1985**, *21*, 653.

Acknowledgment. We thank RPSC for financial suport and ATOCHEM for generous gifts of products.

Registry No. **1** (Ar = 4-$CH_3OC_6H_4$), 56830-32-1; **1** (Ar = 3-$CH_3OC_6H_4$), 97675-10-0; **1** (Ar = 2-$CH_3OC_6H_4$), 97675-11-1; **1** (Ar = 3-$H_2NC_6H_4$), 79576-16-2; **1** (Ar = 4-$CH_3CONHC_6H_4$), 97675-12-2; **1** (Ar = 3-$CF_3C_6H_4$), 97675-13-3; **3** (Ar = C_6H_5; X′ = CF_3), 65538-00-3; **3** (Ar = 4-$CH_3C_6H_4$; X′ = C_5F_{11}), 97675-14-4; **4**, 3111-52-2; **5a**, 355-43-1; **5b**, 335-56-8; **6**, 69127-72-6; **7**, 75-63-8; **8** (Ar = C_6H_5), 456-56-4; **8** (Ar = 4-$CH_3C_6H_4$), 352-68-1; **8** (Ar = 4-$CH_3OC_6H_4$), 78914-94-0; **8** (Ar = 3-$CH_3OC_6H_4$), 97675-15-5; **8** (Ar = 2-$CH_3OC_6H_4$), 75168-99-9; **8** (Ar = 3-$H_2NC_6H_4$), 369-68-6; **8** (Ar = 4-$CH_3CONHC_6H_4$), 351-81-5; **8** (Ar = 3-$CF_3C_6H_4$), 370-48-9; **9**, 40645-42-9; **10**, 407-16-9; **11**, 97675-16-6; **12**, 354-55-2; **13**, 31367-69-8; **14**, 75-71-8; **15a**, 85554-53-6; **15b**, 94169-13-8; **16a**, 1535-67-7; **16b**, 3447-50-5; **17a**, 80351-59-3; **17b**, 94169-14-9; **18**, 76-13-1; **19** (Ar = C_6H_5), 91122-73-5; **19** (Ar = 4-$CH_3C_6H_4$), 94221-44-0; **19** (Ar = 4-$CH_3OC_6H_4$), 97675-17-7; **19** (Ar = 4-ClC_6H_4), 97675-18-8; **20** (Ar = C_6H_5), 100-67-4; **20** (Ar = 4-$CH_3C_6H_4$), 1192-96-7; **20** (Ar = 4-$CH_3OC_6H_4$), 1122-93-6; **20** (Ar = 4-ClC_6H_4), 1121-74-0; **21** (Ar = C_6H_5), 95519-55-4; **21** (Ar = 4-$CH_3C_6H_4$), 97675-19-9; **21** (Ar = 4-$CH_3OC_6H_4$), 97675-20-2; **21** (Ar = 4-ClC_6H_4), 97675-22-4; **22** (Ar = C_6H_5), 456-62-2; **22** (Ar = 4-$CH_3C_6H_4$), 350-59-4; **22** (Ar = 4-$CH_3OC_6H_4$), 97675-21-3; **22** (Ar = 4-ClC_6H_4), 456-65-5; C_6H_5SH, 108-98-5; $C_6H_5NO_2$, 98-95-3.

(21) Yagupolskii, L. M.; Kondratenko, N. V.; Sambur, V. P. *Synthesis* **1975**, 721.