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The Preparation of Several Copper(I) and Silver Polyfluoroalkanethiolates and of Polyfluoroalkyl Aryl (or Alkyl) Sulfides

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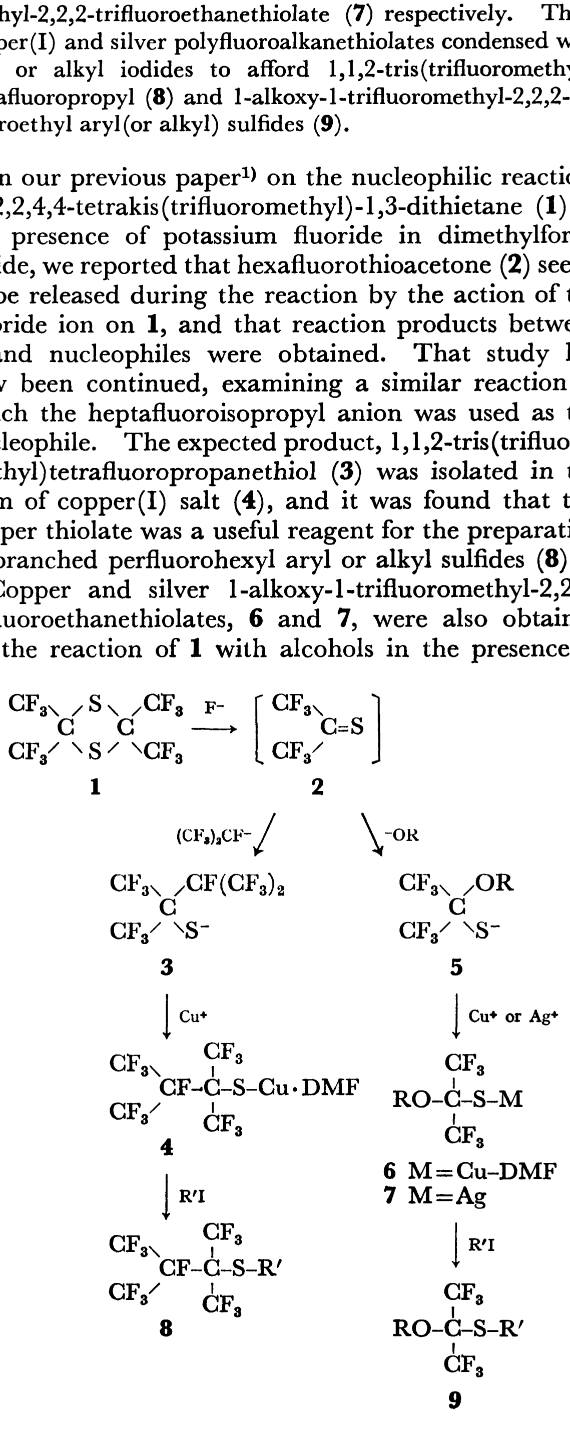
Synopsis. 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane (**1**) in the KF–DMF system was treated with hexafluoropropene in the presence of CuBr to give copper(I) 1,1,2-tris(trifluoromethyl)tetrafluoropropanethiolate (**4**). A similar reaction of **1** with alcohols in the presence of CuBr or $AgNO_3$ gave copper(I) (**6**) and silver 1-alkoxy-1-trifluoromethyl-2,2,2-trifluoroethanethiolate (**7**) respectively. These copper(I) and silver polyfluoroalkanethiolates condensed with aryl or alkyl iodides to afford 1,1,2-tris(trifluoromethyl)tetrafluoropropyl (**8**) and 1-alkoxy-1-trifluoromethyl-2,2,2-trifluoroethyl aryl(or alkyl) sulfides (**9**).

In our previous paper[1] on the nucleophilic reactions of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**) in the presence of potassium fluoride in dimethylformamide, we reported that hexafluorothioacetone (**2**) seems to be released during the reaction by the action of the fluoride ion on **1**, and that reaction products between **2** and nucleophiles were obtained. That study has now been continued, examining a similar reaction in which the heptafluoroisopropyl anion was used as the nucleophile. The expected product, 1,1,2-tris(trifluoromethyl)tetrafluoropropanethiol (**3**) was isolated in the form of copper(I) salt (**4**), and it was found that this copper thiolate was a useful reagent for the preparation of branched perfluorohexyl aryl or alkyl sulfides (**8**).

Copper and silver 1-alkoxy-1-trifluoromethyl-2,2,2-trifluoroethanethiolates, **6** and **7**, were also obtained by the reaction of **1** with alcohols in the presence of metal ion, and these thiolates condensed easily with aryl iodides to give 1-alkoxy-1-trifluoromethyl-2,2,2-trifluoroethyl aryl sulfides, **9**.



The Preparation of Copper(I) 1,1,2-Tris(trifluoromethyl)-tetrafluoropropanethiolate. The heptafluoroisopropyl anion, which is formed readily by the action of the fluoride ion on hexafluoropropene, is known to be an effective nucleophile.[2] The reaction between 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**) and hexafluoropropene was examined in the presence of potassium fluoride in dimethylformamide. Since the resulting perfluoroalkanethiol was presumed to be readily oxidized, we carried out the reaction in the presence of copper(I) bromide in order to trap the thiol in the form of copper(I) thiolate. The reaction proceeded smoothly at 50 °C, and the expected copper thiolate was isolated from the reaction products in a yield of 52% by acetone extraction. This compound was a fairly stable solid, with a melting point of 78—80 °C; it was an adduct with one mole of dimethylformamide. The structure was evident from its IR, NMR, and mass spectra. In the IR spectrum, the presence of an amide group was revealed by the strong band at 1650 cm^{-1}. In the ^{19}F NMR spectrum, three signals appeared, at −18.8 (doublet), −17.0 (singlet), and 124.7 (multiplet) ppm;* they are probably due to $\mathrm{CF(C}\mathit{F}_3)_2$, $\mathrm{C(C}\mathit{F}_3)_2$, and $\mathrm{C}\mathit{F}\mathrm{(CF_3)_2}$, respectively. In the mass spectrum, two important fragment peaks, m/e 415 ($C_6F_{13}SCu^+$) and m/e 73 ($C_3H_7NO^+$), appeared, in addition to the molecular ion, M^+ 488. The other fragment peaks at m/e 351 and m/e 344 can be explained by the elimination of Cu and CF_3 respectively from m/e 415. The ions of m/e 182 (C_3F_6S), 132 (C_2F_4S), and 113 (C_2F_3S), which are characteristic of hexafluorothioacetone derivatives, also appeared.

The Preparation of Copper(I) and Silver 1-Alkoxy-1-trifluoromethyl-2,2,2-trifluoroethanethiolates. In our investigation of the reactions between 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**) and alcohols in the potassium fluoride–dimethylformamide system, 1-alkoxy-1-trifluoromethyl-2,2,2-trifluoroethanethiols (**5**) seemed to be formed; however, they were finally oxidized and isolated as disulfides.[1]

As we desired to capture the thiol, **5**, in the form of metal thiolates as evidence of the reaction pass, these reactions were carried out in the presence of silver or copper salt. When silver nitrate was used, silver thiolates were obtained as stable white crystals, which were isolated from the reaction products by extraction with acetone.

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* All the ^{19}F NMR chemical shifts throughout this article are given in ppm from external trifluoroacetic acid.

Table 1. Preparation of **8**

R′	Yield (%)	Bp (°C/mmHg) (mp °C)	^{19}F NMR$^{a)}$			F-Anal (%)	
			$(CF_3)_2CF$	$-(CF_3)_2$	$>CF$	Found	(Calcd)
C_6H_5	69	58—60/26	−12.6	−10.7	108.5	57.4	(57.7)
m-Me·C_6H_4	50	96—99/24	−12.0	−10.7	110.0	55.6	(55.9)
p-Me·C_6H_4	42	86—89/25	−11.8	−10.3	110.2	55.3	(55.9)
o-O_2N·C_6H_4	45	(63—65)	−13.0	−11.0	105.5	51.9	(52.2)

a) δ ppm from ext. CF_3CO_2H in CCl_4.

Table 2. Preparation of **9** (R=OMe)

R′	Yield (%)	Bp (°C/mmHg) (mp °C)	^{19}F NMR$^{a)}$ CF_3	F-Anal(%)	
				Found	(Calcd)
C_6H_5	57	73—75/32	−8.70	39.6	(39.3)
o-MeC_6H_4	60	107—108/27	−8.70	37.8	(37.3)
p-MeC_6H_4	64	98—99/19	−8.75	36.8	(37.3)
p-FC_6H_4	70	108—110/71	−8.70	43.0	(43.2)
o-$O_2NC_6H_4$	75	(69—70)	−8.84	33.4	(34.0)
m-$O_2NC_6H_4$	51	114—115/4	−8.70	33.7	(34.0)
p-$O_2NC_6H_4$	56	(41—43)	−8.76	33.0	(34.0)
o-$HO_2CC_6H_4$	59	(105—106)	−8.75	34.4	(34.1)
o-$MeO_2CC_6H_4$	55	107—108/4	−8.70	32.5	(32.7)
p-$MeOC_6H_4$	67	86—89/3	−8.65	35.2	(35.6)

a) ^{19}F Chemcal shifts are given in δ ppm from ext. CF_3CO_2H in CCl_4.

Copper thiolates were also obtained by using copper(I) bromide instead of silver nitrate in the above reaction. The product isolated from the acetone extract was an adduct with one mole of dimethylformamide, as in the case of **4**. The IR spectrum revealed a strong band at 1640 cm^{-1} due to the amide group; the other major bands were similar to those of **7**.

The Condensation of Silver and Copper(I) Thiolates with Aryl(or Alkyl) Iodides. The condensation of silver and copper alkanethiolates with aryl or alkyl iodides is well known.[3–5] The silver and copper thiolates mentioned above also underwent condensation with aryl and alkyl iodides to give polyfluoroalkyl aryl or alkyl sulfides (Tables 1 and 2). The reactions proceeded in dimethylformamide at 80—100 °C under a nitrogen atmosphere. Especially, the condensation of various substituted aryl iodides and the copper perfluorohexanethiolate (**4**) seems to be a useful synthetic method for higher perfluoroalkyl thiobenzenes, which are valuable intermediates for surface-active compounds.

Experimental

Copper(I) 1,1,2-Tris(trifluoromethyl)tetrafluoropropanethiolate-DMF Adduct (4). Hexafluoropropene was bubbled into a mixture of the dimer of hexafluorothioacetone, **1** (7.3 g, 0.02 mol), copper(I) bromide (5.7 g, 0.04 mol), potassium fluoride (4.5 g, 0.077 mol), and dimethylformamide (50 ml) at 50 °C until no more absorption of the gas took place. The reaction mixture was then poured into water, and the precipitates were separated by filtration and washed with water. This black solid was subjected to extraction with hot acetone, and the solvent was removed by evaporation to give an orange product; mp 78—80 °C (10 g, 52%). This was a 1:1 adduct of **4** with dimethylformamide. Found: C, 21.5; H, 1.71; N, 2.48; F, 50.5%. Calcd for $C_9H_7F_{13}NOSCu$: C, 22.2; H, 1.44; N, 2.87; F, 50.7%.

Copper(I) 1-Methoxy-1-trifluoromethyl-2,2,2-trifluoroethanethiolate (6). A mixture of **1** (3.64 g, 0.01 mol), methyl alcohol (0.64 g, 0.02 mol), copper(I) bromide (2.86 g, 0.02 mol), and potassium fluoride (1.71 g, 0.029 mol) in dimethylformamide (30 ml) was stirred for 24 hr at room temperature. The resulting mixture was worked up as above to give **6** (yield, 63%); mp 68—70 °C. Found: C, 24.3; H, 2.95; N, 4.21; F, 32.4%. Calcd for $C_7H_{10}F_6NO_2SCu$: C, 24.1; H, 2.88; N, 4.01; F, 32.6%. IR: 1640 cm^{-1} (-CO-N-).

Silver 1-Methoxy-1-trifluoromethyl-2,2,2-trifluoroethanethiolate (7) (R=Me). A mixture of **1** (3.64 g, 0.01 mol), methyl alcohol (0.64 g, 0.02 mol), silver nitrate (3.4 g, 0.02 mol), potassium fluoride (1.30 g, 0.022 mol), and dimethylformamide (30 ml) was worked up as above, giving a white product; mp 132—133 °C (4.04 g, 57%). Found: C, 15.2; H, 0.76; F, 35.2%. Calcd for $C_4H_3F_6OSAg$: C, 15.0; H, 0.94; F, 35.5%. NMR (in DMSO-d_6): ^{1}H, 5.76 (OMe, s); ^{19}F, −6.00 (CF_3, s).

The reaction with ethanol was run similarly; here the product (mp 150—151 °C) was obtained in a yield of 34%.

Condensation Reactions. *A)*: A mixture of **4** (5.32 g, 0.011 mol), *o*-iodonitrobenzene (2.50 g, 0.01 mol), and DMF (50 ml) was stirred under an atmosphere of nitrogen at 80—90 °C for 24 hr. After the copper iodide had been removed by filtration, the filtrate was poured into water, and the precipitates were collected and recrystallized from *n*-hexane to give **8** (R′=*o*-$NO_2C_6H_5$) (mp 63—65 °C) in a yield of 45%. Found: C, 30.7; H, 0.96; N, 2.73; F, 51.9%. Calcd for $C_{12}H_4F_{13}NO_2S$: C, 30.5; H, 0.85; N, 2.96; F, 52.2%. IR: 1510, 1358 (NO_2) cm^{-1}.

B): A mixture of **6** (R=Me, 7.0 g, 0.025 mol), *o*-iodonitrobenzene (5.0 g, 0.02 mol) and DMF (50 ml) was worked up such as has been described above at 90—100 °C for 24 hr. The product was recrystallized from *n*-hexane to give **9** (R′=*o*-$NO_2C_6H_5$, 75%); mp 69—70 °C. Found: C, 36.0; H, 2.31; N, 4.25; F, 33.9%. Calcd for $C_{10}H_7F_6NO_3S$: C, 35.8; H, 2.10; N, 4.18 F, 34.0%. IR: 1525, 1358 (NO_2) cm^{-1}.

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