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The Reactions of the Hexafluorothioacetone Dimer with Nucleophiles in the Presence of the Fluoride Ion

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In the KF–DMF system, the hexafluorothioacetone dimer (**1**) reacted with alcohols, alkanethiols, and thiophenols under mild conditions. The products, **2**, **3**, **10**, and **12**, were assumed to have resulted from the hexafluorothioacetone monomer (**4**) and the nucleophiles. Cycloadducts of **4** and anthracene or styrene were also obtained readily from the dimer (**1**) and the dienes.

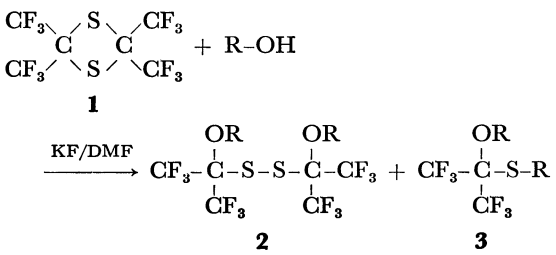
2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithiethane (**1**), a dimer of hexafluorothioacetone, is a stable compound derived from hexafluoropropene and sulfur.[1] In an earlier communication,[2] we reported on the reactions between the dimer and amines or carbonyl reagents, which gave *N*-substituted hexafluoroisopropylideneimines. However, attempts to have other nucleophiles, such as alcohols and thiols, react with the dimer were unsuccessful.

In our continued studies of the nucleophilic reactions of the dimer, we have found that, in the presence of potassium fluoride, **1** in dimethylformamide reacted with alcohols and thiols, thus giving the reaction products of these nucleophiles with hexafluorothioacetone itself.

Results and Discussion

Reaction of Hexafluorothioacetone Dimer with Alcohols. Although the dimer, **1**, reacted with aryl or alkyl amines in dimethylformamide at room temperature,[2] no reaction was observed with alcohols even at a higher temperature. The presence of a small amount of potassium fluoride, however, promoted the reaction very much, and it proceeded smoothly at room temperature. The products of this reaction were bis-[1-alkoxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl] disulfide (**2**) and 1-alkoxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl alkyl sulfide (**3**).

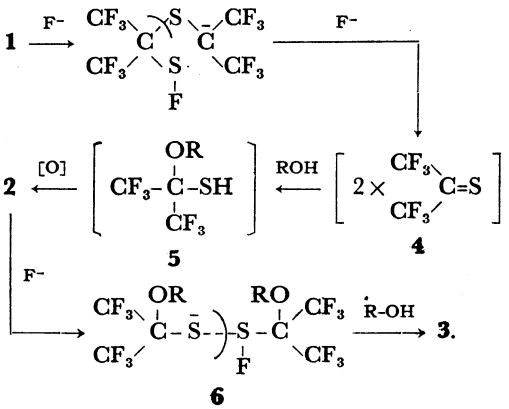
1) I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **183**, 598 (1968).
2) N. Ishikawa and T. Kitazume, This Bulletin, submitted for publication.



The structures of these compounds were elucidated by a study of the ^1H and ^{19}F NMR and the mass spectra. The ^{19}F NMR spectra of both **2** and **3** showed only one singlet signal each, *i.e.*, −9.2 ppm for **2** (R=Me) and −7.20 ppm for **3** (R=Me), from ext. CF_3CO_2H in CCl_4. The patterns of the ^1H NMR spectra were also simple. Only one singlet signal at τ 6.28 (OMe) for **2** (R=Me) and two singlet signals at τ 6.40 (OMe) and 7.80 (SMe) for **3** (R=Me) appeared. In the mass spectrum of **2** (R=Me), the base peak, *m/e* 181 ($C_4H_3F_6O$), and other fragment peaks, such as *m/e* 213 ($C_4H_3F_6OS$), 69 (CF_3), 64 (S_2), and 31 (OMe), appeared appropriately. The parent peak, M^+ 426, was not observed, but this is not strange because, in di-*tert*-alkyl disulfides, it is known that the parent peak appears very weakly.[3]

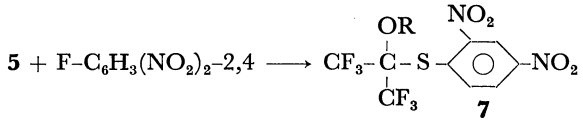
Among the various catalysts examined in connection with the above reaction, only alkali metal fluorides such as potassium and sodium flouride, were effective; alkalies, such as potassium and sodium hydroxide or potassium carbonate, had no catalytic activity. Further, in protonic solvents such as alcohols, no reaction occurred even in the presence of potassium fluoride. These results made it evident that the fluoride ion, especially the unsolvated active ion, catalyzed the reaction.

We presumed that the reaction proceeded according to the following scheme:



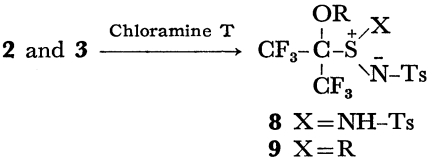
It was initiated by the active fluoride ion in the polar aprotic solvent, which attacked the sulfur atom of the dimer, **1**; it thus accelerated the formation of the reactive hexafluorothioacetone monomer, **4**. Alcohol as a nucleophile reacted with **4**, thus giving 1-alkoxy-1-(trifluoromethyl)-2,2,2-trifluoroethanethiol (**5**), which was subsequently oxidized to disulfide, **2**. The attack of the fluoride ion on sulfur occurred again, and the resulting anionic sulfur (**6**) probably reacted with alcohol to give **3**.

In order to obtain evidence for this scheme, we carried out the following reactions. To capture the intermediate thiol, **5**, the **1** and methanol in the KF–DMF system were reacted in the presence of 2,4-dinitrofluorobenzene; the 2,4-dinitrophenyl sulfide (**7**) (R=Me) was thus obtained in a good yield.

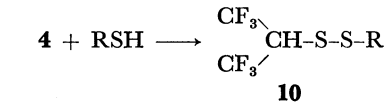


Further, the disulfide **2** (R=Me) reacted with methanol in the KF–DMF system to give **3** (R=Me), proving **2** and **3** were formed successively.

It is well known that sulfides[4] and disulfides[5] give *N*-sulfonylsulfilimines and sulfonimidosulfinsulfonylimine derivatives with Chloramine T. From disulfides, **2**, and sulfides, **3**, these derivatives were obtained as two crystalline compounds, (**8**) and (**9**) (Table 1).



Reaction of the Dimer with Thiols. Middleton *et al.* reported that, in the reaction of the hexafluorothioacetone monomer with alkanethiols, the thiocarbonyl group behaves as would be expected if sulfur were positive; the following addition reaction was observed:



Since hexafluorothioacetone was assumed to be formed during the reaction of the dimer **1** in the KF–DMF system, we carried out the reaction using alkanethiols as the nucelophile. For example, *n*-butanethiol and **1**, together with potassium fluoride, were allowed to react in dimethylformamide at room temperature; the disulfide **10** (R=*n*-Bu) was thus obtained as the main product. Ethanethiol also gave a similar product, **10** (R=Et).

When thiophenol and thiocresol were used in the above reaction, the main products were 3:1 (C_3F_6S:ArSH) and 4:1 adducts, **12** (*n*=**2** and **3**) respectively. Adducts of this kind were also reported by Middleton *et al.*, although they did not make clear on which side the disulfide bonding was.[6]

We elucidated the structure of **12** by studying the NMR and mass spectra. For example, the ^{19}F NMR of **12** (Ar=Ph, *n*=2) revealed three signals, one doublet and two singlets of the same intensity, and the ^1H NMR contained one multiplet signal at τ 6.24 in addition to the aromatic-proton signal. The mass spectrum gave the molecular ion and other fragment ions, as is

3) D. H. Williams, J. H. Bowie, S. O. Lawesson, J. ϕ, Madsen, C. Nolde, and G. Schrole, *J. Chem. Soc. B*, **1966**, 946.

4) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

5) G. Leandri and D. Spinelli, *Ann. Chem.*, **49**, 964 (1959).

6) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

Table 1. Preparation of disulfide **2** and monosulfide **3**, and their chloramine T derivatives, **8** and **9**

R		Yield (%)	Bp (°C/mmHg)	^{19}F NMR (δ ppm[a])	F-Anal (%) Obsd	F-Anal (%) Calcd		Yield (%)	Mp (°C)	IR (cm^{-1}) N=S (IV)	IR (cm^{-1}) N-H	F-Anal (%) Obsd	F-Anal (%) Calcd
Me	2	68	113—115/24	−9.20	51.9	52.1	8	37	124—126	956	3452	20.4	20.7
Et		69	131—132/43	−8.40	50.8	50.2		64	125—126	978	3480	20.0	20.1
n-Pr		77	132—134/24	−8.20	47.5	47.3		58	135—135.5	958	3442	19.3	19.7
i-Pr		46	138—140/20	−8.40	47.7	47.3		60	121.5—122	945	3438	19.6	19.7
n-Bu		66	155—156/23	−8.80	45.1	44.7		65	122—123	958	3422	19.0	19.2
i-Am		51	159—160/23	−8.62	42.6	42.4		56	131.5—132	963	3418	18.7	18.8
Me	3	23	101—102/120	−7.20	50.3	50.0	9	68	109—110	945	——	28.9	28.7
Et		27	125—126/43	−8.00	44.7	44.5		66	129.5—130	956	——	27.1	26.8
n-Pr		23	118—120/24	−7.40	40.6	40.1		47	126—127	943	——	25.4	25.2
i-Pr		15	128—131/20	−7.35	40.3	40.1		44	127—129	938	——	25.6	25.2
n-Bu		21	148—149/24	−7.65	36.1	36.5		45	120—121	964	——	23.7	23.7
i-Am		33	131—134/23	−7.90	32.9	33.5							

a) Erom ext. CF_3CO_2H in CCl_4.

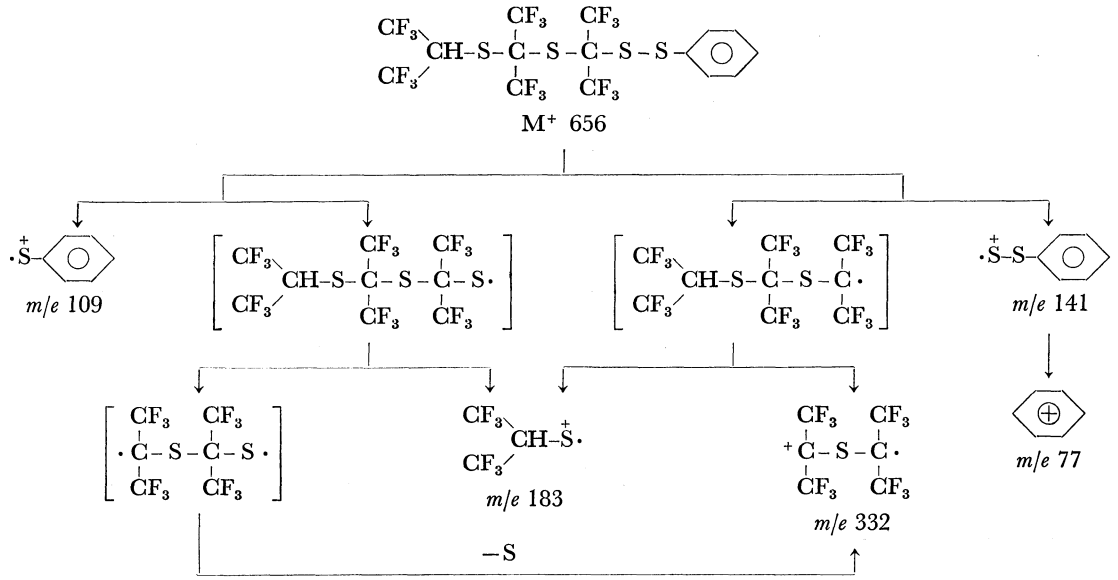
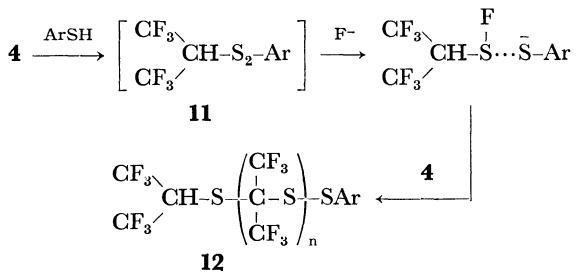
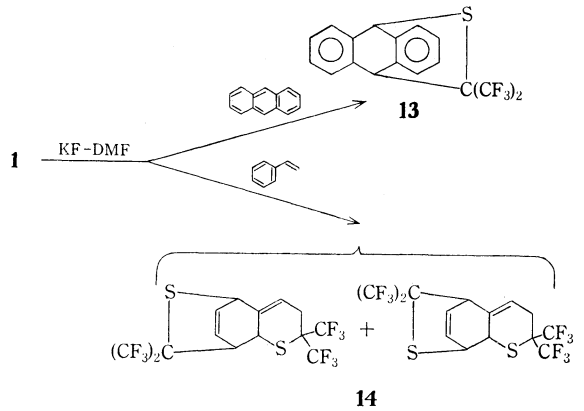


Fig. 1. Mass fragmentation of 12 (Ar=Ph).

shown in Fig. 1. On the other hand, the fragment peaks, $C_6H_5S_2^+$ and $C_3HF_6S_2^+$, which are characteristic of the disulfide bond,[3,7,8] appeared in considerable strength and no fragment corresponding to $C_3HF_6S_2^+$ was observed. This means that there is C–S_2–Ar group, but no C–S_2–CH$(CF_3)_2$ group, in the molecule.

From these results, the reaction scheme and the structures of the products were estimated to be as is shown below:





Preparation of Cycloadducts from the Hexafluorothioacetone Dimer. Further confirmation of hexafluorothioacetone as an intermediate was made by the formation of the cycloadducts with dienes.

7) S. Kozuka, H. Takahashi, and S. Oae, This Bulletin, **43**, 129 (1970).

8) I. L. Knunyants and L. S. German, *Dokl. Akad. Nauk SSSR*, **201**, 603 (1971).

Since Middleton reported that hexafluorothioacetone gives cycloadducts with dienes very easily,[9] we carried out the reaction of the dimer **1** with anthracene and with styrene in the KF–DMF system. As expected, the **13** and **14** cycloadducts were obtained respectively; they were similar to those prepared by Middleton.

Experimental

Reaction of 1 with Methyl Alcohol. Into a mixture of potassium fluoride (4.6 g, 0.08 mol), **1** (14.6 g, 0.04 mol), and dimethylformamide (30 ml), methyl alcohol (3.8 g, 0.12 mol) was added, drop by drop; the whole was then stirred for 24 hr at room temperature. The reaction mixture was poured into water, and the separated oily matter was extracted with ethyl ether. The extract was dried over magnesium sulfate, and the solvent was removed. The vacuum distillation of the residue gave **3** (R=Me) (bp 101—102 °C/120 mmHg (3.8 g, 23%)) and **2** (R=Me) (bp 113—115 °C/24 mmHg (5.8 g, 68%)).

The reactions with other alcohols were run similarly; two products, **2** and **3**, were obtained in each case (Table 1).

1-Alkoxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl 2',4'-dinitrophenyl Sulfide (7). A mixture of **1** (7.3 g, 0.02 mol), potassium fluoride (2.4 g, 0.041 mol), methanol (1.4 g, 0.04 mol), 2,4-dinitrofluorobenzene (3.7 g, 0.02 mol), and dimethylformamide (30 ml) was stirred for 48 hr at room temperature, and then the reaction mixture was poured into water. The resulting precipitate was collected and recrystallized from cyclohexane, thus giving crystals of **7** (R=Me) (mp 76—77 °C) in a yield of 73%. Found: F, 29.5%. Calcd: F, 30.0%. IR: 1526, 1352 (NO_2) cm^{-1}. NMR: ^1H, τ 1.62 (Ph), 6.16 (OMe); ^{19}F, −8.80 ppm from ext. CF_3CO_2H in CCl_4.

The sulfide, **7** (R=Et) (mp 82—83 °C), was also prepared in a similar way. Found: F, 28.6%. Calcd: F, 28.9%.

S-[*1-Ethoxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl*]-S-p-*toluenesulfonamide*-N-p-*toluenesulfonylsulfilimine (8).* Into a solution of **2** disulfides (R=Et, 1.0 g, 2 mmol) in ethanol (30 ml), we added Chloramine T (3.0 g, 10 mmol) at room temperature, and then the whole was stirred for 48 hr. The reaction mixture was then poured into a cold dilute sodium hydroxide solution. The precipitate was filtered and recrystallized from benzene to give **8** (R=Et, 1.6 g, 64%) (mp 125—126 °C).

9) W. J. Middleton, *J. Org. Chem.*, **30**, 1390 (1965).

S-[*1-Ethoxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl*]-S-*ethyl*-N-p-*toluenesulfonylsulfilimine (9).* To a mixture of the **3** sulfide (R=Et, 2.05 g, 8 mmol), Chloramine T (3.0 g, 10 mmol), and methanol (30 ml), we added, drop by drop, a mixture of acetic acid (1.0 ml) and methanol (5 ml) at room temperature. The whole was then stirred for 48 hr and poured into a cold dilute sodium hydroxide solution. The precipitate was collected and washed with water. Recrystallization from benzene gave **9** (R=Et, 2.24 g, 66%) (mp 129—130 °C).

Other Chloramine T derivatives were obtained by a similar procedure (Table 1).

Reaction of 1 with Butanethiol. A mixture of **1** (7.3 g, 0.02 mol), butanethiol (3.6 g, 0.04 mol), potassium fluoride (2.4 g, 0.04 mol), and dimethylformamide (20 ml) was stirred for 24 hr at room temperature, and then the whole was poured into water. An oily matter was subsequently extracted with ethyl ether, and the solvent was removed. The vacuum distillation of the residue gave **10** (R=*n*-Bu) (bp 85—86 °C/21 mmHg (2.0 g, 55% on the basis of the consumed BuSH.)) and di-*n*-butyl disulfide (2.4 g, bp 118—119 °C/21 mmHg). **10** (R=*n*-Bu): Found: F, 41.4%, Calcd for $C_7H_{10}F_6S_2$: F, 41.9%. NMR: ^1H, τ 6.2 (m, $(CF_3)_2$-CH); ^{19}F, δ −12 ppm (d) (from ext. CF_3CO_2H in CCl_4).

When ethanthiol was used in the above reaction, a similar disulfide, **10** (R=Et) (bp 74—76 °C/58 mmHg), was obtained in a 47% yield. Found: F, 46.3%. Calcd: F, 46.7%. NMR: ^1H, τ 6.31 (m); ^{19}F, δ −11.6 ppm (d).

Reaction of 1 with Thiophenol. A mixture of thiophenol (2.2 g), **1** (3.6 g), potassium fluoride (1.2 g), and dimethylformamide (20 ml) was allowed to react as has been described above. A subsequent work-up gave an oil, **12** (Ar=Ph, n=2) (2.2 g, 51%, bp 94—95 °C/70 mmHg, Found: F, 51.6%, Calcd for $C_{15}H_6F_{18}S_4$: F, 52.1%).

p-Thiocresol gave a similar product, **12** (Ar=*p*-MeC_6H_4, n=3) (bp 87—89 °C/19 mmHg, 40%; Found: F, 53.3%. Calcd: F, 53.5%).

Hexafluorothioacetone–anthracene Adduct (13). A mixture of **1** dimer (7.3 g, 0.02 mol), anthracene (7.2 g, 0.04 mol), potassium fluoride (2.4 g), and dimethylformamide (30 ml) was stirred at room temperature for 48 hr, and then the mixture was poured into water. The precipitate was collected and recrystallized from *n*-hexane, thus, giving **13** (mp 121—122 °C (lit,[9] mp 123—124 °C)) in a yield of 82%.

Styrene reacted in a similar way, thus giving a mixture of isomers (**14**) (bp 125—127 °C/3 mmHg (lit,[9] bp 103—104 °C/1.2 mmHg)) in a 24% yield.