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REACTIONS OF BIS(BISTRIFLUOROMETHYLAMINO-OXY)-MERCURY(II) AND NN-BIS(TRIFLUOROMETHYL)NITROXIDE WITH THIO-CARBONYL COMPOUNDS

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SUMMARY

   Thiobenzophenone, 9-thiocarbonylfluorene and carbonyl sulphide react with the mercurial, $Hg[ON(CF_3)_2]_2$, to form HgS and the compounds $Ph_2C[ON(CF_3)_2]_2$, $(C_6H_4)_2C[ON(CF_3)_2]_2$ and $[(CF_3)_2NO]_2CO$ respectively. The last compound is also formed as the major product on mixing the mercurial with carbon disulphide. With thiophosgene, reaction occurs to form $HgCl_2$ and a mixture of the compounds $(CF_3)_2NSCOCl$ and $(CF_3)_2NSCOON-(CF_3)_2$, which are thought to arise by rearrangement of the intermediates $(CF_3)_2NOC(S)Cl$ and $[(CF_3)_2NO]_2CS$. A similar rearrangement may also occur during the reactions of thio-benzoyl chloride and aryl chlorothionoformates with the mercurial but the product mixtures from these reactions are more complex and pure compounds have not been isolated.

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[*] For part XX see ref. 27
[‡] Dedicated to Professor H.J. Emeléus on the occasion of his
   80th birthday.
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Reaction between thiophosgene dimer and the mercurial results in a simple chlorine exchange to afford the 1,3-dithietane $[(CF_3)_2NO]_2\overline{CSC[ON(CF_3)_2]_2S}$. The low temperature reaction of thiophosgene with $(CF_3)_2NO$ gives a thermally unstable product believed to be $(CF_3)_2NOCCl_2S(O)ON(CF_3)_2$, while the similar reaction with thiobenzophenone appears to give $(CF_3)_2NOCPh_2SON-(CF_3)_2$, which decomposes above 0 °C.

INTRODUCTION

(Bistrifluoromethylamino-oxy)mercury(II) (1), first reported by Eméleus and co-workers [1] in 1969, has proved to be a versatile reagent for the introduction of the $(CF_3)_2NO$ group into organic and inorganic molecules [2]. Apart from isolated reports of the reaction of thiazyl fluoride [3] and $CF_3S(O)F$ [4] reactions of (1) with sulphur compounds have received little attention, although several reactions of the nitroxide radical, $(CF_3)_2NO$, with sulphur derivatives are known [2,5-8]. We now describe a comparative study of the reactions of (1) and $(CF_3)_2NO$ with some thiocarbonyl and thioacyl chloride derivatives [9].

RESULTS AND DISCUSSION

When an equimolar mixture of (1) and carbonyl sulphide in a sealed tube was allowed to warm to room temperature from -196 °C a rapid reaction occurred to give the known compound $[(CF_3)_2NO]_2CO$ [1] in 99% yield and mercury(II) sulphide. Under similar conditions (1) reacted with thiobenzophenone and 9-thiocarbonylfluorene to produce the new compounds (2) and (3) in 55% and 81% yields respectively. Both these compounds are stable in air and stable thermally up to at least 150 °C. Little or no reaction occurred between carbon disulphide and (1) between -196 °C and -46 °C, but above -23 °C reaction took place to give $[(CF_3)_2NO]_2CO$ as one of the major volatile products, together with $(CF_3)_2NON(CF_3)_2$, and several minor products which were not identified. An opaque, viscous, high-
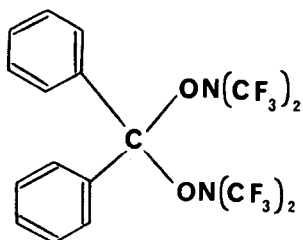
(2)
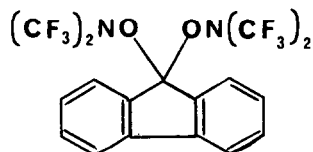
(3)

boiling liquid was also isolated from this reaction, and from the ^{19}F NMR spectrum this appeared to contain one major $(CF_3)_2NO-$ containing product [-12.0 p.p.m.], and at least five other minor products. Attempts to obtain a pure sample of the major product were not successful as it decomposed on attempted vacuum distillation. It is possible that this is the expected product $C[ON(CF_3)_2]_4$, which, according to earlier reports [1,2(a)] is unstable thermally. The reaction between (1) and 9-thiocarbonylfluorene in benzene is quite slow, and it was possible to observe the olive-green starting material react at 5 °C over 2 min. to give an orange suspension, which finally turned black due to formation of HgS after a further 10 min. This orange suspension may be an adduct of the type $\{Ar_2C=S \rightarrow Hg[ON(CF_3)_2]_2\}$, although this was not confirmed; similar adduct formation has been noted previously during the reaction of 9-thiocarbonylfluorene with mercury(II) chloride [10].

In contrast, reaction of the mercurial (1 mol equivalent) with thiophosgene (2 mol equivalent) takes place by chlorine atom exchange producing mercury(II) chloride rather than the sulphide. The major volatile products from this reaction were identified as $(CF_3)_2NSCOCl$ (4) and $(CF_3)_2NSCOON(CF_3)_2$ (5), rather than the expected products of a metathetical exchange reaction, namely, $(CF_3)_2NOCSCl$ (6) and $(CF_3)_2NOCSON(CF_3)_2$ (7) respectively. There is no doubt about the assigned structures since the ^{19}F NMR spectra of both (4) and (5) show a singlet in the region of -19.6 to -20.0 p.p.m. typical of a $(CF_3)_2NS-$ group [11]. In addition the spectrum of (5) has a singlet at
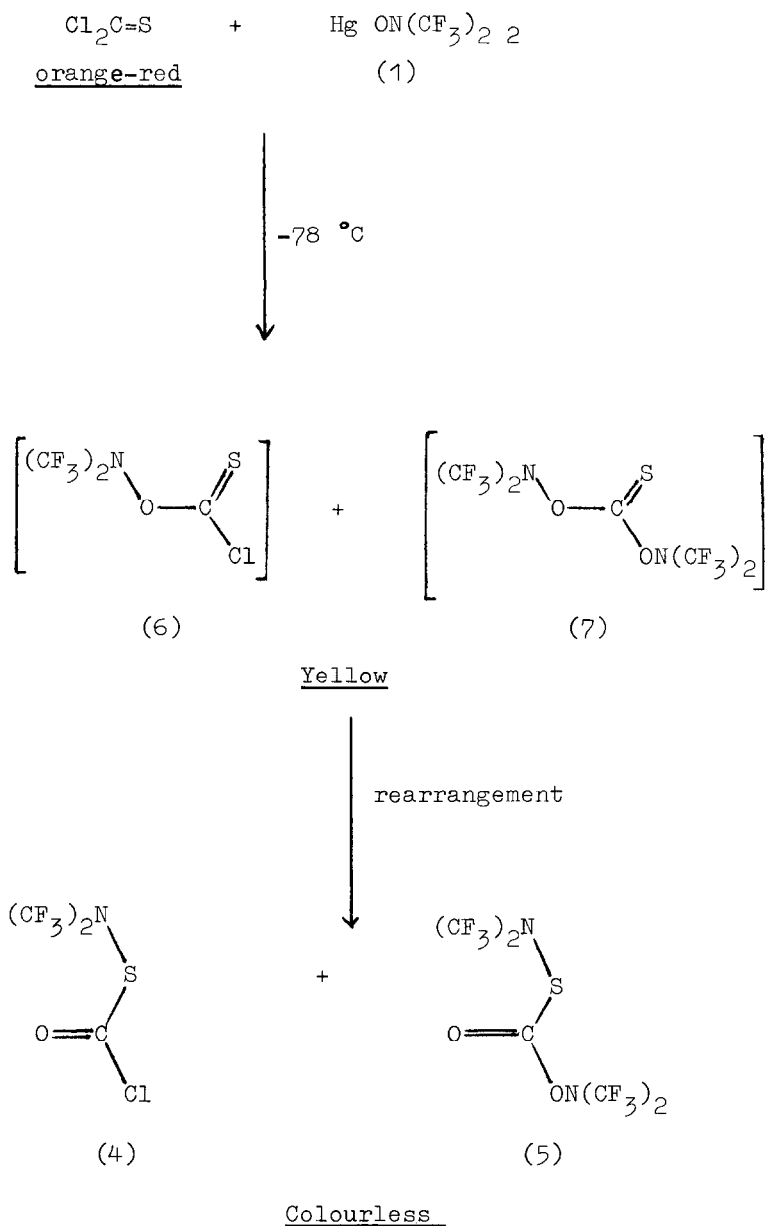
-8.0 p.p.m. for the $(CF_3)_2NO$ group [12]. The high resolution mass spectra of (4) and (5) add further support to the structural assignments, and eliminate the possible alternative structures $(CF_3)_2NCOSCl$ and $(CF_3)_2NCOSON(CF_3)_2$. An interesting feature of the IR spectrum of (5) is that both in the neat liquid and the vapour phase it shows two strong $\nu(C=O)$ bands at 1835 and 1804 cm^{-1}. These are tentatively attributed to an equilibrium between a monomer [$\nu(CO)$ 1835 cm^{-1}] and a dimer [$\nu(CO)$ 1804 cm^{-1}] in which the monomer predominates at room temperature (Scheme 1). As the vapour pressure of (5) was reduced from 9.0 to 0.1 mm Hg the ratio of the intensities of these bands [$I(1835)/I(1804)$] increased in a linear manner from 1.47 to 3.64 as expected for a monomer/dimer equilibrium.
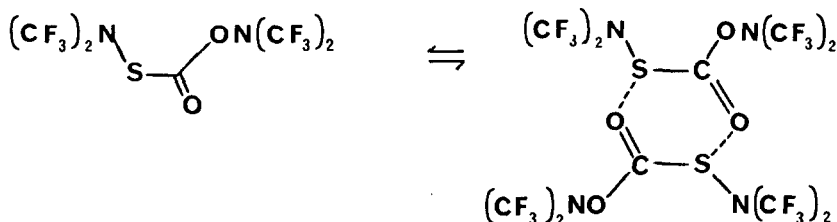
Scheme 1

The acid chloride (4) reacted only slowly with water to form COS, HCl, F⁻ and sulphur, and after 20 h at room temperature 79 % of (4) was recovered unchanged. It also failed to react with $(CF_3)_2NO$, $(CF_3)_2NOH$ or $(CF_3)_2NOH/CsF$ over several days at room temperature, but complete decomposition occurred after 15 min. with aqueous potassium hydroxide.

The characterisation of (4) and (5) as $(CF_3)_2NSCO-$ rather than $(CF_3)_2NOCS-$ derivatives raised the possibility that these could be formed from (6) and (7) by rearrangement (see Scheme 2). Since monomeric thiocarbonyls are usually highly coloured, e.g. FCSCl is a yellow gas [13], while (4) and (5) are colourless, the intermediate formation of (6) and (7) could explain the intense yellow colour which developed during the

$$Cl_2C=S \quad + \quad Hg\ ON(CF_3)_2\ _2$$

orange-red   (1)

$\downarrow$ -78 °C

$$\left[(CF_3)_2N\diagdown O\text{---}C \diagup^{S}_{\diagdown Cl} \right] \quad + \quad \left[(CF_3)_2N\diagdown O\text{---}C \diagup^{S}_{\diagdown ON(CF_3)_2} \right]$$

(6)   (7)

Yellow

$\downarrow$ rearrangement

$$(CF_3)_2N\diagdown S \diagup C \diagup^{O}_{\diagdown Cl} \quad + \quad (CF_3)_2N\diagdown S \diagup C \diagup^{O}_{\diagdown ON(CF_3)_2}$$

(4)   (5)
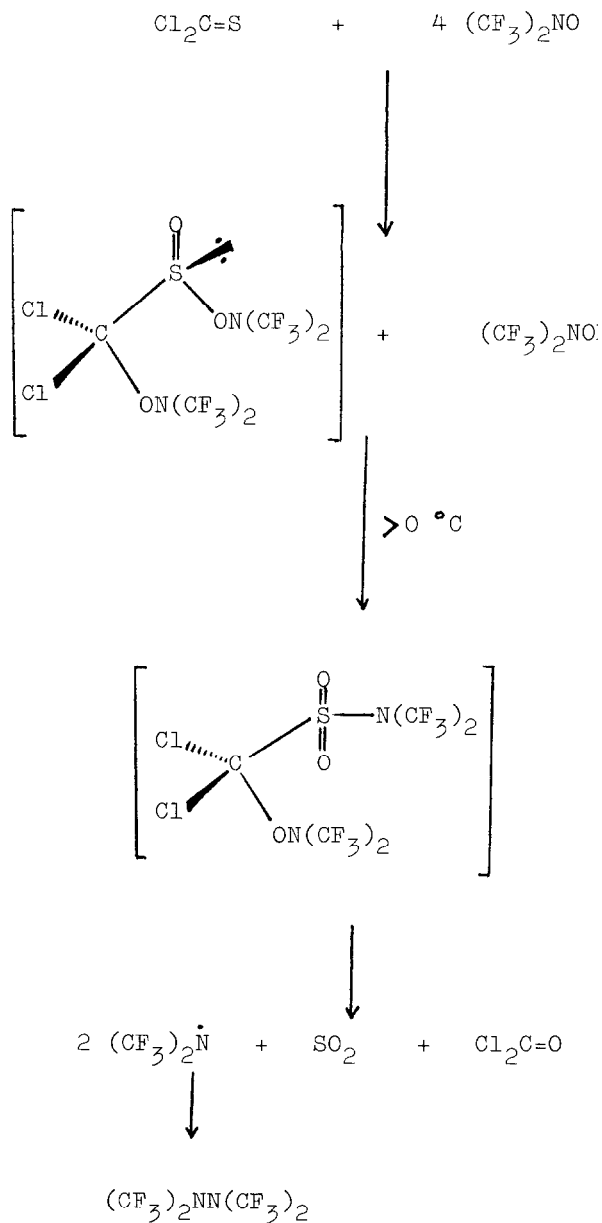
Colourless

Scheme 2

reaction of (1) with thiophosgene. It is also possible that
(5) could be formed by reaction between (4) and the mercurial,
but a control experiment carried out at room temperature
showed that this reaction required 7 days for a 95 % con-
version to (5), and is too slow to account for the formation
of (5) in the thiophosgene reaction. Thiono-thiolo rearrange-
ments of thio-esters and thiocarbonates are well known and have
been studied in some depth [14]. Rearrangements of thioesters
and thionocarbonates usually require temperatures in the range
of 200 - 400 °C, but some thiocarbamoylated oximes,
$R_2^1C=NOC(S)R^2$ and thiocarbamoylated hydroxamic acids,
$R^1CONMeOC(S)R^2$ rearrange to $R_2^1C=NSC(O)R^2$ and $R^1CONMeSC(O)R^2$
respectively at, or near, room temperature by a mechanism
involving caged radical pairs [15].

    The $(CF_3)_2NOC(S)-$ to $(CF_3)_2NSC(O)-$ rearrangement appears
to be quite general. So, for example, chlorothionoformates,
$ArOC(S)Cl$ (Ar = Ph, $4-ClC_6H_4$, $4-MeC_6H_4$) reacted with (1) at
low temperature to give the corresponding rearrangement products
$ArOC(O)SN(CF_3)_2$, in 59 - 78 % yields. Unfortunately, these
reactions are not as clean as that of thiophosgene, and the
products are always contaminated by appreciable amounts of the
bistrifluoromethylaminocarbonates, $ArOC(O)ON(CF_3)_2$, and
$(CF_3)_2NON(CF_3)_2$. It is thought that these last products arise
by competing attack by (1) at sulphur to form the intermediates
$[ArOC\{ON(CF_3)_2\}_2Cl]$, which are expected to be thermally
unstable and decompose to give $(CF_3)_2NON(CF_3)_2$ and the aryl
chloroformates, ArOCOCl. In separate experiments it has been
demonstrated that aryl chloroformates react rapidly with (1)
to form aryl bistrifluoromethylaminocarbonates [16]. Reaction
between thiobenzoyl chloride and (1) (2:1 molar ratio) in
$CFCl_3$ gave a mixture of four products. ^{19}F NMR spectroscopy
indicated that the major product contained a $(CF_3)_2NS-$ group
[-23.4 p.p.m.], and this was possibly the expected rearrange-
ment product $PhCOSN(CF_3)_2[\nu(C=O)$ 1720 vs $cm^{-1}]$ but it could not
be isolated in a pure state. The other products all contained
$(CF_3)_2NO-$ groups but were not identified.

Reaction of (1) with thiophosgene dimer in $CFCl_3$ occurred by simple chlorine exchange to give the dithietane (8) in 90 % yield as a white crystalline solid which is soluble in petroleum ether and $CFCl_3$, but immiscible with CCl_4 and $CHCl_3$; in acetone it appears to form a trimer. Unlike some other dithietanes [13,17] compound (8) did not revert to a monomer on heating, but decomposed ca. 108 °C to give at least nine products, none of which corresponded to (4) or (5).

The nitroxide radical, $(CF_3)_2NO$, does not react with either carbon disulphide [18] or carbonyl sulphide at room temperature over 13 days, but with thiobenzophenone in $CFCl_3$ solvent it reacted within 5 mins. at -78 °C to give a product shown by ^{19}F NMR spectroscopy at -30 °C to contain only two broad resonances in the region of -10 p.p.m.; this was possibly $(CF_3)_2NOCPh_2SON(CF_3)_2$. Above rapid 0 °C rapid decomposition occurred to give a mixture of at least 10 products, which included $(CF_3)_2NH$, $(CF_3)_2N.N(CF_3)_2$, $CF_3N=CF_2$ and benzophenone. With thiophosgene the nitroxide radical reacted at -23 °C over 4 h to give $(CF_3)_2NON(CF_3)_2$ and a viscous, colourless liquid shown by ^{19}F NMR spectroscopy at -25 °C to contain one major product having a sharp singlet at -12.5 p.p.m. and two quartets centred at -10.2 and -10.8 p.p.m. (J_{F-F} = 11 Hz). When the sample was allowed to warm up to 0 °C the quartets coalesced to a broad singlet at -10.5 p.p.m.; this change was completely reversible. This behaviour is typical of a $(CF_3)_2NO-$ group bonded to a chiral centre [19], and since the ^{19}F chemical shifts of the two quartet resonances are close to those of the CF_3- groups in $(CF_3)_2NOS(O)ON(CF_3)_2$ (-10.3 p.p.m.) and $(CF_3)_2NOS(O)F$ (-10.5 p.p.m.) [20] a reasonable structure for the major product is $(CF_3)_2NOCCl_2S(O)ON(CF_3)_2$ (9) having a chiral sulphur atom. Above 0 °C this product decomposed to give a mixture containing $(CF_3)_2NN(CF_3)_2$, $COCl_2$, SO_2 and several other products which were not identified. It is interesting that the related compound $CF_3S(O)ON(CF_3)_2$ is also reported to be unstable at 25 °C and apparently rearranges to $CF_3SO_2N(CF_3)_2$ [4]. A similar mode of decomposition could explain the thermal instability of (9) (Scheme 3).

$$Cl_2C=S \quad + \quad 4 \ (CF_3)_2NO$$

$$\left[\begin{array}{c} Cl_{\cdots\cdots}C \overset{\displaystyle O}{\underset{\displaystyle ON(CF_3)_2}{\overset{\displaystyle |}{S}}} {ON(CF_3)_2} \\ Cl \end{array} \right] \quad + \quad (CF_3)_2NO$$

$$> 0 \ ^\circ C$$

$$\left[\begin{array}{c} Cl_{\cdots\cdots}C \overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\displaystyle \|}{S}}} {-N(CF_3)_2} \\ Cl \qquad ON(CF_3)_2 \end{array} \right]$$

$$2 \ (CF_3)_2\dot{N} \quad + \quad SO_2 \quad + \quad Cl_2C=O$$

$$(CF_3)_2NN(CF_3)_2$$

Scheme 3

On the limited available evidence it appears that the nitroxide radical reacts with thiocarbonyl compounds by addition to the $\rangle$C=S bond, but since $(CF_3)_2NO$ is a powerful oxidising agent capable of oxidising S^{II} to S^{IV}, and even to S^{VI} [5], added to the fact that many of the compounds formed are thermally unstable these reactions can lead to complex product mixtures.

EXPERIMENTAL

Infra red spectra were recorded on a Perkin-Elmer 621 spectrophotometer and NMR spectra were recorded either on a Perkin-Elmer R10 or a Hitachi-Perkin-Elmer R20A spectrometer operating at 60 MHz (^{1}H) and 56.46 MHz (^{19}F; trifluoroacetic acid external reference; chemical shifts to low field of the reference are designated negative). Mass spectra were determined using an AEI MS902 spectrometer, and GLC analyses were effected using either a Pye 104 instrument fitted with a flame ionisation detector, or, for preparative separations a Perkin-Elmer Fraktometer, model 251. Molecular weights of volatile compounds were determined either by Regnault's method or by mass spectrometry, but the molecular weights of less volatile products were determined by the isopiestic method using a Perkin-Elmer model 115 molecular weight apparatus.

Bistrifluoromethylhydroxylamine [21] and bis(bistrifluoromethylaminooxy)mercury(II) [22] were prepared by literature methods. Carbonyl sulphide was prepared by dropwise addition of an aqueous solution of potassium thiocyanate to cold 50 % v/v aqueous sulphuric acid at room temperature. Thiobenzophenone [19], 9-thiocarbonylfluorene [10], and thiobenzoyl chloride [24] were synthesised by reported routes, and thiophosgene was a commercial sample purified by distillation under nitrogen. Phenyl chlorothionoformate [82 % yield; b.p. 79 ^{o}C/0.5 mmHg (lit. [25] b.p. 101-3 ^{o}C/18 mmHg)], 4-tolyl chlorothionoformate [80 % yield; b.p. 88 ^{o}C/0.5 mmHg (lit. [26] b.p. 110-120 ^{o}C/ 760 mmHg)], 4-chlorophenyl chlorothionoformate [76 % yield; b.p. 82-86 ^{o}C/0.5 mmHg] and 4-methoxyphenyl chlorothionoformate [72 % yield; b.p. 118 ^{o}C/0.5 mmHg (lit. [26] b.p. 108 ^{o}C/ 2 mmHg)] were prepared by addition of a solution of the corresponding phenol (0.25 mol) in aqueous sodium hydroxide (250 cm^3) over 45 minutes to a solution of thiophosgene (0.25 mol) in chloroform (200 cm^3).

Reactions of Bis(bistrifluoromethylamino-oxy)mercury(II)

(a) With Carbonyl Sulphide

Carbonyl sulphide (0.36 g, 6.01 mmol) was condensed under vacuum on to the mercurial (3.23 g, 6.01 mmol) held at -196 $^{\circ}$C in a Pyrex ampoule (150 cm^3) fitted with a Rotaflo valve; reaction started at -130 $^{\circ}$C i.e. the melting point of carbonyl sulphide. When the reaction mixture reached room temperature it was shaken for a further 15 min., and then the volatile products were removed and separated by fractional condensation under vacuum to give bis(bistrifluoromethylamino-oxy)carbonyl (2.03 g, 5.56 mmol, 95 %) [-46 $^{\circ}$C and -78 $^{\circ}$C traps] and bistrifluoromethylamino-oxyl (0.07 g, 0.43 mmol, 3 %) [-120 $^{\circ}$C trap], together with recovered carbonyl sulphide (0.03 g, 0.43 mmol, 7 %) [-196 $^{\circ}$C trap]. The residue in the tube was confirmed as mercury(II) sulphide.

(b) With Thiobenzophenone

Thiobenzophenone (0.76 g, 3.84 mmol), contained in a soda-glass test tube, was transferred quickly under a dry nitrogen atmosphere into an ampoule containing the mercurial (2.08 g, 3.87 mmol). After evacuating the tube sodium-dried benzene (10.8 g) was condensed into it at -196 $^{\circ}$C. The tube was then allowed to warm to room temperature before shaking it vigorously to break the test tube containing the thiobenzophenone. There was an immediate reaction and the white mercurial changed to a black suspension of mercury(II) sulphide. The volatiles, benzene and a little $(CF_3)_2NO$, were removed under vacuum, and the residue was extracted with dry benzene (3 x 15 cm^3). The extract was filtered under nitrogen and the solvent removed from the filtrate to give (2) (1.06 g, 2.11 mmol, 55 %) as white crystals, m.p. 47 $^{\circ}$C, purified by GLC (2 m SE30 column at 150 $^{\circ}$C). Analysis: Found: C, 41.0; H, 2.1; F, 46.1, N, 5.6; $\underline{M}$, 518 (isopiestic; toluene) $C_{17}H_{10}F_{12}N_2O_2$ requires C, 40.7; H, 2.0; F, 46.5 ; N, 5.6%. $\underline{M}$, 502. IR (natural film): 3070 w, 1495 w, 1490 sh, 1450 s, 1300 vs, 1250 vs, 1082 w,1050 s, 1034 sh, 1000 s, 985 w, 958 s, 934 w, 922 w, 896 s, 812 sh, 800 w, 786 w, 758 s, 745 sh, 722 w, 706 s, 697 s, 664 w, 652 w,

650 w cm-1; ^{1}H NMR (CCl$_4$) δ 7.5 s, ^{19}F NMR -13.0 p.p.m.;
MS m/z 502 ⌊M⌋$^+$ not seen, 334 ⌊M-(CF$_3$)$_2$NO]$^+$ 10.9 %, 182 ⌊M-
⌊M-(CF$_3$)$_2$NO-(CF$_3$)$_2$N⌋$^+$ 56.3 %, 105 ⌊C$_6$H$_5$CO]$^+$ 100 %.

(c) With 9-Thiocarbonylfluorene

Using a similar procedure to that described above
9-thiocarbonylfluorene (0.68 g, 3.49 mmol) and the mercurial
(2.32 g, 4.31 mmol) were mixed at room temperature to give a
pale yellow solution, follwed, after 2 min., by the formation
of an orange suspension which turned black after a further
10 min. Removal of the volatiles and extraction with benzene
followed by chromatography [Florisil (60 - 100 mesh) with light
petroleum (b.p. 30 - 40 ^{o}C)/benzene 9/1 as eluant] gave white
cubic crystals of (3) (1.41 g, 2.82 mmol, 82 %) m.p. 91 - 92 ^{o}C
Analysis: Found: C, 41.0; H, 1.7; F, 45.4 %; N, 5.5.
C$_{17}$H$_8$F$_{12}$N$_2$O$_2$ requires: C, 40.8; H, 1.7;   F, 45.6 %; N, 5.6
IR (Nujol and hexachlorobutadiene mulls): 3085 w, 1614 w,
1456 s, 1297 vs, 1258 vs, 1210 vs, 1110 w, 1028 s, 987 w,
936 vs, 948 w, 921 s, 802 w, 760 s, 727 s, 660 w, 639 w cm^{-1};
^{1}H NMR (CCl$_4$) δ 7.4 m; ^{19}F NMR -11.8 p.p.m.; MS m/z 500 [M]$^+$
18.6 %;   332 [M-(CF$_3$)$_2$NO]$^+$ 69.0 %, 180 [M-(CF$_3$)$_2$NO-(CF$_3$)$_2$N]$^+$
100 %.

(d) With Carbon Disulphide

A mixture of carbon disulphide (0.28 g, 3.66 mmol), the
mercurial (3.93 g, 7.32 mmol) and trichlorofluoromethane
(10.6 g) was shaken at -78 ^{o}C for 3 h. The temperature was
then raised to -46 ^{o}C and shaking was continued for a further
2 h, and finally the mixture was allowed to reach room tempera-
ture. Fractional condensation of the volatile products gave
fractions at -46 ^{o}C and -78 ^{o}C (1.136 g) shown by GLC (3 m SE 30
and 2 m PEGA columns at room temperature) to contain [(CF$_3$)$_2$-
NO]$_2$CO (ca. 40 % overall yield) as the major product, together
with (CF$_3$)$_2$NON(CF$_3$)$_2$ and at least seven other minor components
which were not identified.

(e) With Thiophosgene

When thiophosgene (2.45 g, 21.30 mmol) and trichlorofluoro-
methane (7.30 g) were condensed separately in vacuo on to the
mercurial (5.67 g, 10.06 mmol) the orange colour of the thio-

phosgene gradually changed over 1 h to a pale yellow
suspension and ultimately to a white suspension (3 h) on warming
from -196 °C to -78 °C. Fractional condensation of the vola-
tile products gave a colourless liquid (4.85 g) [-46 °C and
-78 °C traps] shown by preparative GLC (SE 30 column, 20 °C)
to consist of (4) (3.21 g, 13.0 mmol, 61 %) b.p. 82.5 °C/758 mm
(Siwoloboff).

Analysis: Found: C, 14.7; F, 46.3; N, 5.9. C_3ClF_6ONS
requires: C, 14.6; F, 46.2; N, 5.7; F. IR (vapour)
3605 w, 2575 w, 2400 w, 2150 w, 1881 sh, 1814 vs, 1770 sh,
1731 w, 1628 w, 1417 w, 1354 s, 1322 vs, 1257 vs, 1212 vs,
1180 sh, 1063 w, 1022 w, 998 w, 974 vs, 910 sh, 884 s, 825 vs,
775 s, 708 vs, 648 w, 580 s, 563 sh, 472 s, 444 s cm^{-1}; ^{19}F
NMR (neat liquid) -20.0 p.p.m.; U.V. (cyclohexane) λ_{max} 212
(ε 1700), 299.5 - 303 inf (ε 216), 285 (ε 350) nm; MS (high
resolution) 246.9306 $[M]^{+}$ 0.1 %, 183.9653 $[(CF_3)_2NS]^{+}$ 9.3 %,
114.9703 $[CF_3NS]^{+}$ 0.7 %, 95.9716 $[CF_2NS]^{+}$ 4.3 %, 94.9354
$[COSCl]^{+}$ 5.8 %, 81.9680 $[CF_2S]^{+}$ 0.2 %, 78.9646 $[COSF]^{+}$ 0.3 %,
66.9414 $[SCl]^{+}$ 2.1 %, 65.9653 $[CFCl]^{+}$ 0.1 %, 64.0012 $[CNF_2]^{+}$
0.4 %, 62.9652 $[COCl]^{+}$ 31.4 %, 59.9688 $[COS]^{+}$ 19.4 % and (5)
(1.40 g, 3.68 mmol, 35 %), b.p. 105.5 °C/752 mm (Siwoloboff).

Analysis: Found: C, 16.1; F, 59.7; N, 7.3; S, 8.3; M
(Regnault) 380. $C_5F_{12}O_2N_2S$ requires: C, 15.8; F, 60.0;
N, 7.4; S, 8.4 %; $\underline{M}$ 380. IR (vapour) 1835 vs, 1804 s, 1360 w,
1315 vs, 1266 vs, 1218 vs, 1099 s, 1068 vs, 1040 vs, 1022 s,
978 vs, 863 w, 835 s, 793 w, 771 w, 753 w, 727 s, 715 vs,
645 w, 584 s, 554 w, 511 w, 483 w, 424 s, 405 s cm^{-1}. U.V.
(hexane) λ_{max} 207.5 mm (ε 180); M.S. (high resolution) m/z
380 $[M]^{+}$ not seen, 335.9588 $[CF_3)_2NSN(CF_3)_2]^{+}$ 4.0 %, 227.9553
$[(CF_3)_2NSCO_2]^{+}$ 9.7 %, 211.9604 $[(CF_3)_2NSCO]^{+}$ 44.3 %, 195.9832
$[(CF_3)_2NOCO]^{+}$ 1.7 %, 185.9655 $[(CF_3)_2NS]^{+}$ 100 %, 167.9883
$[(CF_3)_2NO]$ 10.9 %, 164.9671 $[CF_2=N(CF_3)S]^{+}$ 1.1 %, 132.9950
$[CF_2=NCF_3]^{+}$ 23.0 %.

Three other minor products (total 0.14 g) from this reac-
tion were not identified. The residue was shown to be mercury(II)
chloride.

(f) With Thiobenzoyl Chloride

Reaction between the mercurial (3.35 g, 6.25 mmol) and thiobenzoyl chloride (1.96 g, 12.5 mmol) in trichlorofluoromethane (10.56 g) at -78 °C over 5 h gave a yellow suspension which gradually changed to buff as the temperature rose to ambient temperature over 2 h. Removal of the volatiles, and extraction with benzene gave a pale yellow, viscous liquid (3.4 g) shown to contain five components which could not be separated by GLC (2 m SE 30 or 2 m PEGA at 122 °C). The ^{19}F NMR spectrum (CCl_4) showed singlets at -23.4, -13.4, -11.2 and -9.2 p.p.m. in the integration ratio of 34:18:2:1. The IR spectrum (neat liquid) had bands at 3030 w, 1795 w, 1721 s, 1447 w, 1346 w, 1300 vs, 1250 vs, 1205 vs, 1179 vs, 1042 w, 966 s, 892 w, 769 w, 736 w, 709 w, 701 s and 678 s cm^{-1} .

(g) With Phenyl Chlorothionoformate

Phenyl chlorothionoformate (12.5 g, 67.5 mmol) and the mercurial (18.1 g, 33.8 mmol) in $CFCl_3$ (10 cm^3) were shaken in a tube at room temperature for 48 h. The products were extracted into diethyl ether and were shown by GLC (3 m SE 30 150 °C) to contain $PhOCOON(CF_3)_2$ (3.80 g, 13.5 mmol, 28 %) [IR (neat liquid) $\nu(C=O)$ 1835 vs cm^{-1}; ^{19}F NMR $(CFCl_3)$ -9.00 p.p.m.], $(CF_3)_2NON(CF_3)_2$ (4.32 g, 13.5 mmol, 14 %) and $PhOCOSN(CF_3)_2$ (4.12 g, 28.4 mmol, 59 %), [IR $\nu(C=O)$ 1785 vs cm^{-1} ^{19}F NMR -21.0 p.p.m.] together with recovered PhOCOSCl (4.32 g, 25.7 mmol, 38 %). Attempts to separate the mixture by GLC and by repeated fractional distillation using a 50 cm spinning-band column were unsuccessful and led to appreciable thermal decomposition of $(CF_3)_2NON(CF_3)_2$ and $PhOCOSN(CF_3)_2$.

(h) With 4-Chlorophenyl Chlorothionoformate

Under similar conditions a vigorous, exothermic reaction occurred between the mercurial (16.2 g, 30.1 mmol) and 4-chlorophenyl chlorothionoformate (12.4 g, 60.0 mmol) in $CFCl_3$ (5 cm^3) to give a mixture containing $4\text{-}ClC_6H_4OCOON(CF_3)_2$ (2.3 g, 7.1 mmol, 12 %) [IR (neat liquid) $\nu(C=O)$ 1840 vs cm^{-1}; ^{19}F NMR $(CFCl_3)$ -8.9 p.p.m.; MS m/z 323 $[M]^{+}$ 7.7 %]. $(CF_3)_2NON\text{-}(CF_3)_2$ (2.3 g, 7.1 mmol, 12 %), $4\text{-}ClC_6H_4OCOSN(CF_3)_2$ (13.5 g, 39.0 mmol, 65 %) [IR $\nu(C=O)$ 1795 cm^{-1}; ^{19}F NMR -22.8 p.p.m.; MS m/z 339 $[M]^{+}$ 4.8 %], and recovered $4\text{-}ClC_6H_4OCOCl$ (2.7 g, 13.8 mmol, 23 %).

(i)   With 4-Tolyl Chlorothionoformate

Reaction between 4-tolyl chlorothionoformate (8.40 g, 45.0 mmol) and the mercurial (12.7 g, 23.6 mmol) in $CFCl_3$ (10 cm^3) at room temperature for 2 h gave 4-$MeC_6H_4OCOON(CF_3)_2$ (1.2 g, 3.9 mmol, 9 %) [IR (neat liquid) ν(C=O) 1835 cm^{-1}; ^{19}F NMR ($CFCl_3$) -8.9 p.p.m.;   MS m/z 303 [M]$^{+}$ 34 %] $(CF_3)_2$-$NON(CF_3)_2$ (1.2 g, 3.9 mmol, 11 %), 4-$MeC_6H_4OCOSN(CF_3)_2$ (11.2 g, 35.2 mmol, 78 %) [IR ν(C=O) 1775 vs cm^{-1}; ^{19}F NMR -21.1 p.p.m.] and recovered 4-MeC_6H_4OCOCl (1.1 g, 6.0 mmol, 13 %).

(j)   With S-[bistrifluoromethylamino-oxy] Carbonyl Chloride

The mercurial (2.61 g, 4.58 mmol) and (4) (0.79 g, 3.22 mmol) in $CFCl_3$ (6.52 g) were shaken at room temperature in the dark, and the reaction was monitored by IR spectroscopy. After 7 days the volatile products were separated by fractional condensation in vacuo to give (5) (1.12 g, 4.53 mmol, 91 %) which collected mainly in the -46 °C trap, but a small quantity was collected in the -78 °C trap mixed with $[(CF_3)_2NO]_2CO$ (0.05 g, 0.137 mmol).

(k)   With 2,2,4,4-Tetrachloro-1,3-dithietane

Freshly sublimed thiophosgene dimer (0.91 g, 3.96 mmol) was added in two small test tubes to preformed mercurial (4.46 g, 8.33 mmol) and $CFCl_3$ (11.45 g).   The reactants were mixed at -78 °C by vigorous shaking and were held at this temperature for ca. 16 h, before allowing the mixture to warm to room temperature (4 h) and shaking for a further 24 h. The solvent was removed under vacuum and the white solid residue was extracted under nitrogen with light petroleum (b.p. 30 - 40 °C) to give white needles of (8) (2.70 g, 3.55 mmol, 90 %) m.p. 33 °C. Analysis: Found: C, 15.9; F, 60.2; N, 7.5; S, 8.0; M (isopiestic, acetone) 2279. $C_{10}F_{24}N_4O_4S_2$ requires: C, 15.8; F, 60.0; N, 7.4;   S, 8.4 %, M 760. IR (film) 1325 s, 1255 vs, 1205 vs, 1165 vs, 1050 s, 965 s, 935 w, 886 w, 828 w, 795 w, 753 w, 738 w, 716 s, 699 w, 635 w cm^{-1}; ^{19}F NMR ($CFCl_3$) -12.0 p.p.m.; MS m/z 760 [M]$^{+}$ not seen, 592 [M-$(CF_3)_2NO$]$^{+}$ 1.0 %, 380 [{$(CF_3)_2NO$}$_2CS$]$^{+}$ 34.4 %, 212 [$(CF_3)_2NOCS$]$^{+}$ 44.0 % 196 [$(CF_3)_2NOCO$]$^{+}$ 3.8 %, 184 [$(CF_3)_2NS$]$^{+}$ 24.6 %].

Reaction of NN-Bis(trifluoromethyl)nitroxide

(a) With Thiobenzophenone

A mixture of thiobenzophenone (0.93 g, 4.69 mmol) and the nitroxide (1.58 g, 9.40 mmol) in $CFCl_3$ (10.1 g) was allowed to warm up from -196 $^{\circ}$C to -78 $^{\circ}$C with shaking to give a colourless solution within 5 min. The ^{19}F NMR spectrum of this solution was examined at -30 $^{\circ}$C. The volatiles were transferred to a vacuum system and shown to contain $(CF_3)_2NH$, and $(CF_3)_2$-$N=CF_2$. When the temperature of the mixture reached ca. 0 $^{\circ}$C the viscous liquid residue decomposed suddenly with gas evolution to leave a pale yellow liquid shown to contain $(CF_3)_2NN(CF_3)_2$, benzophenone and six other products by GLC (2 m SE 30 and 2 m PEGA at 184 $^{\circ}$C).

(b) With Thiophosgene

Thiophosgene (0.80 g, 6.95 mmol) and the nitroxide (3.51 g, 20.9 mmol) were allowed to stand at -23 $^{\circ}$C for 4 h, before transferring the volatile products to a vacuum system. Fractional condensation of the volatiles gave a colourless liquid (2.28 g) [-46 $^{\circ}$C trap] which is possibly $(CF_3)_2NOCCl_2$-$SOON(CF_3)$, and which decomposed on warming to room temperature in the dark to give $(CF_3)_2NN(CF_3)_2$, Cl_2CO, SO_2, and seven other products which could not be identified. The -78 $^{\circ}$C and the -96 $^{\circ}$C traps contained mainly $(CF_3)_2NON(CF_3)_2$ (1.38 g, 4.31 mmol, 41 %) and traces of recovered thiophosgene (0.43 mmol) and $(CF_3)_2NN(CF_3)_2$ (0.13 g, 0.43 mmol, 4 %). The -196 $^{\circ}$C trap consisted of recovered $(CF_3)_2NO$ (0.16 g, 0.95 mmol, 5 %), phosgene (0.18 g, 1.84 mmol, 27 %) and sulphur dioxide (0.07 g, 1.09 mmol, 16 %).

REFERENCES

1 H.J. Emeléus, J.M. Shreeve, and P.M. Spaziante, J. Chem.
Soc. (A), (1969) 431.

2 (a) P.M. Spaziante, M.T.P. International Review of
Science, Inorg. Series 1, 3 (1972) 145;
(b) H.J. Emeléus, Record Chem. Progress, 32 (1971) 135;
(c) D.P. Babb and J.M. Shreeve, Intra-Science Chemistry
Reports, 5 (1971) 55.

3 H.J. Emeléus and R.J. Poulet, J. Fluorine Chem., 1 (1971/2)
13.

4 C.A. Burton and J.M. Shreeve, Inorg. Chem., 16 (1977) 1039.

5 M.D. Vorob'ev, A.S. Filatov and M.A. Englin, J. Org. Chem.
(U.S.S.R.), 9 (1973) 326; 10 (1974) 1009.

6 J. Varwig and R. Mews, J. Chem. Research (S), (1977) 245.

7 R.E. Banks, J.M. Birchall, R.N. Haszeldine and S.N. Nona,
J. Fluorine Chem., 16 (1980) 391.

8 R. Mews, J. Fluorine Chem., 18 (1981) 155.

9 Presented in part at the 5th European Fluorine Symposium,
Aviemore, Scotland, September 1974.

10 E. Campaigne and W.B. Reid, J. Amer. Chem. Soc., 68 (1946)
769.

11 H.J. Emeléus and B.W. Tattershall, J. Inorg. Nucl. Chem.,
28 (1966) 1823.

12 R.E. Banks, R.N. Haszeldine, and B. Justin, J. Chem. Soc.
(C), (1971) 2777.

13 W.J. Middleton, E.G. Howard, and W.H. Sharkey, J. Org.
Chem., 30 (1965) 1375.

14 A. Schonberg and L. Vargha, Ber., 63 (1930) 178;
S.G. Smith, Tetrahedron Letters, (1962) 979;
M.S. Newman and H.A. Karnes, J. Org. Chem., 31 (1966) 3980;
E.J. Hedgley and N.H. Leon, J. Chem. Soc. (C), (1970) 467.

15 R.F. Hudson, C.J.M. Stirling (Editor), Organic Sulphur
Chemistry, Butterworths, London, (1975) p. 131.

16 R.F. Browne, Ph.D. Thesis (Manchester) 1979.

17 E. Campaigne, in S. Patai (Editor) 'The Chemistry of the
Carbonyl Group', Interscience, New York, 1966, p. 917.

18 J. S. Coombes and P.M. Spaziante, J. Inorg. Nucl. Chem.,
31 (1969) 2634.

19 R.E. Banks, K.W. Cheung and R.N. Haszeldine, unpublished
    results.
20 A. Ginsberg, K.N. Smirnov and M.A. Vasileva, J. Gen. Chem.
    (U.S.S.R.), 39 (1964) 1304.
21 R.E. Banks and C. Oppenheim, J. Fluorine Chem., 12 (1978)
    27.
22 R.E. Banks and D.R. Choudhury, J. Chem. Soc., Perkin
    Trans. I, (1981) 1443.
23 B.F. Gofton and E.A. Braude, Org. Syntheses, Coll. Vol. IV,
    (1963) 127.
24 J. Houben, Ber., 39 (1906) 3224;
    H. Staudinger and J. Siegwart, Helv. Chim. Acta, 3 (1920)
    824.
25 A. Kaji and M. Miyazaki, Nippon Kagaku Zasshi, 87 (1966)
    727;
    Chem. Abs., 65 (1966) 15256 d.
26 Y. Yokai, Jap. patent no. 7 037 968/1970;
    Chem. Abs., 74 (1971) 141334 b.
27 B.L. Booth, R.N. Haszeldine, and C.A. Nwadinigwe,
    J. Chem. Soc., Perkin Trans. 1, (1982) 835.