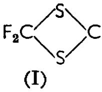
846. *Thiocarbonyl Fluoride.*

By A. J. Downs.

Tensimetrically pure thiocarbonyl fluoride, SCF_2, has been prepared by the decomposition of silyl trifluoromethyl sulphide. It is stable in glass apparatus, in the liquid phase, at room temperature, and, in the gaseous phase, at temperatures up to 300°. The C–F bonds are unusually reactive, being broken by water, hydrogen iodide, and ammonia, whereas addition occurred with chlorine, trimethylamine, and mercuric and argentous fluoride; the reactions with certain other fluorides, dienes, trifluoromethanethiol, hydrogen chloride, silane, and mercuric chloride have also been investigated.

There has been some confusion about the preparation of thiocarbonyl fluoride, as summarised in a recent review.[1] Recently, however, Yarovenko and Vasil'eva [2] claim to have isolated the compound by the reduction of chlorodifluoromethanesulphenyl chloride, $CF_2Cl\cdot SCl$, giving a boiling point of −57° to −54°. Pyrolysis of the cyclic dimer (I) is said [3] to give thiocarbonyl fluoride (b. p. −54°) almost quantitatively. There are, further, two patents [4] referring to the formation of the fluoride, but physical data are generally lacking.



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[1] Cady, " Fluorine-containing Compounds of Sulphur," in " Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press, New York, 1960, Vol. II, p. 105.

[2] Yarovenko and Vasil'eva, *Zhur. obshchei Khim.*, 1959, **29**, 3792.

[3] Middleton, Howard, and Sharkey, *J. Amer. Chem. Soc.*, 1961, **83**, 2589.

[4] Lipscomb, U.S.P. 2,952,706; *Chem. Abs.*, 1961, **55**, 3442; Marquis, U.S.P. 2,962,529; *Chem. Abs.*, 1961, **55**, 7285.

We have confirmed that interaction of trifluoromethanethiol with ammonia or sodium fluoride gives small amounts of thiocarbonyl fluoride,[5] but the pure material could not be isolated in this way. Attempts to prepare the compound by the fluorination of thiocarbonyl chloride with mercuric, zinc, lead, or antimony(III) fluoride were also unsuccessful, thereby confirming earlier results.[5] Moreover, it has been shown that bis(trifluoromethyl)-mercury reacts with sulphur in the temperature range 400—700°, and that thiocarbonyl fluoride is one of the numerous products, but it could not be obtained pure by the conventional methods of trap-to-trap distillation.

Silyl trifluoromethyl sulphide, $SiH_3{\cdot}S{\cdot}CF_3$,[6] is known to decompose according to the equation: $SiH_3{\cdot}S{\cdot}CF_3 \longrightarrow SiH_3F + SCF_2$; a partial separation of the products has been described, together with the infrared and fluorine resonance spectra of the material believed to be thiocarbonyl fluoride. It has now been shown that silyl trifluoromethyl sulphide vapour undergoes smooth decomposition at room temperature when passed repeatedly over solid bis(trifluoromethylthio)mercury suspended on glass wool, and that tensimetrically pure thiocarbonyl fluoride can be obtained by fractional distillation of the products in yields of up to 90%. No carbonyl sulphide or silicon tetrafluoride (the usual impurities accompanying thiocarbonyl fluoride) was present in the product, but silyl fluoride could not be totally eliminated and may have influenced the apparent stability of the compound with respect to glass. There is evidence[5] that the impure fluoride attacks glass at room temperature: $2SCF_2 + SiO_2 \longrightarrow SiF_4 + 2COS$. Samples prepared from silyl trifluoromethyl sulphide were quite stable in glass apparatus in the liquid or vapour phase at room temperature; and appreciable reaction of the vapour with glass did not occur at <300°.

The major features of the infrared spectrum tally with those already recorded;[6] evidence supporting the original vibrational assignment will be published later. The fluorine resonance spectrum consists of a single line at —40·74 p.p.m. relative to trichlorofluoromethane as solvent and internal standard;[7] ^{13}C–F satellites are also observed. The appropriate parameters are compared in the Table with analogous values for carbonyl fluoride. The unusual low-field value for the fluorine resonance of the thiocarbonyl compound is attributable to the existence of suitable low-lying excited states associated with the sulphur atom.[8] Thus, whereas thiocarbonyl fluoride undergoes an electronic transition in the near-ultraviolet region (352 mμ), carbonyl fluoride does not absorb at wavelengths greater than 200 mμ. Although few measurements have been made on analogous compounds, the values of $J(^{13}C\text{–}F)$ conform to the pattern described for saturated trifluoromethyl compounds,[9] and increasing the atomic number of the substituent X in the $>C{=}X$ bond increases the coupling constant.

Fluorine resonance spectra of thiocarbonyl and carbonyl fluorides.

Compound	$\phi(^{19}F)$ [7] (p.p.m.) ($CCl_3F = 0$)	$J(^{13}CF)$ (*c*/sec. ± 0·3)	Isotopic shift $\sigma(^{13}C^{12}C)$ (p.p.m. ± 0·004) ($CCl_3F = 0$)
SCF_2	−40·74 ± 0·01 *	366·0	0·143
OCF_2	+21·54 ± 0·10 †	308·4	0·121

* No significant change in chemical shift was observed between the pure liquid containing a drop of CCl_3F and a ~20% solution in CCl_3F. † Value extrapolated to infinite dilution since a significant change (~3%) in chemical shift was observed between a ~20% and ~50% solution in CCl_3F.

In the ultraviolet region, thiocarbonyl fluoride vapour shows two bands ($\lambda_{max.}$ 204 and 352 mμ; ε 7800 ± 100 and 4·5 ± 0·2, respectively). The 352 mμ band exhibits fine structure associated with vibrations of the excited state of the molecule; by analogy with similar

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[5] Haszeldine and Kidd, *J.*, 1955, 3871.

[6] Downs and Ebsworth, *J.*, 1960, 3516.

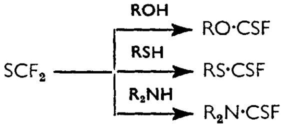
[7] Filipovich and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.

[8] Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.

[9] Harris, *J. Phys. Chem.*, 1962, **66**, 768.

cases,[10] it is ascribed to a $n \longrightarrow \pi^*$ transition. An additional band at 264 mμ, the intensity of which varied irregularly with pressure, could be accounted for by the presence of traces of trifluoromethyl fluorodithioformate, $CF_3S{\cdot}CSF$,[5] resulting from the photolytic dimerisation of thiocarbonyl fluoride. No appreciable change occurred, however, on prolonged irradiation of the fluoride vapour in a Pyrex vessel.

The fluorine atoms of thiocarbonyl fluoride appear comparable in reactivity with those of the carbonyl compound.[11] Reference has already been made to the readiness with which the thiocarbonyl compound reacts with water, alcohols, thiols, and amines:[2]



It has now been shown that the gaseous compound is relatively stable in dry air at room temperature, but that it is rapidly hydrolysed by water: $SCF_2 + H_2O \longrightarrow COS + 2HF$. Hydrogen iodide reacted at −78° to give a mixture of products; the initial reaction $SCF_2 + 2HI \longrightarrow SCI_2 + 2HF$ probably being followed by $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$, and $SCI_2 \longrightarrow CS_2$, I_2, etc. With hydrogen chloride, however, there was no reaction. Ammonia broke the C–F bonds producing, not thiourea as expected, but the isomeric ammonium thiocyanate; the process can be formulated as $SCF_2 + 4NH_3 \longrightarrow NH_4SCN + 2NH_4F$. By contrast, trimethylamine reacted with the fluoride in a 1 : 1 molar ratio to give a solid product which appeared to attack glass at room temperature. This suggests that the reaction of thiocarbonyl fluoride with ammonia, amines, etc., may well involve preliminary formation of an unstable adduct from which hydrogen fluoride is then eliminated. An analogous reaction occurs between carbon disulphide and triethylphosphine,[12] but few stable adducts of thiocarbonyl compounds have otherwise been described. Unlike other thiols,[2] trifluoromethanethiol did not react with thiocarbonyl fluoride at room temperature in the absence of a hydrogen fluoride-acceptor such as sodium fluoride; less direct evidence of this [5] has been clearly confirmed. Other instances have been cited [13] where the S–H bond of trifluoromethanethiol is appreciably less reactive than that of its alkyl analogues.

Addition across the $>$C=S bond of thiocarbonyl fluoride occurred with chlorine; bromine has previously been shown to behave similarly;[2] iodine did not react. With mercuric and argentous fluoride at −78°, the thiocarbonyl compound gave bis(trifluoromethylthio)mercury, $Hg(S{\cdot}CF_3)_2$, and trifluoromethylthiosilver, $AgS{\cdot}CF_3$, respectively. This behaviour is analogous to the addition of fluoroalkenes [14] and perfluoro(methylenemethylamine), $CF_3{\cdot}N{:}CF_2$,[15] to mercuric fluoride. It also suggests that thiocarbonyl fluoride may be the principal intermediate in the synthesis of bis(trifluoromethylthio)-mercury [16] and trifluoromethylthiosilver [17] from carbon disulphide and the corresponding fluoride; the thiocarbonyl compound has been postulated as an intermediate in the formation and decomposition of other trifluoromethylthio-derivatives,[5,18] but so far without much direct experimental foundation. There was no similar reaction between thiocarbonyl fluoride and sodium, boron, or antimony(III) fluoride; mercuric chloride also failed to react. The readiness with which mercuric and silver fluoride combine with thiocarbonyl fluoride probably reflects upon the relative stabilities of the corresponding

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[10] Sidman, *Chem. Rev.*, 1958, **58**, 689; Janssen, *Rec. Trav. chim.*, 1960, **79**, 454, 464.
[11] Emeléus and Wood, *J.*, 1948, 2183.
[12] Hofmann, *Ber.*, 1880, **13**, 1732.
[13] Pugh (1959), Downs (1961), and Haas (1962), Theses, Cambridge.
[14] Krespan, *J. Org. Chem.*, 1960, **25**, 105.
[15] Young, Tsoukalas, and Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.
[16] Man, Coffman, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.
[17] Emeléus and MacDuffie, *J.*, 1961, 2597.
[18] Haszeldine and Kidd, *J.*, 1953, 3219; Jellinek, *Proc. Chem. Soc.*, 1959, 319.

trifluoromethylthio-derivatives and also upon the preference of mercury(II) and silver(I) to adopt the covalent form. The ability of thiocarbonyl fluoride to act as a dienophile has been mentioned elsewhere.[3] The addition [3] of cyclopentadiene in a 1 : 1 molar ratio at −20° has been confirmed, though at room temperature the product seemed to dissociate slowly. No well-defined derivative was obtained from butadiene and the fluoride. The reactivity of the $>$C=S bond towards dienes is not, however, peculiar to fluorine-containing thiocarbonyl compounds, since thiocarbonyl chloride and thiofluorenone are said to undergo similar reactions.[3]

EXPERIMENTAL

Attempted Preparations.—The reactions of trifluoromethanethiol with (*a*) sodium fluoride and (*b*) ammonia were reinvestigated with carefully dried reagents; the results were essentially the same as those of Haszeldine and Kidd.[5] The reaction of thiocarbonyl chloride with zinc, lead, or antimony(III) fluoride at 100° failed to yield an appreciable amount of thiocarbonyl fluoride; carbonyl sulphide, silicon tetrafluoride, carbon disulphide, and carbon tetrachloride were the principal volatile products. Mercuric fluoride (5 g.) reacted with thiocarbonyl chloride (0·50 g.) at room temperature with the evolution of much heat; the volatile products (0·12 g.) were shown spectroscopically to be primarily silicon tetrafluoride, carbonyl sulphide, carbon dioxide, and carbonyl fluoride. Extraction of the solid with methanol gave, on evaporation of the solution, trifluoromethylthiomercuric chloride, $CF_3S{\cdot}HgCl$ (0·40 g.), identified spectroscopically.[19]

In a typical reaction between sulphur and bis(trifluoromethyl)mercury, a stream of dry nitrogen was used to sweep sulphur vapour over the mercury compound (1 g.) in a copper tube at 500°. The volatile products (0·2 g.), collected in a glass trap at −196°, were identified by their infrared spectra as thiocarbonyl fluoride, silicon tetrafluoride, carbonyl sulphide, hexafluoroethane, and carbonyl fluoride, which could not be separated by distillation. A similar reaction has been successfully applied to the preparation of perfluoro-thioketones.[3]

Preparation of Thiocarbonyl Fluoride from Silyl Trifluoromethyl Sulphide.—Silyl trifluoromethyl sulphide, prepared from silyl iodide (2·14 g.) and an excess of bis(trifluoromethylthio)-mercury (11·2 g.) as described elsewhere,[6] was distilled about fifty times through a U-tube containing the mercury compound suspended on glass wool at room temperature. Blackening of the solid was observed as the reaction proceeded. From the volatile products, thiocarbonyl fluoride, barely volatile at −145°, was obtained (1·00 g.) (Found: *M*, 82; C, 14·8; S, 39·4; F, 46·3%. Calc. for CF_2S: *M*, 82; C, 14·6; S, 39·1; F, 46·3%). The fraction volatile at −145° (650 mg.) was identified by its infrared spectrum [20] and vapour density as silyl fluoride containing a small amount of thiocarbonyl fluoride (Found: *M*, 52. Calc. for SiH_3F: *M*, 50). Some trifluoromethanethiol (~10 mg.) (involatile at −132°) was also formed, probably from a trace of moisture in the reaction system. No unchanged silyl trifluoromethyl sulphide was recovered. Bis(trifluoromethylthio)mercury with liquid silyl trifluoromethyl sulphide (for a few minutes at room temperature) gave relatively little thiocarbonyl fluoride; instead, the dimer, trifluoromethyl fluorodithioformate, was formed together with both silyl and silylene fluorides.

Properties were determined on samples that had been repeatedly distilled at −132° and collected at −145°. The temperatures were measured with a copper–constantan thermocouple calibrated against suitable gas thermometers; the melting point was determined by the Stock plunger method.

Pure thiocarbonyl fluoride has m. p. −163·5° ± 1·0°, b. p. −62·1° ± 0·5°; the v. p. (−95° to −62°) is given by $\log_{10} p$ (mm.) $= 7{\cdot}182 - 908/T$; the heat of vaporisation (−95° to −62°) = 4150 ± 50 cal. mole^{-1}; Trouton's constant = 19·7.

Tensimetrically pure thiocarbonyl fluoride was shown spectroscopically always to contain $<0{\cdot}1\%$ of silyl fluoride [20] which might have served to stabilise the material with respect to glass. The compound was stable in clean glass apparatus, even in the liquid phase, for up to 24 hr. After 36 hr. at 300°, the gaseous fluoride decomposed to the extent of only ~5% based on the

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[19] Emeléus and Pugh, *J.*, 1960, 1108.

[20] Newman, O'Loane, Polo, and Wilson, *J. Chem. Phys.*, 1956, **25**, 855; Onyszchuck, Ph.D. Thesis, Cambridge, 1956.

equation: $SiO_2 + 2SCF_2 \longrightarrow 2COS + SiF_4$. Ultraviolet irradiation (36 hr.) in a Pyrex tube also caused negligible decomposition.

The fluorine resonance spectra of thiocarbonyl and carbonyl fluorides were recorded with a Varian Associates V-4300B high-resolution nuclear magnetic resonance spectrometer with flux stabiliser, operating at 40 Mc./sec. with the sample-spinning technique. The samples were contained in Pyrex tubing of 5 mm. external diameter. The ^{13}C–F coupling constants were measured for the pure liquids, and the chemical shifts obtained from dilute solutions in trichlorofluoromethane. The ultraviolet spectrum of thiocarbonyl fluoride vapour was recorded at wavelengths between 190 and 400 mμ on a Cary model 14 recording spectrophotometer with a 10 cm. gas cell fitted with quartz end-plates.

Reactions. (1) The gaseous compound did not react with dry air, hydrogen chloride, iodine, boron trifluoride, antimony trifluoride, or mercuric chloride at room temperature; with sodium fluoride, there was no reaction at room temperature even in the liquid phase; silane also failed to react with thiocarbonyl fluoride at 200° or when irradiated with ultraviolet light at room temperature. In each case, the volatile material taken was recovered unchanged (although a little thiocarbonyl fluoride was lost by polymerisation when irradiated in the presence of silane).

(2) Water (100 mg.) and thiocarbonyl fluoride (39 mg.) at 0° (2 min.) gave carbonyl sulphide (25 mg.) (Found: *M*, 61; v. p. at −78°, 18·2 cm. Calc. for COS: *M*, 60; v. p.[21] at −78°, 17·2 cm.) as the only product volatile at −95°; its identity was confirmed spectroscopically. The aqueous solution contained fluoride (18 mg.), estimated by precipitation as lead chloride fluoride; this corresponded to complete hydrolysis of the thiocarbonyl fluoride: $SCF_2 + H_2O \longrightarrow COS + 2HF$.

(3) Hydrogen iodide (200 mg.) and the thiocarbonyl compound (53 mg.) at −78° (18 hr.) gave unchanged hydrogen iodide (33 mg.) (Found: *M*, 125. Calc. for HI: *M*, 128), silicon tetrafluoride (32 mg.) (Found: *M*, 102. Calc. for SiF_4: *M*, 104), and a trace of carbon disulphide (~1 mg.). The infrared spectra confirmed this identification. The residue was a black solid (185 mg.) involatile at −63°; it was inhomogeneous, containing free iodine and carbon disulphide, together with unidentified materials. The overall combining ratio, HI : SCF_2 was 2·01 : 1. Thus, the reaction appears to be: $SCF_2 + 2HI \longrightarrow SCI_4$ ($\longrightarrow CS_2, I_2$, etc.) + 2HF (+$SiO_2 \longrightarrow SiF_4$).

(4) Thiocarbonyl fluoride (35 mg.) immediately gave a white solid when mixed with ammonia (40 mg.) at −78°. Ammonia (10 mg.) was recovered (Found: *M*, 18; v. p. at −63°, 13·60 cm. Calc. for NH_3: *M*, 17; v. p.[22] at −63°, 13·7 cm.), and its identity confirmed spectroscopically. Qualitative tests and its infrared spectrum [23,24] showed that the solid was a mixture of ammonium thiocyanate and fluoride. The combining ratio ammonia : thiocarbonyl fluoride was 4·06 : 1; accordingly, the reaction can be formulated as: $SCF_2 + 4NH_3 \longrightarrow NH_4SCN + 2NH_4F$.

(5) Trimethylamine (120 mg.) and thiocarbonyl fluoride (57 mg.) also gave a white solid when mixed at −78°. Trimethylamine (77 mg.) was recovered (Found: *M*, 59; v. p. at 0°, 68·0 cm. Calc. for C_3H_9N: *M*, 59; v. p.[25] at 0°, 68·5 cm.); its identity was confirmed spectroscopically. From an attempted analysis of the solid for carbon, hydrogen, and nitrogen, and from its infrared spectrum, which showed the presence of the SiF_6^{2-} ion,[23] it appeared that the adduct attacked glass at room temperature. The infrared spectrum resembled that of the adduct $(Me_3N)_2TiCl_3$ [26] in the shape and position of the bands due to trimethylamine, but showed no strong absorption definitely attributable to C–F stretching modes. The combining ratio, trimethylamine : thiocarbonyl fluoride, was 1·02 : 1.

(6) Trifluoromethanethiol and thiocarbonyl fluoride did not react at room temperature even in the liquid phase (18 hr.), and the starting materials were recovered unchanged. In the presence of anhydrous sodium fluoride (200 mg.), however, liquid thiocarbonyl fluoride (36 mg.) and trifluoromethanethiol (47 mg.) gave at room temperature (18 hr.) no more than a trace of the volatile starting materials. The volatile products were mainly carbonyl sulphide (15 mg.) (Found: *M*, 63. Calc. for COS: *M*, 60) and trifluoromethyl fluorodithioformate

[21] Kemp and Giauque, *J. Amer. Chem. Soc.*, 1937, **59**, 79.
[22] Overstreet and Giauque, *J. Amer. Chem. Soc.*, 1937, **59**, 254.
[23] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[24] Plumb and Hornig, *J. Chem. Phys.*, 1955, **23**, 947.
[25] Aston, Sagenkahn, Szasz, Moessen, and Zuhr, *J. Amer. Chem. Soc.*, 1944, **66**, 1171.
[26] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

(42 mg.) (Found: *M*, 162. Calc. for $C_2F_4S_2$: *M*, 164); the identities of these and small amounts of bis(trifluoromethyl) trithiocarbonate and the unchanged volatile reactants were confirmed spectroscopically. The solid residue was also shown by its infrared spectrum [23] to contain SiF_6^{2-} and HF_2^- ions.

(7) Chlorine (29 mg.) and thiocarbonyl fluoride (33 mg.) at −78° (36 hr.) gave chlorodifluoromethanesulphenyl chloride, $CF_2Cl{\cdot}SCl$ (62 mg.) (Found: *M*, 152; Cl, 47·7%. Calc. for CCl_2F_2S: *M*, 153; Cl, 46·7%). The infrared spectrum and v. p. at 0° (~11 cm.) [27] were consistent with this identification.

(8) From thiocarbonyl fluoride (34 mg.) and mercuric fluoride (200 mg.) at −78° (18 hr.) no volatile material was recovered. The solid was extracted with carbon tetrachloride, and evaporation of the solution gave bis(trifluoromethylthio)mercury (70 mg.) (m. p. found, 37°; lit.,[16] 39°), the identity of which was confirmed spectroscopically; [28] the amount was 85% of that based on the equation $HgF_2 + 2SCF_2 \longrightarrow Hg(S{\cdot}CF_3)_2$.

(9) Thiocarbonyl fluoride (51 mg.) and argentous fluoride (400 mg.) reacted at −78° (18 hr.). Thiocarbonyl fluoride (26 mg.) was recovered (Found: *M*, 80. Calc. for CF_2S: *M*, 82), and its identity checked spectroscopically.[6] By extraction of the solid residue with acetone and evaporation of the solution, trifluoromethylthiosilver (47 mg.) (Found: Ag, 51·0. Calc. for $CAgF_3S$: Ag, 50·7%) was obtained; the infrared spectrum was identical with that recorded elsewhere.[29] The yield, based on the weight of thiocarbonyl fluoride consumed according to an equation such as that given above, was 74%. At room temperature (2 hr.), no unchanged thiocarbonyl compound was recovered from the reaction mixture.

(10) Cyclopentadiene (22·5 mg.) and thiocarbonyl fluoride (35 mg.) at −22° (4 hr.) gave a white solid. The volatile material was unchanged fluoride (8 mg.) (Found: *M*, 80. Calc. for CF_2S: *M*, 82), also identified by its infrared spectrum.[6] The reacting ratio, R = $C_5H_6 : SCF_2$, was thus 1·03 : 1. The m. p. of the freshly prepared solid adduct (~46°) agreed with that previously reported,[3] but the material deteriorated with time at room temperature. When the reaction was carried out at room temperature (48 hr.), the solid was a polymeric material which did not melt, but decomposed with charring at ~100°. In this case, R was 1·56 : 1, indicating that the equimolar adduct was relatively unstable to dissociation at ordinary temperatures: $nC_5H_6,SCF_2 \longrightarrow (C_5H_6)_n + nSCF_2$.

(11) At −20° (10 hr.), butadiene and the fluoride did not react, and the starting materials were recovered unchanged. Even in the liquid phase at room temperature (18 hr.), the diene (52 mg.) and the fluoride (80 mg.) reacted incompletely. Unchanged thiocarbonyl fluoride (41 mg.) (Found: *M*, 78. Calc. for CF_2S: *M*, 82) and butadiene (29 mg.) (Found: *M*, 55. Calc. for C_4H_6: *M*, 54) were recovered, and their identities checked spectroscopically; small amounts of carbonyl sulphide and silicon tetrafluoride were also detected. The residue was a deep red, involatile liquid (63 mg.), which was inhomogeneous and was not characterised.

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[27] Yarovenko, Motornyi, Vasil'eva, and Gershzon, *Zhur. obshchei Khim.*, 1959, **29**, 2163.
[28] Downs, Ebsworth, and Emeléus, *J.*, 1961, 3187.
[29] MacDuffie, Ph.D. Thesis, Cambridge, 1961.