639. *Reactions of Fluorocarbon Radicals. Part XI.* Synthesis and Some Reactions of Trifluoromethanethiol and Trifluoromethanesulphenyl Chloride.*

By R. N. Haszeldine and J. M. Kidd.

Reaction of carbon disulphide with iodine pentafluoride gives mainly bistrifluoromethyl disulphide and sulphur tetrafluoride. Bistrifluoromethyl trisulphide is a by-product and together with bistrifluoromethyl tetrasulphide is a product from the reaction of trifluoroiodomethane with sulphur. Chemical and spectroscopic evidence is presented to show that the sulphur chain in these compounds is unbranched. The compound hitherto reported as thiocarbonyl fluoride is actually thionyl fluoride.

Bis(trifluoromethylthio)mercury with hydrogen chloride gives trifluoromethanethiol, and with chlorine gives trifluoromethanesulphenyl chloride, both in high yield. The sulphenyl chloride is obtained quantitatively by direct chlorination of bistrifluoromethyl disulphide. The properties and reactions of these compounds, and relevant ultra-violet and infra-red spectra, are discussed.

It was shown earlier that trifluoroiodomethane and sulphur react, probably by a free-radical mechanism, to give bistrifluoromethyl disulphide in high yield (Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198, 2549). The present communication describes a more convenient route to this compound and the synthesis from it of trifluoromethanethiol and trifluoromethanesulphenyl chloride.

Carbon disulphide reacts with pure iodine pentafluoride at temperatures from 60° to 200° to give three products: bistrifluoromethyl disulphide (80%), sulphur tetrafluoride, and bistrifluoromethyl trisulphide (7%); carbon tetrafluoride is formed only at the higher temperatures. The disulphide can thus be obtained in high yield by a reaction which does not involve the relatively expensive trifluoroiodomethane. The following intermediates, which produce trifluoromethylthio-radicals, are proposed:

$$\begin{tikzcd}
& SF_4 + CF_2{:}S \arrow[dr, "I^+F^-"] & \\
S{:}C{:}S \arrow[ur, "IF_5"] \arrow[dr, "I_2", equal] & & CF_3{\cdot}SI \\
& CI_3{\cdot}SI \arrow[ur, "IF_5"'] &
\end{tikzcd}$$

$$CF_3{\cdot}SI \longrightarrow CF_3{\cdot}S\cdot + I\cdot$$

$$2CF_3{\cdot}S\cdot \longrightarrow CF_3{\cdot}S_2{\cdot}CF_3$$

Iodine pentafluoride is a mild fluorinating agent and, if the initial attack of iodine pentafluoride on carbon disulphide removes sulphur (as the tetrafluoride), thiocarbonyl fluoride could be an intermediate which, by addition of iodine monofluoride, could yield trifluoromethanesulphenyl iodide. Iodine monofluoride has never been isolated, but evidence that it can exist in equilibrium with iodine pentafluoride will be presented later. An alternative method of formation of the sulphenyl iodide is by the intermediate formation of tri-iodosulphenyl iodide by reaction of carbon disulphide with iodine (cf. $CS_2 \xrightarrow{Cl_2} CCl_3{\cdot}SCl$), followed by replacement of iodine by fluorine (cf. $CI_4 \xrightarrow{IF_5} CF_3I$). Combination of two trifluoromethylthio-radicals would yield bistrifluoromethyl disulphide. The formation of the trisulphide involves radical reactions such as

$$CF_3{\cdot}S\cdot + CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \longrightarrow CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3 + CF_3\cdot$$

or

$$2CF_3{\cdot}S\cdot \longrightarrow CF_3\cdot + CF_3{\cdot}S{\cdot}S\cdot \xrightarrow{CF_3{\cdot}S\cdot} CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3$$

Bistrifluoromethyl sulphide is not a reaction product, so that combination of a trifluoromethyl and a trifluoromethylthio-radical does not occur to any extent.

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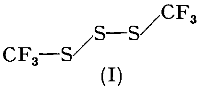
* Part X, Haszeldine, *J.*, 1953, 2075.

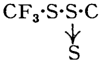
A report of unpublished work by Ruff (B.I.O.S. Final Report 1595, Item 22; F.I.A.T. Final Report 1114, p. 26) states that thiocarbonyl fluoride (b. p. —40°) is formed together with the compounds $C_2S_2F_6$ (b. p. —33°) and $C_3S_3F_6$ (b. p. —26°) when carbon disulphide is treated with iodine pentafluoride. The present work has shown, however, that iodine pentafluoride and carbon disulphide react only at temperatures greater than 60°, and that use of reaction temperatures up to 200° serves only to increase the rate; thiocarbonyl fluoride cannot be detected. Ruff's compound was very probably thionyl fluoride (b. p. —44°), which has sulphur and fluoride contents (37·2, 44·2%) very similar to those which would be shown by thiocarbonyl fluoride (39·0, 46·3%). Thionyl fluoride is, in fact, isolated on use of iodine pentafluoride which has been exposed to air and moisture and thus contains iodine oxytrifluoride. Sulphur tetrafluoride is produced only when the oxygen-containing compounds in the iodine pentafluoride have been destroyed.

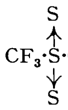
The disulphide prepared from carbon disulphide was shown to be identical with bistrifluoromethyl disulphide, synthesised earlier from trifluoroiodomethane, by its ultra-violet and infra-red spectra, by the fact that it gave bistrifluoromethyl sulphide quantitatively on exposure to ultra-violet light, and by its reaction with mercury to give bis-(trifluoromethylthio)mercury. The trisulphide (b. p. 86·5°) was shown to contain two trifluoromethyl groups by irradiation to give bistrifluoromethyl sulphide and sulphur; bistrifluoromethyl disulphide was isolated as an intermediate:

$$CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow{h\nu} CF_3{\cdot}S{\cdot}CF_3 + CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow{h\nu} CF_3{\cdot}S{\cdot}CF_3 + S$$

The reaction of trifluoroiodomethane with sulphur is best carried out in an autoclave at 310°, since the yield of bistrifluoromethyl disulphide is then high (75%), and the formation of carbon disulphide (found as by-product when glass vessels are used, or at a temperature >320° in an autoclave) is avoided. Bistrifluoromethyl tri- and tetra-sulphides are also obtained, but not the monosulphide. Like the disulphide, both of the poly-sulphides are decomposed rapidly and quantitatively into fluoride, sulphide, sulphur, and carbonate when treated with aqueous sodium hydroxide. Bent (*e.g.*, I) or branched (*e.g.*, II or III) sulphur chains are possible, but two lines of evidence—the synthesis of the trisulphide from trifluoromethanesulphenyl chloride and hydrogen sulphide (see below), and electron-diffraction results—show that the unbranched structure (I) is correct. It is to be expected that the tetrasulphide will have a similar structure.


(I)


$$CF_3{\cdot}\underset{\overset{\downarrow}{S}}{S}{\cdot}S{\cdot}CF_3$$
(II)


$$CF_3{\cdot}\overset{\overset{S}{\uparrow}}{\underset{\underset{S}{\downarrow}}{S}}{\cdot}CF_3$$
(III)

The electron-diffraction results, which will be published in full by Dr. L. E. Sutton and Mr. H. Bowen, are summarised in Table 1. The S–S bond in sulphur is 2·1 Å long (Warren and Burwell, *J. Chem. Phys.*, 1935, **3**, 6; Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, **67**, 818), and dimethyl trisulphide has similarly been shown to contain an unbranched sulphur chain with C–S 1·78 Å and S–S 2·04 Å (Donohue and Schomaker, *J. Chem. Phys.*, 1948, **16**, 92). That the structure of diethyl tetrasulphide involves an unbranched chain is shown by its synthesis from sulphur dichloride and ethanethiol.

TABLE 1.

	Bond lengths (Å)					Bond lengths (Å)			
$(CF_3)_2X_n$	C–F	C–X	$X\hat{C}X$		$(CF_3)_2X_n$	C–F	C–X	$X\hat{C}X$	
$(CF_3)_2S$	$1{\cdot}32_8$	$1{\cdot}82_8$	—	105·6°	$(CF_3)_2Se$	$1{\cdot}35_6$	$1{\cdot}95_8$	—	104·4°
$(CF_3)_2S_2$	$1{\cdot}33_4$	$1{\cdot}82_9$	$C\hat{S}S$	105·4	$(CF_3)_2Se_2$	$1{\cdot}33_6$	$1{\cdot}93_4$	Se–Se	$2{\cdot}33_5$
			S–S	$2{\cdot}05_3$					
$(CF_3)_2S_3$	$1{\cdot}34_0$	$1{\cdot}84_8$	$S\hat{S}S$	103·8					
			S–S	$2{\cdot}06_5$					

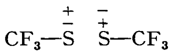
The electron-diffraction results obtained with bistrifluoromethyl selenide and bistrifluoromethyl diselenide are included in Table 1 for comparison.

The ultra-violet spectra of the compounds $CF_3{\cdot}[S]_n{\cdot}CF_3$, ($n$ = 1—4) are shown in

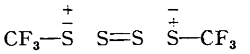
Table 2. Since the chemical evidence for the unbranched structure for bistrifluoromethyl disulphide presented earlier (*J.*, 1952, 2198, 2549) is confirmed by electron-diffraction measurements, the shift in absorption maximum from 250 (for dialkyl disulphides) to 235 mμ in $(CF_3)_2S_m$ (m = 2—4) must be attributed to a decrease, caused by the fluorine atoms, in the contribution of structures of type (IV) in the excited state. The similarity of the spectra of the bistrifluoromethyl tri- and tetra-sulphide to that of the disulphide is strong evidence that the polysulphides contain unbranched chains. The slight shift to longer wave-length is attributed to additional structures involving hyperconjugation such as (V) which stabilises the excited level. For comparison $\varepsilon_{max.}$ for the tri- and tetra-sulphides should be divided by the number of S–S bonds present; it is clear that there is a marked increase in intensity of absorption relative to that of the disulphide. The ultra-violet spectra of other polysulphides (Table 3) show that the shift in the absorption maximum to longer wave-length is much less with the fluorine compounds than with the unsubstituted compounds.

TABLE 2.

	Solvent	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$
$(CF_3)_2S$	Vapour	210	6·85	—	—
$CF_3{\cdot}SH$	Vapour	218	46	215	45
$(CF_3)_2S_2$	Vapour	235	290	212	110
	Light petroleum	236	390	—	—
	Ethanol	237	360	212	160
$(CF_3)_2S_3$	Vapour	236	670	220	600
	Ethanol	238	1500	221	1330
	Light petroleum	240·5	1550	221	1250
$(CF_3)_2S_4$	Light petroleum		Infl. 232—242, ε 2500		
$CF_3{\cdot}SCl$	Vapour	333	25	277	1·5
		214	235	—	—
$CCl_3{\cdot}SCl$	Light petroleum	322	10·0	293	6·5
	$CHCl_3$	324	12·0	290	7·5

(IV) 

$$\mathrm{CF_3{-}}\overset{\overset{+}{-}}{\mathrm{S}}\ \ \overset{\overset{-}{+}}{\mathrm{S}}\mathrm{{-}CF_3}$$

 (V)

$$\mathrm{CF_3{-}}\overset{\overset{+}{-}}{\mathrm{S}}\ \ \mathrm{S{=}S}\ \ \overset{\overset{-}{+}}{\mathrm{S}}\mathrm{{-}CF_3}$$

TABLE 3.

Compound	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$
Et_2S_2 [1]	250	440	226	235
Et_2S_4 [2]		Infl. 280, ε 2700		
*cyclo*Hexyl disulphide [2]	246	560	230	410
*cyclo*Hexyl hexasulphide [2]		Infl. 300, ε 7000		
Dibenzyl disulphide [3]		Infl. 258, ε 1550		
Dibenzyl trisulphide [3]		Infl. 272, ε 2140		
Dibenzyl tetrasulphide [3]		Infl. 286, ε 3550		

[1] Brandt *et al.*, *loc. cit.* [2] Koch, *J.*, 1949, 397. [3] Minoura, *Chem. Abs.*, 1953, **47**, 3118.

Infra-red spectroscopic evidence for the unbranched structure of bistrifluoromethyl disulphide was reported earlier (*J.*, 1952, 2549). The infra-red spectra of bistrifluoromethyl tri- and tetra-sulphide (C.S. 51 and 52 *) are very similar to that of the disulphide, with C–F stretching vibrations in the 8—9-μ region (Table 4). The band which appears at *ca.* 13·2 μ in bistrifluoromethyl mono- and di-sulphide was ascribed earlier to either the C–S stretching vibration or a CF_3 deformation frequency. The tri- and tetra-sulphides show a similar band (Table 4), and, since trifluoromethyl-selenium, -phosphorus (*J.*, 1953, 1565), and -arsenic (*J.*, 1953, 1552) compounds show a similar band, it is now probable that it is a deformation and not a stretching vibration. Studies on the Raman spectra of other tri- and tetra-sulphides suggest that a co-ordinate S–S double bond is not present, *i.e.*, that the chain is unbranched (Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publ. Corp., New York, 1939, p. 259).

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* Spectra thus designated have been deposited with the Chemical Society. Photocopies may be obtained from the General Secretary on application which must state the C.S. number.

TABLE 4.

Compound	C–F bands (μ)		CF_3 deformation (μ)
$(CF_3)_2S$ ...	8·17 8·35 8·60	9·25	13·10 13·35
$(CF_3)_2S_2$ ...	8·43	9·10	13·12 13·18
$(CF_3)_2S_3$	8·50	9·05	13·24
$(CF_3)_2S_4$	8·65	9·17	13·25

Bis(trifluoromethylthio)mercury, prepared almost quantitatively from bistrifluoromethyl disulphide, is a valuable intermediate; from it have been synthesised trifluoromethane-thiol (infra-red spectrum, C.S. 53) and -sulphenyl chloride. The thiol (b. p. −37°; cf. MeSH, b. p. 6°) is obtained quantitatively by reaction with anhydrous hydrogen chloride :

$$\mathrm{CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow{Hg,\ \mathit{h\nu}} (CF_3{\cdot}S)_2Hg \xrightarrow{HCl} 2CF_3{\cdot}SH + HgCl_2}$$

it can be stored in a vacuum indefinitely. Its constitution follows from its method of preparation, and from its infra-red spectrum which shows the S–H stretching vibration at 3·84 μ (cf. alkanethiols, 3·72—3·90 μ), the C–F stretching bands at 8·49, 8·57, and 8·76, 8·80 μ, and the CF_3 deformation bands at 12·95, 13·10, 13·25 μ. The ultra-violet spectrum of the thiol (Table 2) is similar to that of bistrifluoromethyl sulphide.

Trifluoromethanethiol, the sulphur analogue of the still unknown trifluoromethanol was postulated as an intermediate in the hydrolysis by bases of bistrifluoromethyl disulphide to fluoride, carbonate, sulphide, and sulphur (*J.*, 1952, 2198) :

$$\mathrm{CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow{H_2O} CF_3{\cdot}SH + CF_3{\cdot}S{\cdot}OH}$$

$$\mathrm{CF_3{\cdot}SH \xrightarrow{NaOH} F^-,\ CO_3^{--},\ S^{--}}$$

$$\mathrm{CF_3{\cdot}S{\cdot}OH \xrightarrow{NaOH} F^-,\ CO_3^{--},\ S^{--}}$$

This scheme is supported by the fact that synthetic trifluoromethanethiol is decomposed fairly slowly (12 hr.) by water with complete liberation of fluorine as fluoride, but very rapidly by aqueous sodium hydroxide; sulphur is not a reaction product from trifluoromethanethiol so that the sulphur liberated from the disulphide must be produced by further reactions of trifluoromethanesulphenic acid.

Photochemical decomposition of the thiol yields hydrogen, sulphur, fluoroform, bistrifluoromethyl sulphide, and bistrifluoromethyl disulphide, by a series of reactions clearly involving $CF_3{\cdot}S{\cdot}$ and $CF_3{\cdot}$ radicals.

Chlorine reacts with bis(trifluoromethylthio)mercury at −22°, to give the golden-yellow trifluoromethanesulphenyl chloride :

$$\mathrm{(CF_3{\cdot}S)_2Hg \longrightarrow 2CF_3{\cdot}SCl + HgCl_2}$$

Trifluoromethylthiomercuric chloride and bistrifluoromethyl disulphide are by-products and the yield of the latter is greater at 20°. Trifluoromethylthiomercuric chloride, which is readily distinguished from bis(trifluoromethylthio)mercury by comparison of infra-red spectra (C.S. 54 and 55), is formed as follows :

$$\mathrm{(CF_3{\cdot}S)_2Hg + CF_3{\cdot}SCl \longrightarrow CF_3{\cdot}S{\cdot}HgCl + (CF_3)_2S_2}$$

Trifluoromethanesulphenyl chloride can also be prepared directly from the disulphide by reaction with chlorine in Pyrex vessels on exposure to ultra-violet light ($\mathrm{CF_3{\cdot}S_2{\cdot}CF_3 \xrightleftharpoons{Cl_2,\ \mathit{h\nu}} 2CF_3{\cdot}SCl}$); this is an equilibrium reaction and the final product contains *ca.* 50% of the sulphenyl chloride. In silica reaction vessels [*i.e.*, transmitting light of wave-length >220 mμ instead of only >300 mμ (Pyrex)] extensive decomposition of the trifluoromethanesulphenyl chloride to chlorotrifluoromethane and sulphur chlorides occurs. These products are also formed when the pure sulphenyl halide is irradiated in a silica vessel.

The infra-red spectrum of the sulphenyl chloride (C.S. 56) shows the presence of the

CF_3 group (cf. $CCl_3{\cdot}SCl$, C.S. 57), and the ultra-violet spectrum (Table 2) the presence of the S–Cl bond. The shift to the red relative to trichloromethanesulphenyl chloride (Table 2) is attributed to the contribution of structures such as $F^{-}CF_2{:}S{:}Cl^{+}$ to the excited state; comparison should also be made with sulphur dichloride ($\lambda_{max.}$ *ca.* 260 mμ, ε *ca.* 900) and sulphur monochloride ($\lambda_{max.}$ *ca.* 300 mμ, ε *ca.* 1000) (Koch, *J.*, 1949, 397).

Trifluoromethanesulphenyl chloride readily combines with mercury or with compounds which contain the S–H bond:

$$2CF_3{\cdot}SCl + Hg \longrightarrow (CF_3)_2S_2 + HgCl_2$$

$$CF_3{\cdot}SCl + CF_3{\cdot}SH \longrightarrow CF_3{\cdot}S{\cdot}S{\cdot}CF_3$$

$$CF_3{\cdot}SCl + H_2S \longrightarrow CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3$$

The last two reactions prove that the di- and tri-sulphides contain unbranched sulphur chains.

The few alkanesulphenyl halides known at present are unstable compounds. 2-Methylpropane-2-sulphenyl bromide and chloride are best prepared from the *NN*-dimethylsulphenamide (Rheinbolt and Mott, *Ber.*, 1939, **72**, 668), and trichloromethanesulphenyl chloride is best obtained by chlorination of carbon disulphide. The unstable methanesulphenyl chloride (b. p. 22°/60 mm.) has been prepared only recently by chlorination of dimethyl disulphide or of methanethiol at −15° (Schneider, *Chem. Ber.*, 1951, **84**, 911; Douglas and Brower, *J. Amer. Chem. Soc.*, 1951, **73**, 5787); reaction at higher temperatures results in attack on the alkyl groups. The fluoro-sulphenyl halides, $CF_3{\cdot}[CF_2]_n{\cdot}SCl$, are relatively stable compounds, however, and with the corresponding thiols open up a route to an extensive chemistry of perfluoroalkyl-sulphur compounds.

EXPERIMENTAL

The compounds were manipulated in a conventional vacuum system fitted with mercury manometers or, for compounds which attack mercury, with spoon gauges. Molecular weights were determined by Regnault's method, and b. p.s in an isoteniscope. Unless otherwise stated, reactions were carried out in Pyrex tubes of 30—40-ml. capacity. Trifluoroiodomethane was prepared as described earlier (*J.*, 1951, 584).

Reaction of Iodine Pentafluoride with Carbon Disulphide.—(a) *Under anhydrous conditions.* Iodine pentafluoride was prepared by passing fluorine over dry iodine in a water-cooled nickel vessel until a colourless product was obtained. This was transferred to a silica apparatus and was distilled *in vacuo* immediately before use.

Iodine pentafluoride (90 g.) and carbon disulphide (10 g.) were sealed with exclusion of air in a 100-ml. autoclave and heated at 195° for 12 hr. The products were pumped from the autoclave and given a preliminary distillation by passage *in vacuo* through a trap cooled to −95°. The material which condensed in this trap was washed with water, distilled once *in vacuo* to remove water, then redistilled through a low-temperature fractionating column, to give bistrifluoromethyl disulphide (10·1 g., 76% based on carbon disulphide), b. p. 34° (Found: F, 31·5; S, 56·8%; *M*, 202. Calc. for $C_2F_6S_2$: F, 31·6; S, 56·4%; *M*, 202), and *bistrifluoromethyl trisulphide* (1·1 g., 7%), b. p. 86·4°, n_D^{20} 1·4023 (Found: F, 48·9; S, 41·2%; *M*, 234. $C_2F_6S_3$ requires F, 48·7; S, 41·1%; *M*, 234). The compounds were heated at 60° for 12 hr. with 15% aqueous sodium hydroxide to cause breakdown to fluoride, sulphide, sulphur, and carbonate. For analysis an aliquot was treated with hydrogen peroxide in alkaline solution to convert sulphide and sulphur into sulphate, and the fluoride was then distilled from the acidified solution as fluorosilicic acid, which was titrated with thorium nitrate solution; a second aliquot was treated with hydrogen peroxide, acidified (hydrochloric acid), and, after removal of the fluoride by evaporation several times to dryness, sulphide was determined as barium sulphate.

Brandt, Emeléus, and Haszeldine (*loc. cit.*) report b. p. 34·6° for bistrifluoromethyl disulphide prepared from trifluoroiodomethane. The infra-red and ultra-violet spectra of the disulphides prepared by the two routes were identical. Bistrifluoromethyl trisulphide, isolated as a product of reaction of trifluoroiodomethane with sulphur, shows the same b. p. and ultra-violet and infra-red spectra as the compound described above.

The more volatile products were fractionated in a vacuum, to give carbon tetrafluoride and sulphur tetrafluoride (9·0 g., 65%, based on carbon disulphide), b. p. −38·4° (Found:

F, 69·0; S, 29·1%; *M*, 106·5. Calc. for F_4S: F, 70·4; S, 29·6%; *M*, 108). Fischer and Jaenckner (*Angew. Chem.*, 1929, **42**, 810) report b. p. −40° for sulphur tetrafluoride. Sulphur tetrafluoride was decomposed for analysis by 15% aqueous sodium hydroxide.

Carbon disulphide (5 g.) and iodine pentafluoride (100 g.) showed negligible reaction after 24 hr. at 20° and then 24 hr. at 50°, but after being heated at 80° for 5 days all the carbon disulphide had been converted into bistrifluoromethyl disulphide and sulphur tetrafluoride as above. Carbon tetrafluoride was not produced. Thiocarbonyl fluoride was sought at every stage but was not found.

(b) *In presence of oxygen-containing compounds.* Carbon disulphide (5 g.) was sealed with iodine pentafluoride (60 g.) which had been stored for several weeks in a steel container and had absorbed moisture. After 12 hr. at 50° the volatile reaction products were distilled, to give thionyl fluoride (2·4 g., 21%), b. p. −44° to −46° (Found: F, 44·5; S, 38·0%; *M*, 86. Calc. for OF_2S: F, 44·2; S, 37·2%; *M*, 86). Analysis was carried out as for sulphur tetrafluoride. Reaction of sulphuryl fluoride (0·161 g.) with water (5 ml.) in a 30-ml. tube at 20° for 12 hr. gave sulphur dioxide (0·067 g., 56%) (Found: *M*, 64. Calc. for SO_2: *M*, 64), identified by its infra-red spectrum.

Reaction of Trifluoroiodomethane with Sulphur.—Trifluoroiodomethane (45 g.) and sulphur (60 g.), heated at 310° for 36 hr. in a 300-ml. stainless-steel autoclave, gave unchanged trifluoroiodomethane (18 g., 39%) (shown by infra-red spectroscopic examination to be free from bistrifluoromethyl sulphide), bistrifluoromethyl disulphide (10·5 g., 75%), b. p. 34·5° (Found: *M*, 202. Calc. for $C_2F_6S_2$: *M*, 202), bistrifluoromethyl trisulphide (2·0 g., 12%), b. p. 86·2—86·4°, n_D^{20} 1·4023 (Found: *M*, 234. Calc. for $C_2F_6S_3$: *M*, 234), *bistrifluoromethyl tetrasulphide* (0·2 g., 1%), b. p. 135°, n_D^{20} 1·4608 (Found: F, 42·5; S, 48·6. $C_2F_6S_4$ requires F, 42·8; S, 48·2%), and a residue (*ca.* 0·3 g.) which probably contained higher polysulphides. The trisulphide was identical with the compound obtained from carbon disulphide as above. The tetrasulphide was completely decomposed by 15% aqueous sodium hydroxide after 15 hr. at 55°. Both the tri- and the tetra-sulphide are stable to air, water, or mercury at room temperature. The above yields of polysulphides are based on the combined products from several experiments.

Photochemical Decomposition of Bistrifluoromethyl Trisulphide.—The trisulphide (1·07 g.), sealed in a silica tube, was exposed to ultra-violet light for 17 days. A viscous liquid, deposited soon after irradiation started, was slowly converted into rhombic sulphur (0·289 g., 66%). Fractionation of the volatile products gave bistrifluoromethyl sulphide (0·384 g., 49%) (*M*, 170), identified spectroscopically, bistrifluoromethyl disulphide (0·313 g., 34%) (*M*, 202), and an unidentified fraction (0·061 g.) (Found: *M*, 89). The disulphide was sealed in a 10-ml. silica tube and irradiation was continued for 5 days, to give unchanged disulphide (0·021 g.) (Found: *M*, 199) and bistrifluoromethyl sulphide (0·163 g., 62%). The total yield of the monosulphide is 70%.

Reaction of Bis(trifluoromethylthio)mercury with Hydrogen Chloride.—The mercurial was prepared by the irradiation for 4 days of bistrifluoromethyl disulphide (5·0 g.) and mercury (80 g.) in a vigorously shaken 100-ml. silica tube. The residual bistrifluoromethyl disulphide (4%) and the small amount of bistrifluoromethyl sulphide formed (5%) were removed, and the solid products were extracted with ether. Evaporation of the dried (P_2O_5) ethereal extracts at room temperature in a dried atmosphere gave the pure mercurial (90%), m. p. 37—38°. Anhydrous hydrogen chloride was purified in a vacuum system.

Bis(trifluoromethylthio)mercury (1·05 g.) and anhydrous hydrogen chloride (0·228 g.) were sealed in a 30-ml. Pyrex tube. An immediate reaction was apparent as the tube warmed to room temperature, and the mercurial was converted into a white amorphous powder (mercuric chloride). After 48 hr. the volatile products were distilled, to give *trifluoromethanethiol* (0·53 g., 99%), b. p. −36·7° (Found: F, 56·0; S, 31·7%; *M*, 102. CHF_3S requires F, 55·9; S, 31·4%; *M*, 102), and unchanged hydrogen chloride (22%). Trifluoromethanethiol was completely decomposed to fluoride, sulphide, and carbonate by 15% aqueous sodium hydroxide at 20° in 6 hr.

Photochemical or Hydrolytic Decomposition of Trifluoromethanethiol.—The thiol (0·4844 g.), sealed in a silica tube and exposed to ultra-violet light for 10 days, gave hydrogen (0·0019 g., 40%) (Found: *M*, 2), unchanged trifluoromethanethiol (0·0323 g., 7%), fluoroform (0·1489 g., 44%) (Found: *M*, 70. Calc. for CHF_3: *M*, 70) identified by its infra-red spectrum, bistrifluoromethyl sulphide (0·0161 g., 4%) (Found: *M*, 167. Calc. for C_2F_6S: *M*, 170) identified by its infra-red spectrum, bistrifluoromethyl disulphide (0·2057 g., 43%) (Found: *M*, 202. Calc. for $C_2F_6S_2$: *M*, 202), and sulphur (0·0618 g., 41%). The unchanged trifluoromethanethiol and bistrifluoromethyl sulphide were obtained as a mixture from which the thiol was removed by treatment at 70° for 24 hr. with 15% aqueous sodium hydroxide.

Trifluoromethanethiol (0·131 g.) was sealed with water (2 ml.) in a 10-ml. Carius tube, and allowed to warm to room temperature. As soon as the ice melted, fumes were evolved and a yellow oil was formed. This had disappeared after 12 hr. at room temperature. The aqueous solution was made alkaline and treated with an excess of hydrogen peroxide, and the fluoride was determined as described above (Found : F, 54·8. Calc. for CHF_3S : F, 55·9%).

Preparation of Trifluoromethanesulphenyl Chloride.—(a) *From bis(trifluoromethylthio)mercury.* In a typical reaction the mercurial (4·99 g.) and dry chlorine (1·60 g.) were condensed into a Carius tube which was sealed and allowed to warm to −22°. An immediate reaction was apparent and the crystalline mercurial changed into a white amorphous powder. After 3 hr. the volatile products were distilled in a vacuum, to give bistrifluoromethyl disulphide (0·29 g., 11%) and *trifluoromethanesulphenyl chloride* (2·44 g., 72%), b. p. −0·7° (Found : Cl, 25·9; F, 41·7; S, 23·1%; *M*, 137. $CClF_3S$ requires Cl, 26·0; F, 41·8; S, 23·4%; *M*, 136·5). The last compound was decomposed by sodium fusion for analysis. When treated with 15% sodium hydroxide, trifluoromethanesulphenyl chloride liberated its chlorine quantitatively as chloride, but not all its fluorine as fluoride. The following vapour pressures have been recorded for the sulphenyl chloride, which condenses to a golden-yellow liquid : −25·1°, 262·2 mm.; −21·3°, 316·0 mm.; −17·3°, 379·4 mm.; −13·7°, 446·0 mm.; −3·3°, 684·4 mm.; −1·3°, 740·3 mm.

Reaction of chlorine (0·37 g.) with the mercurial (1·13 g.) at room temperature for 4 days gave bistrifluoromethyl disulphide (0·301 g., 60%) (Found : *M*, 202) and a correspondingly lower yield of trifluoromethanesulphenyl chloride.

The solid product from the first reaction above was extracted with ether; evaporation of the ether followed by fractional sublimation gave *trifluoromethylthiomercuric chloride* (Found : Cl, 11·6. $CClF_3SHg$ requires Cl, 10·5%), slightly contaminated with mercuric chloride. Attempts to separate the mercurial from mercuric chloride by differential solvent extraction failed.

(b) *From bistrifluoromethyl disulphide and chlorine.* The disulphide (10·0 g.) and dry chlorine (10·0 g.) were sealed in a 100-ml. Pyrex Carius tube and exposed to ultra-violet light for 14 days. Distillation gave unchanged disulphide (45%) (Found : *M*, 203), chlorine (Found : *M*, 71), and trifluoromethanesulphenyl chloride (100%) (Found : *M*, 138).

When irradiated in a 100-ml. silica tube for 10 days, bistrifluoromethyl disulphide (1·51 g.) and chlorine (0·80 g.) gave unchanged chlorine (0·11 g., 14%), trifluoromethanesulphenyl chloride (0·94 g., 46%), chlorotrifluoromethane (0·50 g., 32%) (Found : *M*, 105. Calc. for $CClF_3$: *M*, 104·5), disulphur dichloride (0·20 g.), and a mixture of unchanged bistrifluoromethyl disulphide and sulphur dichloride. This mixture was treated with water and redistilled, to give bistrifluoromethyl disulphide (0·17 g., 11%) (Found : *M*, 200).

Reactions of Trifluoromethanesulphenyl Chloride.—(a) *With mercury.* The chloro-compound (0·52 g.), shaken with mercury (10 g.) at room temperature for 4 hr., gave bistrifluoromethyl disulphide (0·37 g., 96%), identified by its molecular weight (202) and vapour pressure.

(b) *With trifluoromethanethiol.* The sulphenyl halide (0·29 g.) and trifluoromethanethiol (0·23 g.) were sealed in a Carius tube and set aside for 14 days. The now colourless liquid was distilled to give hydrogen chloride and bistrifluoromethyl disulphide (0·429 g., 94%) (Found : *M*, 202).

(c) *With hydrogen sulphide.* Hydrogen sulphide (0·171 g.) and trifluoromethanesulphenyl chloride (0·75 g.) reacted slowly (1 month) with disappearance of the yellow colour, to give bistrifluoromethyl trisulphide (0·57 g., 92%), b. p. 87°, n_D^{20} 1·4020 (Found : *M*, 233. Calc. for $C_2F_6S_3$: *M*, 234), identical with the material described earlier.

(d) *Photolysis.* Trifluoromethanesulphenyl chloride (0·789 g.) was exposed to ultra-violet light in a silica tube for 14 days, to give sulphur (0·136 g., 73%), chlorotrifluoromethane (0·419 g., 69%) (Found: *M*, 104), and liquid products (S_2Cl_2, SCl_2, $CF_3{\cdot}S_2{\cdot}CF_3$) which were not examined further.

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