410. *Organometallic and Organometalloidal Fluorine Compounds. Part III.* Trifluoromethyl Derivatives of Sulphur.*

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The interaction of sulphur and trifluoroiodomethane yields bistrifluoromethyl disulphide, $(CF_3)_2S_2$, carbon disulphide, thiocarbonyl fluoride, and polysulphides. The structure of bistrifluoromethyl disulphide is proved chemically and its unusual hydrolysis is considered. On irradiation in presence of mercury the disulphide yields bis(trifluoromethylthio)mercury, $(CF_3S)_2Hg$; irradiation in absence of mercury gives bistrifluoromethyl sulphide, $(CF_3)_2S$.

The synthesis and reactions of trifluoromethylmercuric iodide and of bistrifluoromethylmercury were described in Parts I and II (Emeléus and Haszeldine, *J.*, 1949, 2948, 2953). The present communication describes the use of perfluoroalkyl iodides, as typified by trifluoroiodomethane, for the preparation of perfluoroalkyl derivatives of sulphur (preliminary publication, *Nature*, 1950, **166**, 225).

Application of the general methods for the preparation of alkyl sulphides to trifluoroiodomethane is unlikely to give good yields of the fluoroalkyl sulphides, since heterolytic fission of the carbon–iodine bond in trifluoroiodomethane involves the so-called "positive-iodine" mechanism (Banus, Emeléus, and Haszeldine, *J.*, 1951, 60):

$$OH^- + I - CF_3 \longrightarrow HOI + CF_3^-$$

Very few polyhalogenated alkyl sulphides and polysulphides are known. Riche (*Annalen*, 1854, **92**, 353; *Ann. Chim. Phys.*, 1854, **43**, 283) prepared bistrichloromethyl sulphide by the action of chlorine on dimethyl sulphide, and Feichtinger and Moos (*Ber.* 1948, **81**, 371) showed that it readily decomposed into carbon tetrachloride and thiocarbonyl chloride:

$$CCl_3{\cdot}S{\cdot}CCl_3 \longrightarrow CCl_4 + CSCl_2$$

Polyhalogenated methyl di- and tri-sulphides can be prepared by the action of chlorine or bromine on carbon disulphide (Klason, *Ber.*, 1887, **20**, 2379; Hell and Urech, *Ber.*, 1882,

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* Part II, Emeléus and Haszeldine, *J.*, 1949, 2953.

15, 273; Sanna and Stefano, *Gazzetta*, 1942, **72**, 305), and bistrichloromethyl disulphide has also been obtained by the action of silver dust on perchloromethanethiol :

$$2CCl_3{\cdot}SCl + 2Ag \longrightarrow CCl_3{\cdot}S{\cdot}S{\cdot}CCl_3 + 2AgCl$$

The last compound decomposes on distillation at atmospheric pressure to give perchloromethanethiol and thiocarbonyl chloride :

$$CCl_3{\cdot}S{\cdot}S{\cdot}CCl_3 \longrightarrow CCl_3{\cdot}SCl + CSCl_2$$

In view of the instability of bistrichloromethyl sulphide and disulphide, it is probable that their conversion into the corresponding fluorine compounds by halogen exchange with, say, antimony trifluoride would be difficult, if not impossible.

The fluorination of aliphatic ethers to the corresponding perfluoro-ethers $[CF_3{\cdot}[CF_2]_n]_2O$ has been described (Haszeldine, *Research*, 1951, **4**, 378, and XIIth Meeting, Int. Congr. Pure & Appl. Chem., New York, 1951), but the similar treatment of aliphatic sulphides or polysulphides has not been reported. In fact, only one trifluoromethyl derivative of sulphur has been described : Silvey and Cady (*J. Amer. Chem. Soc.*, 1950, **72**, 3624) have shown that the fluorination of carbon disulphide by cobalt trifluoride yields trifluoromethylsulphur pentafluoride, $CF_3{\cdot}SF_5$, as the main product. Chlorofluoroethyl sulphides and disulphides have been obtained from tetrafluoroethylene by reaction (at 100—150° under pressures up to 1000 lb./sq. in.) with sulphur dichloride or disulphur dichloride, *e.g.*, $(CF_2Cl{\cdot}CF_2)_2S$ and $(CF_2Cl{\cdot}CF_2)_2S_2$ (Raasch, U.S.P. 2,451,411; *Chem. Abs.*, 1949, **43**, 6646).

It has now been shown that trifluoroiodomethane and sulphur react at temperatures above 200° to give a product whose composition depends on the temperature and on the vessel used. In a stainless-steel autoclave at 260° the main product is $C_2S_2F_6$, b. p. 35°, which has been shown to be bistrifluoromethyl disulphide; the same product is produced in smaller yield in glass vessels at 205—210° : the other products are discussed below. Bistrifluoromethyl disulphide has a normal value for Trouton's constant and is insoluble in, and unaffected by, water or hydrochloric acid at room temperature. With aqueous sodium hydroxide at room temperature, however, it is rapidly and completely hydrolysed to fluoride, carbonate, sulphide, and polysulphides, but fluoroform is not produced. The mechanism of this unusual hydrolysis is discussed below.

The structure of bistrifluoromethyl disulphide was proved by establishing the number of trifluoromethyl groups present by the series of reactions now described. Bistrifluoromethyl disulphide was substantially unchanged when heated to 300° with hydrogen in the absence of a catalyst and neither trifluoromethanethiol nor fluoroform was detected. Partial decomposition of the disulphide to metal fluoride and sulphide without the formation of fluoroform was brought about in a single experiment with hydrogen and Raney nickel. Passage of bistrifluoromethyl disulphide over cobalt trifluoride at low temperature yielded trifluoromethylsulphur pentafluoride, however :

$$CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{CoF_3} CF_3{\cdot}SF_5$$

and indicated the presence of at least one CF_3 group. Structures for $C_2S_2F_6$ such as $CF_2(SF){\cdot}CF_2{\cdot}SF$ could not be completely eliminated, however, on basis of this fluorination reaction.

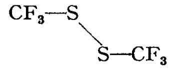
Treatment of bistrifluoromethyl disulphide with iodine at temperatures up to 290° failed to yield trifluoroiodomethane. The resistance of the CF_3–S bonds to fission by iodine may be compared with the ready conversion of trifluoromethyl derivatives of arsenic and phosphorus into trifluoroiodomethane at moderate temperatures (unpublished observations in this laboratory). The disulphide was stable to chlorine at 120°, but at higher temperatures sulphur chlorides and chlorotrifluoromethane were formed :

$$CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{Cl_2} 2CF_3Cl + S_2Cl_2,\ \text{etc.}$$

At 360°, more than 1·65 moles of chlorotrifluoromethane were formed per mole of bistrifluoromethyl disulphide, and on the basis of this reaction structures for $C_2S_2F_6$ which contained $-SF$, $=SF_2$, $-SF_3$, or $=SF-$ groups and might therefore have explained the ready attack by alkali, could be eliminated, since they contained no, or only one, CF_3 group.

The presence of two trifluoromethyl groups in the disulphide being established, it remained to show whether the sulphur atoms were arranged linearly or were branched, *i.e.*,

(I)



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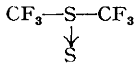
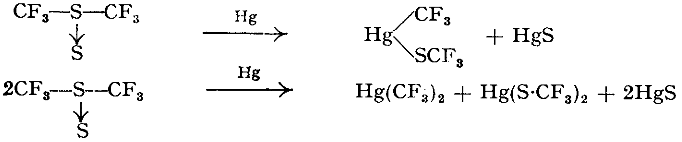


(II)

There is little evidence of branched sulphur chains in any of the known polysulphides. Electron-diffraction and *X*-ray data show that the sulphur chain normally has a zig-zag structure, although the possibility of isomerisation to the branched-chain structure on thermal or photochemical activation cannot be eliminated. Bistrifluoromethyl disulphide has a maximum absorption in the ultra-violet at 235 mμ (Part IV, following paper), and strong evidence for the absence of a branched chain was afforded (on the assumption of no isomerisation on irradiation) by its reaction with mercury in ultra-violet light to give a good yield of bis(trifluoromethylthio)mercury :

$$CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow{Hg} Hg(S{\cdot}CF_3)_2$$

Bistrifluoromethylmercury or trifluoromethyl(trifluoromethylthio)mercury which might be expected from structure (II) :



were not formed.

Bis(trifluoromethylthio)mercury resembles bistrifluoromethylmercury (Emeléus and Haszeldine, *loc. cit.*), since it is a white crystalline solid which sublimes readily at atmospheric pressure and is soluble in organic solvents but is also soluble in water, and is not decomposed by dilute nitric acid. These properties may be compared with those of bismethylthiomercury, which has a high melting point (175°) and is insoluble in water and most solvents (Klason, *Ber.*, 1887, **20**, 3410). Similarly, bisethylthiomercury (m. p. 76—77°) is only slightly soluble in hot alcohol and is insoluble in water (Otto, *Ber.*, 1880, **13**, 1289).

The evidence given above shows that the compound $C_2S_2F_6$ has the structure $CF_3{\cdot}S{\cdot}S{\cdot}CF_3$. This is also consistent with the infra-red absorption spectrum of the compound which is discussed in detail, together with its ultra-violet spectrum and spectra of $(CF_3)_2S$ and related compounds in Part IV (following paper).

The hydrolysis of bistrifluoromethyl disulphide by dilute alkali thus involves the destruction of two CF_3 groups. Compounds containing such groups can be divided into three classes, based on their reaction with aqueous alkali : (1) Those which show great stability, *e.g.*, $CF_3{\cdot}[CF_2]_n{\cdot}CF_3$, $C_6H_5{\cdot}CF_3$, CF_3Cl, CF_3Br, CF_3I, CF_3H, $CF_3{\cdot}O{\cdot}CF_3$, $CF_3{\cdot}S{\cdot}CF_3$, $CF_3{\cdot}SF_5$, $(CF_3)_3N$, $(CF_3)_2NF$, $CF_3{\cdot}NF_2$, $CF_3{\cdot}N{:}N{\cdot}CF_3$, $CF_3{\cdot}CO_2H$. (2) Those which liberate fluoroform, *e.g.*, $(CF_3)_3As$, $(CF_3)_3P$, $(CF_3)_3Sb$ (unpublished results, this laboratory), $CF_3{\cdot}CO{\cdot}CF_3$, $CF_3{\cdot}CHO$, $C_6H_5{\cdot}CO{\cdot}CF_3$. (3) Those which give fluoride ion, completely or partly, *e.g.*, $CF_3{\cdot}OF$, $(CF_3)_2As{\cdot}As(CF_3)_2$, $(CF_3)_2NH$, $CF_3{\cdot}O{\cdot}O{\cdot}CF_3$. Class (1) includes the majority of the CF_3 compounds now known, but Class (3), to which bistrifluoromethyl disulphide must now be added, has only a few members. Bistrifluoromethyl disulphide is the sulphur analogue of the bistrifluoromethyl peroxide isolated by Swarts (*Bull. Soc. chim. Belg.*, 1933, **42**, 102). This peroxide, although more stable to alkali than the disulphide, is slowly hydrolysed with complete decomposition. The peroxidic nature of the compound was established by its reaction with aqueous iodide solution :

$$CF_3{\cdot}O{\cdot}O{\cdot}CF_3 + 2I^- + 2H_2O \longrightarrow I_2 + 2CO_2 + 4HF + 2F^-$$

Bistrichloromethyl disulphide is also completely decomposed by aqueous alkali (Hell and Urech, *loc. cit.*) and the monosulphide is even more unstable (Feichtinger and Moos, *loc. cit.*). Since bistrifluoromethyl sulphide (see below) is stable to aqueous alkali, however, the instability of the chloro-compounds may be due to the instability of the CCl_3 group itself.

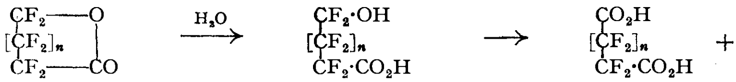
It is postulated that the hydrolysis of bistrifluoromethyl disulphide takes place by the mechanism :

$$\begin{tikzcd} \mathrm{CF_3{\cdot}S{\cdot}S{\cdot}CF_3} \arrow[r, "\mathrm{NaOH}"] & \mathrm{CF_3{\cdot}SH} \arrow[d] & + & \mathrm{CF_3{\cdot}S{\cdot}OH} \arrow[d] \\ \mathrm{F^-, CO_3^{=}, S^{=}} & \mathrm{F_2C{:}S + HF} \arrow[l] & & \mathrm{F^-, CO_3^{=}, S^{=}} \end{tikzcd}$$

that is, hydrolytic fission of the S–S bond by alkali to give trifluoromethanethiol and trifluoromethanesulphenic acid which react further to give fluoride, carbonate, and sulphides. Alternatively, since sulphur is liberated in the hydrolysis, we may have

$$\begin{tikzcd} \mathrm{CF_3{\cdot}S{\cdot}S{\cdot}CF_3} \arrow[r, "\mathrm{NaOH}"] & \mathrm{CF_3{\cdot}SH} \arrow[d] & + \mathrm{S} + & \mathrm{CF_3{\cdot}OH} \arrow[d] & \\ & \mathrm{F^-, CO_3^{=}, S^{=}} & & \mathrm{HF + F_2C{:}O} \arrow[r] & \mathrm{F^-, CO_3^{=}, S^{=}} \end{tikzcd}$$

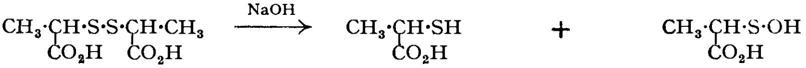
The mechanism for the hydrolysis of trifluoromethanethiol is analogous to that proposed for the decomposition of perfluoro-lactones (Haszeldine, *Nature*, 1951, **168**, 1028) :



Alkyl sulphides and disulphides are usually stable towards dilute alkali. At temperatures above 100°, however, the disulphide bond is broken and the initial products are probably mercaptides and sulphenic acids which react further with alkali to give mercaptides and sulphinates (Price and Twiss, *J.*, 1910, **97**, 1175; Schöberl, *Annalen*, 1933, **507**, 111; *Ber.*, 1934, **67**, 1545; *Naturwiss.*, 1935, **24**, 291) :

$$\mathrm{R{\cdot}S{\cdot}S{\cdot}R + KOH \longrightarrow R{\cdot}SK + R{\cdot}S{\cdot}OH}$$
$$\mathrm{2R{\cdot}S{\cdot}OH + 2KOH \longrightarrow R{\cdot}SK + R{\cdot}SO_2K + H_2O}$$

When the disulphide group has an adjacent negative group, *e.g.*, carboxyl (cf. CF_3), hydrolysis to sulphide takes place. Thus, dimethylthiodiglycollic acid with N-sodium hydroxide at 100° (Schöberl, *Ber.*, 1937, **70**, 1186) reacts as follows :



$$\mathrm{CH_3{\cdot}\underset{CO_2H}{CH}{\cdot}S{\cdot}S{\cdot}\underset{CO_2H}{CH}{\cdot}CH_3 \xrightarrow{NaOH} CH_3{\cdot}\underset{CO_2H}{CH}{\cdot}SH + CH_3{\cdot}\underset{CO_2H}{CH}{\cdot}S{\cdot}OH}$$

$$\mathrm{CH_3{\cdot}CH(S{\cdot}OH){\cdot}CO_2H \xrightarrow{NaOH} CH_3{\cdot}CO{\cdot}CO_2H + H_2S}$$

Bistrifluoromethyl disulphide is the main product from the reaction of trifluoroiodomethane with sulphur. Amongst the other products still under investigation are carbon disulphide, the polysulphides $CF_3{\cdot}S_3{\cdot}CF_3$ and $CF_3{\cdot}S_4{\cdot}CF_3$, and thiocarbonyl fluoride. The formation of the last compound apparently involves the glass of the reaction vessel since it is not formed in an autoclave reaction. It was not completely separated from the silicon tetrafluoride which was also formed in the reaction in glass vessels. The formation of thiocarbonyl fluoride is analogous to that of carbonyl fluoride from trifluoroiodomethane and oxygen in ultra-violet light (Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041) :

$$\mathrm{CF_3I \xrightarrow[h\nu]{O_2} COF_2 + \ldots}$$
$$\mathrm{CF_3I \xrightarrow[heat]{S} CSF_2 + \ldots}$$

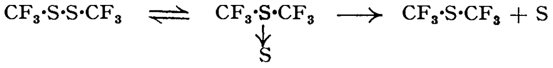
Thiocarbonyl fluoride is not formed when bistrifluoromethyl disulphide is heated to 250° (cf. the preparation of thiocarbonyl chloride from bistrichloromethyl disulphide). It has been reported (B.I.O.S. Final Report 1595, Item No. 22) that Ruff prepared carbonyl fluoride from carbon disulphide and iodide pentafluoride, but details have not yet been published.

The photolysis of bistrifluoromethyl disulphide in a silica vessel yields bistrifluoromethyl sulphide and sulphur:

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

apparently *via* the formation of an intermediate viscous liquid which on further irradiation changes into rhombic sulphur. Irradiation of bistrifluoromethyl disulphide in Pyrex glass gave no reaction as is to be expected from the ultra-violet spectrum (Part IV, where the infra-red spectrum is also recorded).

The mechanism of the photolysis of bistrifluoromethyl disulphide is not yet clear. Possibly irradiation leads to isomerisation of the disulphide followed by S→S bond fission:



$$CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \rightleftharpoons CF_3{\cdot}\underset{\underset{S}{\downarrow}}{S}{\cdot}CF_3 \longrightarrow CF_3{\cdot}S{\cdot}CF_3 + S$$

It seems, however, more probable that homolytic cleavage of the S–S bond occurs to give two $CF_3{\cdot}S{\cdot}$ free radicals, a view which is supported by the smooth formation of bis(trifluoromethylthio)mercury in the presence of mercury. To determine whether the photolysis of the disulphide involved attack on it by free trifluoromethyl radicals produced by carbon–sulphur bond fission, a mixture of it with trifluoroiodomethane was irradiated in Pyrex; it is known that the fluoroiodide produces trifluoromethyl radicals under such conditions. Neither bistrifluoromethyl sulphide nor hexafluoroethane was produced. A tentative reaction mechanism is:

$$\begin{array}{rcl}
CF_3{\cdot}S{\cdot}S{\cdot}CF_3 & \longrightarrow & 2CF_3{\cdot}S{\cdot} \\
CF_3{\cdot}S{\cdot} + CF_3{\cdot}S{\cdot}S{\cdot}CF_3 & \longrightarrow & CF_3{\cdot}S{\cdot}CF_3 + CF_3{\cdot}S{\cdot}S{\cdot} \\
CF_3{\cdot}S{\cdot}S{\cdot} & \longrightarrow & CF_3{\cdot}S{\cdot} + S \\
 & & \qquad\quad \downarrow \\
 & & \qquad\quad \text{etc.} \\
2CF_3{\cdot}S{\cdot}S{\cdot} & \longrightarrow & CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3 \\
CF_3{\cdot}S{\cdot} + CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3 & \longrightarrow & CF_3{\cdot}S{\cdot}CF_3 + CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot} \\
2CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot} & \longrightarrow & CF_3{\cdot}[S]_8{\cdot}CF_3,\ \text{etc.}
\end{array}$$

The formation of polysulphides would explain the intermediate viscous oil. The photolysis of bistrifluoromethyl disulphide is being investigated further.

Bistrifluoromethyl sulphide is a colourless liquid, b. p. $-22°$, which is perfectly stable to aqueous alkali at 150°. It thus differs sharply from the disulphide and indicates that the S–S bond is necessary to obtain complete destruction of the CF_3 groups.

EXPERIMENTAL

Preparation of Trifluoroiodomethane.—Trifluoroiodomethane was prepared by interaction of carbon tetraiodide and iodine pentafluoride (Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2190) or by interaction of iodine and silver trifluoroacetate (Haszeldine, *Nature*, 1950, **166**, 192; *J.*, 1951, 584).

Apparatus and Technique.—Volatile materials were manipulated in a vacuum system, and molecular weights were obtained by Regnault's method. B. p.s were calculated from vapour-pressure curves determined in isoteniscopes with temperatures measured by vapour-pressure thermometers. Small-scale reactions were carried out in Carius tubes of *ca.* 50-ml. capacity; reactions on a larger scale utilised a stainless-steel autoclave of 100-ml. capacity. Air was excluded from reactions, and all manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen.

Analysis was effected either by decomposition of the compound to fluoride ion by means of aqueous sodium hydroxide or by fusion with sodium at 600°, distillation of the fluoride as fluorosilicic acid, and titration with thorium nitrate solution.

Interaction of Sulphur and Trifluoroiodomethane.—(a) *In sealed tubes.* There was only slight reaction when trifluoroiodomethane and excess of sulphur were heated to 170° for 27 hours; after 48 hours at 205°, however, trifluoroiodomethane (4·0 g.) and sulphur (8·0 g.) underwent appreciable reaction and only 30% of the fluoroiodide was recovered unchanged. Reaction at 260—270° for 96 hours caused considerable attack on the glass with formation of silicon tetrafluoride.

The combined products from eight tubes of the type described above for reaction at 205° were fractionated to give (1) unchanged trifluoroiodomethane (20%), *M*, 196; (2) material boiling in the range $-30°$ to $-80°$ (20%); (3) b. p. *ca.* 34°/760 mm. (50%); (4) material, b. p. $>35°$ (10%). Iodine and a hard mass of sulphur–iodine mixture were left in the reaction vessels.

(b) *In an autoclave.* Trifluoroiodomethane (30 g.) and sulphur (25 g.) were charged into the autoclave, which was filled with nitrogen to atmospheric pressure before being sealed. After 30 hours' heating to 220°, *ca.* 10% reaction occurred; further heating to 265° for 24 hours brought about almost complete reaction. Distillation gave the fractions described above: (1) 3%, (2) 0%, (3) 70%, (4) 20%.

Bistrifluoromethyl Disulphide.—Redistillation of fraction (3) obtained as described above gave *bistrifluoromethyl disulphide* (60% yield in the autoclave) (Found: C, 11·2; F, 55·8; S, 31·8%; *M*, 202. $C_2F_6S_2$ requires C, 11·9; F, 56·4; S, 31·7%; *M*, 202), b. p. 34·6°, whose structure was proved by the reactions described below. Bistrifluoromethyl disulphide is a colourless dense liquid with a sharp odour, stable in air and glass. In direct light mercury is attacked very slowly with formation of mercuric sulphide. Analysis was effected by treatment of bistrifluoromethyl disulphide (0·2—0·3 g.) with 15% sodium hydroxide solution (5 ml.) in a sealed tube, whereupon sodium fluoride was rapidly precipitated and the solution became yellow. After the mixture had been kept at 50° for 12 hours no volatile material remained. The contents of the tube were treated with hydrogen peroxide solution (10 ml., 20-vol.) and heated to 100° for 2 hours. Aliquots were used to determine fluoride by distillation, and sulphur as sulphate after removal of fluoride by evaporation to dryness with concentrated hydrochloric acid.

Vapour Pressure of Bistrifluoromethyl Disulphide.—The vapour-pressure equation, calculated by the method of least squares, is $\log p$ (mm.) $= 7{\cdot}765 - 1503{\cdot}1/T$, whence the b. p. is calculated as 34·6°, the latent heat of vaporisation as 6880 cal./mole, and Trouton's constant as 22·4.

Examination of Fractions (2) *and* (4).—The material, b. p. $-80°$ to $-30°$, *M* 70—100, obtained by reaction of trifluoroiodomethane and sulphur in glass vessels contained silicon tetrafluoride and a volatile sulphur compound. The proportion of silicon tetrafluoride increased with the reaction temperature. Absorption by aqueous alkali was complete and silicic acid, sulphide, fluoride, and carbonate were then present in solution. The sulphur compound is *thiocarbonyl fluoride* but, even after prolonged rectification *in vacuo*, a sample completely free from silicon tetrafluoride could not be obtained (faintly positive test for Si) (Found: S, 38·8%; *M*, 82. CF_2S requires S, 39·0%; *M*, 82). The reactions of thiocarbonyl fluoride are being investigated.

The crude bistrifluoromethyl disulphide fraction often consisted of two layers. The small upper layer was separated by condensation of the mixture into a narrow tube, freezing the lower layer, and allowing the upper layer to evaporate *in vacuo* into a separate container. It was shaken with sodium hydroxide solution to remove traces of bistrifluoromethyl disulphide, redistilled, and shown to be carbon disulphide (*ca.* 3% yield) (Found: *M*, 73. Calc. for CS_2: *M*, 76), b. p. 46°.

The material with b. p. $>50°$ is rapidly decomposed by alkali into sulphides, fluoride, and carbonate and consists of polysulphides; it is being examined further.

Reaction of Bistrifluoromethyl Disulphide with Water, Alkali, and Hydrochloric Acid.—The disulphide is insoluble in, and not decomposed by, water or dilute acids at room temperature. The reaction with 15% sodium hydroxide has been described above; a similar but slower decomposition is brought about by N-sodium carbonate solution.

When the disulphide (0·1—0·2 g.) was heated in Carius tubes with 3N-hydrochloric acid (5 ml.) to 50° for 20 hours, to 100° for 48 hours, and to 200° for 48 hours, the amounts of disulphide recovered were 90, 40, and 0%, respectively. Elementary sulphur and fluoride ions were formed in the last two experiments, the walls of the vessels were etched, and the volatile products (carbon dioxide, and traces of silicon tetrafluoride and possibly carbonyl fluoride) were readily absorbed by alkali.

Reaction of Bistrifluoromethyl Disulphide with Hydrogen.—The disulphide (0·073 g.) and hydrogen (30 ml./650 mm.) were heated in a Carius tube from 100° up to 200° during 10 days. Distillation showed that 90% of the disulphide was unchanged. After 3 days at 300°, 87% of the bistrifluoromethyl disulphide was recovered.

Raney nickel (5 g.), thoroughly washed and carefully dried *in vacuo*, was sealed with bistrifluoromethyl disulphide (0·119 g.) and hydrogen (150 ml./650 mm.) and heated to 150° for 48 hours. Only 15% of the disulphide was recovered, but no fluoroform was obtained; the Raney nickel contained sulphide and fluoride.

Fluorination of Bistrifluoromethyl Disulphide.—Cobalt trifluoride was prepared by passage of fluorine over cobalt difluoride at 250° in a 15-cm. horizontal copper tube furnace; the amount of available fluorine was 12 g. During 8 hours bistrifluoromethyl disulphide (0·889 g.) was carried into the reaction vessel, heated to 150°, by a slow stream of nitrogen. Distillation *in vacuo* gave: (1) unchanged bistrifluoromethyl disulphide (10%), (2) carbon tetrafluoride (not estimated), (3) sulphur fluorides, etc. (0·20 g.; *M*, 101) completely decomposed by 15% sodium hydroxide solution, (4) material condensing *in vacuo* in a trap cooled to −130° (0·719 g.; *M*, 148). After further distillation, fraction (4) was treated with 15% sodium hydroxide solution (5 ml.) for 12 hours in a sealed tube to give, after distillation, trifluoromethylsulphur pentafluoride (0·209 g.; 12%) (Found: F, 76·2; S, 16·8%; *M*, 195. Calc. for CF_8S: F, 77·6; S, 16·3%; *M*, 196) whose vapour pressure could be represented by the equation $\log p$ (mm.) = $6{\cdot}71988 - 757{\cdot}795/T - 53791{\cdot}9/T^2$ reported by Silvey and Cady (*loc. cit.*). Sulphur was determined as barium sulphate after sodium fusion.

Reaction of Bistrifluoromethyl Disulphide with Iodine.—The disulphide (0·485 g.) and iodine (5 g.) were heated to 280° for 48 hours in a Carius tube; 75% of the disulphide was unchanged. Further heating at 290° for 48 hours failed to yield trifluoroiodomethane, and 41% of the bistrifluoromethyl disulphide was still unchanged.

Reaction of Bistrifluoromethyl Disulphide with Chlorine.—Bistrifluoromethyl disulphide (0·550 g.) was sealed with chlorine (1·0 g.) and heated to 120° for 3 days; chlorotrifluoromethane was not formed, and the bulk of the disulphide was recovered.

Chlorine (3·0 g.) and bistrifluoromethyl disulphide (0·777 g.) were heated to 160—210° for 30 hours and the volatile products were then passed through 25% sodium hydroxide solution to remove sulphur chlorides and excess of chlorine. Distillation then gave chlorotrifluoromethane (30%) (Found: *M*, 104. Calc. for $CClF_3$: *M*, 104·5), b. p. −81·7° (lit., −81·1°).

Treatment of the disulphide (0·279 g.) with chlorine (1·33 g.) in a sealed tube at 240—260° for 72 hours similarly gave light brown sulphur chlorides and chlorotrifluoromethane (50%) (Found: Cl, 33·1%; *M*, 104·5. Calc. for $CClF_3$: Cl, 34·0%; *M*, 104·5). Treatment of the sulphur chlorides fraction with a further quantity of chlorine at 250—260° for 4 days failed to yield more chlorotrifluoromethane.

When bistrifluoromethyl disulphide (0·202 g.) and chlorine (1·0 g.) were heated at 330—360° for 5 days in a Carius tube, chlorotrifluoromethane (*M*, 105) was formed in 83% yield.

Interaction of Bistrifluoromethyl Disulphide and Mercury.—(a) *On heating.* The disulphide (0·421 g.) and mercury (2 ml.) underwent no reaction at room temperature during 3 days. After 6 hours at 130°, no attack on the mercury could be observed, but after 3 days at 205° red and black solids had been formed. The volatile reaction products were recovered, *viz.*, bistrifluoromethyl disulphide (48%) and a mixture of silicon tetrafluoride and a volatile sulphur compound (probably thiocarbonyl fluoride) which was completely absorbed by aqueous alkali. Examination of the solid products of reaction failed to reveal the presence of a mercurial containing CF_3 groups.

(b) *On irradiation.* Bistrifluoromethyl disulphide (0·892 g.) and mercury (30 g.) were sealed in a silica tube of 100-ml. capacity. which was then shaken and irradiated for 4 days by unfiltered radiation from a Hanovia lamp (code name YEKUL; with an S250 U-type self-starting arc) at a distance of 10 cm. The walls of the tube were then lightly covered in a black powder (mercuric sulphide). The volatile product was bistrifluoromethyl sulphide (7%) (see below). The solid products were extracted with ether, the extract was dried (Na_2SO_4), and the ether evaporated at room temperature over silica gel. The solid residue was purified by sublimation at 65° at atmospheric pressure to give *bistrifluoromethylthiomercury* (0·931 g., 53%) (Found: F, 27·5; S, 16·0; Hg, 49·4. $C_2F_6S_2Hg$ requires F, 28·3; S, 15·9; Hg, 49·8%), translucent shiny plates, m. p. 37·5°. Analysis was effected by sodium fusion followed by determination of sulphur and fluorine, and by heating a sample with excess of nitric acid at 100° in a sealed tube followed by determination of mercury with thiocyanate.

The mercurial, which has a pungent odour, is soluble in water; mercuric ions could not be detected after dissolution of the substance in dilute nitric acid.

Reaction of Bistrifluoromethyl Disulphide with Trifluoroiodomethane.—(a) *On heating.* The disulphide (0·315 g.) and trifluoroiodomethane (4·0 g.) were heated in a sealed tube to 205° for 92 hours. Only a small amount of iodine and of hexafluoroethane (0·041 g.) (*M*, 138) were formed and the disulphide (0·314 g.) and fluoroiodide (3·8 g.) were recovered almost quantitatively.

(b) *On irradiation.* Trifluoroiodomethane (1·70 g.) and bistrifluoromethyl disulphide (0·315 g.) were irraidated in Pyrex glass for 30 days. A small amount of iodine was liberated. Distillation *in vacuo* removed *ca.* 80% of the disulphide, and treatment of the trifluoroiodomethane fraction with 15% sodium hydroxide solution to destroy disulphide, followed by redistillation, gave trifluoroiodomethane (1·66 g., 98%).

Preparation of Bistrifluoromethyl Sulphide by Irradiation of Bistrifluoromethyl Disulphide.—In a typical experiment, bistrifluoromethyl disulphide (1·140 g.) was irradiated for 13 days in a silica tube of 100-ml. capacity by a Hanovia lamp placed 10 cm. distant. As reaction proceeded, a viscous oil was deposited on the walls of the vessel and on further irradiation it crystallised to a yellow solid. The volatile products were distilled *in vacuo* to give: (1) bistrifluoromethyl disulphide (0·364 g., 32%) (*M*, 202), (2) volatile material (0·093 g., 8%) (*M*, 87), (3) *bistrifluoromethyl sulphide* (0·449 g., 39%) (Found: F, 67·2; S, 19·1%; *M*, 170. C_2F_6S requires F, 67·1; S, 18·8%; *M*, 170).

The yellow solid produced in the reaction was dissolved by carbon disulphide, the solution filtered, and the solvent evaporated to leave rhombic sulphur, m. p. 112·5°. Fraction (2) was completely decomposed by aqueous alkali and contained silicon tetrafluoride, carbon dioxide, and possibly thiocarbonyl fluoride.

The recovered disulphide [fraction (1)] was irradiated in a silica tube of 15-ml. capacity by ultra-violet light for 8 days, to give sulphur (*ca.* 10%), volatile material decomposed by alkali (5%), a non-volatile viscous oil (34%) on the wall of the tube, and bistrifluoromethyl sulphide (0·186 g., 52%). The total yield of bistrifluoromethyl sulphide was thus 0·635 g. (66%).

No reaction occurred when bistrifluoromethyl disulphide (0·310 g.) was sealed in a Pyrex tube and irradiated for 8 days, or when the disulphide and trifluoroiodomethane were similarly irradiated.

Properties of Bistrifluoromethyl Sulphide.—For analysis, the bistrifluoromethyl sulphide was freed from traces of the disulphide by treatment with aqueous alkali, then fused with sodium at 600°.

The vapour pressure of bistrifluoromethyl sulphide is given by the equation $\log p$ (mm.) = $7{\cdot}816 - 1239{\cdot}1/T$, whence the b. p. is calculated as $-22{\cdot}2°$, the latent heat of vaporisation as 5650 cal./mole, and Trouton's constant as 22·5.

When bistrifluoromethyl sulphide (0·244 g.) was treated with 15% sodium hydroxide (3 ml.) at room temperature, no reaction could be detected after 12 hours. After 20 hours at 100°, 98% of the sulphur compound was recovered unchanged, whilst after heating to 150° for 24 hours, over 97% of the bistrifluoromethyl sulphide was recovered.

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