Reactions of Chlorotrifluoromethyldisulphane

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Chlorotrifluoromethyldisulphane undergoes metathetical reactions with MeSH, EtSH, AcSH, CF3-C(O)SH, $CF_3 \cdot SH$, AgNCO, and $(CF_3)_2 C$:NLi to form MeS $\cdot S \cdot S \cdot CF_3$, EtS $\cdot S \cdot S \cdot CF_3$, AcS $\cdot S \cdot S \cdot CF_3$, $CF_3 \cdot C(0) \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot CF_3$, $CF_3 \cdot S \cdot S \cdot CF_3$, CF_3 which are formed by attack of CI and CF3SS on the olefin. With tetrafluoroethylene, hexafluoropropene, hexafluorocyclobutene, chlorotrifluoroethylene, and 1,2-dichloro-1,2-difluoroethylene, CF₃·S·S·CF₂·CF₂CI, CF₃·S·S·

 $CF(CF_3) \cdot CF_2CI, CF_3 \cdot S \cdot S \cdot CF_2 \cdot CFCI \cdot CF_3, CF_3 \cdot S \cdot S \cdot CF \cdot CF_2 \cdot CFCI, CF_3 \cdot S \cdot S \cdot CFCI \cdot CF_2CI, CF_3 \cdot S \cdot S \cdot CFCI_2, and CF_3 \cdot S \cdot S \cdot CFCI \cdot CFCI_2 were prepared. Only tetrafluoroethylene gives a higher telomer, CF_3 \cdot S \cdot S \cdot [CF_2 \cdot CF_2]_2CI.$ Insertion into the sulphur-sulphur bond does not occur.

THE preparation and characterisation of chlorotrifluoromethyldisulphane has been reported recently.¹ Direct fluorination techniques could not be used to prepare this compound from its chlorinated analogue owing to the ease of sulphur-sulphur bond rupture and the simultaneous oxidation of sulphur. A method established by Feher² was utilized to produce this precursor of some novel mixed polyfluoroalkyl-di- and -trisulphanes,

RESULTS AND DISCUSSION

Trisulphanes.—The preparation of bis(polyfluoroalkyl)trisulphanes has generally been limited to methods which involve the reaction of sulphur with polyfluoroalkyl iodides ^{3,4} or olefins ^{4,5} at high temperatures and which produce numerous other sulphides and polysulphanes. While these methods usually can be used to prepare symmetric trisulphanes, e.g. CF₃I and sulphur are used to produce bis(trifluoromethyl)trisulphane, there has been no convenient route reported for the synthesis of non-symmetric polyfluoroalkyltrisulphanes. Reactions of chlorotrifluoromethyldisulphane, which behaves as a relatively reactive acid chloride, provide a convenient route to new trisulphanes.

Methanethiol, ethanethiol, thioacetic acid, trifluorothioacetic acid, and trifluoromethanethiol react smoothly with CF₃·S·SCl to produce the respective trisulphanes, CF_3 ·S·S·SMe, CF_3 ·S·S·SEt, AcS·S·S·CF₃, CF_3 ·C(0)S·S·S·- CF_3 , and $CF_3 \cdot S \cdot S \cdot CF_3$ in high yields. In contrast to the data presented below and those reported ⁵ for disulphanes, there is no spin-spin coupling of proton or fluorine substituents across the trisulphane linkage. A low temperature ¹H and ¹⁹F n.m.r. spectral study of methyltrifluoromethyltrisulphane demonstrates that no conformation arises where interaction can occur across the sulphur bonds, even when rotation about the bonds is substantially reduced.

The gas-phase reaction of hydrogen sulphide with CF₃·S·SCl produces high yields of bis(trifluoromethyl)pentasulphane even when the ratio of H₂S to CF₃·S·SCl is large. Under various conditions, reactions of CF₃-S-SCl with polyfluoro-alcohols, NN-bis(trifluoromethyl)-

¹ N. R. Zack and J. M. Shreeve, Inorg. Nuclear Chem. Letters, 1974, **10**, 619.

³ G. A. R. Brandt, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1952, 2198.

⁴ G. G. Krespan and C. M. Longkammer, J. Org. Chem., 1962, 27, 3584.

hydroxylamine, and trifluoroacetic acid failed to yield the analogous substitution products.

Disulphanes.—Dimethylamine reacts with the active chlorine of CF_3 ·S·SCl (2:1 molar ratio) to produce dimethylaminotrifluoromethyldisulphane. The ¹H and $^{19}\mathrm{F}$ n.m.r. spectra show a quartet centred at δ 2.66 for the methyl protons and a septet at 42.8 p.p.m. for the trifluoromethyl group, respectively. As the temperature is lowered, no change occurs in the ¹⁹F spectrum. The amino-disulphane reacts with HCl to regenerate CF₃·S·SCl.

 CF_3 ·S·SCl will undergo metathetical reactions with several salts. Bis(trifluoromethylthio)mercury reacts quantitatively to produce CF3.S.S.S.CF3, and metallic mercury decomposes the disulphane to HgS and unidentified solid products. The reaction of silver salts with CF₃·S·SCl provides a convenient method of preparing perfluoropseudohalogenoids.⁶ Silver cyanide forms the previously reported ⁷ unstable CF₃·S·S·CN, which decomposes at 25° . Freshly prepared silver isocyanate is used to synthesise CF₃·S·S·NCO. I.r. and n.m.r. spectral data indicate that only the monomer is formed at room temperature.

The reaction of lithium salts with CF₃·S·SCl provides a means of introducing the CF₃SS unit into usually unreceptive systems. The lithio-imine (I)⁸ reacts with CF₃·S·SCl to form the disulphane (II) in high yield. Other lithium salts can be employed to form

$$(CF_3)_2C:NLi \xrightarrow{CF_3:SCI} CF_3:S:S:N:C(CF_3)_2 + LiCi$$
(I)
(II)

non-symmetric disulphanes, e.g. n-butyl-lithium forms CF_3 ·S·SBuⁿ in moderate yield (68%).

Alkali metal fluorides either do not react with CF₃·S·-SCl or cause it to decompose to CF3.S.S.CF3 or CF3.-S·S·S·CF₃. No evidence for the formation of CF_3 ·S·SF was obtained under the conditions employed. Although the use of chlorine monofluoride as an oxidising agent for sulphur-containing compounds is well established,⁹ ClF severs the sulphur-sulphur bond to form CF₃·SF₃,

⁵ C. G. Krespan and W. R. Brasen, J. Org. Chem., 1962, 27, 3995.

² F. Feher and D. Grodau, Z. Naturforsch., 1971, 26b, 614.

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7 H. J. Emeléus and A. Haas, J. Chem. Soc., 1963, 1273.
8 R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, *Inorg. Chem.*, 1972, 11, 242.
9 D. T. Sauer and J. M. Shreeve, J. Fluorine Chem., 1971/72, 1, 1; T. Abe and J. M. Shreeve, *ibid.*, 1973/74, 3, 187.

SF₄, and Cl₂, at 0, -78, and -120° in either a metal or a glass vessel.

The ease with which the sulphur-chlorine bond of CF₂·S·SCl is broken suggests that insertion of inorganic materials into this bond should occur. However, irradiation of CF₃·S·SCl in the presence of a large excess of SF_4 , PF_3 , or SO_2 failed to give products which would be expected from insertion into either the S-Cl or the S-S bond.

Harris ^{10,11} has shown that trifluoromethanesulphenyl chloride and trifluoromethanethiol add across polyfluoro-olefins by a free-radical process involving cleavage of the S-Cl and S-H bonds, respectively. For CF₃·SCl, the major attacking species is considered to be Cl., and CF_3S assumes that role for CF_3SH . Sharp and his co-workers 12 studied the reactions of chlorotetrafluoro(trifluoromethyl)sulphur with olefins and found, that under photolytic conditions, CF_3SF_4 is the attacking radical. Thermal reactions of fluoro-olefins with disulphur dichloride carried out by Knunyants et al.¹³ resulted in severing of the S-S bond and the S-Cl bond as well as rearrangement of the products.

Analogous to CF₃·SCl, CF₃·S·SCl reacts with polyhalogeno-olefins in Pyrex vessels when exposed to sunlight or a medium-pressure u.v. source to give new non-symmetric disulphanes in yields of 10-60%. No trisulphanes or products derived from cleavage of the sulphur-sulphur bond of CF₃·S·SCl are obtained. Highest yields of addition products are obtained when the olefins used are totally fluorinated, and the yields decrease rapidly as fluorine is replaced by chlorine or hydrogen. No reaction occurs without photolysis.

When tetrafluoroethylene reacts with CF₃·S·SCl, the adducts $CF_3 \cdot S \cdot S \cdot [CF_2 \cdot CF_2]_n Cl$ (n = 1 or 2) are formed. No higher telomers are detected. With the other olefins, telomerisation does not occur. These m/e 330 is observed in the mass spectrum of the adduct formed with the latter. The two possible structural isomers (IIIa and b) expected from the reaction with CF, CFCl were not separable by g.l.c. but were clearly identifiable by their ¹⁹F n.m.r. spectra. Compound (IIIa) constitutes 80% of the total addition products found. Initial radical attack in radical additions to perfluoro-olefins usually occurs on the terminal CF₂ group but various factors (steric effects, stability of intermediate radical, electronic character of the radical, etc.) influence orientation of the attacking reagent so that mixtures are often obtained. Addition products in this case indicate that both CF3.S.S. and Cl. must participate in initiating the reaction sequence (Scheme 1). Reaction (iii) must be of lesser importance than (ii) since (IIIb) is formed in low yield and no

$$CF_{3} \cdot S \cdot SCl \xrightarrow{h\nu} CF_{3} \cdot S \cdot S + Cl \qquad (i)$$

$$CI \cdot + CF_{2} \cdot CFCl \longrightarrow CF_{2}Cl \cdot CFCl \xrightarrow{CF_{3} \cdot S \cdot SCl} CF_{2}Cl \cdot CFCl \cdot S \cdot S \cdot CF_{3} \qquad (ii)$$

$$(IIIa)$$

$$CF_{3} \cdot S \cdot S + CF_{2} \cdot CFCl \longrightarrow CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot CFCl \xrightarrow{CF_{3} \cdot S \cdot S} CF_{2} \cdot CFCl_{2} \qquad (iii)$$

$$(IIIb)$$

$$SCHEME 1$$

 $CF_3 \cdot S \cdot S \cdot CF_2 \cdot CFC1 \cdot S \cdot S \cdot CF_3$ is isolated. Small amounts of $CF_2Cl \cdot CFCl_2$ and $CF_3 \cdot S \cdot S \cdot S \cdot S \cdot CF_3$ are formed.

The reaction of CF3.S.SCl with hexafluoropropene is analogous. The major isomer formed is CF3.S.CF- (CF_3) ·CF₂Cl, which suggests that most often the initial attack is by Cl. on the terminal CF₂ group to form the more stable intermediate radical, $ClCF_2 \cdot CF(CF_3)$.¹⁵ However, radical additions to unsymmetrical fluoroolefins are frequently bidirectional, especially when heteroatom radicals are involved.¹⁶ Since the products

$$Cl \cdot + CF_{3} \cdot CF; CF_{2} \xrightarrow{major} ClCF_{2} \cdot \mathring{C}F \cdot CF_{3} + CF_{3} \cdot CFCl \cdot \mathring{C}F_{2}$$

$$(minor)$$

$$(minor)$$

$$CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \xrightarrow{minor} CF_{3} \cdot S \cdot S \cdot CF(CF_{3}) \cdot \mathring{C}F_{2} + CF_{3} \cdot S \cdot S \cdot CF_{2} \cdot \mathring{C}F \cdot CF_{3}$$

$$(CF_{3} \cdot S \cdot S + CF_{3} \cdot CF; CF_{2} \cdot S \cdot S \cdot CF_{3} \cdot CF_{3}$$

results are in contrast to the olefin addition reactions of CF_3 ·S·CF₃,¹⁴ which with C_2F_4 , gives as main products the adducts $CF_3 \cdot S[CF_2 \cdot CF_2]_n SCF_3$ (n = 2 and a large number). A 1 : 1 adduct is not reported.

Photolysis of CF₃·S·SCl in the presence of chlorotrifluoroethylene or 1,2-dichloro-1,2-difluoroethylene produces disulphanes in low yields. A molecular ion at

¹⁰ J. F. Harris, J. Amer. Chem. Soc., 1962, 84, 3148.

¹¹ J. F. Harris and F. W. Stacey, J. Amer. Chem. Soc., 1961, 83, 840.

¹² J. I. Darragh, G. Haran, and D. W. A. Sharp, J.C.S. Dalton, 1973, 2289.

from the CF₂:CFCl reaction show that both CF·S·S· and Cl. attack the olefin, it is likely that the products from the hexafluoropropene reaction are formed via bidirectional addition of both attacking species (Scheme 2). Compound (IVa) constitutes 70% of the total

- ¹⁶ R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley, New York, 1973, pp. 173-176 and references therein.

¹³ I. L. Knunyants and A. V. Fokin, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1966, 627; I. L. Knunyants and E. G. Vykhous-kaya, *ibid.*, 1955, 769.
 ¹⁴ G. Haran and D. W. A. Sharp, J.C.S. Perkin I, 1972, 34.
 ¹⁵ R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1957, 2193.

addition products. The 17 eV mass spectrum of (IVa) contains an intense peak at m/e 85 {[CF₂Cl]⁺} and a peak at m/e 233 {[CF₃SSCF(CF₃)]⁺}. A peak at m/e183 {[CF₃SSCF₂]⁺} is observed in the spectrum of (IVb). The mass and ¹⁹F n.m.r. spectra confirm the structural assignments for (IVa and b).

Photolysis of CF_3 ·S·SCl in the presence of ethylene through Pyrex yields only the monosulphur addition product, CF₃·S·CH₂·CH₂Cl,¹¹ and sulphur. Similarly, no addition occurs in the reaction with (CF₃)₂C:NH; the major products are bis(trifluoromethyl)disulphane and disulphur dichloride. Reaction of CF₃·S·SCl with hexafluorocyclobutene produces a compound, CF₃·S·S·-

 $\dot{C}F \cdot CF_2 \cdot CF_2 \cdot \dot{C}FCl$, with a complex n.m.r. spectrum similar to that of the product of addition of CF₃·O·OF to octafluorocyclopentene.¹⁷

All the foregoing reactions of CF₃·S·SCl with olefins were also studied under thermal conditions. After 3 h at 220°, only tetrafluoroethylene formed an addition product (32% yield). At 125°, for longer periods, a small amount of product was formed with C_2F_4 ; no reaction occurred with the other olefins tested.

Although telomers are observed only with the tetrafluoroethylene reaction, the olefin addition reactions do occur via a free-radical process involving formation of CF₃S·S· and Cl· by photolysis through Pyrex. Particularly in the reactions involving the polychloroolefins, CF_3 ·S·S·S·S·CF₃ is observed as a major product, and some Cl₂ addition products are also formed. Such a free-radical process must be closely related to those outlined in the literature.^{11,13}

The reactions of CF₃·S·SCl with olefins are analogous to those recently reported for CF_3 ·O·OCl.¹⁸ The peroxy-compound is far more reactive in that it adds across olefinic double bonds below -78° .

EXPERIMENTAL

A standard Pyrex high-vacuum system equipped with a Heise-Bourdon tube gauge was used in all manipulations. Quantities of gaseous materials were measured on the assumption of ideal gas behaviour. I.r. spectra were recorded on Perkin-Elmer 237 and 457 spectrometers. A Varian HA-100 spectrometer (internal references tetramethylsilane and trichlorofluoromethane as needed) was used to obtain ¹H and ¹⁹F n.m.r. spectral data. Mass spectra were recorded with a Perkin-Elmer RMU-6E spectrometer operating at 17 and 70 eV. Molecular weights were determined generally by mass spectrometry.

All reaction materials are available commercially and,

with the exception of AgOCN, were used as received. The latter was prepared before each reaction.¹⁹ CF₃·S·SCl was obtained as previously described.1 All new compounds were purified by g.l.c. (gas injection system; 2.3, 2.7, and 4.2 m columns of 20% Kel-F on Chromosorb P or 0.8 m column of 15% DMS on Chromosorb P).

Equimolar quantities of CF₃·S·SCl and thiols or acids were condensed together into small glass vessels and allowed to remain at 20° for 0.5 h, after which the mixture was fractionated. As indicated by the disappearance of the yellow colour due to CF₃·S·SCl, reactions were complete within 5 min.

Salt reactions were carried out by condensing a known amount of CF_3 ·S·SCl onto an excess of the dried salt in a glass or stainless steel vessel, with the exception of the reaction of (CF₃)₂C:NLi, in which CF₃·S·SCl was used in slight excess. The reactants were then allowed to warm slowly from -196 to 20° and the product mixture was separated and examined.

Preparation of the disulphanes from olefins was generally accomplished by placing equimolar quantities of CF₃·S·SCl and the olefin in a 350 ml Pyrex vessel and irradiating the mixture with sunlight or a Hanovia utility ultraviolet quartz lamp for 16-24 h. Usually mixtures were irradiated until no further change was observed in the yellow colour. Thermal reactions were attempted by condensing a slight excess of the olefin with CF₃·S·SCl into a small glass tube, which was sealed and placed in a controlled temperature oven for 3-12 h. The polychloro-olefin and hexafluorocyclobutene addition products could not be separated from CF₃·S·S·S·CF₃ by either low temperature distillation or g.l.c. techniques.

With the exception of CF_3 ·S·S·NCO, all the new polysulphanes are stable in air and at room temperature. They are colourless, evil-smelling compounds and probably extremely toxic.

Elemental analyses were obtained from Mikroanalytisches Laboratorium Beller. These data, as well as i.r., mass, and n.m.r. spectra data, are available as Supplementary Publication No. SUP 21247 (3 pp.).†

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† For details of Supplementary Publications, see Notice to Authors No. 7 in J.C.S. Perkin I, 1974, Index issue.

¹⁷ F. A. Hohorst, Ph.D. Thesis, Northeastern University, 1973.

¹⁸ D. D. DesMarteau, F. A. Hohorst, and N. Walker, presented at the 7th International Symposium on Fluorine Chemistry, Santa Cruz, California, July 1973. ¹⁹ R. G. Neville and J. J. McGee. Inorg. Synth., 1966. 8, 23.

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