Reactions of Chlorotrifluoromethyldisulphane

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Chlorotrifluoromethyldisulphane undergoes metathetical reactions with MeSH, EtSH, AcSH, $CF_3{\cdot}C(O)SH$, $CF_3{\cdot}SH$, AgNCO, and $(CF_3)_2C{:}NLi$ to form $MeS{\cdot}S{\cdot}S{\cdot}CF_3$, $EtS{\cdot}S{\cdot}S{\cdot}CF_3$, $AcS{\cdot}S{\cdot}S{\cdot}CF_3$, $CF_3{\cdot}C(O)S{\cdot}S{\cdot}S{\cdot}CF_3$, $CF_3S{\cdot}S{\cdot}S{\cdot}CF_3$, $CF_3{\cdot}S{\cdot}S{\cdot}NCO$, and $CF_3{\cdot}S{\cdot}S{\cdot}N{:}C(CF_3)_2$, respectively. Free-radical addition to olefins gives products which are formed by attack of Cl· and $CF_3SS{\cdot}$ on the olefin. With tetrafluoroethylene, hexafluoropropene, hexafluorocyclobutene, chlorotrifluoroethylene, and 1,2-dichloro-1,2-difluoroethylene, $CF_3{\cdot}S{\cdot}S{\cdot}CF_2{\cdot}CF_2Cl$, $CF_3{\cdot}S{\cdot}S{\cdot}CF(CF_3){\cdot}CF_2Cl$, $CF_3{\cdot}S{\cdot}S{\cdot}CF_2{\cdot}CFCl{\cdot}CF_3$, $CF_3{\cdot}S{\cdot}S{\cdot}\overline{CF{\cdot}CF_2{\cdot}CF_2{\cdot}CFCl}$, $CF_3{\cdot}S{\cdot}S{\cdot}CFCl{\cdot}CF_2Cl$, $CF_3{\cdot}S{\cdot}S{\cdot}CF_2{\cdot}CFCl_2$, and $CF_3{\cdot}S{\cdot}S{\cdot}CFCl{\cdot}CFCl_2$ were prepared. Only tetrafluoroethylene gives a higher telomer, $CF_3{\cdot}S{\cdot}S{\cdot}[CF_2{\cdot}CF_2]_2Cl$. 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 Feher [2] 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.* CF_3I 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 $CF_3{\cdot}S{\cdot}SCl$ to produce the respective trisulphanes, $CF_3{\cdot}S{\cdot}S{\cdot}SMe$, $CF_3{\cdot}S{\cdot}S{\cdot}SEt$, $AcS{\cdot}S{\cdot}S{\cdot}CF_3$, $CF_3{\cdot}C(O)S{\cdot}S{\cdot}S{\cdot}CF_3$, and $CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3$ 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 ^{19}F 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 $CF_3{\cdot}S{\cdot}SCl$ produces high yields of bis(trifluoromethyl)pentasulphane even when the ratio of H_2S to $CF_3{\cdot}S{\cdot}SCl$ is large. Under various conditions, reactions of $CF_3{\cdot}S{\cdot}SCl$ with polyfluoro-alcohols, *NN*-bis(trifluoromethyl)hydroxylamine, and trifluoroacetic acid failed to yield the analogous substitution products.

Disulphanes.—Dimethylamine reacts with the active chlorine of $CF_3{\cdot}S{\cdot}SCl$ (2 : 1 molar ratio) to produce dimethylaminotrifluoromethyldisulphane. The ^1H and ^{19}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 ^{19}F spectrum. The amino-disulphane reacts with HCl to regenerate $CF_3{\cdot}S{\cdot}SCl$.

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

The reaction of lithium salts with $CF_3{\cdot}S{\cdot}SCl$ provides a means of introducing the CF_3SS unit into usually unreceptive systems. The lithio-imine (I) [8] reacts with $CF_3{\cdot}S{\cdot}SCl$ to form the disulphane (II) in high yield. Other lithium salts can be employed to form non-symmetric disulphanes, *e.g.* n-butyl-lithium forms $CF_3{\cdot}S{\cdot}SBu^n$ in moderate yield (68%).

$$\underset{\text{(I)}}{(CF_3)_2C{:}NLi} \xrightarrow{CF_3{\cdot}S{\cdot}SCl} \underset{\text{(II)}}{CF_3{\cdot}S{\cdot}S{\cdot}N{:}C(CF_3)_2} + LiCl$$

Alkali metal fluorides either do not react with $CF_3{\cdot}S{\cdot}SCl$ or cause it to decompose to $CF_3{\cdot}S{\cdot}S{\cdot}CF_3$ or $CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3$. No evidence for the formation of $CF_3{\cdot}S{\cdot}SF$ 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 $CF_3{\cdot}SF_3$,

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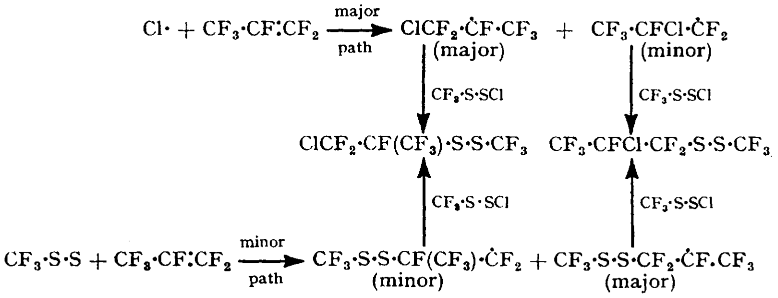
SF_4, and Cl_2, at 0, −78, and −120° in either a metal or a glass vessel.

The ease with which the sulphur–chlorine bond of $CF_3{\cdot}S{\cdot}SCl$ is broken suggests that insertion of inorganic materials into this bond should occur. However, irradiation of $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}SCl$, the major attacking species is considered to be Cl•, and $CF_3S{\cdot}$ assumes that role for $CF_3{\cdot}SH$. Sharp and his co-workers [12] studied the reactions of chlorotetrafluoro(trifluoromethyl)sulphur with olefins and found, that under photolytic conditions, $CF_3SF_4{\cdot}$ 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 $CF_3{\cdot}SCl$, $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}SCl$, the adducts $CF_3{\cdot}S{\cdot}S{\cdot}[CF_2{\cdot}CF_2]_nCl$ ($n = 1$ or 2) are formed. No higher telomers are detected. With the other olefins, telomerisation does not occur. These results are in contrast to the olefin addition reactions of $CF_3{\cdot}S{\cdot}S{\cdot}CF_3$,[14] which with C_2F_4, gives as main products the adducts $CF_3{\cdot}S[CF_2{\cdot}CF_2]_nSCF_3$ ($n = 2$ and a large number). A 1 : 1 adduct is not reported.



SCHEME 2

Photolysis of $CF_3{\cdot}S{\cdot}SCl$ in the presence of chlorotrifluoroethylene or 1,2-dichloro-1,2-difluoroethylene produces disulphanes in low yields. A molecular ion at *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 $CF_2{:}CFCl$ were not separable by g.l.c. but were clearly identifiable by their ^{19}F 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 CF_2 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 $CF_3{\cdot}S{\cdot}S{\cdot}$ 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 $CF_3{\cdot}S{\cdot}S{\cdot}CF_2{\cdot}CFCl{\cdot}S{\cdot}S{\cdot}CF_3$ 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.

$$CF_3{\cdot}S{\cdot}SCl \xrightarrow{h\nu} CF_3{\cdot}S{\cdot}S{\cdot} + Cl \qquad \text{(i)}$$

$$Cl{\cdot} + CF_2{:}CFCl \longrightarrow CF_2Cl{\cdot}\dot{C}FCl \xrightarrow{CF_3{\cdot}S{\cdot}SCl} \underset{\text{(IIIa)}}{CF_2Cl{\cdot}CFCl{\cdot}S{\cdot}S{\cdot}CF_3} \qquad \text{(ii)}$$

$$CF_3{\cdot}S{\cdot}S + CF_2{:}CFCl \longrightarrow CF_3{\cdot}S{\cdot}S{\cdot}CF_2{\cdot}\dot{C}FCl \xrightarrow{CF_3{\cdot}S{\cdot}SCl} \underset{\text{(IIIb)}}{CF_3{\cdot}S{\cdot}S{\cdot}CF_2{\cdot}CFCl_2} \qquad \text{(iii)}$$

SCHEME 1

The reaction of $CF_3{\cdot}S{\cdot}SCl$ with hexafluoropropene is analogous. The major isomer formed is $CF_3{\cdot}S{\cdot}S{\cdot}CF(CF_3){\cdot}CF_2Cl$, which suggests that most often the initial attack is by Cl• on the terminal CF_2 group to form the more stable intermediate radical, $ClCF_2{\cdot}\dot{C}F(CF_3)$.[15] However, radical additions to unsymmetrical fluoro-olefins are frequently bidirectional, especially when heteroatom radicals are involved.[16] Since the products from the $CF_2{:}CFCl$ reaction show that both $CF{\cdot}S{\cdot}S{\cdot}$ 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

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addition products. The 17 eV mass spectrum of (IVa) contains an intense peak at *m/e* 85 $\{[CF_2Cl]^+\}$ and a peak at *m/e* 233 $\{[CF_3SSCF(CF_3)]^+\}$. A peak at *m/e* 183 $\{[CF_3SSCF_2]^+\}$ is observed in the spectrum of (IVb). The mass and ^{19}F n.m.r. spectra confirm the structural assignments for (IVa and b).

Photolysis of $CF_3{\cdot}S{\cdot}SCl$ in the presence of ethylene through Pyrex yields only the monosulphur addition product, $CF_3{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$,[11] and sulphur. Similarly, no addition occurs in the reaction with $(CF_3)_2C{:}NH$; the major products are bis(trifluoromethyl)disulphane and disulphur dichloride. Reaction of $CF_3{\cdot}S{\cdot}SCl$ with hexafluorocyclobutene produces a compound, $CF_3{\cdot}S{\cdot}S{\cdot}\overline{CF{\cdot}CF_2{\cdot}CF_2{\cdot}C}FCl$, with a complex n.m.r. spectrum similar to that of the product of addition of $CF_3{\cdot}O{\cdot}OF$ to octafluorocyclopentene.[17]

All the foregoing reactions of $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3S{\cdot}S{\cdot}$ and $Cl{\cdot}$ by photolysis through Pyrex. Particularly in the reactions involving the polychloro-olefins, $CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3$ is observed as a major product, and some Cl_2 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 $CF_3{\cdot}S{\cdot}SCl$ with olefins are analogous to those recently reported for $CF_3{\cdot}O{\cdot}OCl$.[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 ^{19}F 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] $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}SCl$, reactions were complete within 5 min.

Salt reactions were carried out by condensing a known amount of $CF_3{\cdot}S{\cdot}SCl$ onto an excess of the dried salt in a glass or stainless steel vessel, with the exception of the reaction of $(CF_3)_2C{:}NLi$, in which $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}SCl$ 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 $CF_3{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}CF_3$ by either low temperature distillation or g.l.c. techniques.

With the exception of $CF_3{\cdot}S{\cdot}S{\cdot}NCO$, 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.

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