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Trifluoromethylthiolation of aromatic substrates using thiophosgene—fluoride salt reagents, and formation of byproducts with multi-carbon chains

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Abstract

Reaction of potassium fluoride or tetramethylammonium fluoride with thiophosgene leads to the formation of a nucleophilic source of trifluoromethanethiolate, suitable for the preparation of trifluoromethyl aryl sulfides from activated haloaromatics. Analysis of the by-products in the system demonstrates that complex molecules with up to C_4 chains may be formed by the reaction of fluoride salts with thiophosgene.

Keywords: Trifluoromethylthio; Tetramethylammonium fluoride (TMAF); Dithiine; Dithione

1. Introduction

Trifluoromethyl aryl sulfides are important target molecules for the pharmaceutical and agrochemical industries [1,2], because of the lipophilicity [3] and electronic effects [4] imparted by the $–SCF_3$ group. These compounds have traditionally been prepared using Swartz chemistry which involves photochemical chlorination of a methyl aryl sulfide followed by fluorination with either anhydrous HF at high pressure and temperature, or SbF_3 [1,2]. As these harsh reaction conditions limit the variety of other functional groups which may be attached to the ring, several milder methods have been developed, including the use of trifluoromethanesulfenyl chloride and substituted aromatics [5], and Grignard reagents [6]. Nucleophilic sources of trifluoromethanethiolate include $Hg(SCF_3)_2$ [7,8], and $CuSCF_3$ [9–12], both of which have been used in the preparation of aryl trifluoromethyl sulphides. $AgSCF_3$ is only suitable for reactions with highly polarised C–X bonds, reacting, for example, with benzotrichloride to form the trithiolated product, $PhC(SCF_3)_3$ [13].

Dmowski and Haas [14,15] found that potassium and cesium trifluoromethanethiolates may be formed at low (−15°C) temperatures from the reaction of thiocarbonyl fluoride (F_2CS) with the alkali metal fluoride, and used this to introduce $–SCF_3$ groups to pentafluoropyridine, tetrafluoropyridazine and tetrafluoropyrimidine, although large scale reactions gave a red-brown polymeric tar as a by-product. We recently reported that the reaction between thiophosgene (Cl_2CS) and KF provides a cheap and convenient source of trifluoromethanethiolate anion in solution, which can be used to perform nucleophilic aromatic substitution reactions on activated aromatic substrates [16] (Scheme 1). We have now investigated this reaction in more detail, and have investigated the effects of using an organic fluoride source in place of KF, and studied the by-products formed.

2. Results and discussion

2.1. The reactions of thiophosgene with tetramethylammonium fluoride (TMAF) and potassium fluoride

The reaction of haloaromatics with Cl_2CS and KF was found to be limited to substrates which are highly activated to nucleophilic substitution [16]. Although product yields for the relatively inactive substrate, 2-chloro-5-nitrobenzonitrile, could be improved by heating the reaction, this also decreased the selectivity of the reaction. The $KSCF_3$ formed in situ decomposes on warming, forming F_2CS and KF, and this is likely to thwart attempts to extend the range of

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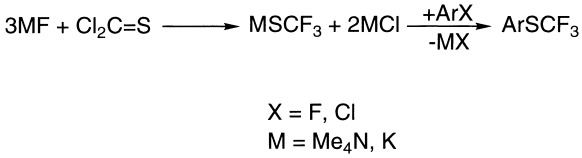


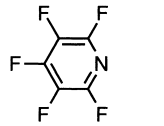
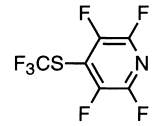
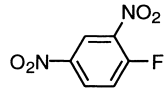
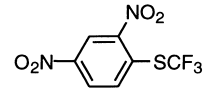
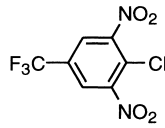
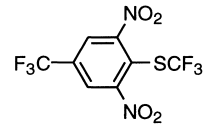
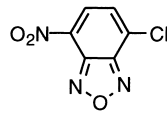
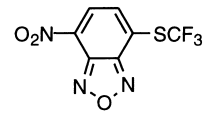
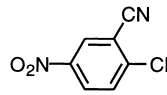
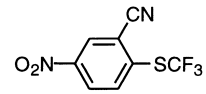
Scheme 1.

substrates simply by heating the reaction. We thought that a bigger cation might help stabilise the relatively large trifluoromethanethiolate anion. Since the reaction needs to be performed under anhydrous conditions, tetramethylammonium fluoride (TMAF) was chosen as this may be dried efficiently [17].

When Cl_2CS was added to a suspension of dry TMAF (three equivalents) in acetonitrile at −15°C, the reaction mixture rapidly turned pink, indicating the formation of $(F_3CS)_2CS$ (which has been reported elsewhere as being red when undiluted [18,19]): the presence of this compound was confirmed by ^{19}F NMR spectroscopy and GCMS. By the time the reaction had warmed to −10°C, it had taken on a dark brown colour, and showed a large number of peaks in the ^{19}F NMR spectrum. By contrast, the reaction between Cl_2CS and KF does not turn pink until it reaches 0°C. TMAF is a more active source of fluoride than KF, in terms of both nucleophilicity and basicity [20], and fluoride is known to catalyse the condensation of thiocarbonyl fluoride [18]. The lower temperature for formation of condensation products demonstrates that the greater activity of the TMAF outweighs any stabilisation effects imparted by use of the larger cation. Addition of dichloromethane to the TMAF/Cl_2CS solution causes precipitation of tetramethylammonium chloride, (the identity of which was confirmed by infrared spectroscopy and $AgNO_3$ titration), indicating that salt formation is the fate of the thiophosgene's chlorine atoms.

Like the KF/Cl_2CS system, TMAF/Cl_2CS may be used as a nucleophilic source of trifluoromethanethiolate, but better results are obtained with the latter system if the reactions are started at −40°C (rather than −15°C used for KF). Several substrates were studied, and compared to the KF/Cl_2CS system (Table 1). Good conversions to the aryl trifluoromethyl sulphide products were observed for the simple activated substrates pentafluoropyridine, 2,4-dinitrofluorobenzene and 4-chloro-3,5-dinitrobenzotrifluoride. However, the use of TMAF led to destruction of the furazan ring in 4-chloro-7-nitrobenzofurazan (which was left intact when KF was used), and a large number of unidentified products were seen in the GC trace for this reaction. It appears that, whilst dry TMAF may be used as a fluoride source for this reaction, it offers no advantages over KF, and in some situations its increased activity can be a drawback.

Table 1
Reaction of haloaromatic substrates with thiophosgene and fluoride

Substrate	Product	Yield/% (GC area) [a]	
		KF [b]	TMAF [c]
		70	>90
		85	96
		83[d]	78
		80	0 [e]
		5	0

[a] The area not accounted for is starting material, unless otherwise noted.
[b] Conditions: KF (78 mmol), substrate (13 mmol) and thiophosgene (13 mmol). The reaction was kept at −15°C for 4 h, and then stirred at room temperature overnight.
[c] Conditions: TMAF (2.4 mmol), substrate (0.79 mmol) and thiophosgene (0.79 mmol). The reaction was kept at −48°C for 4 h, and then stirred at room temperature overnight.
[d] 14% 4-fluoro-3,5-dinitrobenzotrifluoride also observed.
[e] A complex mixture of products was formed, many of which were unidentified.

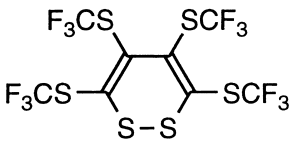
2.2. By-product formation

Haas and Klug [18] reported that thiocarbonyl fluoride reacts in the presence of alkali-metal fluorides to form $F_3CSC(S)F$, $(F_3CS)_2CS$, and heavier condensation products of formula $(CSF_2)_n$ which were not identified. We found that the KF/Cl_2CS reactions always contained F_3CSSCF_3, $F_3CSSSCF_3$ and $(F_3CS)_2CS$ as by-products, along with a compound with a molecular weight of 516 and an MS fragmentation pattern consistent with a compound of formula $C_8F_{12}S_6$ (**1**).

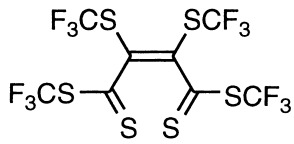
In order to investigate the thermal stability of the $KSCF_3$ formed in situ, a reaction between KF and $Cl_2C=S$ without substrate was sampled from −40°C ($MeCN–CO_2$ bath) to 20°C at 5°C intervals. These samples were filtered to remove solid KF, and analysed by ^{19}F NMR spectroscopy. There was no peak in any of the spectra which could be assigned to $KSCF_3$ itself: presumably the active source of trifluoromethanethiolate is formed at the surface of the KF, and is either insoluble, or unstable in solution. At −40°C, the solution showed no fluorine containing compounds, but at −5°C the spectrum showed the presence of F_3CSSCF_3 and traces of $F_3CSC(S)F$ (**3**) and $(F_3CS)_2CS$ (**4**). By the time the reaction reached room temperature the major component was **4**, and on stirring for 4 h most of this was converted to **1**, with some disulphide, F_3CSSCF_3.

The final product distribution was not affected either by light or by the presence of oxygen, although increasing the initial ratio of KF to Cl_2CS was found to increase the final ratio of **1** to the disulphide, as determined by ^{19}F NMR spectroscopy.

A large-scale (50 g KF, 20 g Cl_2CS) reaction was run without substrate, from which compound **1** (8% yield) was isolated after removal of volatiles on a rotary evaporator and purification by column chromatography. **1** was obtained as an orange oil with an odour of garlic, which crystallised slowly, and showed two peaks in the ^{19}F NMR spectrum, at $\delta = -40.9$ and -42.6 ppm. This was identified as 3,4,5,6-tetrakis(trifluoromethylthio)-1,2-dithiine, with melting point, ^{19}F NMR and IR spectra in good agreement with values available in the literature [21]. The data could also be assigned to a but-2-ene-1,4-dithione structure (**2**) [22], but such compounds are known to be thermodynamically less stable, and spontaneously cyclise to dithiines [23], hence the dithiine structure is more likely. Unfortunately, attempts to obtain a crystal of **1** of sufficient quality for an X-ray structure were unsuccessful.



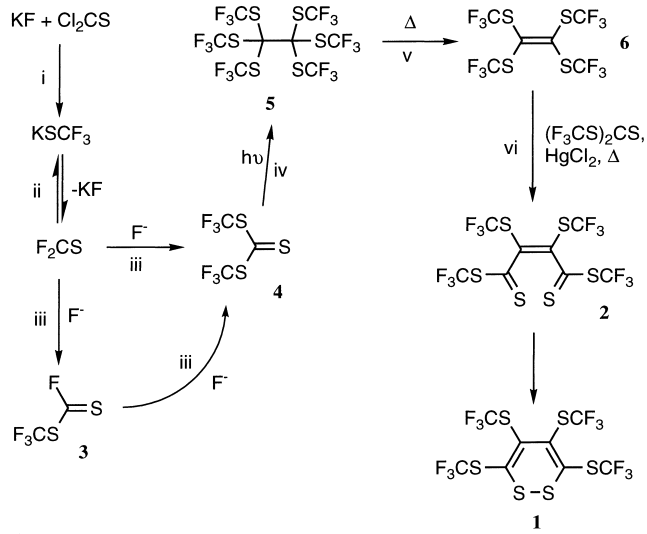
1



2

Compound **1** is not a simple oligomer of formula $(CSF_2)_n$, being deficient in sulphur: the missing sulphur atoms are accounted for by the presence of the trisulphide, $F_3CSSSCF_3$. Remarkably, it contains a 4-carbon chain, which has been generated from a C_1 molecule under relatively mild conditions. Although it may seem surprising that a molecule as complex as **1** is formed simply from KF and thiophosgene, there is literature precedent for a number of reaction steps which could lead to the formation of **1,** most of which may occur in the presence of fluoride or light: only the final step was reported as proceeding under more forcing conditions (Scheme 2). Compounds **4**, **5** and **6** were all detected as by-products in reactions involving KF/Cl_2CS, although they were typically found at low levels (1–5% of **1**). Whilst investigating the reactions of silver(I) trifluoromethanethiolate with halosilanes, we observed a different cyclic condensation product, of formula $(CS)_3(SCF_3)_2$ [24]. However, that compound was not detected in any of the reactions involving KF/Cl_2CS or TMAF/Cl_2CS.

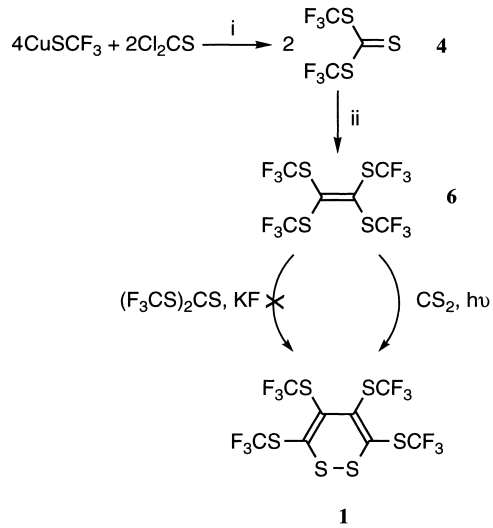
In order to confirm the identities of some of the by-products, alternative methods were devised for their preparation (Scheme 3). Copper(I) trifluoromethanethiolate reacted readily with thiophosgene in acetonitrile to form bis(trifluoromethyl)trithiocarbonate (**4**) in quantitative yield. This was purified by co-distillation with the acetonitrile: the two compounds formed a low-boiling azeotrope at 60–70°C, which was collected as a red solution. Addition of



i ref 16; ii refs 14, 15, 16; iii ref 18, iv ref 27;, v ref 8, 27; vi ref 22.

Scheme 2.

four equivalents of triphenylphosphite [$P(OPh)_3$] to this solution caused conversion of the trithiocarbonate (**4**) to tetrakis(trifluoromethanethio)ethene (**6**), which again co-distilled with acetonitrile (70–80°C). The alkene (**6**) has been reported to react with trithiocarbonate (**4**) to form the dithione (**2**, which presumably cyclises to **1**) in the presence of $HgCl_2$ at 170°C [22]. However, mixing **4** and **6** together under less forcing conditions, in the presence of KF (with or without UV irradiation) did not lead to any detectable products (by GCMS, ^{19}F NMR), although a colour change from pink to orange was observed. Photolysis of **6** in the presence of carbon disulphide led to the formation of **1** in 5% yield (GC areas), along with a roughly equal quantity of tris(trifluoromethanethio)ethene, $(F_3CS)_2C{=}CH(SCF_3)$, **7**.



i: acetonitrile, room temperature; ii: $P(OPh)_3$, acetonitrile, room temperature

Scheme 3.

Exactly what role the carbon disulphide plays in this reaction is, as yet, unclear, but it should be noted that carbon disulphide is formed on photolysis of **4** [25], and is therefore likely to be present in the KF/Cl_2CS reactions, and so may be involved in the formation of **1** in this system.

3. Conclusions

Trifluoromethanethiolate salts of potassium and tetramethylammonium fluoride cations may be formed in acetonitrile at low temperatures by reaction of the corresponding fluoride with Cl_2CS. Either of these may be used as a source of nucleophilic trifluoromethanethiolate for the preparation of trifluoromethyl aryl sulphides. The tetramethylammonium salt is less thermally stable than the potassium salt, but both decompose even at 0°C to form a range of SCF_3-containing by-products. Reaction of thiophosgene with fluoride salts may result in multiple carbon–carbon bond formation: the major by-product, 3,4,5,6-tetrakis(trifluoromethylthio)-1,2-dithiine, contains a C_4 backbone.

4. Experimental

4.1. Instrumentation

^{19}F NMR spectra were recorded at 20°C in CH_3CN with a few drops of C_6D_6 added as a signal lock and referenced to $CFCl_3$ on a Jeol EX270 spectrometer operating at 254 MHz, unless otherwise stated. The ^{19}F and ^{13}C NMR spectra of **1** were obtained in C_6D_6 on a Bruker AMD 400 operating at 376 MHz for ^{19}F and 100 MHz for ^{13}C. Connectivity was proved by ^{19}F–^{13}C 2D gradient assisted HMQC technique [26], running an experiment optimised for long-range coupling to adjacent carbons. Mass spectra were obtained on a VG analytical Autospec instrument or on a Finnegan MAT Magnum GC-MS instrument. IR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer.

4.2. Chemicals

Anhydrous solvents stored under nitrogen were obtained from Aldrich and used without further purification, unless otherwise stated. Copper(I) trifluoromethanethiolate ($CuSCF_3{\cdot}CH_3CN$) was prepared by a previously reported method [10].

4.3. Reactions with TMAF and thiophosgene

Typical reaction conditions: TMAF was dried by the method of Christe [17]. TMAF (0.22 g, 2.4 mmol) and a stirrer bar were transferred in an inert-atmosphere glovebox to a reaction flask, which was fitted with a rubber septum. Acetonitrile (8 ml) was added and the reaction cooled to −42°C (acetonitrile/CO_2 bath). The substrate (0.79 mmol) was dissolved in acetonitrile (2 ml) and injected into the reaction flask. Thiophosgene (0.091 g, 0.79 mmol, 60 μl) was then injected into the cold, stirring reaction mixture. The reaction was kept at −42°C for 4 h, and then allowed to warm to room temperature. The reaction mixture was separated using diethylether and washed with aqueous sodium hydrogen carbonate solution, to neutralise any residual thiophosgene. The ether layer was dried over magnesium sulfate, filtered, and reduced on a rotory evaporator. Products were identified by GCMS and ^{19}F NMR spectroscopy.

4.4. Analytical data for reaction products

2,3,5,6-Tetrafluoro-4-(trifluoromethylthio)pyridine
^{19}F NMR (CD_3CN): $\delta = -41.5$ (s, 3F, SCF_3), −90.2 (m, 2F, *ortho* to pyridine N), −133.6 (m, 2F, *meta* to pyridine N) ppm
MS: $m/z = 251$ (53%), 69 (100), 138 (27), 87 (18), 93 (12), 163 (12), 232 (12), 182 (9)
2,4-Dinitro(trifluoromethylthio)benzene
^{19}F NMR (CD_3CN): $\delta = -42.0$ (s) ppm
MS: $m/z = 268$ (23%), 199 (100), 69 (88), 63 (87), 95 (45), 183 (26), 79 (24), 137 (20).
2,6-Dinitro-4-(trifluoromethylthio)benzotrifluoride
^{19}F NMR (CD_3CN): $\delta = -39.2$ (s, 3F, SCF_3); −62.4 (s, 3F, CF_3) ppm
MS: $m/z = 336$ (4%), 267 (100), 251 (86), 69 (22), 175 (18), 106 (15), 317 (12), 81 (11)
4-Nitro-7-(trifluoromethylthio)benzofurazan
^{19}F NMR (CD_3CN): $\delta = -39.6$ (s) ppm
MS: $m/z = 265$ (92%), 69 (100), 196 (68), 120 (28), 180 (27), 80 (23), 207 (19), 136 (16)
5-Nitro-2-(trifluoromethylthio)benzonitrile
^{19}F NMR (CD_3CN): $\delta = -40.8$ (s) ppm
MS: $m/z = 248$ (100%), 69 (98), 133 (50), 152 (22), 218 (20), 82 (15), 202 (13), 229 (10).

4.5. Reactions with KF and thiophosgene

Typical reaction conditions: KF (spray dried, 4.53 g, 78 mmol) was oven-dried at 300°C for at least 4 h. This was placed in a flask with a magnetic stirrer bar, the substrate (13 mmol) and acetonitrile (30 ml, freshly distilled from calcium hydride), and fitted with a rubber septum. The reaction was flushed with argon and cooled to −15°C in an ethylene glycol–dry ice bath, at which point Cl_2CS (1.50 g, 13 mmol, 1.0 ml) was injected through the septum. The reaction was kept at −15°C for 4 h, and then allowed to warm to room temperature. The reaction mixture was separated using diethylether and washed with aqueous sodium hydrogen carbonate solution, to neutralise any residual thiophosgene. The ether layer was dried over magnesium sulfate, filtered, and reduced on a rotory evaporator. Products were identified by GCMS and ^{19}F NMR.

For the isolation of compound **1**, a large scale reaction was performed without an aromatic substrate, under conditions similar to those mentioned, but using 50 g of KF and 20 g of thiophosgene. Isolation was performed by removal of volatiles on a rotary evaporator, followed by column chromatography on Kieselgel 60 silica gel using cyclohexane as the eluent.

3,4,5,6-Tetrakis(trifluoromethylthio)-1,2-dithiine, $C_8F_{12}S_6$, **1**
Elemental analysis: expected for $C_8F_{12}S_6$: 18.60% C; found 19.14%; m.p. 40°C
^{19}F NMR (C_6D_6): $\delta = -40.9$ (s, 6F, C–C–SCF_3), −42.6 (s, 6F, S–C–SCF_3) ppm
^{13}C NMR (C_6D_6): $\delta = 127.5$ (q, $J = 313.8$ Hz, 2C, C–C–S**C**F_3), 129.1 (q, $J = 313.7$ Hz, 2C, S–C–S**C**F_3), 130.5 (s, 2C, C–**C**=C), 85.5 (s, 2C, S–C=C) ppm
MS: $m/z = 516$ (42%), 69 (100), 447 (81), 145 (70), 346 (63), 88 (55), 277 (26), 189 (23)
IR: 1500 (m), 1449 (s), 1153 (vs, broad), 1097 (vs), 1016 (m), 975 (m), 911 (m), 876 (m), 755 (s), 477 (s) cm^{-1}.

4.6. Reaction of $CuSCF_3$ with thiophosgene

$CuSCF_3 \cdot CH_3CN$ (2.0 g, 9.2 mmol) was dissolved in acetonitrile (10 ml). The solution was degassed with argon and then Cl_2CS (0.52 g, 4.5 mmol, 345 μl) was added with a microsyringe. The reaction was stirred for 10 min, during which time it developed a deep red colour and CuCl precipitated. The reaction mixture was the filtered and distilled at ambient pressure. A red fraction was collected between 60° and 80°C, which contained a mixture of acetonitrile and product **4**.

Copper(I) trifluoromethanethiolate, $CuSCF_3$
^{19}F NMR (CD_3CN): $\delta = -25$ (s) ppm
IR: 1084 (s, C–F), 751 (s, C–S) cm^{-1}
Bis(trifluoromethyl)trithiocarbonate, $(F_3CS)_2CS$, **4**
^{19}F NMR (CH_3CN): $\delta = -41.8$ (s) ppm
MS: $m/z = 246$ (5%), 145 (100), 69 (55), 72 (35).

4.7. Reaction of bistrifluoromethyltrithiocarbonate with triphenylphosphite

A quarter of the solution (≈1 mmol) collected from the reaction of $CuSCF_3$ with Cl_2CS was reacted with $P(OPh)_3$ (4 mmol, 1.2 g) in a sample tube at room temperature for 1 h. The reaction mixture was then distilled at ambient pressure. The colourless product, **6**, formed a low-boiling azeotrope with the acetonitrile and was collected at 70°C.

Tetrakis(trifluoromethylthio)ethene, $(F_3CS)_2C=C(SCF_3)_2$, **6**
^{19}F NMR (C_6D_6): $\delta = -39.5$ (s) ppm
MS: $m/z = 428$ (100%), 145 (82), 69 (62), 258 (57), 88 (55), 189 (48), 359 (42), 327 (35).

4.8. Reaction of bis(trifluoromethyl)trithiocarbonate with tetrakis(trifluoromethylthio)ethene

The solution of **6** obtained from the distillation described above was combined with equimolar quantities of **4** and KF. The reaction was allowed to stand in a sample tube overnight, during which time no products formed. This was then irradiated with a 300-W UV lamp for 1 h. Again, no products were observed by GCMS. Finally, two drops of carbon disulphide were added to the reaction, which was re-irradiated. After an hour, a small quantity of **1** (5%) could be detected by GCMS, along with a compound with a mass spectrum consistent with tris(trifluoromethylthio)ethene (5%), **7**.

Tris(trifluoromethylthio)ethene, $(F_3CS)_2C=CHSCF_3$, **7**
MS: $m/z = 328$ (98%), 69 (100), 158 (74), 89 (48), 215 (40), 259 (28), 145 (18), 227 (12).

4.9. Analytical data for other observed by-products

Trifluoromethylfluorodithionoformate, $(F_3CS)C(S)F$, **3**
^{19}F NMR (CH_3CN): $\delta = +43.2$ (s, 1F, C–F), −40.2 (s, 3F, SCF_3) ppm
Hexakis(trifluoromethylthio)ethane, $(F_3CS)_3CC(SCF_3)_3$, **5**
MS: $m/z = 630$ (10%), 459 (100), 145 (42), 461 (25), 390 (4), 321 (4)
Bis(trifluoromethyl)disulphide, F_3CSSCF_3
^{19}F NMR (CH_3CN): $\delta = -46.1$ (s) ppm
MS: $m/z = 202$ (69%), 183 (100), 69 (65), 64 (48), 114 (32), 133 (15), 63 (23), 95 (14)
Bis(trifluoromethyl)trisulphide, $F_3CSSSCF_3$
^{19}F NMR (C_6D_6): $\delta = -44.5$ (s) ppm
MS: $m/z = 234$ (72%), 83 (100), 64 (34), 115 (29), 133 (27), 165 (18), 69 (17), 215 (4).

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