

Reactions of trifluoromethylthiocopper with halomethanes

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Abstract

The reaction of trifluoromethylthiocopper with halomethanes, namely di- and triiodo-, dibromodichloro-, dibromochlorofluoro-, dibromodifluoro-, bromochlorofluoro-, phenyltrichloro-, bromocyano- and dibromofluoro-methanes, has been investigated in detail. In addition to the expected compounds, the formation of unusual products such as bis(trifluoromethyl)trithiocarbonate, dimethyl(trifluoromethylthio)benzene, bis(trifluoromethylthio)fluoromethane, (trifluoromethylthio)carbonyl fluoride, carbon disulfide, carbon tetrachloride, trifluoromethylthio-benzoate, etc. was observed. In some cases, bis(trifluoromethylthio)mercury has been used instead of trifluoromethylthiocopper. The mechanism of formation of the various products and their mass spectral fragmentation behavior are described.

Keywords: Trifluoromethylthiocopper; Halomethanes; Reactions; NMR spectroscopy; Mass spectrometry

1. Introduction

The usefulness of organocopper compounds and organocuprates in organic synthesis has been rather well documented [1]. The enhancement of biopharmacological properties of organic compounds upon the introduction of fluorine, trifluoromethyl and trifluoromethylthio groups has created considerable interest in the preparation and use of perfluoroorganocopper reagents [2,3]. Although copper reagents were used to introduce the trifluoromethyl functionality into aromatic compounds some 25 years ago, it was Burton and coworkers who developed elegant methods for the synthesis of perfluoro-organometallics [3b]. It was also Burton and coworkers who not only prepared trifluoromethylcopper from the metathesis of trifluoromethylcadmium with copper(I) salts, but also provided conclusive proof of the involvement of 'trifluoromethylcopper' species in these reactions [4].

Until recently, only two procedures were available for the introduction of the trifluoromethylthio group into organic compounds. One method required four steps [5] and the other required two steps [2b,6]. A third method, involving the reaction of arylmagnesium halides with trifluoromethanesulfenyl chloride, is of limited application [7]. Customarily, trifluoromethylthiocopper (**1**) has been prepared and used in situ from the reaction of bis(trifluoromethyl-

thio)mercury or its silver counterpart with copper powder in dimethylformamide [6a–c]. Yagupolskii and coworkers obtained CuSCF_3 (**1**) via the metathesis of trifluoromethylthiosilver with copper(I) salts [6d]. However, trifluoromethylthiosilver is relatively expensive and requires the reaction to be carried out in an autoclave. Bis(trifluoromethylthio)mercury, on the other hand, is extremely moisture-sensitive and highly corrosive. It is highly toxic as well [6a]. Although the reaction of copper with bis(trifluoromethyl)disulfide in DMF or *N*-methylpyrrolidone or hexamethylphosphoramide has been reported to give CuSCF_3 (**1**) [8], we were unable to prepare it according to this procedure. Though expensive, it is commercially available [9].

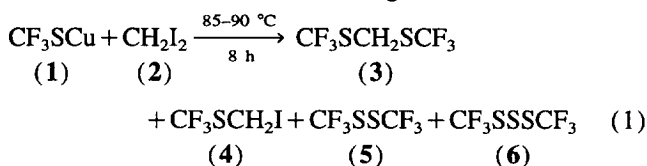
We have recently described a relatively simple procedure for the synthesis of CuSCF_3 (**1**) as an acetonitrile adduct in a highly pure crystalline state, as well as some of its reaction [10a,b]. We have also observed a solvent exchange between the acetonitrile moiety of the adduct with DMF on an NMR time scale [11]. The X-ray crystallographic structure determination of the trifluoromethylthiocopper–acetonitrile adduct has shown it to consist of a discrete molecular aggregate complex containing 10 copper thiolate units and eight molecules of acetonitrile, namely $[(\text{CF}_3\text{SCu})_{10} \cdot (\text{CH}_3\text{CN})_8]$ [12]. The cluster framework of CuSCF_3 (**1**) is composed of alternating copper–sulfur atoms in a centrosymmetric arrangement and can be described as a member of the tritwistane series of an all-carbon pentacyclic system [13].

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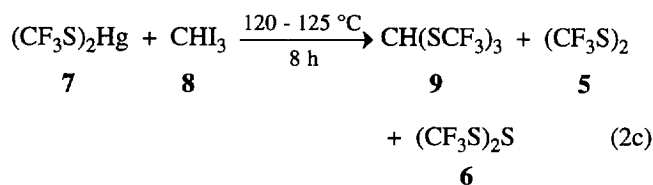
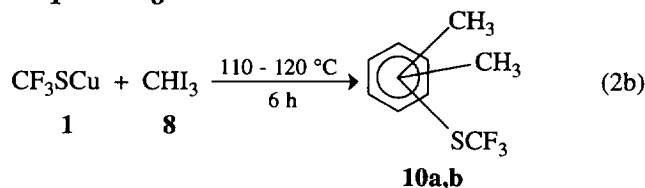
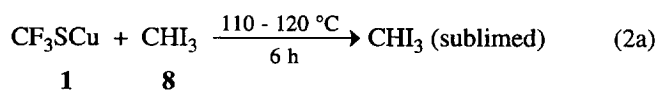
Although the CF₃SCu-acetonitrile adduct is not stable in the crystalline form for a prolonged period, the vacuum-dried material is stable and active even after several years [14a]. In continuation of our interest in the chemistry of the trifluoromethylthio group [10,11b,14], we have now investigated the reactions of CuSCF₃ (1) with halomethanes.

2. Results and discussion

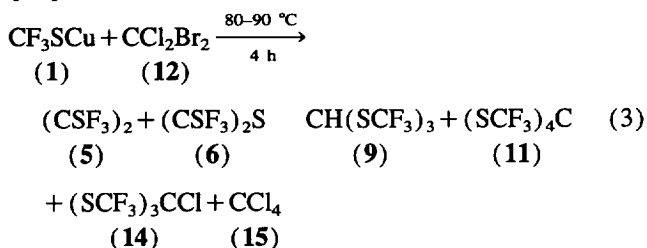
The reaction of CuSCF₃ (1) with diiodomethane (2) at 85-90 °C for 8 h gave, in addition to the expected bis(trifluoromethylthio)methane (3), (trifluoromethylthio)methyl iodide (4), bis(trifluoromethyl di- and tri-sulfides (5 and 6) [Eq. (1)]. The synthesis of 5 has been described [15]. The formation of di- and poly-sulfides in the reactions of 1 has been rationalized as arising from a cascade of free-radical reactions [10c and references cited therein]. Compound 3 has been prepared from Hg(SCF₃)₂ (7) and 2 [16]. The mass spectral fragmentation of the products described in this communication is given in Table 1.



Heating a mixture of CuSCF₃ (1) and iodoform (8) [Eq. (2a)] at 110-120 °C for 6 h resulted only in the sublimation of 8 and no tris(trifluoromethylthio)methane (9) was detected. Using dry xylene (commercial xylene contains all three isomers though the *para* isomer is the major constituent) as a solvent resulted in the formation of two aromatic compounds, namely two trifluoromethylthiolated isomeric xylenes (10a,b) as shown by GC-MS [Eq. 2(b)]. Compounds 10a and 10b are not formed when xylene is heated with CuSCF₃ (1). The desired product, tris(trifluoromethylthio)methane (9), was obtained in 82% yield (99.5% pure by GC) by heating a mixture of Hg(SCF₃)₂, 7 and 8 [16] [Eq. 2(c)].



The reaction of CuSCF₃ (1) with dibromodichloromethane (12) proved to be complex. Six compounds, i.e. (1 and 2), bis(trifluoromethyl di- and tri-sulfides (5 and 6); (3), tris(trifluoromethylthio)methane (9); (4), tetrakis(trifluoromethylthio)methane (11); (5) tris(trifluoromethylthio)chloromethane (14); and (6) carbon tetrachloride (15), were detected and characterized by GC-MS [Eq. (3)]. However, it has been reported that only 11 was formed from the reaction of bis(trifluoromethylthio)mercury (7) and 12 [16].



The formation of 9, 11 and 14 from the reaction of 1 and 12 can be rationalized as shown in Scheme 1. The fact that tris(trifluoromethylthio)chloromethane (14) (step 7), tris(trifluoromethylthio)methane (9) and tetrakis(trifluoromethylthio)methane (11) (steps 9 and 10) have been identified by GC-MS appears to lend support to the proposed scheme. However, it is conceivable that the tris(trifluoromethylthio)methyl radical (step 8) could have originated from tetrakis(trifluoromethylthio)methane (11). In fact such a suggestion has been made previously to account for the formation of another compound from 11 [17]. What is interesting in this reaction is the characterization of carbon tetrachloride (15) as one of the products of the reaction. Compound 9 is formed from the abstraction of hydrogen from the solvent by the tris(trifluoromethylthio)methyl radical (cf. steps 8 and 9). There are precedents for the participation of solvents in chemical reactions [18 and refs. cited therein]. GC-MS analysis of the starting material, 12 and acetonitrile (the solvent) confirmed the absence of 15 as an impurity.

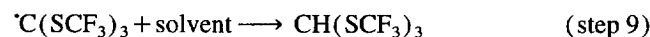
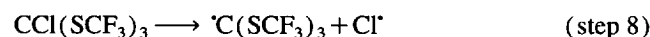
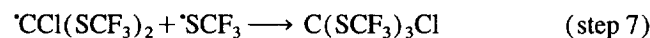
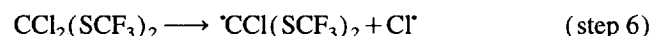
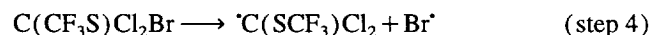
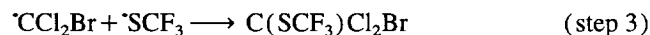
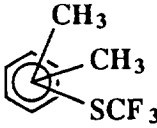


Table 1
Mass spectral fragmentation behavior of various compounds

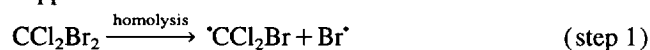
CF ₃ SCH ₂ SCF ₃ (3)	M ⁺ = 216; 147 (M – CF ₃); 115 (M – SCF ₃); 101 (SCF ₃); 82 (CSF ₂); 69 (CF ₃); 63 (CSF); 50 (CF ₂); 45 (CSH)
CF ₃ CH ₂ I (4)	M ⁺ = 242; 141 (M – SCF ₃); 128 (HI); 127 (I); 115 (M – I); 114 (M – HI); 101 (SCF ₃); 82 (CSF ₂); 63 (CSF)
CH(SCF ₃) ₃ (9)	M ⁺ = 316; 247 (M – CF ₃); 215 (M – SCF ₃); 146 (215 – CF ₃); 82 (CSF ₂); 69 (CF ₃); 63 (CSF); 45 (SCH)
 10 a, b	(a) M ⁺ = 206; 101 (SCF ₃); 91 (C ₇ H ₇); 82 (CSF ₂) (b) M ⁺ = (not seen); 77 (C ₆ H ₅); 69 (CF ₃) + ring-fission products
C(SCF ₃) ₄ (11)	M ⁺ = 416 (not seen); 347 (M – CF ₃); 315 (M – SCF ₃); 145 [C(S)SCF ₃]; 101 (SCF ₃); 76 (CS ₂); 69 (CF ₃); 63 (CSF); 50 (CF ₂)
CF ₃ SC(S)F (13)	M ⁺ = 164; 95 (M – CF ₃); 76 (CS ₂); 69 (CF ₃); 63 (CSF)
C(SCF ₃) ₃ Cl (14)	M ⁺ = 350 (not seen); 315 (M – Cl); 251, 249 (M – SCF ₃); 180 (249 – CF ₃); 145 [C(S)SCF ₃]; 79 (CSCl); 69 (CF ₃); 63 (CSF); 47 (CCl); ³⁵ Cl and ³⁷ Cl isotopes are seen in the ratio of their natural abundance
CCl ₄ (15)	M ⁺ = 152 (not seen); 117 (M – ³⁵ Cl); 115 (M – ³⁷ Cl); 84 (C ³⁵ Cl ³⁷ Cl); 82 (C ³⁵ Cl ₂); 49 (C ³⁷ Cl); 44 (C ³⁵ Cl)
FC(SCF ₃) ₃ (16)	M ⁺ = 334 (not seen); 233 (M – F); 164 (233 – CF ₃); 145 (164 – F); 101 (SCF ₃); 95 [FC(S)CS]; 82 (CSF ₂); 76 (CS ₂); 69 (CF ₃); 63 (CSF); 50 (CF ₂); 44 (CS)
Cl ₂ CF(SCF ₃) (19)	M ⁺ = 202 (not seen); 167 (M – Cl); 101 (SCF ₃); 98 (167 – CF ₃); 81 [C(S) ³⁷ Cl]; 79 [C(S) ³⁵ Cl]; 69 (CF ₃); 66 (CClF); 63 [C(S)F]; 50 (CF ₂); 47 (CCl)
ClCF(SCF ₃) ₂ (20)	M ⁺ = 268 (not seen); 233 (M – Cl); 169 [F ³⁷ ClC(SCF ₃)]; 167 (F ³⁵ ClC(SCF ₃)); 145 [C(S)SCF ₃]; 111 [ClC(S)S]; 101 (SCF ₃); 95 [C(S)SCL]; 82 (CSF ₂); 76 (CS ₂); 69 (CF ₃); 63 (CSF)
ClCFBr(SCF ₃) (21)	M ⁺ = 247 (not seen); 167 (M – Br); 147 (ClC ⁸¹ Br); 145 (ClCF ⁷⁹ Br); 101 (SCF ₃); 82 (CSF ₂); 66 (CFCl); 47 (CCl); 44 (CS)
CF ₃ SC(S)SCF ₃ (22)	M ⁺ = 246; 177 (M – CF ₃); 145 (M – SCF ₃); 133 (CF ₃ SS); 101 (SCF ₃); 82 (CSF ₂); 78 (CS ₂); 69 (CF ₃); 64 (SS)
CF ₃ SCBr (27)	M ⁺ = 180 (181, Cl) and 182 (⁸¹ Br); 163 (CF ₂ C ⁸¹ Br); 161 (CF ₂ SCBr); 129 (161 – S); 101 (SCF ₃); 79 (⁷⁹ Br)
HCF(SCF ₃) ₂ (28)	M ⁺ = 234 (not seen); 215 (M – F); 146 [CH(S)SCF ₃]; 101 (SCF ₃); 69 (CF ₃); 63 (CSF); 45 (CSH)
CSF ₂ (32)	M ⁺ = 82; 63 [C(S)F]; 50 (CF ₂)
C ₆ H ₅ C(O)F (33)	M ⁺ = 125 (Cl) and 124 (EI); 105 (M – F); 96 (M – CO); 77 (C ₆ H ₅); 51 (C ₄ H ₃); 39 (C ₃ H ₃)
C ₆ H ₅ C(O)SCF ₃ (34)	M ⁺ = 207 (Cl); 105 (M – SCF ₃) + fragments of ring cleavage
CF ₃ SCH ₂ CN (39)	M ⁺ = 142 (Cl); 122 (M – F); 115 (M – CN); 101 (SCF ₃); 82 (CSF ₂); 72 (M – CF ₃); 69 (CF ₃); 63 (CSF); 46 (CSH ₂); 40 (CH ₂ CN)

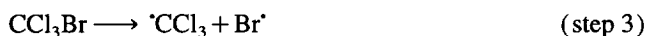


Scheme 1. Formation of tris(trifluoromethylthio)chloromethane (14), tris(trifluoromethylthio)methane (9) and tetrakis(trifluoromethylthio)methane (11) from the reaction F₃CSCu (1) with CCl₂Br₂ (12).

Scheme 2 attempts to explain the formation of carbon tetrachloride (15) during the above reaction. The homolysis

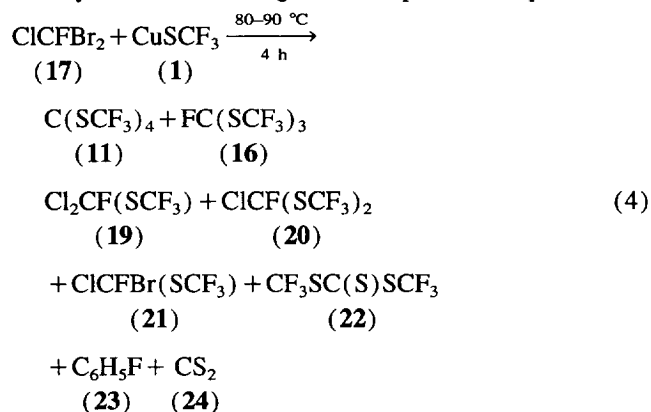
of Br₂CCl₂ (12) (step 1 of Scheme 2) is common to Schemes 1 and 2. The Cl[•] radical formed in steps 6 and 8 (Scheme 1) serves as a source of Cl[•] radicals needed for steps 2 and 4 of Scheme 2. The Br[•] radicals (step 3) could then react with Cu[•] (generated from the dissociation of F₃CSCu) to form the copper salts.



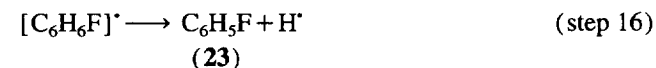
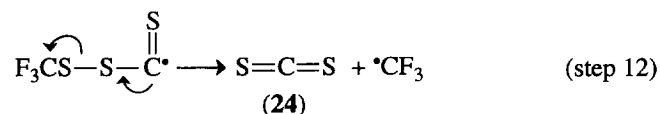
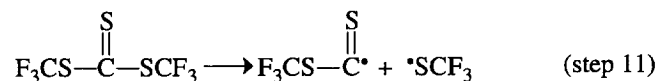
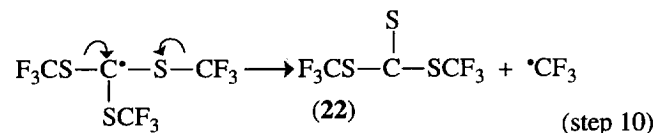
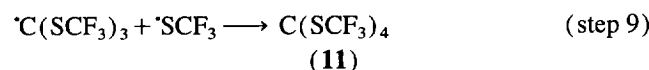
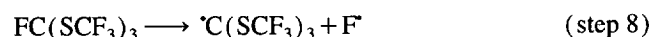
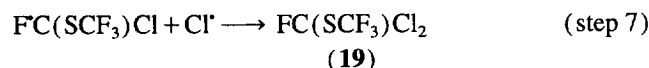
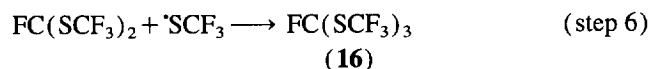
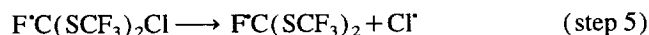
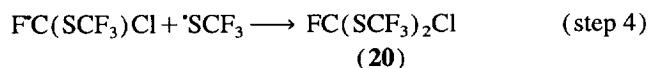
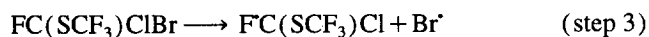
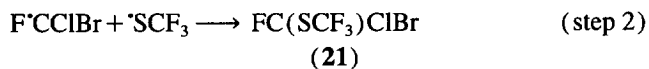


Scheme 2. Formation of carbon tetrachloride (15).

The reaction of dibromochlorofluoromethane (17) with CuSCF_3 (1) [Eq. (4)] was even more complex than that of Br_2CCl_2 (12) with 1 [Eq. (3)]. In all, eight products, i.e. (1), tetrakis(trifluoromethylthio)methane (11); (2), tris(trifluoromethylthio)fluoromethane (16); (3), dichlorofluoro(trifluoromethylthio)methane (19); (4), bis(trifluoromethylthio)chlorofluoromethane (20); (5), bromochlorofluoro(trifluoromethylthio)methane (21); (6) bis(trifluoromethyl)trithiocarbonate (22); (7), fluorobenzene (23); and (8), carbon disulfide (24), have been characterized by their GC–MS fragmentation patterns [Eq. (4)].

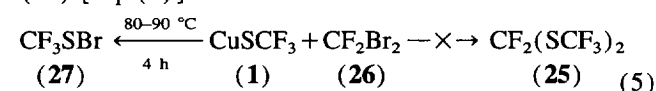


GC–MS analysis of the starting material, namely chlorodibromofluoromethane (17), confirmed the fact that carbon disulfide (24) is a product of the reaction and not an impurity in the starting material. The formation of fluorobenzene (23) is due to the presence of C_6H_6 as an impurity in the starting material 17, as shown by its GC–MS analysis. The trithiocarbonate 22 has been previously prepared by the reaction of trifluoromethylthiol with ammonia [19a] and by treatment of CsF with CSF_2 at $-40 \text{ }^\circ\text{C}$ in a stainless steel bomb [19b]. The pyrolysis of 11 has been reported to yield 22 quantitatively [16]. Scheme 3 endeavors to rationalize the products of the reaction of CuSCF_3 (1) with ClCFBr_2 (17) [Eq. (4)], namely the formation of 11, 16, 18, 19, 20, 21, 22, 23 and 24. The trifluoromethylthiyl radical is formed according to step 1 of Scheme 1. The origin of carbon disulfide (24) appears to be 22 (steps 10–12). Hexafluoroethane (step 13) was not detected. The origin of fluorobenzene (23) (step 15) was traced to the presence of benzene as an impurity in dibromochlorofluoromethane (17). The participation of similar aromatic free-radical processes (step 15) has been invoked to rationalize the products of the aromatic free-radical substitution reactions [18d].

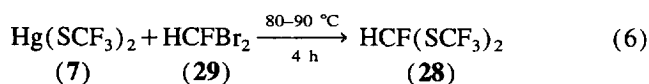


Scheme 3. Formation of compounds 11, 19, 20, 21, 22, 23, 24 and 32 [cf. Eq. (4)].

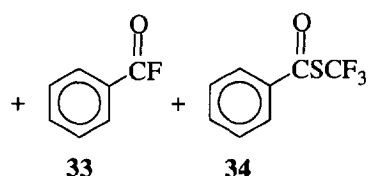
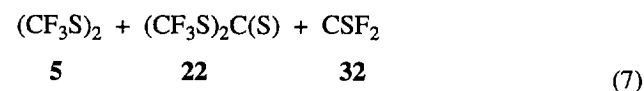
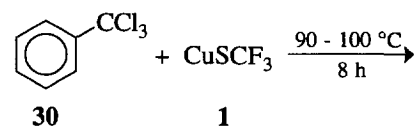
Our attempts to prepare bis(trifluoromethylthio)difluoromethane (25) by the treatment of CuSCF_3 (1) with dibromodifluoromethane (26) yielded only the starting material and a small amount of trifluoromethylsulfenyl bromide (27) [Eq. (5)].



Bis(trifluoromethylthio)fluoromethane (**28**) was prepared by heating dibromofluoromethane (**29**) with $\text{Hg}(\text{SCF}_3)_2$ (**7**):

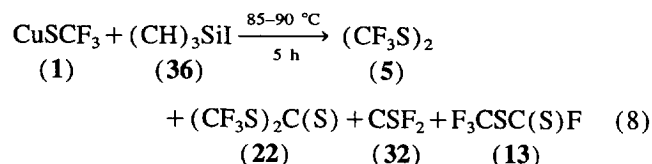


The reaction of CuSCF_3 (**1**) with phenyltrichloromethane (**30**), instead of the expected phenyltris(trifluoromethylthio)methane (**31**) furnished **5**, **22**, thiocarbonyl fluoride (**32**), benzoyl fluoride (**33**) and trifluoromethylthiobenzoate (**34**) [Eq. (7)].

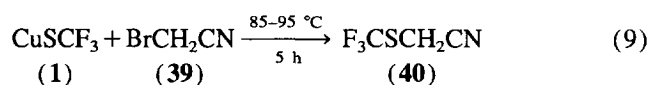


The source of **34** must be the trifluoromethylthiyl radical [10d,17]. The origin of the benzoyl moiety of **33** and **34** must be due to partial hydrolysis. In view of the report that the reaction of $\text{Hg}(\text{SCF}_3)_2$ (**7**) with phenyltrichloromethane (**30**) gave the expected product, namely phenyltris(trifluoromethylthio)methane (**31**), as the only product [20], the above reaction of CuSCF_3 with phenyltrichloromethane (**30**) appears to be unusual.

The reaction of CuSCF_3 (**1**) with trimethylsilyl iodide (**36**) gave the disulfide **5**, the trithiocarbonate **22**, thiocarbonyl fluoride (**32**), trifluoromethylthiocarbonyl fluoride (**13**), an unknown compound with a molecular weight of 248 and a couple of silyloxy derivatives rather than the desired (trifluoromethylthio)trimethylsilane (**35**) [Eq. (8)]. Under similar experimental conditions, the reaction of hexamethyldisilane (**37**) with trifluoromethylsulfenyl chloride (**38**) resulted in the recovery of the disilane **37**.



Finally, the reaction of CuSCF_3 (**1**) with bromocyanomethane (**39**) gave the expected cyano(trifluoromethylthio)methane (**40**) [Eq. (9)], which was previously prepared in three steps starting from trifluoromethanesulfonyl chloride (**38**) and ketene to give (trifluoromethylthio)acetyl chloride [17].



The mass spectra of **5** and **6** [14,21] and the mass spectral fragmentation of **13**, **22** and **32** have been reported [10d]. In general, molecular ion peaks of the compounds with more than one trifluoromethylthio group attached to the same carbon are not observed. The loss of CF_3 , SCF_3 , CSF , CF_2 and F appears to be common characteristic of these compounds. In the fragmentation pattern of compound **22** and chlorotris(trifluoromethylthio)methane (**14**), a molecule of CS_2 is split off. The presence of thiocarbonyl fluoride (**32**) implies the participation of trifluoromethylthiyl radicals.

3. Experimental details

3.1. General procedures

Warning! Bis(trifluoromethyl) di-, -tri- and poly-sulfides formed as byproducts of the reactions of **1 are highly toxic. The disulfide itself has been reported to have a lethal toxicity index of 200 ppm min⁻¹ [15]. Therefore, extreme care should be exercised in working with these compounds and all reactions should be carried out in efficient hoods.** NMR spectra (¹H, ¹³C and ¹⁹F) were recorded in CDCl_3 on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz, respectively, with TMS serving as the internal reference. The external reference for the ¹⁹F spectra was CCl_3F . Mass spectra were obtained on a Finnigan model 5100 GC-MS instrument equipped with a silica 25 m × 0.31 mm (i.d.) SE-54 capillary column (J. & W. Scientific, Rancho Cordova, CA). Routine GC analyses were carried out on a Hewlett Packard 5890A gas chromatograph equipped with a 30 m × 0.53 mm (i.d.) DB-5 column (J & W. Scientific, Folsom, CA).

Reactions were carried out in a flame-dried argon-purged 10 or 25 ml round-bottom flask equipped with a magnetic stirrer, gas inlet, pressure equalizing funnel and a reflux condenser attached to a Dry Ice/acetone-cooled Dewar condenser. The coolant circulating in the cooling coils was maintained at $-20 \text{ }^\circ\text{C}$. All reactions were carried out by the addition of stoichiometric amounts of the reagents (usually on a 10 mmol scale) under argon. Acetonitrile was freshly distilled prior to use. After the addition was complete, the reaction mixtures were heated (as noted in the narrative section), allowed to come to ambient temperature and then flash-distilled under reduced pressure. The flash-distillate was collected in a receiver precooled to $-78 \text{ }^\circ\text{C}$ and processed as usual. The product(s) were then fractionally distilled and analyzed by GC and GC-MS methods.

3.2. Bis(trifluoromethylthio)methane (**3**)

A mixture of trifluoromethylthiocopper (**1**, 4.5 g) and diiodomethane (**2**, 2.68 g, 0.01 mol) was heated at $85-90 \text{ }^\circ\text{C}$

for 8 h. The mixture was cooled to room temperature, flash-distilled under reduced pressure and the distillate collected in a receiver cooled to -78°C . GC–MS analysis of the flash-distillate indicated that the mixture consisted of: (1), the title compound **3** (b.p. $78\text{--}80^{\circ}\text{C}$, 44.2% [16]); (2), trifluoromethylthioiodomethane (**4**, 45.4%); (3), bis(trifluoromethyl) disulfide (**5**, 0.3%); and (4), bis(trifluoromethyl) trisulfide (**6**, 0.2%). Compound **3** (b.p. $78\text{--}80^{\circ}\text{C}$) has been prepared earlier via the reaction of **2** with bis(trifluoromethylthio)mercury (**7**) [16]. $^1\text{H NMR}$ δ : 4.28 (s) ppm. $^{13}\text{C NMR}$ δ : 28.6 (d, $J=3.1$ Hz, CH_2); 129.9 ($J=307$ Hz, SCF_3) ppm [14d].

3.3. Tris(trifluoromethylthio)methane (9)

(a) When a mixture of stoichiometric amounts of trifluoromethylthiocopper (**1**) and iodoform (**8**) was similarly heated at $110\text{--}120^{\circ}\text{C}$ for 6 h, most of **8** had sublimed and condensed on the walls of the condenser and the residue remaining in the flask did not contain the desired product, **9**.

(b) The above procedure was repeated, except that commercial xylene was added as a solvent, and the reaction mixture was processed as before. GC–MS analysis of the flash-distillate showed it to contain a small amount (about 2.0%) of an isomeric mixture of trifluoromethylthio xylene isomers **10a,b**. Since xylene when used as a solvent contained all three isomers, no attempt was made to separate the isomers formed.

(c) Finally, a mixture of stoichiometric amounts of bis(trifluoromethylthio)mercury (**7**) and iodoform (**8**) was heated at $120\text{--}125^{\circ}\text{C}$ for 8 h and the reaction mixture processed as described above. GC–MS analysis of the flash-distillate permitted the identification of the following components: (1), bis(trifluoromethyl) disulfide (**5**, 0.2%); (2), bis(trifluoromethyl) trisulfide (**6**, 0.3%); and (3), tris(trifluoromethylthio)methane (**9**, 95.5%). The latter was further purified by fractionation under reduced pressure and distillation, b.p. $105\text{--}107^{\circ}\text{C}$ [16]. NMR of **10**: ^1H δ : 5.93 (s) ppm. ^{13}C δ : 46.7 (d, $J=3.1$ Hz, ^{13}CH); 128 ($J=312$ Hz, S^{13}CF_3) ppm.

3.4. Tetrakis(trifluoromethylthio)methane (11)

A mixture of dibromodichloromethane (**12**) and trifluoromethylthiocopper (**1**) was heated at $80\text{--}90^{\circ}\text{C}$ for 4 h. The mixture was cooled to room temperature and processed as before. Routine GC analysis of the mixture indicated it to be a complex mixture of eight compounds. GC–MS examination of the mixture permitted the characterization of all but one. The eight compounds are: (1 and 2), bis(trifluoromethyl) di- and -trisulfide (**5** and **6**, 8.4%); (3), trifluoromethylthiocarbonyl fluoride (**13**, 2.5%); (4), tris(trifluoromethylthio)methane (**9**, 8.8%); (5), tetrakis(trifluoromethylthio)methane (**11**, 61.1%); (6), tris(trifluoromethylthio)chloromethane (**14**, 1.4%); and (7), carbon tetrachloride (**15**, 15.1%). The eighth component was the starting

material. The preparation of **9** and **11** has been described previously [16].

3.5. Fluoro-tris(trifluoromethylthio)methane (16)

(a) With a view to preparing the title compound **16**, a mixture of stoichiometric amounts of chlorodibromofluoromethane (**17**) and trifluoromethylthiocopper (**1**) in freshly distilled dry toluene was heated at $100\text{--}110^{\circ}\text{C}$ for 6 h. The usual processing of the reaction mixture and GC–MS analysis of the flash-distillate showed it to be composed of five components: (1), bis(trifluoromethyl) disulfide (**5**, 0.6%); (2), tris(trifluoromethylthio)methane (**9**, 0.7%); (3), carbon tetrachloride (**15**, 4.3%); (4), fluorobenzene (**23**, 0.5%); with the remainder corresponding to starting material.

(b) The above reaction was repeated in an analogous manner except that trifluoromethylthiocopper (**1**) was replaced by bis(trifluoromethylthio)mercury (**7**). GC–MS analysis of the flash-distillate led to identification of the following components: (1), dichlorofluoro(trifluoromethylthio)methane (**19**, 0.3%); (2), trifluoromethylthiocarbonyl fluoride (**13**, 0.2%); (3), chlorofluorobis(trifluoromethylthio)methane (**20**, 2.3%); (4), fluoro-tris(trifluoromethylthio)methane (**16**, 3.0%); (5), bromochlorofluoro(trifluoromethylthio)methane (**21**, 0.2%); (6), carbon tetrachloride (**15**, 5.6%); (7), fluorobenzene (**23**, 0.3%); (8), bis(trifluoromethyl)trithiocarbonate (**22**, 0.15%); (9), tetrakis(trifluoromethylthio)methane (**11**, 2.4%); (10), carbon disulfide (**24**, 1.6%); and (11), starting material (**17**).

3.6. Bis(trifluoromethylthio)difluoromethane (25)

Dibromodifluoromethane (**26**) and trifluoromethylthiocopper (**1**) were reacted as described earlier, GC–MS analysis of the flash-distillate showed the presence of four components. Based on the mass spectral fragmentation, the major component was identified as trifluoromethylsulfonyl bromide (**27**, 5.8%). The remaining three were present in trace amounts and the desired product (**25**) was not detected among the products of the reaction.

3.7. Bis(trifluoromethylthio)fluoromethane (28)

A solution of dibromofluoromethane (**29**) and bis(trifluoromethylthio)mercury (**7**) in freshly distilled dry acetonitrile was heated at $80\text{--}90^{\circ}\text{C}$ for 4 h. GC–MS analysis of the flash-distillate indicated the product to consist of: (1), bis(trifluoromethyl) disulfide (**5**, 0.4%); (2), bis(trifluoromethyl) trisulfide (**6**, 0.2%); (3), tris(trifluoromethylthio)methane (**9**, 0.3%); (4), bis(trifluoromethylthio)fluoromethane (**28**, 14.3%); and (5), starting material (**29**).

3.8. Attempted preparation of phenyltris(trifluoromethylthio)methane (31)

A mixture of phenyltrichloromethane (**30**) and CuSCF_3 (**1**) was heated at $90\text{--}100^{\circ}\text{C}$ for 8 h and the reaction mixture

processed as usual. GC–MS analysis of the product showed it to be composed of: (1), bis(trifluoromethyl) disulfide (5); (2), bis(trifluoromethyl)trithiocarbonate (22); (3), thiocarbonyl fluoride (13); (4), benzoyl fluoride (33); and (5), trifluoromethylthiobenzoate (34).

3.9. Attempted preparation of trimethyl(trifluoromethylthio)silane (35)

A stoichiometric mixture of trimethylsilyl iodide (36) and CuSCF_3 (1) was heated at 85–90 °C for 5 h and the reaction processed as before. GC–MS analysis of the product indicated it to consist of: (1), bis(trifluoromethyl) disulfide (5); (2), bis(trifluoromethyl)trithiocarbonate (22); (3), thiocarbonyl fluoride (32); and (4), trifluoromethylthiocarbonyl fluoride (13). Reaction of hexamethyldisilane (37) with trifluoromethylsulfenyl chloride (38) also failed to furnish the desired compound (35).

3.10. Cyano(trifluoromethylthio)methane (39)

To a suspension of CuSCF_3 (5.0 g) in freshly distilled dry acetonitrile (5 ml), a solution of bromocyanomethane (40, 3.0 g, 25 mmol) in dry acetonitrile (5 ml) was added slowly with stirring and the reaction mixture heated at 85–95 °C for 5 h. Flash-distillation of the reaction product under reduced pressure and GC analysis indicated that the desired product (39) was present in 65% yield. This compound had previously been prepared in three steps [17].

References

- [1] (a) J.F. Normant, *Synthesis*, (1972) 63; (b) J.F. Normant and A. Alexakis, *Synthesis*, (1981) 841; (c) R.D. Rieke, *Science*, 246 (1989) 1260.
- [2] (a) R. Filler and Y. Kobayashi (eds.), *Biomedical Aspects of Fluorine Chemistry*, Kodash/Elsevier, New York, 1982; (b) W.C. Randall, P.S. Anderson, E.A. Cresson, C.A. Hunt, T.F. Lyon, K. Hoogsteen, M. Williams, E.A. Risley and J.A. Totaro, *J. Med. Chem.*, 22 (1979) 1222 (and references cited therein); (c) E.A. Nodiff, S. Lipschutz and M. Gordon, *J. Org. Chem.*, 25 (1960) 60.
- [3] (a) J.-P. Belgue and D. Bonnet-Delpon, *Tetrahedron*, 47 (1991) 3207; (b) D.J. Burton and Z.-Y. Yang, *Tetrahedron*, 48 (1992) 189; (c) G.A. McClinton, *Tetrahedron*, 48 (1992) 6555.
- [4] (a) D.M. Wiemers and D.J. Burton, *J. Am. Chem. Soc.*, 108 (1986) 832; (b) M.A. Willert-Paroda, D.J. Burton and N.C. Baenziger, *J. Chem. Soc., Chem. Commun.*, (1989) 1633.
- [5] (a) O. Scherer, *Angew. Chem.*, 52 (1939) 457; (b) *idem*, French Pat. 820 796, 1937.
- [6] (a) F.H. Mann, D.D. Coffman and E.L. Muetterties, *J. Am. Chem. Soc.*, 81 (1959) 3575; (b) *idem*, US Pat. 3 062 894, Nov. 6, 1962; (c) D.C. Remy, K.E. Little, C.A. Hunt and M.B. Freedman, *J. Org. Chem.*, 41 (1976) 1644; (d) L.M. Yagupolskii, N.V. Kondratenko and V.P. Sambur, *Synthesis*, (1975) 721.
- [7] W.A. Sheppard, *J. Org. Chem.*, 29 (1964) 895.
- [8] N.V. Kondratenko, A.A. Kolomeytssev, A.A. Popov and L.M. Yagupolskii, *Synthesis*, (1985) 667.
- [9] TCI America, 91/92 Catalogue No. C1159, \$192.50/1 g.
- [10] (a) S. Munavalli, D.I. Rossman, A.J. Muller, H.S. Aaron, C.P. Ferguson, J.W. King, D.K. Rohrbaugh and L.C. Buettner, *Am. Chem. Soc., 10th Winter Fluorine Conf.*, St. Petersburg, FL, Jan. 28–Feb. 2, 1991, Abs. No. 38; (b) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh, C.P. Ferguson and F.-L. Hsu, *Heteroatom. Chem.*, 3 (1992) 189; (c) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh, C.P. Ferguson and L.J. Szafraniec, *J. Fluorine Chem.*, 59 (1992) 91; (d) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh, C.P. Ferguson and L.C. Buettner, *J. Fluorine Chem.*, 65 (1993) 15; (e) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh and C.P. Ferguson, *206th Am. Chem. Soc. Nat. Meet., Div. Fluorine Chem.*, Chicago, IL, Aug. 21–27, 1993, Abs. No. 17.
- [11] (a) S. Munavalli, D.I. Rossman, L.L. Szafraniec, W.T. Beaudry and C.P. Ferguson, unpublished results; (b) S. Munavalli, A. Hassner, D.I. Rossman, S. Singh, D.K. Rohrbaugh and C.P. Ferguson, *J. Fluorine Chem.*, 73 (1995) 7.
- [12] (a) S. Munavalli, D.I. Rossman, C.P. Ferguson and A.L. Rheingold, *1993 US Army, ERDEC Conf., Chem. Defense Res.*, Aberdeen Proving Ground, MD, Nov. 16–19, 1993, Abs. No. 25; (b) A.L. Rheingold, S. Munavalli, D.I. Rossman and C.P. Ferguson, *Inorg. Chem.*, 33 (1994) 1723.
- [13] M. Nakazaki, K. Naemura, H. Chikamatsu and M. Hashimoto, *J. Org. Chem.*, 46 (1981) 2300.
- [14] (a) S. Munavalli and D.I. Rossman, unpublished results; (b) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh, C.P. Ferguson and H.D. Banks, *J. Fluorine Chem.*, 60 (1993) 85; (c) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh and C.P. Ferguson, *J. Fluorine Chem.*, 61 (1993) 155; (d) S. Munavalli, D.I. Rossman, D.K. Rohrbaugh and C.P. Ferguson, *J. Fluorine Chem.*, 61 (1993) 147; (e) S. Munavalli, A.J. Muller, D.I. Rossman, D.K. Rohrbaugh and C.P. Ferguson, *J. Fluorine Chem.*, 63 (1993) 253.
- [15] C.W. Tullock and D.D. Coffman, *J. Org. Chem.*, 25 (1960) 2016.
- [16] J. Harris, *J. Org. Chem.*, 32 (1967) 2063.
- [17] J.F. Harris, *J. Org. Chem.*, 37 (1972) 1340.
- [18] (a) K. Okuhara, *J. Am. Chem. Soc.*, 102 (1980) 244; (b) M. Moller, P. Bauer and J.E. Dubois, *J. Org. Chem.*, 47 (1982) 4120; (c) H.C. Brown and M.M. Midland, *J. Am. Chem. Soc.*, 93 (1971) 3291; (d) J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, Wiley, New York, 1992.
- [19] (a) R.N. Haszeldine and J.M. Kidd, *J. Chem. Soc.*, (1955) 3871; (b) A. Haas and W. Klug, *Chem. Ber.*, 101 (1968) 2609.
- [20] L.M. Yagupolskii and N.V. Kondratenko, *Zh. Obshch. Khim.*, 39 (1969) 175.
- [21] (a) M.C. Cullen, D.C. Frost and M.T. Pun, *Inorg. Chem.*, 9 (1970) 1976; (b) N.R. Zack and J.M. Shreeve, *J. Fluorine Chem.*, 5 (1975) 153.