Synthesis of bis(trifluoromethyl)trisulfide and bis(trifluoromethylthio)selenide

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(Received December 14, 1992; accepted March 25, 1993)

Abstract

The use of 4-dimethylaminopyridine as a catalyst in the reaction of trifluoromethylsulfenyl chloride with hydrogen sulfide at −78 °C cuts down the time of reaction from 30 d to 1 d and gives up to 70% yield of bis(trifluoromethyl)trisulfide (**1**). Similarly, bis(trifluoromethylthio)selenide (**2**) can be prepared from hydrogen selenide and trifluoromethylsulfenyl chloride. The influence of other catalysts on the course of the reaction, the formation of unusual by-products, the NMR and mass spectral data of **1** and **2** are presented in this paper.

Introduction

In connection with an on-going project [1], bis(trifluoromethyl)trisulfide (**1**) was required in large quantities. An earlier synthesis of **1** took 30 d at room temperature [2]. When a mixture of carbon disulfide and iodine pentafluoride was heated to 200 °C, **1** was isolated as one of the minor products [3]. A 7%–12% yield of **1** was obtained when a mixture of trifluoromethyl iodide and sulfur was heated at 310 °C for 36 h [3–5]. However, trifluoromethanesulfenyl chloride (**3**) reacted slowly with H_2S to give acceptable yields of **1** [2]. The reaction of trifluoromethylchloro-disulfide (CF_3SSCl), obtained via photolysis of a mixture of bis(trifluoromethyl) disulfide (**4**) and sulfur dichloride (**5**), with trifluoromethylthiol (**6**) was shown to furnish **1** [4]. It should be noted that the reaction of **3** with an excess of H_2S has been reported to give trifluoromethyl disulfane and bis(trifluoromethyl)trisulfide [5]. Trifluoromethyl radicals generated from a glow discharge of hexafluoroethane reacted with sulfur vapor under the influence of a radio frequency to yield polysulfides including **1** and carbon disulfide [6]. We now wish to report that the use of 4-dimethylaminopyridine (**7**) in the reaction of **3** with H_2S at −78 °C for 2–3 h gives satisfactory yields (75%–80%) of **1**, accompanied by trace amounts of the di-, tetra- and pentasulfides as well as 1,1-dichlorofluoromethyl trifluoromethyl disulfide (**8**). Replacement of **7** with either pyridine, or triethylamine or *N*,*N*-dimethylaniline lowers the yield of **1** considerably.

Recently, we have developed and described an efficient method for the synthesis of trifluoromethylthiocopper (**9**) in a crystalline form [7]. Reaction of **9** with **5** at room temperature for 45 min also produced **1** though in slightly reduced yields [1a]. In fact, di- and poly-sulfides routinely result as by-products of the reaction of **9** with various substrates [8]. Scheme 1 provides the genesis of di- and poly-sulfides and **8**. Under similar experimental conditions as those described in the use of **7**, hydrogen selenide reacted with **3** to furnish the selenium analog of **1**, namely bis(trifluoromethylthio)selenide (**2**), which has been characterized from its NMR and mass spectral data. In addition, **4** and **8** were identified as minor products of this reaction (Table 1).

Results and discussion

Table 1 lists, in addition to the expected products (**1** and **2**), the various by-products that have been identified from their mass-spectral fragmentation patterns. The examination of the origin, formation and distribution of the by-products listed in Table 1 clearly suggests the involvement of free radicals in these reactions. It has been reported that the reaction between carbon disulfide and iodine pentafluoride follows a free-

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SSDI 0022-1139(93)02928-8

TABLE 1. Products of the reaction of trifluoromethylsulfenyl chloride with H_2S, H_2Se and CF_3SCu

Reactants	Products
$H_2S + CF_3SCl \xrightarrow{-78\,°C}$	$CF_3S_2CF_3{}^a + CF_3S_3CF_3$ (76–80%) $+ CF_3S_4CF_3{}^a + CF_3S_5CF_3{}^a + CF_3S_2CFCl_2$ (1.2%)
$H_2Se + CF_3SCl \xrightarrow{-78\,°C}$	$(CF_3S)_2Se$ (86%) $+ CF_3S_2CF_3 + CF_3S_2CFCl_2$ (7.0%)
$CF_3SCu + CF_3SCl \xrightarrow{25\,°C}$	$CF_3S_2CF_3 + CF_3S_3CF_3$ (61%) $+ CF_3S_4CF_3 + CF_3S_5CF_3$

[a]These compounds were not detected earlier [2].

radical process [3]. A similar suggestion has been made about the reaction between trifluoromethyl iodide and sulfur [6]. Scheme 1 attempts to rationalize the origin and formation of the polysulfides and **8** identified by the GC–MS examination of the flash-distillate of the reaction mixture.

$$H_2S + CF_3SCl \longrightarrow CF_3SSSCF_3 \quad (1)$$

$$CF_3SSSCF_3 \longrightarrow CF_3S^{\bullet} + CF_3SS^{\bullet} \quad (2)$$

$$2CF_3S^{\bullet} \longrightarrow CF_3SSCF_3 \quad (3)$$

$$2CF_3SS^{\bullet} \longrightarrow CF_3SSSSCF_3 \quad (4)$$

$$CF_3SSSSCF_3 \longrightarrow CF_3SSSS^{\bullet} + {}^{\bullet}CF_3 \quad (5)$$

$$CF_3SSSS^{\bullet} + {}^{\bullet}SCF_3 \longrightarrow CF_3SSSSSCF_3 \quad (6)$$

$$CF_3SCl + {}^{\bullet}SCF_3 \longrightarrow CF_3SSCF_3 + Cl^{\bullet} \quad (7)$$

$$CF_3SSCF_3 + Cl^{\bullet} \longrightarrow CF_3SSCF_2Cl + F^{\bullet} \quad (8)$$

$$CF_3SSCF_2Cl + Cl^{\bullet} \longrightarrow CF_3SSCCl_2F + F^{\bullet} \quad (9)$$

$${}^{\bullet}CF_3 + F^{\bullet} \longrightarrow CF_4{}^{*} \quad (10)$$

$${}^{\bullet}CF_3 + {}^{\bullet}CF_3 \longrightarrow C_2F_6{}^{*} \quad (11)$$

$$CF_3S^{\bullet} + {}^{\bullet}CF_3 \longrightarrow CF_3SCF_3{}^{*} \quad (12)$$

*Were not detected.

Scheme 1. Genesis of bis(trifluoromethyl)polysulfides and other by-products.

In a sense, Scheme 1 is an extension of an earlier suggestion [2] made to account for the formation of tri- and tetra-sulfides. The disulfide, **4**, is a ubiquitous product of the reaction of trifluoromethylthiocopper (**9**) with various substrates [7, 8]. It is often accompanied by polysulfides. All of the compounds listed in steps 1–6 have been characterized from their mass-spectral fragmentation patterns. Steps 7–9 describe the formation of **8**, initiated by the attack of the trifluoromethylthiyl radical on **3**. Tetrafluoromethane, hexafluoroethane and bis(trifluoromethyl)sulfide (steps 10–12) were not detected. The origin of **8** may be **3** itself (Scheme 2) instead of steps 8 and 9 of Scheme 1. The initially formed difluoromethylene sulfenyl chloride radical (step 1 of Scheme 2) may undergo a rearrangement to give the thiyl radical.

$$CF_3SCl \longrightarrow F_2C^{\bullet}SCl + F^{\bullet} \quad (1)$$

$$F_2C^{\bullet}SCl \longrightarrow F_2(Cl)CS^{\bullet *} \quad (2)$$

$$F_2(Cl)CS^{\bullet} \longrightarrow F(Cl)C(S) + F^{\bullet} \quad (3)$$

$$CF_3SCl \longrightarrow F_3CS^{\bullet} + Cl^{\bullet} \quad (4)$$

$$F(Cl)C(S) + Cl^{\bullet} \longrightarrow FCl_2CS^{\bullet} \quad (5)$$

$$FCl_2CS^{\bullet} + {}^{\bullet}SCF_3 \longrightarrow FCl_2CSSCF_3 \quad (6)$$

*Undergoes a rearrangement.

Scheme 2. Postulated route to dichlorofluoromethyl trifluoromethyl disulfide (**8**).

There are precedents for this type of arrangement. The rest of the free-radical process (steps 3–6) follows the accepted course. The formation of **8** can be attributed to the participation of free radicals. The free-radical intermediate $Cl_2FCS^{\bullet}$ proposed in this mechanism (Scheme 2) has also been implicated in the formation of chlorofluoro-disulfides [9]. The origin of **8** is **3** itself (cf. Scheme 2). Scheme 1 is an extension of an earlier suggestion by Haszeldine and Kidd [2].

Irradiation of a mixture of stoichiometric amounts of **3** and thiocarbonyl fluoride (**10**) has been described to furnish chlorodifluoromethyl trifluoromethyl disulfide [ClF_2CSSCF_3 (**11**)] in 67% yield [9]. Similar treatment of **3** with thiocarbonyl chlorofluoride [FC(S)Cl (**12**)] was also reported to give **8** in 56% yield. It is conceivable that the $F_2C(S)^{\bullet}Cl$ thiyl radical might have been formed from **3** and directly resulted in **11** (cf. Scheme 3).

$$CF_3SCl \longrightarrow F_3CS^{\bullet} + Cl^{\bullet} \quad (1)$$

$$F_3CS^{\bullet} \longrightarrow F_2CS + F^{\bullet} \quad (2)$$

$$F_2CS^{\bullet} + Cl^{\bullet} \longrightarrow CF_2ClS^{\bullet} \quad (3)$$

$$CF_2ClS^{\bullet} + F_3CS^{\bullet} \longrightarrow F_3CSSCF_2Cl \quad (4)$$

Scheme 3. Postulated route to chlorodifluoromethyl trifluoromethyl disulfide (**11**).

It is worth noting that both **8** and **11** are formed at −78 °C in the reaction of **3** with dry NH_3 and without the assistance of irradiation [10].

The ^{13}C and ^{19}F chemical shifts of **1** and **2** are consistent with the structures assigned to these compounds. The introduction of Se in **2** shifted the ^{19}F signal upfield by 3 ppm, whereas the ^{13}C chemical shift

TABLE 2. Mass-spectral fragmentation data

$CF_3S_3CF_3$ (**1**)	$M^+=234$; 215 $(M-F)$; 165 $(M-CF_3)$; 133 $(M-SCF_3)$; 96 (SSS); 82 (CSF_2); 69 $(CF_3$, 100%); 64 (SS); 44 (CS)
$CF_3SSeSCF_3$ (**2**)	$M^+=282$; 263 $(M-F)$; 213 $(M-CF_3)$; 101 (SCF_3); 82 (CSF_2); 69 $(CF_3$, 100%); 63 (CSF); 50 (CF_2); 44 (CS); 32 (S)
CF_3SSCF_2Cl (**8**)	$M^+=234$; 215 $(M-F)$; 199 $(M-Cl)$; 133 $(M-SCF_3)$; 117 $(199-CSF_2)$; 101 $(SCF_3$, 100%); 98 (CSFCl); 79 (CSCl); 69 (CF_3); 64 (SS); 63 (CSF); 44 (CS)
CF_3SSCF_2Cl (**11**)[a]	$M^+=218$; 149 $(M-CF_3)$; 117 $(M-SCF_3)$; 101 (SCF_3); 82 (CSF_2); 69 $(CF_3$, 100%); 64 (SS); 44 (CS)

[a] This compound was identified along with **8** in the products of the reaction of dry ammonia with **3** at −78 °C.

was unaffected. The ^{19}F chemical shift of bis(trifluoromethyl)disulfide itself appears as a singlet at 46.0 ppm [9]. Thus, the insertion of Se into the sulfur–sulfur bond of the disulfide to form **2** elicits a more pronounced effect on the ^{19}F chemical shift than does the insertion of S to yield **1**. The identity of the polysulfides has been confirmed from their mass-spectral fragmentation patterns, which are similar to the data reported by others [6, 11]. The mass-spectral fragmentation behavior of **1**, **2**, **8** and **11** is given in Table 2 and supports the structures assigned to them. All of the polysulfides give the parent peak $[M^+]$ and the peak corresponding to $m/e=69[CF_3]^+$. In the case of di- and tri-sulfides, the peak corresponding to $[M-F]$ is seen. However, this peak is absent in the spectra of tetra- and pentasulfides. Other conspicuous peaks correspond to $[CF_3SSS]^+$, $[CF_3SS]^+$, $[CF_3S]^+$ and $[CSF_2]^+$ fragments.

Experimental

General procedure

Warning!! Because of the high toxicity associated with inhalation of 1 and 4, extreme care should be exercised and all reactions should be carried out in efficient hoods. ^{19}F and ^{13}C spectra were recorded on a Varian VXR-400S spectrometer using CCl_3F as an external reference [machine frequencies, 100.58 MHz (^{13}C) and 376.29 MHz (^{19}F)]. A positive chemical shift value δ (ppm) is taken downfield from the external reference. Mass spectra were obtained on a Finnigan model 5100 GC–MS spectrometer equipped with a silica 25 m × 0.31 mm i.d. SE-54 capillary column (J and W Scientific, Rancho Cordova, CA). Routine GC analyses were accomplished with a Hewlett Packard 5890A gas chromatograph equipped with a 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA). The solvents were dried and freshly distilled before use. The reactions were carried out in a flame-dried, argon-purged 10 or 25 ml three-necked round-bottom flask equipped with a magnetic stirrer, a gas inlet, a pressure equalizing dropping funnel and a reflux condenser carrying a Dry Ice/acetone trap. The temperature of the coolant passing through the reflux condenser was maintained at −20 °C. After the reaction was over, the mixture was cooled to room temperature, flash-distilled under reduced pressure, the distillate collected into a receiver cooled to −78 °C and finally fractionally distilled through a silvered, vacuum-jacketed, metal-helix-packed column.

Bis(trifluoromethyl)trisulfide

Hydrogen sulfide (0.68 g, 0.02 M) was sparged into a solution of **3** (5.14 g, 0.04 M) in freshly distilled dry CH_2Cl_2 (5 ml) cooled to −78 °C. A solution of **7** (1.2 g, 0.01 M) in dry CH_2Cl_2 was added dropwise. The reaction mixture was stirred at −78 °C for 2 h and then at ambient temperature for 0.5 h. The reaction mixture was flash-distilled and the distillate collected in a receiver cooled to −78 °C. The material was fractionally distilled through a silvered, vacuum-jacketed, metal-helix-packed column, b.p. 85–87 °C (lit. value [2], 86.2 °C) to give the desired product in 75% yield and with a purity of 96% as estimated by GLC methods. ^{13}C NMR δ: 128.7 (quartet) ($J=314\pm1$ Hz) ppm. ^{19}F NMR δ: 44.5 (singlet) ppm.

Preparation of bis(trifluoromethyl)trisulfide using trifluoromethylthiocopper

To a slurry of trifluoromethylthiocopper (**9**) (3.1 g, 0.19 M) in 5 ml of dry xylene was added dropwise at ambient temperature a solution of sulfur dichloride (**5**) (3.1 g, 80% 0.024 M) in 5 ml of dry xylene. The reaction was exothermic. After addition was complete, the reaction was stirred for an additional 30–45 min and flash-distilled into a Dry Ice/alcohol-cooled receiver. GC–MS analysis of the distillate indicated the presence of the di, tetra- and pentasulfides as minor impurities. Further purification furnished the pure product (61%).

Bis(trifluoromethylthio)selenide

To a solution containing **3** (5.14 g, 0.04 M) and hydrogen selenide (0.8 g, 0.01 M) in 5 ml of dry CH_2Cl_2 cooled to −78 °C was added a solution of **7** (1.2 g

0.01 M) in 5 ml of dry CH_2Cl_2 with stirring. After addition was complete, the reaction mixture was stirred at -78 °C for 3 h and then allowed to warm to ambient temperature spontaneously. The reaction mixture, after flash-distillation, was fractionally distilled to yield the title compound in 86% yield, b.p. 100–102 °C with a purity of 94% as estimated by GLC methods. ^{13}C NMR δ: 128.6 (quartet) ($J = 312.5 \pm 1$ Hz) ppm. ^{19}F NMR δ: 41.5 (singlet) ppm.

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