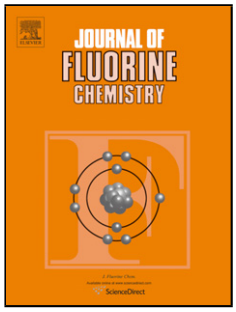

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Author: Shay Potash Shlomo Rozen

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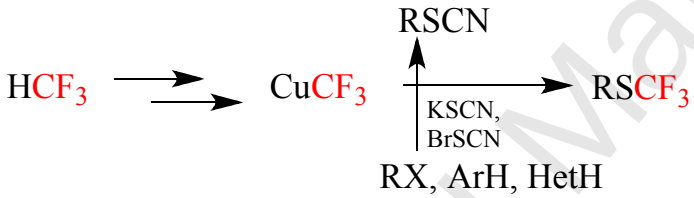
A New Synthesis of Trifluoromethyl Sulfides Utilizing Thiocyanates and Fluoroform

Shay Potash and Shlomo Rozen*

School of Chemistry, Tel-Aviv University, Tel-Aviv, Israel 69978. Fax: +972 3 640 9293; Tel: +972 3 640 8378; E-mail: rozens@post.tau.ac.il

Graphical Abstract



Highlights

- An efficient and general way developed for preparing the most lipophilic SCF_3 group.
- The cheap fluoroform has been used as a source for the CF_3 group.
- $CuCF_3$ was prepared with no stabilizers (e.g. Et_3N/xHF) under atmospheric pressure.
- Aliphatic, aromatic and heterocyclic (trifluoromethyl)thio derivatives were made.
- $RSCF_3$ are made by reacting thiocyanates, readily made from halides, with $CuCF_3$.

Abstract

Fluoroform is a potent greenhouse gas which should not be released to the atmosphere. Large amounts of it are stored and wait for new and useful reactions to be based on it. One such general reaction that is described in this paper, is its use in preparation of the important organic trifluoromethyl sulfides. Aliphatic, aromatic and heterocyclic thiocyanates are easy to prepare. They were reacted with fluoroform based $CuCF_3$ to form the corresponding (trifluoromethyl)thio derivatives.

Introduction

Fluorinated compounds are continuously taking more prominent place in various fields since they usually considerably modify molecules' physical, chemical and biological properties. These modifications result in materials, which are suitable for diverse applications in the areas of medicinal chemistry materials science, agrochemistry, and much more [1–3]. It is not surprising, thus, that a large number of existing pharmaceuticals and agrochemicals and up to 50% of those under development contain at least one fluorine atom [4].

The trifluoromethyl group is very much associated with remarkable biological properties, mainly due to the increased lipophilicity it offers [5,6]. Two main methods are used for constructing such trifluoromethylated compounds. One consists of transferring the whole CF_3 group from an appropriate reagent such as Ruppert-Prakash Me_3SiCF_3 [7], CF_3I [8], (trifluoromethyl)dibenzothio or seleno salt systems [9], CF_3COOK [10], Togni reagent [11] and alike. The other main route focuses on constructing the CF_3 group at desired sites [12].

Among the various trifluoromethyl moieties the trifluoromethylthio one, SCF_3, is of special interest since it has one of the highest lipophilicity's parameter values [13]. Due to the importance of these trifluoromethylated sulfides, several

synthetic methods have been developed for their preparation. Billard compiled an impressive review describing the formation of the C-SCF_3 bond by either electrophilic or nucleophilic trifluorothiomethylating agents based on the toxic CF_3SCl and some of its metal derivatives CF_3SM (M = Ag, Cu or NR_2) [14]. Another approach, mostly confined to aromatics, use CF_3SiMe_3/S_8 mixture which was reacted either with aryl boronic acid derivatives or aryl iodides [15]. Trifluorothiomethyl-iodonium reagents have also been successfully employed [16]. It should be pointed out that most of these reactions proceed with racemization of asymmetric carbon centers when relevant. Other synthetic methods for the preparation of trifluoromethyl sulfides used CF_3I or the now banned CF_3Br [17]. One of the current industrial method for the preparation of trifluoromethyl sulfides is by chlorination followed by chlorine–fluorine exchange reactions of the trichloromethyl sulfides with $HF/SbF_3/SbF_5$ a method requiring harsh conditions frequently responsible to undesired side reactions [**Error! Bookmark not defined.**,18].

The use of fluoroform, CHF_3, has long been recognized as an attractive trifluoromethylation method. Fluoroform is a side product of manufacturing Teflon®, PVDF, refrigerants and fire extinguishing agents. It is generated in large volumes of over 20000 tons yearly [19,20]. However, although nontoxic and with zero ozone depleting potential, it is a very potent greenhouse compound. As a result, the 1997 Kyoto protocol obligated industrialized countries to reduce its emissions. Consequently, as the disposal of this stable compound by destruction is rather expensive [**Error! Bookmark not defined.**], large quantities of fluoroform are currently in storage waiting for new reactions to utilize it [**Error! Bookmark not defined.**].

In an effort to put fluoroform to good use, research efforts have been invested

to take advantage of it as a synthetic reagent. Indeed CHF_3, along with strong bases, was reacted with carbonyls to form new C-CF_3 bonds [21]. Prakash and Olah reported the fluoroform-derived trifluoromethylation of C, Si and B centers using suitable electrophiles and amide bases at very low temperatures and mild reaction conditions [**Error! Bookmark not defined.**]. Other contributions have recently been published by Grushin, who prepared the relatively stable $CuCF_3$ reagent using fluoroform and *t*-BuOK/CuCl system for trifluoromethylation of aromatic halides, aryl boronic acid and formation of α-trifluoromethyl ketones [**Error! Bookmark not defined.**,22]. The use of this fluoroform based nucleophilic trifluoromethylating agent, has attracted our attention, while considering construction RS-CF_3 derivatives. This task requires besides the trifluoromethyl nucleophile, an appropriate sulfur electrophile. Disulfides have been used as such electrophiles and indeed formed trifluoromethyl sulfides, but the fact is that half of the organic disulfide is lost as a leaving group while the trifluoromethylating nucleophile was Me_3SiCF_3 [23] and the base phosphazene [24] both quite expensive agents. Organic thiocyanates seemed a natural contender for this function, as they possess electrophilic sulfur. Such thiocyanates are easy to prepare from inexpensive thiocyanate salts such as KSCN, from electrophilic XSCN reagents (X = Cl, Br, SCN) or from the corresponding thiols and BrCN [25].

Results and Discussion

Our initial substrate was the commercial n-dodecyl thiocyanate, **1a** which was reacted with 1.5 molar equivalents of the fluoroform derived $CuCF_3$. After a few experiments it was found that the best conditions for the reaction were using non-stabilized $CuCF_3$, rather than the $CuCF_3/Et_3N{\cdot}3HF$ combination that was previously employed mainly to suppress side products containing the O-*t*-Bu moiety [**Error! Bookmark not defined.**b]. It was also found that unlike several previous works, there

was no need for reaction vessels suitable for high-pressure procedures using CHF_3 and *t*-BuOK/CuCl system for the preparation the active $CuCF_3$ species. This simplified procedure produced the desired trifluoromethyldodecyl sulfide (**2a**) in quantitative yield within 5h at room temperature. 3-Phenylpropyl thiocyanate (**1b**) [26] was similarly reacted with the $CuCF_3$ suspension to form 3-phenylpropyltrifluoromethyl sulfide (**2b**) also in quantitative yield. This compound was previously prepared by the reaction of the corresponding disulfide with Me_3SiCF_3 but no yield was reported [27]. In order to demonstrate the efficiency of this reaction, the doubly thiocyanate, 1,10-dithiocyanatodecane (**1c**) [28], was reacted with 3 mole-equivalents of the fluoroform derived $CuCF_3$ (50% excess) for 6h at room temperature yielding the previously unknown 1,10-bis(trifluoromethylthio)decane (**2c**) in 90% yield.

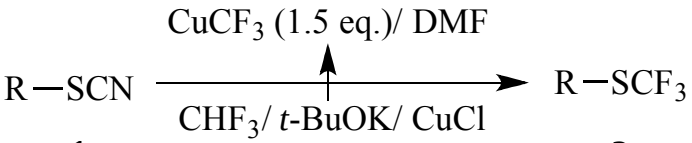
Secondary thiocyanates are also reactive towards the nucleophilic trifluoromethylating reagent $CuCF_3$. The reaction rate, however, seem to be affected from steric factors as the reactions are slower and require moderate heating to reach full conversion. Nonetheless, (3-thiocyanatobutyl)benzene (**1d**) [29] yielded the previously unknown secondary 3-[(trifluoromethyl)thio]-1-phenylbutane (**2d**) in 6h at 45 ^{o}C and in 75% yield. Similarly, the reaction of the trifluoromethylating agent $CuCF_3$ with the cyclic thiocyanatocyclohexane (**1e**) [30] yielded under similar conditions the 1-[(trifluoromethyl)thio]cyclohexane (**2e**) (Scheme 1).

Aromatic thiocyanates could also be readily prepared and then successfully employed in this reaction. 4-*Tert*-butylphenyl thiocyanate (**1f**) was formed by electrophilic aromatic substitution of *tert*-butylbenzene using lead (II) thiocyanate [31]. Its reaction with 1.5 molar equivalents of $CuCF_3$ provided 1-[(trifluoromethyl)thio]-4-*tert*-butylbenzene (**2f**) in 90% yield after 14h at 45 ^{o}C. The

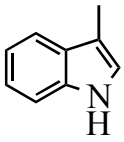
2-thiocyanatonaphthalene (**2g**) was recently reported to be formed in 47% yield by the reaction of the in-situ prepared sodium naphthalene-2-thiolate with CF_3I [32]. As with **1f**, we have used CHF_3 based $CuCF_3$ on 2-naphthyl thiocyanate (**1g**) and obtained the desired **2g** in 80% yield.

In one of his pioneering works, Grushin reported trifluoromethylation of some chloro-aryl derivatives by $CuCF_3$, reactions which required heating of up to 80 ^oC [**Error! Bookmark not defined.**]. Since the substitution of aromatic thiocyanate is much faster, it is possible to get a clean reaction of 1,2-dichloro-4-thiocyanatobenzene (**1h)** with 1.5 equivalent of the fluoroform based copper reagent, yielding 1-[(trifluoromethyl)thio]-3,4-dichlorobenzene (**2h**) in 85% yield without affecting the aromatic halogens. Heterocyclic trifluoromethyl sulfides such as 3-[(trifluoromethyl)thio]-indole (**2i**) could also be obtained by starting with the unprotected 3-indole thiocyanate, (**1i**), which in its turn, was prepared by electrophilic aromatic substitution of indole with KSCN and Br_2 (BrSCN) [33] (Scheme 1).

Scheme 1: From thiocyanates to trifluoromethyl sulfides



1 **2**

a	R = n-$C_{12}H_{25}$	5h, R.T	> 95%
b	R = $Ph(CH_2)_3$	5h, R.T	> 95%
c	R = —$(CH_2)_{10}$—	6h, R.T	90%[a]
d	R = $Ph(CH_2)_2CHMe$	6h, 45 °C	75%
e	R = cyclo-C_6H_{11}	6h, 45 °C	60%
f	R = 4-*t*-BuC_6H_4	14h, 45 °C	90%
g	R = 2-naphtyl	14h, 45 °C	80%
h	R = 3,4-*di*-Cl-C_6H_3	14h, 45 °C	85%
i	R = 	14h, 45 °C	50%

(a) using 3 mol/eq of $CuCF_3$

Conclusion

In conclusion, a diverse series of trifluoromethyl sulfides was prepared from the corresponding alkyl, aryl and heterocyclic thiocyanates. As these trifluoromethylthio compounds gain popularity, it is important to find sustainable and relatively easy procedure for their preparation. The use of fluoroform fulfills this condition, as the disposal of this greenhouse gas has become a major issue in the last decade.

Experimental

General Procedures:

^{1}H, ^{19}F, and ^{13}C NMR spectra were obtained with $CDCl_3$ as solvent at 400, 376, and 100 MHz, respectively, with Me_4Si as an internal standard for the ^{1}H and ^{13}C NMR and $CFCl_3$ for the ^{19}F NMR spectra. HRMS sample of **2i** was measured under ESI conditions. In all other cases this method could not detect the molecular ion, so we used successfully Amirav's supersonic GC-MS technique. In these cases, the isotope abundance analysis provided very satisfactory results, as shown for the specific compounds. This type of analysis confirmed the proposed elemental formulas as it ranked them in first place and hence as the best choice, with very good matching factors of better than 940 (out of 999) [34].

General Trifluoromethylation Procedure:

To a two necked flask equipped with a glass pipette inlet for argon, 40 ml of DMF were inserted and the solvent was degassed for 5 minutes. Then, 4.7 gr of finely ground potassium *tert*-butoxide were added into the solution and stirred for about 5 minutes until most of the solid was dissolved. Two gr of copper (I) chloride were added and the suspension turned black within a minute. This suspension was vigorously stirred while argon was passed through for 1h at room temperature. The argon inlet was replaced with a fluoroform inlet which was bubbled through the black solution for 5 minutes at a rate of about 600 ml per minute (about 6 mole equivalents, based of Cu). This procedure produced about 16mmol $CuCF_3$ (calibrated using ^{19}FNMR with $PhCF_3$ as a standard). A measured volume was added to a DMF solution of the thiocyanate ensuring about 50% excess of $CuCF_3$ over the starting thiocyanate and the suspension was stirred under argon atmosphere. The suspension was added to cold water and extracted with ether. The ethereal solution was passed through a short pad of celite to remove inorganic salts and evaporated. The product was purified by flash column chromatography using Petrol Ether/EtOAc. Specific

amounts of thiocyanates, $CuCF_3$ suspension, reaction times and temperatures are specified herein.

Thiocyanates formation:

Numerous thiocyanates have been prepared in the past. We have referenced the known ones. In particular the primary thiocyanate **1b** was prepared by us via the substitution of (3-bromopropyl)benzene with 1.2 equiv. potassium thiocyanate in a refluxing ethanolic solution for 2h. Bis–thiocyanate **1c** was similarly prepared using 3 equivalent potassium thiocyanate and 1,10-dibromodecane. The secondary thiocyanate **1d** was made by the substitution of the corresponding tosylate with 1.5 equivalent potassium thiocyanate in a refluxing ethanol for 6h. Thiocyanates **1e**,**g**,**h** were prepared by drop-wise addition of an acetone solution of BrCN (1 equiv.) into a solution of the corresponding thiol (1 equiv.) and triethylamine (1.5 equiv.) at 0^oC. The preparations of the electron-rich thiocyanates **1f** and **1i** were obtained by electrophilic aromatic substitutions using in-situ prepared BrSCN as described in reference **Error! Bookmark not defined.**.

1-[(trifluoromethyl)thio]dodecane (**2a**) [35]. Prepared from commercial thiocyanate **1a** (1.00 g) and about 6.6 mmol $CuCF_3$ as described in the general procedure, in quantitative yield: 1.19 g, clear oil, ^{1}H NMR 2.87 (2 H, t, J = 7.2 Hz), 1.68 (2 H, quin, J = 7.2 Hz), 1.39 (2 H, m), 1.26 (16 H, m), 0.88 (3 H, t, J = 6.8 Hz) ppm. ^{13}C NMR 131.3 (q, J = 304 Hz), 32.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.0, 28.6, 22.4, 14.1 ppm. ^{19}F NMR -41.8 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 270.1 $(M)^+$ with an isotope abundance analysis matching factor of 982 out of 999.

1-[(trifluoromethyl)thio]-3-phenylpropane (**2b**) [**Error! Bookmark not defined.**]. Prepared from thiocyanate **1b [Error! Bookmark not defined.**] (1.24 g) and fluoroform derived $CuCF_3$ (about 10.5 mmol) as described in the general procedure, in quantitative yield: 1.53 g, clear oil, ^{1}H NMR 7.31 (2 H, m), 7.22 (1 H, m), 7.19 (2 H, m), 2.89 (2 H, t, *J* = 7.2 Hz), 2.75 (2 H, t, *J* = 7.2 Hz), 2.04 (2 H, quin, *J* = 7.2 Hz), ppm. ^{13}C NMR 141.2, 131.9 (q, *J* = 311 Hz), 192.3, 129.2, 35.1, 31.7, 29.9 ppm. ^{19}F NMR -41.6 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 220.0 $(M)^+$ with an isotope abundance analysis matching factor of 996 out of 999.

1,10-bis[(trifluoromethyl)thio]decane (**2c**). Prepared from thiocyanate **1c** [**Error! Bookmark not defined.**] (0.80 g) and the fluoroform derived $CuCF_3$ (about 9.4 mmol) as described in the general procedure, in 90% yield: 0.96 g, clear oil, ^{1}H NMR 2.87 (4 H, t, *J* = 7.2 Hz), 2.87 (2 H, t, *J* = 7.2 Hz), 1.69 (4 H, quin, *J* = 7.2 Hz), 1.3-1.4 (12 H, m) ppm. ^{13}C NMR 131.3 (q, *J* = 304 Hz), 29.9, 29.4, 29.3, 28.9, 28.5 ppm. ^{19}F NMR -40.0 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 342.1 $(M)^+$ with an isotope abundance analysis matching factor of 989 out of 999. Anal. calc. for $C_{12}H_{20}F_6S_2$: C, 42.09; H, 5.89; S, 18.73; F, 33.29. Found: C, 42.12; H, 5.88; S, 18.77; F, 33.64.

3-[(trifluoromethyl)thio]-1-phenylbutanane (**2d**). Prepared from thiocyanate **1d** [**Error! Bookmark not defined.**] (0.62 g) and the fluoroform derived $CuCF_3$ (about 4.9 mmol) as described in the general procedure, in 75% yield: 0.57 g, clear oil, ^{1}H NMR 7.29-7.32 (2 H, m), 7.19-7.23 (3 H, m), 3.31 (1 H, sextet, *J* = 6.8 Hz), 2.77 (2 H, t, *J* = 6.8 Hz), 1.88-2.00 (2 H, m), 1.47 (3 H, d, *J* = 6.8 Hz) ppm. ^{13}C NMR 140.9, 131.2 (q, *J* = 304 Hz), 128.6, 128.4, 126.2, 40.7, 38.6, 32.9, 22.5 ppm. ^{19}F

NMR -39.4 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 234.1 $(M)^+$ with an isotope abundance analysis matching factor of 992 out of 999. Anal. calc. for $C_{11}H_{13}F_3S$: F, 24.33. Found: F, 23.83.

1-[(trifluoromethyl)thio]cyclohexane (**2e**) [**Error! Bookmark not defined.**]. Prepared from thiocyanate **1e** [**Error! Bookmark not defined.**] (1.14 g) the fluoroform derived $CuCF_3$ (about 12.1 mmol) as described in the general procedure, in 60% yield: 0.89 g, clear oil, ^{1}H NMR 3.25 (1 H, m), 2.05 (2 H, m), 1.76 (2 H, m), 1.37-1.63 (5 H, m) ppm. ^{13}C NMR 131.3 (q, J = 304 Hz), 44.0, 33.9, 25.7, 25.3 ppm. ^{19}F NMR -39.7 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 184.0 $(M)^+$ with an isotope abundance analysis matching factor of 958 out of 999.

1-[(trifluoromethyl)thio]-4-*tert*-butylbenzene (**2f**) [**Error! Bookmark not defined.**b]. Prepared from thiocyanate **1f** [**Error! Bookmark not defined.**] (0.50 g) and the fluoroform derived $CuCF_3$ (about 3.9 mmol) as described in the general procedure, in 90% yield: 0.55 g, clear oil, ^{1}H NMR 7.58 (2 H, d, J = 8.4 Hz), 7.44 (2 H, d, J = 8.4 Hz), 1.34 (9 H, s) ppm. ^{13}C NMR 154.4, 136.2, 129.8 (q, J = 306 Hz), 34.9, 31.2 ppm. ^{19}F NMR -43.3 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 234.1 $(M)^+$ with an isotope abundance analysis matching factor of 942 out of 999.

2-[(trifluoromethyl)thio]-naphthalene (**2g**) [**Error! Bookmark not defined.**]. Prepared from thiocyanate **1g** [**Error! Bookmark not defined.**] (0.70 g) and the fluoroform derived $CuCF_3$ (about 5.7 mmol) as described in the general procedure, in 80% yield: 0.69 g, clear oil, ^{1}H NMR 8.21 (1 H, s), 7.85-7.95 (3 H, m),

7.47-69 (3 H, m) ppm. ^{13}C NMR 137.1, 134.0, 133.4, 131.9, 129.8 (q, J = 310 Hz), 129.3, 128.3, 128.0, 127.9, 127.1, 1259, 121.6. ^{19}F NMR -41.3 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 228.0 $(M)^+$ with an isotope abundance analysis matching factor of 991 out of 999.

1-[(trifluoromethyl)thio]-3,4-dichlorobenzene (**2h**) [**Error! Bookmark not defined.**b]. Prepared from thiocyanate **1h [**36] (0.80 g) and the fluoroform derived $CuCF_3$ (about 5.9 mmol) as described in the general procedure, in 85% yield: 0.82 g, clear oil, ^{1}H NMR 7.76 (1 H, m), 7.47-7.53 (2 H, m) ppm. ^{13}C NMR 137.6, 136.1, 135.2, 133.6, 131.2, 129.1 (q, J = 310 Hz), 124.0 ppm. ^{19}F NMR -42.7 ppm (3 F, s). The common MS methods failed to show any molecular peak. Amirav's supersonic GC-MS revealed a strong molecular ion peak of m/z 245.9 $(M)^+$ with an isotope abundance analysis matching factor of 998 out of 999.

3-[(trifluoromethyl)thio]-indole (**2i**) [37]. Prepared from thiocyanate **1i** [**Error! Bookmark not defined.**] (1.25 g) and the fluoroform derived $CuCF_3$ (about 10.8 mmol) as described in the general procedure, in 50% yield: 0.78 g, yellow oil, ^{1}H NMR 8.54 (1 H, brs), 7.82 (1 H, m), 7.54 (1 H, s), 7.43(1 H, m), 7.28-7.32(2 H, m) ppm. ^{13}C NMR 136.1, 134.2, 131.1, 132.1 (q, J = 330 Hz), 123.5, 121.7, 119.4, 111.7 ppm. ^{19}F NMR -42.7 ppm (3 F, s). HRMS (ASAP): calcd. for $C_9H_5F_3NS$ $(M–H)^-$ 216.0095; found 216.0098.

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