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Metal-Free Oxidative Trifluoromethylthiolation of Terminal Alkynes with CF_3SiMe_3 and Elemental Sulfur

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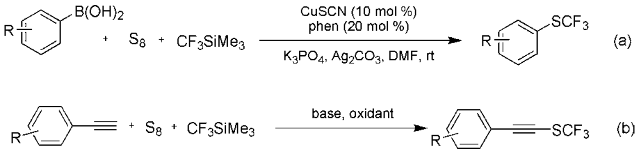
Supporting Information

ABSTRACT: A metal-free oxidative trifluoromethyl-thiolation of terminal alkynes using readily available CF_3SiMe_3 and elemental sulfur at room temperature has been developed. This reaction provides an efficient and convenient method for the preparation of alkynyl trifluoromethyl sulfides bearing a wide range of functional groups. Preliminary investigation revealed that elemental sulfur instead of air acted as the oxidant.

The incorporation of fluorine into organic molecules can result in a profound impact in their physical, chemical, and biological properties. Consequently, this strategy has found a widespread use in the pharmaceutical, agrochemical, and material sciences.[1] As a result, the development of new methodologies for the introduction of fluoroalkyl groups into organic compounds has become the subject of intensive research. Recently, tremendous progress has been made in the development of transition-mediated/catalyzed trifluoromethylation reactions for the construction of carbon−CF_3 bonds.[2−4] However, development of the analogous methods for the introduction of the trifluoromethylthio group (-SCF_3) into organic compounds remains largely unexplored, despite the potential utilization of the SCF_3 group in the pharmaceutical and agrochemical agents because of its strong electron-withdrawing effect and extremely high lipophilicity.[5−8]

Generally, aryl trifluoromethyl sulfides ($ArSCF_3$) can be prepared either by a nucleophilic or radical trifluoromethylation of aryl sulfides or disulfides,[6] or by a nucleophilic reaction of aryl halides or diazonium salts with trifluoromethylthiolate metal reagents ($MSCF_3$).[7] However, these methods are limited by some combination of high temperatures, expensive reagents, and low reactivity with electron-rich arenes. Recently, Buchwald reported the synthesis of aryl trifluoromethyl sulfides by Pd-catalyzed cross-coupling reaction of aryl bromides with $AgSCF_3$ under mild conditions.[8a] Shortly after, we developed a Cu-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids with CF_3SiMe_3 and elemental sulfur at room temperature, providing a complementary and convenient method for the preparation of aryl trifluoromethyl sulfides (Scheme 1a).[8b] Very recently, Vicic described a Ni-catalyzed cross-coupling reaction of aryl iodides with $[NMe_4][SCF_3]$[8c] and later the same group developed a Cu-mediated aerobic oxidative trifluoromethylthiolation of aryl and alkenylboronic acids with $[NMe_4][SCF_3]$.[8d] Despite their great advantages, these reactions typically involved the formation of C_{sp^2}−SCF_3 bonds, while the similar cross-coupling processes that facilitate the construction C_{sp}−SCF_3 bonds has not been described to date, despite the fact that alkynyl trifluoromethyl sulfides have potential use in medicinal chemistry and related areas.[5,9] On the other hand, significant progress has been made recently in metal-mediated oxidative cross-coupling of alkynyl C−H bonds with various nucleophiles due to their atom and step economy.[3c,s,10,11] However, to the best of our knowledge, the oxidative coupling of trifluoromethylthio-based nucleophilic reagent with terminal alkynes has not been reported, albeit this new alternative strategy may provide a direct route to alkynyl trifluoromethyl sulfides. Herein, we report an efficient metal-free oxidative trifluoromethylthiolation of terminal alkynes with (trifluoromethyl)trimethylsilane (CF_3SiMe_3, Ruppert−Prakash reagent)[12] and elemental sulfur at room temperature (Scheme 1b).

Scheme 1. Oxidative Trifluoromethylthiolation



On the basis of the our previous works on copper-mediated oxidative trifluoromethylation of terminal alkynes and copper-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids,[3c,8b] treatment of phenylacetylene **1a** with CF_3SiMe_3 (5.0 equiv), elemental sulfur (7.0 equiv), CuI (1.0 equiv), and 1,10-phenanthroline (phen) (1.0 equiv) in the presence of KF (3.0 equiv) under air atmosphere in DMF at room temperature provided the desired trifluoromethylthiolated product **2a** in 24% yield together with the trifluoromethylated byproduct **3a** in 22% yield (Table 1, entry 1). Previous studies have determined that the stoichiometric amounts of CuI and phen were required for the oxidative trifluoromethylation of terminal alkynes.[3c] Once the loadings of CuI and phen were reduced, the yield of the trifluoromethylated product was decreased dramatically. Experimentally, the yield of product **2a** was increased to 67% without the formation of byproduct **3a** in the

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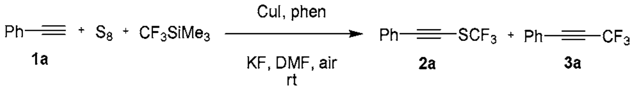
Table 1. Optimization of Oxidative Trifluoromethylthiolation of Phenylacetylene 1a[a]



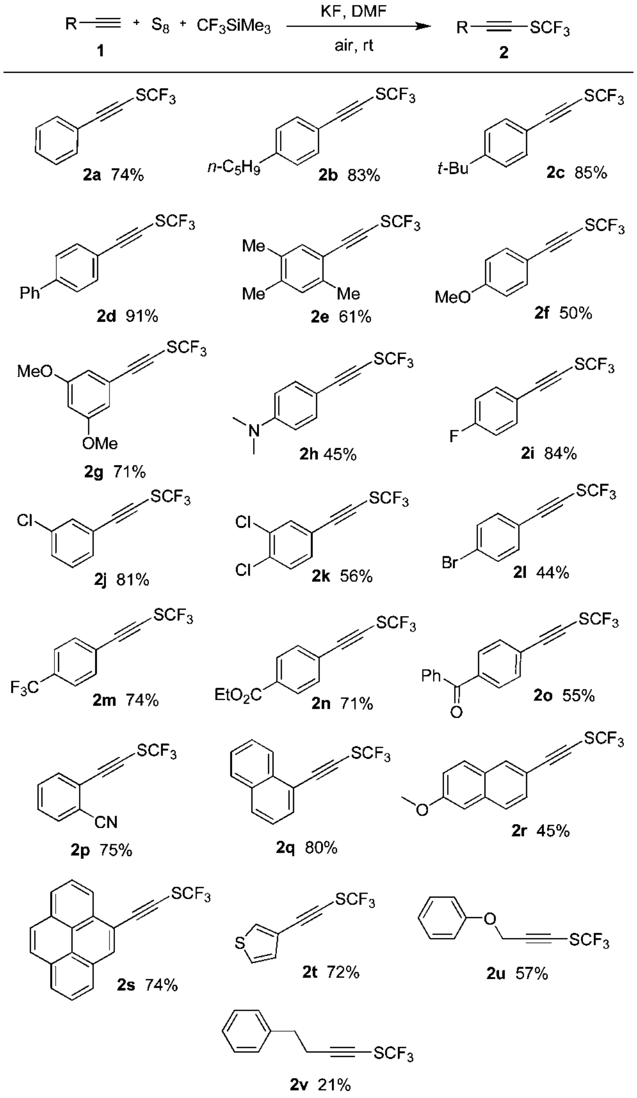
entry	CuI/phen (mol %)	S_8 (equiv)	solvent [0.05 M]	yield of 2a (3a)[b]
1	100	7	DMF	24% (22%)
2	10	7	DMF	67% (/)
3	/	7	DMF	82% (/)
4	/	6	DMF	92% (/)
5	/	5	DMF	62% (/)
6	/	4	DMF	7% (/)
7[c]	/	**6**	**DMF**	**96% (/)**
8[c,d]	/	6	DMF	55% (/)
9[c,e]	/	6	DMF	93% (/)
10[c,f]	/	6	DMF	91% (/)

[a] Reaction conditions: **1a** (0.2 mmol), S_8, CF_3SiMe_3 (5.0 equiv), KF (3.0 equiv), DMF (4 mL), rt, 6 h, under air. [b] Yields determined by ^{19}F NMR using fluorobenzene as an internal standard. [c] KF (2.0 equiv). [d] CF_3SiMe_3 (3.0 equiv). [e] Under Ar atmosphere. [f] Elemental sulfur purified by sublimation.

presence of 10 mol % of CuI and phen (entry 2). Surprisingly, when a control reaction in the absence of CuI and phen was conducted, product **2a** was formed in 82% yield (entry 3). Further investigations showed that the amount of elemental sulfur played an important role in achieving high transformation and high yield. The best yield of **2a** was obtained using 6.0 equiv of elemental sulfur, while only trace amounts of **2a** were observed when the loading of elemental sulfur was decreased to 4.0 equiv (entries 3−6). Exploration of solvents revealed that besides DMF, its analogue DMAC also promoted this transformation, affording product **2a** in moderate yield, whereas little or no product was detected when the reaction was conducted in CH_3CN, dichloromethane, THF, DMSO, or toluene (see Table S1 in Supporting Information). The yield of **2a** was further improved to 96% by decreasing the amount of KF to 2.0 equiv (entry 7). The use of an excess of CF_3SiMe_3 reagent was essential for the high efficiency of this reaction. Reducing the loading of CF_3SiMe_3 to 3.0 equiv resulted in much lower yield of **2a** (entry 8). Interestingly, oxygen was not required for this transformation. When the reaction was conducted in an argon atmosphere, **2a** was still formed in 93% yield (entry 9). The trifluoromethylthiolation with elemental sulfur purified by sublimation gave product **2a** in 91% yield (entry 10). This result precluded the possibility that trace metal impurities in elemental sulfur might be the catalyst for this transformation.

With the optimized conditions in hand (Table 1, entry 7), we next examined the substrate scope of this transformation and found that a series of the electron-rich and electron-deficient terminal alkynes can be transformed into their corresponding alkynyl trifluoromethyl sulfides in modest to good yields (Scheme 2). The mild reaction conditions employed allowed for the oxidative trifluoromethylthiolation of terminal alkynes containing a wide range of functional groups including amino, ester, cyano, and keto (**2h**, **2n−2p**). Moreover, arenes carrying Cl and Br substituents are compatible with the reaction conditions, providing opportunities for further modifications (**2j−2l**). The heterocyclic alkyne derived from thiophene can be trifluoromethylthiolated under the standard condition to afford **2t** in 72% yield. The aliphatic alkynes are also effective to give the desired products in moderate to good yields (**2u**, **2v**). To simplify the manipulation, all reactions were conducted in the atmosphere of dry air (Scheme 2).

Scheme 2. Scope of Metal-Free Oxidative Trifluoromethylthiolation of Terminal Alkynes[a]

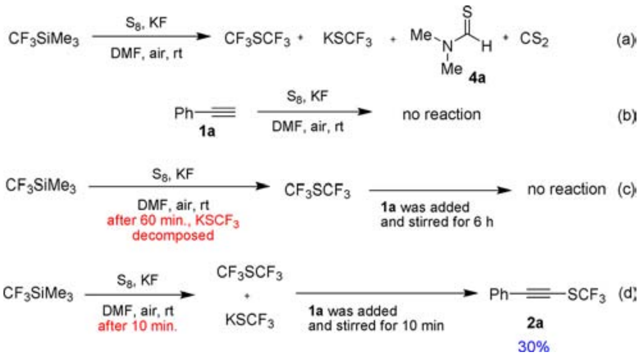


[a] Reaction conditions: **1** (0.2 mmol), S_8 (1.2 mmol), CF_3SiMe_3 (1.0 mmol), KF (0.4 mmol), DMF (4 mL), rt, 6 h, under air, isolated yields.

As mentioned above, an excellent yield of **2a** was still observed when the reaction was conducted in an argon atmosphere (Table 1, entry 9), implying the involvement of an alternative oxidant other than dioxygen. We hypothesized that elemental sulfur might be the real oxidant in this transformation.[13] Under the optimized conditions of entry 7 in Table 1, GC−MS analysis of the reaction mixture revealed the formation of a comparable amount (about 150% yield determined by GC−MS) of *N*,*N*-dimethylmethanethioamide **4a** and a small amount of CS_2. These results suggest that elemental sulfur did act as a stoichiometric oxidant in the current reaction.[13] In addition, these results also explain the observation that the most effective solvent was DMF, which was employed as the trap for the in situ generated S^{2-} species.

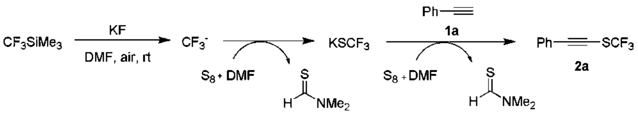
To gain some insight of the reaction mechanism and to further identify the role of elemental sulfur in this transformation, the following experiments were performed (Scheme 3). First, reaction of CF_3SiMe_3 with elemental sulfur and KF in DMF under air at room temperature was monitored by GC−MS and ^{19}F NMR spectroscopy. CF_3SCF_3 (resonated at $\delta = -38.6$ ppm in ^{19}F NMR),[7d] a SCF_3 anion species (the species might be $KSCF_3$, resonated at $\delta = -5.7$ ppm in ^{19}F NMR),[7d] *N,N*-dimethylmethanethioamide **4a**, and CS_2 were clearly observed in the reaction solution, suggesting that trapping of the in situ generated CF_3 anion by elemental sulfur and subsequent trapping of the resulting S^{2-} species by DMF and CO_2 took place under these reaction conditions (Scheme 3a). In contrast, no reaction was observed by GC−MS when a mixture of **1a**, elemental sulfur, and KF in DMF was stirred under air at room temperature (Scheme 3b). The SCF_3 anion species was unstable and underwent decomposition under the reaction conditions.[14] After 1 h at room temperature, only CF_3SCF_3 remained (Scheme 3c). To determine whether CF_3SCF_3 or $KSCF_3$ is the active trifluoromethylthiolating reagent, a mixture of these species was treated at room temperature with **1a**, and the reaction was monitored by ^{19}F NMR spectroscopy. It was found that the peak at $\delta = -5.7$ ppm corresponding to the anionic SCF_3 species disappeared after 10 min while the peak corresponding to CF_3SCF_3 species remained intact, and at the same time, the trifluoromethylthiolated product **2a** was obtained in 30% yield (Scheme 3d). Furthermore, when **1a** was added to the reaction mixture that contained CF_3SCF_3 species, no formation of the desired product was observed (Scheme 3c). These results suggested that the SCF_3 anion species might be the active species in these reactions.

Scheme 3. Mechanical Experiments



On the basis of these preliminary results, we proposed the reaction mechanism outlined in Scheme 4. CF_3SiMe_3 was first converted to the active SCF_3 anion species (might be $KSCF_3$) in the presence of KF, elemental sulfur, and DMF. The SCF_3 anion species then reacted with phenylacetylene **1a** in the presence of elemental sulfur as an oxidant to give the trifluoromethylthiolated product **2a**. However, the detail mechanism of the final oxidation step remains to be elucidated.

Scheme 4. Proposed Mechanism



To further determine whether the final step proceeded via a radical pathway, we conducted a series of inhibition experiments (see Table S2 in Supporting Information). The efficiency of reaction was not affected in the presence or absence of light. Furthermore, the addition of radical inhibitors, including TEMPO and hydroquinone, or an ET scavenger such as 1,4-dinitrobenzene, had a negligible effect on the yield of this reaction. These experiments indicated a radical pathway is less likely in this transformation. Further studies of reaction mechanism are in progress in our laboratory.

In summary, we have developed a metal-free oxidative trifluoromethylthiolation of terminal alkynes using readily available reagents CF_3SiMe_3 and elemental sulfur at room temperature. Preliminary investigation showed that the elemental sulfur instead of air acted as the oxidant in this transformation. Because of the high potential utility of alkynyl trifluoromethyl sulfides to a series of trifluoromethylthiolated compounds as biologically active agents, the metal-free and mild conditions employed, the easy access to reagents, and high compatibility of functional groups, we expect this method to find applications in pharmaceutical and agrochemical fields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data, and copies of ^1H, ^{19}F and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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