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SHORT COMMUNICATION

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Trifluoromethylthiolation of Diazo Compounds through Copper Carbene Migratory Insertion

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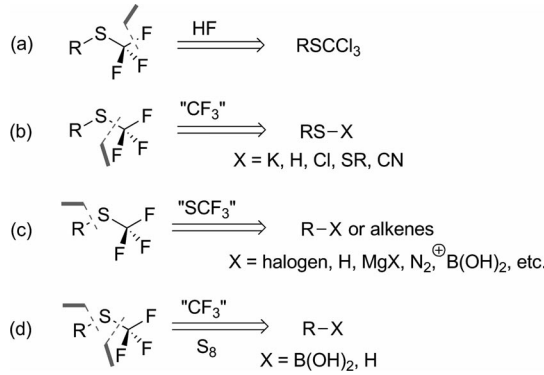
Keywords: Diazo compounds / Carbenes / Fluorine / Migratory insertion

A strategy to introduce the SCF_3 group through the Cu^I-promoted reaction of diazo compounds with the nucleophilic $AgSCF_3$ trifluoromethylthiolation reagent was developed. Various diazo compounds were smoothly converted under mild conditions to form the $C(sp^3)$–SCF_3 bond. Mechanistically, migratory insertion of SCF_3-bearing Cu carbene intermediates is involved in this transformation.

Introduction

Fluorine-containing molecules are valuable in many fields, ranging from agrochemicals and pharmaceuticals to materials science, because introduction of a fluorine or fluorinated functional group into organic moieties will lead to profound changes in their physical and chemical properties, as well as their bioactivity.[1] The trifluoromethylthio group (–SCF_3), privileged in the family of fluorinated functional groups as a result of its unique properties that include a strong electron-withdrawing inductive effect and admirable lipophilicity (π_R = +1.44), has become an important structural element of pharmaceutical and agrochemical agents.[2] However, SCF_3-bearing molecules do not exist in nature. It is therefore significant to develop general and practical methods to introduce a SCF_3 group onto organic moieties.

The trifluoromethylthiolated compounds are traditionally synthesized by the Swarts-type reaction, which involves exhaustive photochemical chlorination of the CH_3 group, followed by Cl/F exchange with anhydrous HF (Scheme 1, a). The harsh conditions in the Swarts-type reaction limit the diversity of functional groups in the substrates.[3] To solve such a problem, many milder methods have been explored. A widely practiced strategy is the trifluoromethylation of RSX sulfides, such as RSK,[4a] RSCl,[4b–4d] RSSR,[4e–4l] RSH,[4m,4n] and RSCN[4o] (Scheme 1, b).



Scheme 1. Retrosynthetic analysis for trifluoromethylthiolation.

Apparently, a more reasonable route to the SCF_3-bearing moiety is the direct incorporation of the SCF_3 group by using trifluoromethylthiolation reagents. In this context, a common approach involves the reaction of nucleophiles with electrophilic trifluoromethylthiolation reagents such as CF_3SCl,[5] RR′$NSCF_3$,[6] hypervalent iodine(III) reagents ("SCF_3^+"),[7] and trifluoromethanesulfonyl hypervalent iodonium ylides[8] or the reaction of electrophiles with nucleophilic trifluoromethylthiolation reagents ("SCF_3^-", Scheme 1, c).[9] More recently, efforts have been directed towards transition-metal-catalyzed or -mediated cross-coupling reactions of aryl iodides[10a,10b] and bromides[10c] and diazonium salts[10d,10e] with "SCF_3" sources and towards direct C–H trifluoromethylthiolation.[11] Moreover, a distinct method is the trifluoromethylthiolation of electron-rich π systems on the basis of a SCF_3 radical process.[12]

In addition to these strategies, aryl-SCF_3 and alkynyl-SCF_3 can also be accessed through the reaction of the corresponding aryl boronic acids or terminal alkynes, respectively, with elemental sulfur and $TMSCF_3$ (Scheme 1, d).[13]

Although remarkable advances in trifluoromethylthiolation have been made, most of the methods so far devel-

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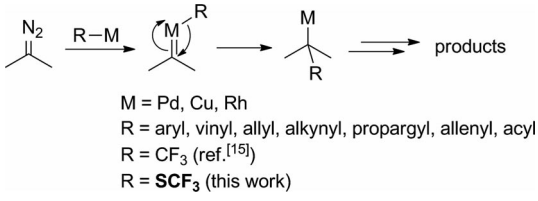
oped are encumbered by at least one of the following limitations: high reaction temperature, limited substrate scope, expensive and/or toxic reagents, costly catalysts/ligands, and cumbersome preparation of the starting materials or reagents.

In contrast, we and others have recently explored a set of transition-metal-catalyzed and -mediated cross-coupling reactions with diazo compounds as coupling partners.[14,15] The key step in these reactions is metal carbene migratory insertion, and the migratory groups include aryl, vinyl, allyl, alkynyl, propargyl, acyl, and allenyl groups (Scheme 2). Recently, Hu and co-workers explored this type of coupling reaction for trifluoromethylation and *gem*-difluoroolefination.[16] In connection to our interest in metal-carbene-based coupling reactions, we report herein a novel strategy for the construction of $C(sp^3)$–SCF_3 bonds through the direct conversion of the diazo group into the SCF_3 group.



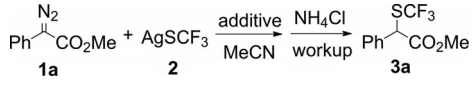
Scheme 2. Trifluoromethylthiolation through metal carbenes.

Results and Discussion

To implement this plan, we initially examined trifluoromethylthiolation by treatment of methyl α-diazophenylacetate (**1a**) with $AgSCF_3$ (**2**) at 0 °C in MeCN. However, only a trace amount of desired product **3a** was observed (Table 1, entry 1). The yield was improved to 10% if **1a** was added dropwise to a solution of **2** in MeCN over a period of 1 h (Table 1, entry 2). We surmised that the failure to obtain the trifluoromethylthiolated product in decent yield could be ascribed to the low efficiency of $AgSCF_3$ on decomposition of the diazo compound. Thus, we conceived that the employment of a copper salt as an additive might lead to an increase in the efficiency of the reaction. After screening copper species, we identified that the addition of 1.0 equiv. CuI to the reaction mixture afforded the coupling product in 45% yield on the basis of ^{19}F NMR spectroscopy analysis (Table 1, entries 3–5). However, reducing the amount of CuI to 20 mol-% led to a diminished yield (Table 1, entry 6).

If **1a** was added more slowly, we observed an increase in the yield of product **3a** from 45 to 53% (Table 1, entry 7). The data show that performing the reaction with a 1.5:1 ratio of **1a/2** at a lower temperature offered a further improvement in the conversion and yield (Table 1, entries 8 and 9). We speculated that the proton source would have a significant effect on the transformation. To our delight, 1.0 equiv. H_2O facilitated the protonation, and expected product **3a** was isolated in 83% yield (Table 1, entry 10). However, the yields of **3a** were appreciably diminished with the use of an excess amount of H_2O or with other sources

Table 1. Optimization of the trifluoromethylthiolation conditions.[a]



Entry	1a/2	Additive (equiv.)	Addition time [h]	T [°C]	Yield[b] [%]
1	1:1	none	0	0	trace
2	1:1	none	1	0	10
3	1:1	CuCl (1.0)	1	0	42
4	1:1	CuBr (1.0)	1	0	40
5	1:1	CuI (1.0)	1	0	45
6	1:1	CuI (0.2)	1	0	19
7	1:1	CuI (1.0)	5	0	53
8	1.5:1	CuI (1.0)	5	0	64
9	1.5:1	CuI (1.0)	5	–25	68
10	1.5:1	CuI (1.0), H_2O (1.0)	5	–25	84 (83)[c]
11	1.5:1	CuI (1.0), H_2O (1.5)	5	–25	73
12	1.5:1	CuI (1.0), MeOH (1.0)	5	–25	71
13	1.5:1	CuI (1.0), *i*PrOH (1.0)	5	–25	74
14[d]	1.5:1	none	5	–25	50
15	1.5:1	H_2O (1.0)	5	–25	10

[a] Reaction conditions: A solution of **1a** in MeCN (1 mL) was added dropwise to a mixture of **2** (0.3 mmol) and the additive in MeCN (0.5 mL) over the indicated time at low temperature. The reaction mixture was stirred for another 2 h at this temperature and then warmed up to r.t. Stirring was continued for another 3 h at r.t. Upon completion of the reaction, saturated aqueous NH_4Cl (3 mL) was added. [b] The yield is based on ^{19}F NMR spectroscopy analysis by using $PhCF_3$ as an internal standard. [c] The yield in parentheses refers to the yield of the isolated product. [d] $CuSCF_3$ was used instead of $AgSCF_3$.

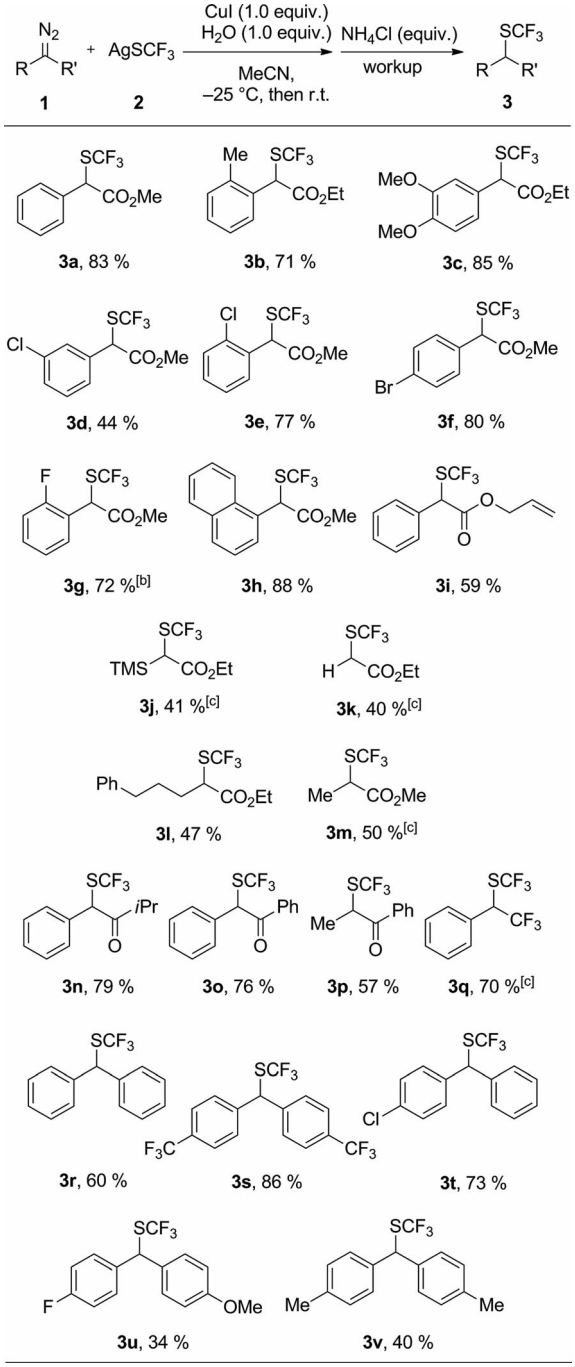
of proton, such as MeOH and *i*PrOH (Table 1, entries 11–13). If $CuSCF_3$ was used in the reaction instead of $AgSCF_3$, product **3a** was obtained in a decreased yield, which was indicative of its moderate reactivity in this reaction (Table 1, entry 14). However, a control experiment conducted in the absence of CuI demonstrated that a copper promoter was necessary (Table 1, entry 15).

With the optimal reaction conditions (Table 1, entry 10) identified, this novel trifluoromethylthiolation method was applied to structurally diverse diazo compounds **1a**–**v** (Table 2).

Generally, α-diazoarylacetates bearing either electron-donating or electron-withdrawing groups underwent the transformation smoothly to afford corresponding SCF_3-bearing products **3b**–**g** in moderate to good yields. Methyl α-diazo(1-naphthyl) acetate and allyl α-diazophenylacetate proved to be suitable substrates, and they gave rise to trifluoromethylthiolated compounds **3h** and **3i**, respectively. For TMS-substituted α-diazo esters and ethyl α-diazoacetate, the yields of **3j** and **3k** were determined on the basis of ^{19}F NMR spectroscopy owing to the volatility of the products.

It is noteworthy that alkyl-substituted **3l** and methyl-substituted **3m** could also be accessed through this strategy, albeit in relatively lower yield, and a small amount of alkene byproducts was generated through the competitive 1,2-H shift of the Cu carbene intermediate (see below). The α-diazo ketones exhibited reactivity similar to that of the α-

Table 2. Optimization of the trifluoromethylthiolation conditions.[a]

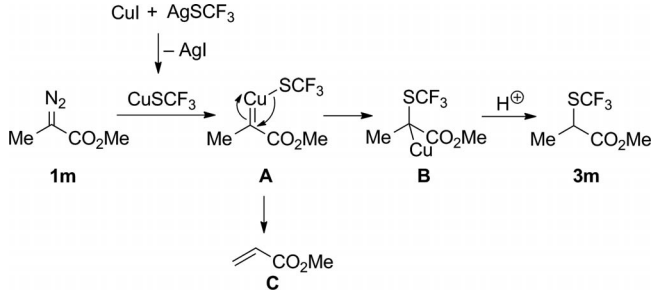


[a] Reaction conditions: A solution of **1a**–**v** (0.45 mmol, 1.5 equiv.) in MeCN (1 mL) was added dropwise to a mixture of **2** (0.3 mmol) and H_2O (1.0 equiv.) in MeCN (0.5 mL) over a period of 5 h at –25 °C. The reaction mixture was stirred for another 2 h at –25 °C and then warmed up to r.t. The stirring was continued for another 3 h at r.t. Upon completion of the reaction, saturated aqueous NH_4Cl (3 mL) was added. The yields refer to isolated products if not otherwise noted. [b] The yield of isolated **3g** is based on **1g**. See the Supporting Information for details. [c] The yield is based on ^{19}F NMR spectroscopy analysis by using $PhCF_3$ as the internal standard.

diazo ester analogues (i.e., **3n**–**p**). Notably, the trifluoromethylthiolation of 1-phenyl-2,2,2-trifluorodiazoethane was successfully achieved, and **3q** was produced in 70% yield.

This novel method was also applied to diaryl diazomethanes **1r**–**v**. In these cases, the efficiency of the reaction seemed to depend on the substituents on the aromatic ring. The conversion of diaryl diazomethane substrates bearing electron-withdrawing substituents on the aromatic ring generally resulted in good yield (i.e., **3s** and **3t**). In contrast, for substrates bearing electron-donating groups on the aromatic ring, the reaction was sluggish and afforded diminished yields (i.e., **3u** and **3v**).

A possible mechanism is proposed as shown in Scheme 3. Treatment of $AgSCF_3$ with CuI leads to the in situ generation of the more reactive $CuSCF_3$ species with the formation of AgI as a precipitate (see the Supporting Information for details).[9a] Decomposition of diazo compound **1m** by $CuSCF_3$ forms SCF_3-containing Cu carbene **A** as the key intermediate. Subsequently, migratory insertion occurs to generate Cu species **B**, protonation of which affords trifluoromethylthiolated product **3m**. From Cu^I carbene intermediate **A**, a competing 1,2-hydride shift occurs to give side product methyl acrylate **C**.



Scheme 3. Mechanistic rationale.

Conclusions

In summary, we demonstrated a novel cross-coupling reaction of various diazo compounds with the nucleophilic $AgSCF_3$ trifluoromethylthiolation reagent under mild conditions. The reaction involves the formation of a Cu^I carbene, migratory insertion of the carbene carbon to the Cu–SCF_3 bond, and finally protonation. The conversion is a valuable complement to the previously established trifluoromethylthiolation methods. In-depth mechanistic studies of the reaction and further exploration of novel methods based on the migratory insertion of transition-metal carbene intermediates will be the focus of future efforts in our laboratories.

Experimental Section

Typical Procedure for the Trifluoromethylthiolation of Diazo Compounds through Cu Carbene Migratory Insertion: An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (57 mg, 0.30 mmol, 1.0 equiv.) and $AgSCF_3$ (**2**; 63 mg, 0.30 mmol, 1.0 equiv.), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfill (three times) before MeCN (0.5 mL) was added. H_2O (6 mg, 0.30 mmol, 1.0 equiv.) was added by microsyringe to the resulting suspension, which was precooled to –25 °C (dry ice/*o*-xylene bath). Then, a solution of 2-

diazo-2-phenylacetate (**1a**; 79 mg, 0.45 mmol) in MeCN (1.0 mL) was added to the resulting suspension over a period of 5 h by using a syringe pump. Upon completion of the addition, the reaction mixture was stirred for 2 h at –25 °C and then warmed up to room temperature. Stirring was continued for an additional 3 h. A saturated aqueous solution of NH_4Cl (3 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic phase was dried with anhydrous Na_2SO_4 and then concentrated in vacuo. The crude residue was purified by silica gel column chromatography to afford methyl 2-phenyl-2-[(trifluoromethyl)-thio]acetate (**3a**) as colorless oil (62 mg, 83%).

Supporting Information (see footnote on the first page of this article): Experimental procedures and copies of the ^1H NMR and ^{13}C NMR spectra.

Acknowledgments

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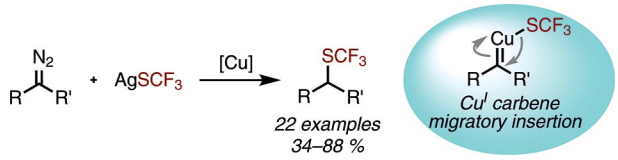

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Keywords: Diazo compounds / Carbenes / Fluorine / Migratory insertion

