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Sandmeyer trifluoromethylthiolation of arenediazonium salts with sodium thiocyanate and Ruppert-Prakash reagent

Trifluoromethyl thioethers are obtained directly from aryl and heteroaryl diazonium salts, sodium thiocyanate and the inexpensive, easy-to-use trifluoromethylating reagent $\text{Me}_3\text{Si}-\text{CF}_3$ in the presence of a copper thiocyanate catalyst. The preparative utility of this Sandmeyer-type trifluoromethylthiolation is demonstrated by the synthesis of 22 aryl and heteroaryl trifluoromethyl thioethers bearing various functionalities from the corresponding anilines.

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Sandmeyer trifluoromethylthiolation of
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In the presence of copper thiocyanate, sodium thiocyanate and the inexpensive, easy-to-use trifluoromethylating reagent $\text{Me}_3\text{Si}-\text{CF}_3$, diazonium salts are smoothly converted into the corresponding aryl trifluoromethyl thioethers. Combined with diazotisation, this convenient and inexpensive method allows the straightforward synthesis of aryl or heteroaryl trifluoromethyl thioethers from the corresponding anilines.

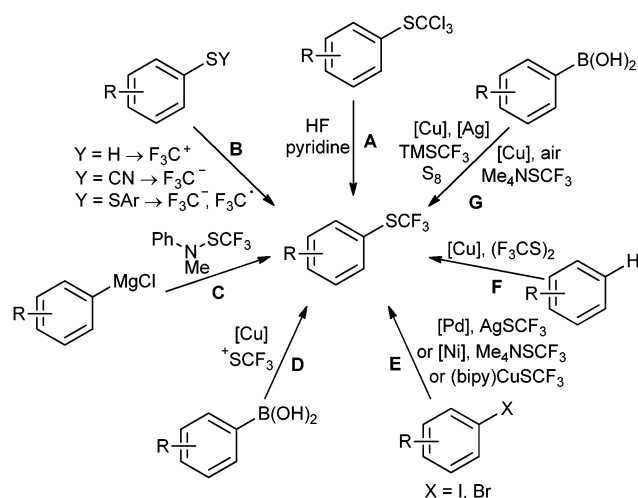
Introduction

In recent years, methods for the introduction of fluorine-containing groups into organic molecules have attracted great attention within organic synthesis, as they can impart desirable properties to bioactive compounds.¹ Substantial progress has recently been achieved in the field of late-stage trifluoromethylations,² whereas the corresponding trifluoromethylthiolations are less developed.³ In general, trifluoromethylthio groups induce even higher lipophilicity than trifluoromethyl substituents (Hansch constant $\pi = 1.44$ versus 0.88),⁴ and are more bulky. This allows a more effective transport of drug molecules through lipid membranes, thereby increasing their bioavailability. Thus, SCF_3 groups are often seen as key functionalities of many pharmaceutical and agrochemical products, such as tiflorex, toltrazuril (Baycox®) or vaniliprole.⁵

Traditional strategies

As shown in Scheme 1, several access routes exist for the formation of trifluoromethyl thioethers. Traditional strategies for the introduction of SCF_3 groups include halogen–fluorine exchange reactions of trihalogenomethyl thioethers (A),⁶ as well as trifluoromethylations of sulfur-containing compounds such as thiols,⁷ thiocyanates⁸ and disulfides,⁹ all of which have to be synthesised in additional steps (B). More modern, one-step trifluoromethylthiolation methods can be divided into four main categories: electrophilic (C and D), nucleophilic (E) and radical (F), as well as oxidative cross-couplings (G). Examples of

electrophilic processes are the reactions of trifluoromethanesulfonamides with aryl–magnesium or lithium reagents reported by Billard *et al.* (Scheme 1, C)¹⁰ and the copper-mediated reaction of arylboronic acids with hypervalent iodine– SCF_3 reagents by Lu and Shen (D).¹¹ Nucleophilic trifluoromethylthiolations include, for example, the palladium-catalysed trifluoromethylthiolation of aryl halides with sensitive AgSCF_3 by Buchwald *et al.*,¹² and the nickel-catalysed coupling of aryl halides either with the similarly unstable Me_4NSCF_3 by Zhang and Vicic,¹³ or with stable, but laborious-to-prepare copper–trifluoromethylthiolate complexes by Huang (E).¹⁴ C–H functionalizations are exemplified by the copper-mediated *ortho*-trifluoromethylthiolation of benzamides with $\text{CF}_3\text{S}-\text{SCF}_3$ by Daugulis *et al.* (F).¹⁵ Oxidative trifluoromethylthiolations have been reported by Qing *et al.*,^{16,17} who treated boronic acids with the Ruppert–Prakash reagent (TMSCF_3) and sulfur in the



Scheme 1 Strategies for the introduction of trifluoromethylthio groups.

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presence of CuSCN and silver carbonate (G). Very recently, Zhang and Vicić developed a similar oxidative trifluoromethylthiolation using $\text{Me}_4\text{N}^+\text{SCF}_3^-$ as the source of SCF_3^- .¹⁸

Although the above approaches provide viable routes for the formation of trifluoromethyl thioethers, they all entail shortcomings, such as the laborious multi-step preparation of starting materials or the use of expensive, air-sensitive or poorly available reagents. As an alternative, we present a cheap and straightforward synthesis of trifluoromethyl thioethers *via* a Sandmeyer-type reaction.

Sandmeyer trifluoromethylthiolation

In the context of our work on new trifluoromethylation reactions,^{19,20} we have developed an effective synthesis of benzotrifluorides *via* a Sandmeyer reaction.²¹ The key advantage of this reaction over related processes²² is that the Cu–CF₃ reagents are generated *in situ* from simple trifluoromethyl silanes or borates. An analogous reaction concept, in which easily accessible diazonium salts are converted into the corresponding trifluoromethyl thioethers *via* a redox-neutral reaction involving a nucleophilic CF₃ reagent in combination with a sulfur source, appeared to be a plausible and attractive way of introducing trifluoromethylthio groups (Scheme 2, bottom). Clark *et al.* have shown the principal feasibility of Sandmeyer trifluoromethylthiolations starting from preformed CuSCF₃. However, they found that their laboriously prepared CuSCF₃ complex transfers its SCF₃ group only reluctantly to diazonium salts, so that only a few electron-poor aryl trifluoromethyl thioethers could be accessed in reasonable yields.²³

Simply combining Clark's process with the *in situ* formation of the Cu–SCF₃ reagents from a trifluoromethylating and a sulfurising agent thus did not appear to be a promising strategy towards a one-step trifluoromethylthiolation process. This assumption was supported by a series of test experiments (Table 1, entries 1–3).

While searching for another straightforward strategy to introduce trifluoromethylthio groups, we reasoned that it should be advantageous to first connect the aryl–C–S and then the S–CF₃ bonds. In search for a viable reaction pathway, we struck upon a report by Langlois *et al.* in which they demonstrated that aryl thiocyanates can be trifluoromethylated with Ruppert–Prakash's reagent.⁸ We reasoned that if we performed a Sandmeyer thiocyanation²⁴ in the presence of a nucleophilic trifluoromethylation reagent, the arenediazonium salts might

Table 1 Optimisation of the reaction conditions^a

Entry	Sulfur source	Additive	Solvent	Yield of 2 ^b [%]
1 ^c	S ₈	CsF	MeCN	5
2 ^c	Lawesson's reagent	CsF	MeCN	Traces
3 ^c	Na ₂ S	CsF	MeCN	0
4	NaSCN	CsF	MeCN	30
5	KSCN	CsF	MeCN	Traces
6	NH ₄ SCN	CsF	MeCN	Traces
7	NaSCN	Cs ₂ CO ₃	MeCN	98
8	NaSCN	Cs ₂ CO ₃	DMF	81
9	NaSCN	Cs ₂ CO ₃	Acetone	18
10	NaSCN	—	MeCN	0
11	—	Cs ₂ CO ₃	MeCN	0
12 ^d	NaSCN	Cs ₂ CO ₃	MeCN	0
13 ^e	NaSCN	Cs ₂ CO ₃	MeCN	34
14 ^f	NaSCN	Cs ₂ CO ₃	MeCN	98
15 ^g	NaSCN	Cs ₂ CO ₃	MeCN	67

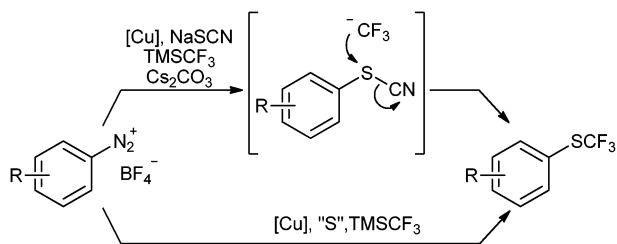
^a Reaction conditions: 0.5 mmol CuSCN, 2 equiv. additive, 1.5 equiv. sulfur source, 2 mL solvent, RT, dropwise addition of 0.5 mmol **1** in 2 mL of solvent, then 2 equiv. TMSCF₃, 12 h. ^b Yields were determined by ¹⁹F NMR using 1,3-difluorobenzene as an internal standard. ^c TMSCF₃ added before **1**. ^d Without CuSCN. ^e 1 equiv. Cs₂CO₃. ^f 0.5 equiv. CuSCN. ^g 0.1 equiv. CuSCN. Lawesson's reagent = 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione.

directly be converted into the corresponding aryl trifluoromethyl thioethers (Scheme 2, top). However, this appeared to be merely a theoretical possibility, since nucleophilic CF₃ sources are known to react smoothly with copper salts.^{2e,19–21} Thus, one would expect that any trifluoromethylating reagent capable of substituting a cyano group in an aryl thiocyanate would also react with CuSCN intermediates to give unwanted Cu–CF₃ or Cu–SCF₃ species. Nevertheless, we were intrigued by the prospects offered by a one-pot trifluoromethylthiolation process and decided to evaluate its feasibility.

Results and discussion

Development of a Sandmeyer trifluoromethylthiolation

We systematically investigated the reaction of 4-methoxybenzenediazonium tetrafluoroborate with sodium thiocyanate and TMS–CF₃ as a model system in the presence of various copper catalysts (see ESI†). As expected, anisole and 4-methoxybenzotrifluoride were formed in most cases, while the desired trifluoromethyl thioether **2** was only a minor product. However, when slowly adding the diazonium salt **1** and TMSCF₃ to a mixture of sodium thiocyanate, CuSCN and CsF in acetonitrile, the desired trifluoromethyl thioether **2** was obtained in an encouraging 30% yield, along with a residual aryl thiocyanate intermediate (Table 1, entry 4). Under these conditions, the formation of 4-(trifluoromethyl)anisole was no longer observed.



Scheme 2 Approaches to Sandmeyer trifluoromethylthiolations.



Further experiments revealed that sodium thiocyanate is the most effective reagent, whereas many other thiocyanate salts suppressed the subsequent trifluoromethylation step (entries 5 and 6). A decisive step-up in the yields was achieved when replacing CsF, which is commonly used to activate TMSCF_3 , with Cs_2CO_3 (entry 7). Acetonitrile was confirmed to be the most effective solvent, which corresponds well with the findings for other Sandmeyer reactions (entries 8 and 9).²⁵

Control experiments revealed that the reaction does not proceed if the copper mediator, the basic additive or sodium thiocyanate are omitted (entries 10–12). Reducing the amount of base to one equivalent led to decreased yields (entry 13). Even when the amount of copper was reduced to 50 mol%, the aryl trifluoromethyl thioether **2** was formed in a near-quantitative yield, with traces of the aryl thiocyanate as the only detectable by-product (entry 14). Reasonable yields were obtained even with only 10 mol% of copper (entry 15), which suggests that future catalyst generations will allow the metal loading to be lowered to truly catalytic amounts.

Scope of the new transformation

Having thus found an effective protocol for the trifluoromethylthiolation of arenediazonium salts, we next investigated its scope. As can be seen from the examples in Table 2, various arenediazonium tetrafluoroborates were smoothly converted into the corresponding aryl trifluoromethyl thioethers in moderate to excellent yields. In contrast to the reaction of diazonium salts with preformed CuSCF_3 , the new process is in no way limited to strongly electron-deficient derivatives.

Common functionalities including ester, ether, amino, keto, carboxylate and cyano groups were tolerated. Substrates containing chloro, bromo or even iodo substituents were trifluoromethylthiolated selectively at the position of the diazonium group. Various heterocycles such as quinoline, thiophene, benzothiazole and carbazole were also smoothly converted. Most products were directly obtained in a sufficiently pure form to allow their straightforward isolation. Only in a few cases did traces of the protodiazotisation products complicate the purification of the crude products. These results demonstrate the utility of the new reaction for the late-stage trifluoromethylthiolation of highly functionalised intermediates.

Mechanistic investigations

In order to gain a deeper mechanistic understanding, the reaction was investigated by ^{19}F NMR. Mixtures of CuSCN , TMS-CF_3 and Cs_2CO_3 in MeCN were found to contain CuCF_3 (-28.1 ppm) and $[\text{Cu}(\text{CF}_3)_2]^-$ (-31.2 ppm), but no CuSCF_3 species.²⁶ This indicates that the SCN^- anion does not react with TMS-CF_3 under the reaction conditions. When NaSCN was added to the above mixture, the formation of CF_3 -copper species was no longer observed. This explains why no trifluoromethylation products are obtained under the optimised conditions. Further experiments confirmed that 4-methoxybenzenediazonium tetrafluoroborate (**1**) is smoothly converted into the aryl thiocyanate by treatment with CuSCN , NaSCN and

Table 2 Scope of the trifluoromethylthiolation of arenediazonium salts^{a,b}

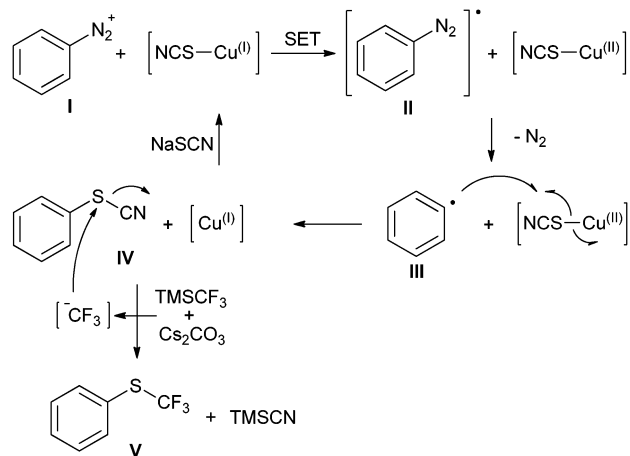
Ar-N_2^+ BF_4^-		TMSCF_3 CuSCN , Cs_2CO_3 NaSCN MeCN, RT	Ar-SCF_3
2 , 82%	3 , ^b 77%		4 , ^b 98%
			5 , ^b 98%
			6 , ^b 92%
			7 , 74%
8 , 86%	9 , 62%		11 , 63%
	10 , 71%		14 , ^b 98%
12 , 79%	13 , 83%		
15 , 74%	16 , 78%		17 , 23%
18 , 62%	19 , 55%		20 , 31%
21 , 66%	22 , 59%		23 , 42%

^a Reaction conditions: 1 mmol of arenediazonium tetrafluoroborate in 4 mL MeCN and 2 equiv. of TMSCF_3 were slowly added to 0.5 equiv. CuSCN and 2 equiv. Cs_2CO_3 in 4 mL MeCN and stirred for 12 h at RT. Isolated yields are noted. ^b Yields determined by ^{19}F NMR using 1,3-difluorobenzene as an internal standard.

Cs_2CO_3 in MeCN in the absence of a nucleophilic CF_3 source. Moreover, preformed aryl thiocyanate quickly reacted to the corresponding aryl trifluoromethyl thioether **2** in the presence of a mixture of TMSCF_3 and Cs_2CO_3 , a process that does not require copper. Thus, a Sandmeyer trifluoromethylthiolation pathway involving CuSCF_3 species was ruled out. Based on these results, we propose a mechanistic cycle, as depicted in Scheme 3.

The diazonium salt is initially converted into the thiocyanate *via* a Sandmeyer process, in which the $\text{Cu}^{\text{I}}\text{SCN}$ species first transfers a single electron to the diazonium salt (I). The resulting diazo radical II releases nitrogen gas with the formation of an aryl radical III, which takes up the thiocyanate group from the copper(II) intermediate to form the aryl thiocyanate IV. The presence of intermediate radicals was confirmed by the finding that the addition of TEMPO resulted in strongly





Scheme 3 Proposed mechanism.

decreased yields (20%). In the presence of Cs_2CO_3 , the nucleophilic trifluoromethylation reagent TMSCF_3 does not interfere with the above reaction steps, but efficiently converts the newly formed aryl thiocyanate to the trifluoromethyl thioether. This nucleophilic displacement of a cyanide leaving group by CF_3 is promoted by Cs_2CO_3 , probably by coordinating to the silicon atom in TMSCF_3 .

Conclusion

In conclusion, we have developed a straightforward, inexpensive and expedient method for the regioselective conversion of arenediazonium salts into the corresponding aryl trifluoromethyl thioethers. The reaction is broadly applicable to electron-rich and electron-poor arene- and heteroarene-diazonium salts and tolerates various functional groups. The availability of the substrates from the large pool of aromatic amines, the use of inexpensive reagents and the mild reaction conditions make this reaction particularly attractive for various applications from drug discovery to industrial-scale syntheses.⁵

Experimental section

The standard procedure for the synthesis of trifluoromethyl thioethers from the corresponding arenediazonium salts is as follows. Under a nitrogen atmosphere, an oven-dried 20 mL crimp cap vessel with a Teflon-coated stirrer bar was charged with copper thiocyanate (61.4 mg, 0.50 mmol), caesium carbonate (652 mg, 2.00 mmol) and sodium thiocyanate (122 mg, 1.50 mmol). Acetonitrile (4 mL) was added *via* syringe and the resulting suspension was stirred at room temperature for 10 minutes. A solution of the arenediazonium tetrafluoroborate (1.00 mmol) in acetonitrile (4 mL) was added dropwise *via* syringe and the reaction mixture was stirred for another 10 minutes. Trifluoromethyl-trimethylsilane (321 μL , 2.00 mmol) was then added *via* syringe and the mixture was stirred at ambient temperature for 16 h. The resulting mixture was filtered through a short pad of Celite (5 g) and rinsed with diethyl ether (20 mL). The resulting organic solution was

washed with water (10 mL) and brine (10 mL). The organic layer was dried over MgSO_4 , filtered and concentrated (700 mbar, 40 °C). The residue was further purified by flash chromatography (SiO_2 , diethyl ether–hexane gradient), yielding the corresponding trifluoromethyl thioethers.

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