Thioether Synthesis

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Copper-Catalyzed Oxidative Trifluoromethylthiolation of Aryl Boronic Acids with $TMSCF_3$ and Elemental Sulfur[**]

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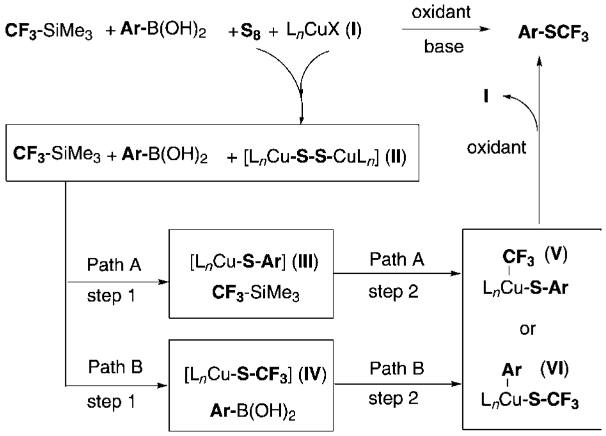
Fluorinated functional groups are key structural units found in various pharmaceuticals and agrochemicals.[1] Approximately 30 % of all agrochemicals and 20 % of all pharmaceuticals on the market contain fluorine. Among these substituents, the trifluoromethylthio group (CF_3S-), especially as an aromatic substituent, plays an important role because of its strong electron-withdrawing effect and high lipophilicity. These characteristics are similar to those of trifluoromethyl (CF_3-) and trifluoromethoxy (CF_3O-) groups.[2] Additionally, aryl trifluoromethyl thioethers (CF_3SAr) are also key intermediates in the preparation of trifluoromethyl sulfoxide and sulfone, which are important trifluoromethylation reagents.[3] Although impressive progress has been made in the trifluoromethylation of arenes in the past several years,[4–7] only a few methods are available for the synthesis of aryl trifluoromethyl thioethers.[8,9] Generally, aryl trifluoromethyl thioethers are prepared either by a nucleophilic reaction of trifluoromethylthiolate with aryl halides,[8] or by a nucleophilic or radical reaction of aryl sulfides and disulfides with a trifluoromethylation reagent.[9] However, these methods are variously limited by a combination of high temperatures, expensive reagents, and low reactivity with electron-rich aromatic groups. Thus, the development of general, safe, and efficient methods to access aryl trifluoromethyl thioethers is highly desirable. Very recently, Buchwald reported a palladium-catalyzed trifluoromethylthiolation of aryl bromides with CF_3SAg.[10] This breakthrough for the preparation of $ArSCF_3$ is highly efficient and compatible with a variety of functional groups. However, from the point view of cost-effectiveness and synthetic convenience, using readily available and inexpensive catalysts and fluorinated reagents, such as copper and (trifluoromethyl)trimethylsilane (the Ruppert–Prakash reagent, $TMSCF_3$), to access aryl trifluoromethyl thioethers would be an attractive alternative.

The present study was inspired by our own and Buchwald's recent investigations into the copper mediated oxidative trifluoromethylation of arylboronic acid with $TMSCF_3$,[11] as well as Karlin's observation of the formation of a stable copper disulfide complex from the reaction of elemental sulfur (S_8) with a Cu^I complex.[12] We hypothesized that a Cu^I disulfide complex generated in situ (**II**; Scheme 1) would react with aryl boronic acid to give intermediate **III** (Path A), which would subsequently react with $TMSCF_3$, providing the key intermediate complex $L_nCu(CF_3)(ArS)$ (**V**). Finally, oxidation of complex **V** to $L_nCu^{III}(CF_3)(ArS)$,[13] followed by reductive elimination would lead to the expected aryl trifluoromethyl thioether. Alternatively, intermediate **IV** could be formed by the reaction of $TMSCF_3$ with complex **II** (Path B). The desired product might still be obtained from oxidation of key intermediate **VI**, generated from complex **IV**.



Scheme 1. Copper(I)-catalyzed formation of aryl trifluoromethyl thioether from aryl boronic acid, $TMSCF_3$, and S_8.

Herein, we report the first example of the copper-catalyzed oxidative trifluoromethylthiolation of arylboronic acids with $TMSCF_3$ and elemental sulfur at room temperature. The notable features of this reaction are its high efficiency, excellent functional group compatibility (bromide is also compatible), operational simplicity, inexpensive catalyst, easily accessible starting materials, and mild reaction conditions.

In accordance with our hypothesis, we began this study by reacting phenyl boronic acid **1**, $TMSCF_3$, and S_8 in the presence of different copper salts, bases, and oxidants to optimize the reaction conditions. To our delight, when the

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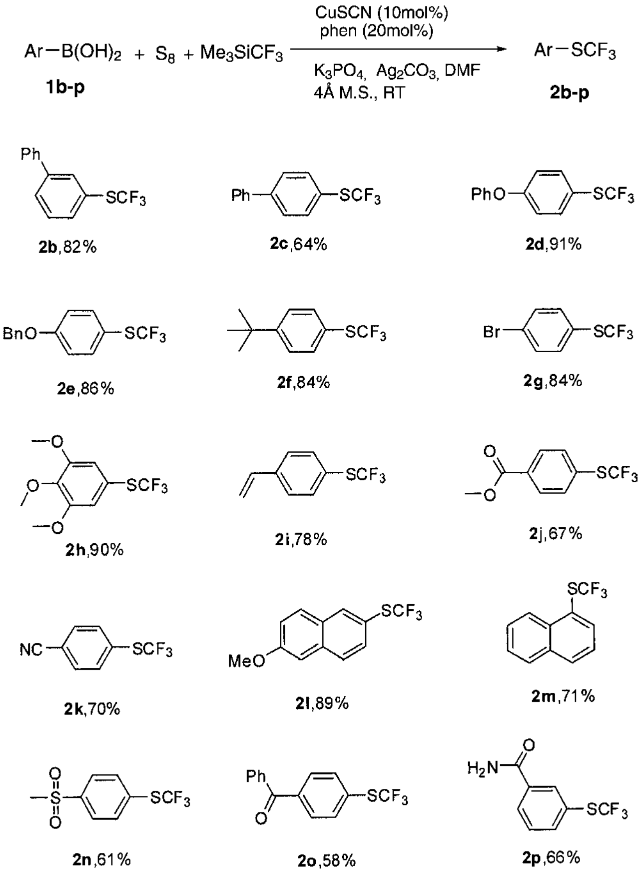
reaction was conducted with CuI (1.0 equiv) and 1,10-phenanthroline (phen; 1.1 equiv) in the presence of Ag_2CO_3 (2.0 equiv) as oxidant, along with K_3PO_4 (1.0 equiv) and KF (1.0 equiv) as bases, and 4 Å molecular sieves (4 Å M.S.), in DMF at room temperature, phenyl trifluoromethyl thioether **2a** was formed in 33 % yield (Table 1, entry 1). The undesired products phenyl disulfide (**3**) and cyclic trimeric phenyl boronic acid anhydride (**4**) were observed in the reaction mixture. Furthermore, reactions without CuI, phen, or Ag_2CO_3 failed to afford desired product **2a**, thus showing the pivotal role of these reagents in the reaction (entries 2–4). Interestingly, when K_3PO_4 was used as both base and initiator for $TMSCF_3$, the yield increased to 43 % (entry 6). The formation of **4** indicated that the intermediate **III** might be generated slowly. Likewise, the formation of **3** arose from the homocoupling of copper complex **III**; an indication that the reaction of **III** with $TMSCF_3$ to form **V** was even slower. Therefore, if a suitable copper salt was used to accelerate step 1 (the formation of copper complexes **III** from intermediate **II**) and step 2 (formation of **V** from **III**), and a proper oxidant was employed to facilitate the reductive elimination of **V** (Scheme 1), the formation of byproducts **3** and **4** would be inhibited and thus lead to improved yield of desired product **2a**. Accordingly, different copper salts and oxidants were examined to improve the reaction efficiency. After many attempts, CuSCN and Ag_2CO_3 were found to be the best choices, providing **2a** in 72 % yield along with a small amount of phenyl disulfide **3** (Table 1, entry 13). To further inhibit the formation of **3**, 5.0 equivalents of $TMSCF_3$ was used, further improving the yield to 85 % (Table 1, entry 14). Notably, a catalytic amount of CuSCN (10 mol %) and phen (10 mol %) still furnished **2a** in a comparable yield (78 %). Further increasing the loading of phen to 20 mol % provided the optimum yield of **2a**, 95 % (entry 16).

Table 1: Optimization of the copper-catalyzed oxidative trifluoromethylthiolation of phenyl boronic acid.[a]

Entry	CuX	Base	Oxidant	Yield [%][b]
1[c]	CuI	K_3PO_4/KF	Ag_2CO_3	33
2[c,d]	CuI	K_3PO_4/KF	Ag_2CO_3	0
3[c]	–	K_3PO_4/KF	Ag_2CO_3	0
4[c]	CuI	K_3PO_4/KF	–	0
5	CuI	KF	Ag_2CO_3	23
6	CuI	K_3PO_4	Ag_2CO_3	43
7	CuCl	K_3PO_4	Ag_2CO_3	19
8	CuBr	K_3PO_4	Ag_2CO_3	19
9	CuOAc	K_3PO_4	Ag_2CO_3	21
10	$(CuOTf)_2C_6H_6$	K_3PO_4	Ag_2CO_3	18
11	$K_4[Cu_2(CN)_6]$	K_3PO_4	Ag_2CO_3	9
12	CuCN	K_3PO_4	Ag_2CO_3	61
13	CuSCN	K_3PO_4	Ag_2CO_3	72
14[e]	CuSCN	K_3PO_4	Ag_2CO_3	85
15[e,f]	CuSCN	K_3PO_4	Ag_2CO_3	78
16[e,g]	CuSCN	K_3PO_4	Ag_2CO_3	95

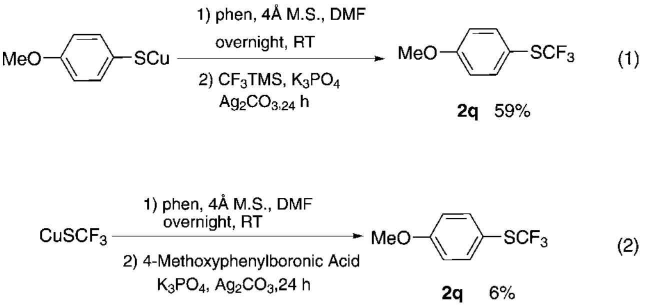
[a] Reaction conditions: **1** (0.2 mmol), S_8 (0.6 mmol), $TMSCF_3$ (0.6 mmol), CuX (0.2 mmol). phen (0.22 mmol), base (0.4 mmol), oxidant (0.4 mmol), 4 Å M.S. (50 mg), DMF (4 mL), 24 h, N_2, RT. [b] Determined by ^{19}F NMR. [c]1.0 equiv of K_3PO_4 and 1.0 equiv of KF. [d] Without phen. [e] With 5.0 equiv of $TMSCF_3$ and 3.0 equiv of K_3PO_4. [f] With 10 mol% of CuSCN and 10 mol% phen. [g] With 10 mol% of CuSCN and 20 mol% phen.

With the optimum reaction conditions (Table 1, entry 16) determined, the substrate scope of the reaction was then investigated (Scheme 2). The mild reaction conditions allowed for the trifluoromethylthiolation of aryl boronic acids containing a range of functional groups, including ester, unprotected amide, ketone, nitrile, and sulfonyl groups. Notably, even for the substrates bearing bromide or vinyl group, which are reactive in the presence of a Pd^0 catalyst, good yields were still obtained, thus providing opportunities for further transformation.



Scheme 2. Scope of the Copper(I)-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids. Reaction conditions: **1** (0.2 mmol), S_8 (0.6 mmol), $TMSCF_3$ (1.0 mmol), CuSCN (0.02 mmol), Phen (0.04 mmol), K_3PO_4 (0.6 mmol), Ag_2CO_3 (0.4 mmol), 4 Å M.S. (50 mg), DMF (3 mL), 24 h, N_2, RT. Yields shown are of isolated products.

To investigate the mechanism of the oxidative trifluoromethylthiolation, several experiments were performed. First, the reaction of 3,4,5-trimethoxyphenyl boronic acid (**1h**) with S_8, CuSCN, and phen in the presence of K_3PO_4 in [D$_7$]DMF at room temperature was monitored by ^1H NMR spectroscopy (see the Supporting Information). A new species corresponding to intermediate **III** was observed. GC/MS analysis of the reaction mixture showed a peak at $m/z = 199$, which was assigned to $Ph(OMe)_3S^-$, suggesting that the formation of intermediate **III** from boronic acid **1**, S_8, and Cu^I is a reasonable proposal. In contrast, neither CF_3S-Cu nor CF_3-Cu was observed when a mixture of $TMSCF_3$, CuSCN, phen, S_8, and K_3PO_4 in DMF was stirred at room temperature (see the Supporting Information). Furthermore, the reaction of copper 4-methoxyphenyl thiolate[14] with $TMSCF_3$ in the presence of Ag_2CO_3 and K_3PO_4 at room temperature proceeded smoothly to give **2q** as the only fluorinated product in 59% yield (determined by ^{19}F NMR; Eq. (1) of Scheme 3). However, only trace **2q** was detected in the reaction of copper trifluoromethyl thiolate ($CuCF_3$)[15] with 4-methoxyphenyl boronic acid (Eq. (2) of Scheme 3). Based on these results, we propose that path A (Scheme 1) is the likely pathway for the copper-catalyzed oxidative trifluomethylthiolation of aryl boronic acids with $TMSCF_3$ and S_8.[16]



Scheme 3. Synthesis of trifluoromethyl 4-methoxyphenyl thioether.

In summary, we have developed the first copper(I)-catalyzed oxidative trifluoromethylthiolation of arylboronic acid using $TMSCF_3$ and S_8 at room temperature. This reaction provides an efficient and convenient method for the preparation of aryl trifluoromethyl thioethers. An organocopper disulfide complex was proposed as the key intermediate in the catalytic cycle.

Experimental Section

General procedure for oxidative trifluoromethylthiolation: In a glove box, 4 Å powdered molecular sieves (50 mg) and K_3PO_4 (128 mg, 0.6 mmol, 3.0 equiv) were added to a test tube equipped with a magnetic stir bar. The vessel was sealed with a septum and flame-dried under vacuum. The tube was cooled to room temperature and backfilled with argon. Then CuSCN (3 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (8 mg, 0.04 mmol, 0.2 equiv), S_8 (20 mg, 0.6 mmol, 3.0 equiv), aryl boronic acid **1** (0.2 mmol, 1.0 equiv), and Ag_2CO_3 (110 mg, 0.4 mmol, 2.0 equiv) were quickly added under a N_2 atmosphere. The tube was then evacuated and backfilled with argon gas. Freshly distilled DMF (5 mL) and $TMSCF_3$ (150 µL, 1.0 mmol, 5.0 equiv) were then added to the reaction tube by syringe, which was then placed under a balloon of N_2 and stirred vigorously for 24 h. Fluorobenzene (56 µL, 0.6 mmol) was added as an internal standard, and the yield of the crude reaction was measured by ^{19}F NMR before workup. The reaction solution was filtered through Celite on silica and the filter cake was washed with diethyl ether. The filtrate was then washed with brine and concentrated. The residue was purified by silica gel column chromatography with hexane to provide pure aryl trifluoromethyl thioether.

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