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# Radical Aromatic Trifluoromethylthiolation: Photoredox Catalysis vs. Base Mediation

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**Abstract:** Trifluoromethyl aryl sulfides (Ar-SCF<sub>3</sub>) constitute highly attractive building blocks due to their exceptional lipophilicity and chemical properties. Related protocols of radical aromatic trifluoromethylthiolation of arenediazonium salts were developed that are based on the facile generation of intermediate aryl radicals. Their reactions with commercial F<sub>3</sub>CS-SCF<sub>3</sub> under very mild conditions afforded a diverse set of Ar-SCF<sub>3</sub> (<90% yield). Direct comparison of photoredox catalysis (eosin Y or [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>) with the weak basemediated dark reaction documented higher synthetic efficiency of the former but higher operational simplicity of the latter strategy.

#### Introduction

Even though fluorine containing compounds are the least spread among naturally occurring organic halides,<sup>1</sup> fluorine-containing substituents have recently emerged as a widespread and significant component in pharmaceuticals,<sup>2</sup> agrochemicals<sup>3</sup> and materials<sup>4</sup>. Beside the introduction of fluorides, trifluoromethyl, and other perfluoroalkyl units, the trifluoromethylsulfanyl (SCF<sub>3</sub>) group has attracted great attention for its exceptional physical and chemical properties. Several well-known drugs, comprising SCF<sub>3</sub>, are depicted in the Scheme 1.<sup>5</sup> The trifluoromethylsulfanyl group (SCF<sub>3</sub>) is a chemically stable, relatively polar and strongly electron-withdrawing substituent that imparts very high lipophilicity to an organic molecule. Despite its polarity ( $\sigma_0$ =0.48, cf. 0.23 (Cl), 0.53 (CF<sub>3</sub>), 0.66 (CN)), SCF<sub>3</sub> exhibits the highest Hansch lipophilicity constant among standard heteroatomic organic substituents ( $\pi_p$ =1.44, cf. 0.88 (CF<sub>3</sub>), 0.14 (F), 1.68 (*t*Bu)).<sup>6</sup> The synthetic procedures for the decoration of arenes residues with the trifluoromethylsulfanyl substituents are manifold (Scheme 1): i) substitution of electron-rich arenes (ArH,<sup>7</sup> ArM, M=Mg,<sup>8</sup> B<sup>9</sup>) with electrophilic SCF<sub>3</sub> reagents; *ii*) metal-mediated trifluoromethylsulfanylation of electrophilic aryl halides and arenediazonium salts with formally anionic SCF3 species such as AgSCF<sub>3</sub> or Me<sub>4</sub>NSCF<sub>3</sub>,<sup>10</sup> iii) reaction of aryl-S precursors with trifluoromethylation reagents;11 iv) halogenfluorine exchange of polyhalogenoalkyl thioethers.<sup>12</sup> Electrophilic SCF<sub>3</sub>-containing reagents include the easy-to-handle trifluoromethanesulfenyl trifluoroacetate, the disulfide (CF<sub>3</sub>S)<sub>2</sub>, the gaseous CISCF<sub>3</sub>, PhN(Me)SCF<sub>3</sub>, and hypervalent aryliodane reagents comprising the SCF<sub>3</sub> group. Copper, silver, and

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ammonium trifluoromethyl thiolates are commonly employed as  $SCF_3$  nucleophiles.



Scheme 1. Important synthesis routes to aryl trifluoromethyl sulfides.

We have recently reported on the photoredox-catalyzed synthesis of arylsulfides from arenediazonium salts and disulfides in the presence of eosin Y under green light irradiation (Scheme 2, top).<sup>13</sup> Later, we have developed a weak basemediated protocol of very similar scope.<sup>14</sup> Most of the examples reported involved unfunctionalized dialkyl and diaryldisulfides. Here, we report the extension of these operationally facile radical aromatic thiolation methods to include the synthesis of trifluoromethylsulfanyl benzenes (Scheme 2, bottom).<sup>10d-f</sup> Both, dark reactions in the presence of weak base and photoredox catalytic conditions were studied.



Scheme 2. Radical thiolations by photoredox catalysis and base mediation.

### **Results and Discussion**

Bis(trifluoromethyl) disulfide, F<sub>3</sub>CS-SCF<sub>3</sub>, is a commercial reagent that can also be freshly prepared on lab scale by a literature procedure. The synthesis involves three sequential halogenation steps starting from carbon disulfide (Scheme 3). However, the low boiling points and toxicity of the intermediates and the product (~34 °C) require special precautions. Trichloromethylsulfenyl chloride was synthesized by chlorination of CS<sub>2</sub> with elemental chlorine.<sup>15</sup> The major side reaction is the decomposition of sulfur dichloride to disulfur dichloride which can be suppressed by the addition of acetylacetone.<sup>16</sup> Halogen exchange with aqueous HBr afforded trichloromethylsulfenyl bromide which underwent fluorination and dimerization by action of KF in hot sulfolane.<sup>17</sup> Pure 1,2-bis(trifluoromethyl) disulfide could be stored in a freezer over longer periods of time without decomposition (<sup>19</sup>F NMR, 282 MHz, CDCl<sub>3</sub>: 45.8 ppm). Our attempt to replace sulfolane with DMSO as the reaction solvent in the final step led to rapid decomposition and gas evolution even below 150 °C.



Scheme 3. Synthesis of 1,2-bis(trifluoromethyl) disulfide.

Initial optimization experiments (Table 1) were performed with equimolar 4-bromobenzenediazonium tetrafluoroborate and  $(F_3CS)_2$ . The dark reactions in the absence of base gave no conversion (entries 1, 3, 5). With sodium acetate (NaOAc) as weak base, moderate conversion to 4-bromotrifluoromethyl-sulfanyl benzene was observed (procedure **A**, entry 2). Significantly higher yields were obtained from photoredox-catalytic reactions with eosin Y (**B**: 2 mol%, 525 nm) and [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>\*6H<sub>2</sub>O (**C**: 0.5 mol%, 450 nm), respectively, under LED (3.8 W) irradiation (entries 4, 6). Employment of 0.5 equiv. (F<sub>3</sub>CS)<sub>2</sub> resulted in slightly lower yields (entry 7). A reaction profile analysis documented the rapid onset of trifluoromethylthiolation for all three procedures (>90% relative product formation within the first 3 h) and the highest reaction rate of the photoredox catalysis with only 0.5 mol% [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (Figure 1).

Then, we subjected a set of five arenediazonium salts to a comparative study of trifluoromethylthiolation under the three reaction conditions **A-C** (Table 2). In all cases, the majority of product formation occurred in the first 3 h of the reaction. Photoredox catalysis conditions with  $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$  fared best for all substrates tested; eosin Y was only slightly less active. While being the operationally most simple strategy, the weak base mediated procedure gave significantly lower yields. The optimized conditions were then applied to eight different arenediazonium salts in the presence of  $[Ru(bpy)_3]Cl_2$  under irradiation with blue light (450 nm, one external 3.8 W LED per reaction). Moderate to good yields of the desired aryl trifluoromethylsulfides were isolated after only 1 h reaction (Scheme 4).

Table 1. Base-mediated and photoredox-catalyzed trifluoromethylthiolation.<sup>a</sup>



[a] Conditions: 4-Bromobenzenediazonium tetrafluoroborate (0.3 mmol), DMSO (1.5 mL), under N<sub>2</sub>, 6 h. Procedure A: NaOAc (0.3 mmol), 20 °C; B: eosin Y (0.012 mmol), irradiation with green LED (525 nm, 3.8 W), 20 °C; C: [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (0.012 mmol, bpy=2,2'-bipyridine), irradiation with blue LED (450 nm, 3.8 W), 20 °C. [b] GC yields vs. internal 1-dodecanenitrile. [c] dark reaction. [d] 0.5 equiv. ( $F_3CS$ )<sub>2</sub>.



Figure 1. Reaction profiles of procedures A-C (for conditions, see Table 1).

Based on recent reports,<sup>13,14</sup> we postulate a radical mechanism that is initiated by the reductive activation of the arenediazonium salt (Scheme 5). With the weak base sodium acetate, this most likely involves the formation of the diazoacetate adduct which thermally releases the aryl radical Ar•. Under photocatalytic conditions, single electron transfer (SET) occurs with the excited photocatalyst PC (eosin Y or [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>). Ar• undergoes rapid reaction with the non-bonding electron donor (SCF<sub>3</sub>)<sub>2</sub>. Cleavage of the resultant disulfide radical generates the trifluoromethylthiyl radical  $F_3CS$ • which readily engages in hydrogen atom transfer or possibly recombines with suitable nucleophiles (not detected). Back-electron transfer (formally from the elusive [NuSCF<sub>3</sub>]<sup>-</sup>) could be a potential pathway of photocatalyst regeneration. Upon addition of TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl,

Table 2. Comparison of procedures A-C for selected arenediazonium salts.<sup>a</sup>



Entry	Ar-SCF₃	<b>A</b> (NaOAc) Yield in % <sup>b</sup> 3 h (24 h)	<b>B</b> (eosin Y) Yield in % <sup>b</sup> 3 h (24 h)	<b>C</b> (Ru(bpy)₃Cl₂) Yield in % <sup>b</sup> 3 h (24 h)
1	4-Br	35 (40)	55 (66)	67 (68)
2 °	4-Br	30 (33)	50 (56)	57 (59)
3	4-OMe	75 (76)	77 (77)	77 (79)
4	4-NO <sub>2</sub>	28 (34)	53 (67)	61 (71)
5	4-F	27 (31)	73 (81)	89 (89)
6	Ph	27 (33)	59 (60)	68 (69)

[a] Conditions: Arenediazonium tetrafluoroborate (0.3 mmol), DMSO (1.5 mL), under N<sub>2</sub>, 24 h. Procedure **A**: NaOAc (0.3 mmol), 20 °C.; **B**: eosin Y (0.006 mmol), green LED (525 nm, 3.8 W), 20 °C; **C**: [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (0.0015 mmol), blue LED (450 nm, 3.8 W), 20 °C. [b] GC yields vs. internal 1-dode-canenitrile. [c] 0.5 equiv. ( $F_3CS$ )<sub>2</sub>.



Scheme 4. Ru-catalyzed photoredox-trifluoromethylthiolation (isolated yields).

both radical intermediates as TEMPO adducts were observed by mass spectrometry.



Scheme 5. Postulated reaction mechanism.<sup>13,14</sup>

#### Conclusions

We have developed three related synthetic protocols that enable the straight-forward trifluoromethylthiolation of readily available arenediazonium salts with the commercial disulfide ( $F_3CS$ )<sub>2</sub>. Weak base-mediated reactions in the presence of one equiv. NaOAc are operationally most simple but afforded only moderate yields. The photoredox-catalyzed protocols gave significantly higher yields of the Ar-SCF<sub>3</sub> products. With only 0.5 mol% [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O, very good yields were obtained after irradiation with blue light at room temperature for 1 h.

#### **Experimental Section**

Synthesis of arenediazonium salts: The parent aniline (30 mmol) was dissolved in 32% aqueous HBF<sub>4</sub> (12 mL) at room temperature. An aqueous solution of NaNO<sub>2</sub> (30 mmol) in water (4 mL) was added dropwise at 0 °C over 5 min. The resulting mixture was stirred for 40 min and the precipitate was collected by filtration and re-dissolved in a minimal amount of acetone. Diethyl ether was added to precipitate the diazonium tetrafluoroborate, which was filtered, washed several times with diethyl ether and dried.

Base-induced trifluoromethylthiolation: A vial (5 mL) was charged with a magnetic stir bar, the arenediazonium salt (0.9 mmol), 1,2-bis(trifluoromethyl)disulfane (0.9 mmol) and sodium acetate (0.9 mmol) and capped with a rubber septum. The vial was purged with N<sub>2</sub> (5 min), and dry DMSO (4.5 mL) was added. After 8 h of stirring at room temperature, water (5 mL) was added to give an emulsion which was extracted with diethylether (3×5 mL). The organic phases were washed with brine (5 mL) and dried over MgSO<sub>4</sub>. Solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (SiO<sub>2</sub>, pentane/ ethyl acetate from 5/0 to 5/1).

Photo-catalytic trifluoromethylthiolation: A vial (5 mL) was charged with a magnetic stir bar, the arenediazonium salt (0.9 mmol) and photocatalyst (0.018 mmol, 2 mol% Eosin Y or 0.0045 mmol, 0.5 mol% [Ru(bpy)\_3]Cl\_2·6H\_2O). Dry DMSO (4.5 mL) was added, and the vial was purged with N<sub>2</sub> (5 min). 1,2-Bis(trifluoromethyl)disulfane (0.9 mmol) was added, and the reaction vessel was sealed with a rubber septum. The mixture was irradiated with green light (eosin Y, LED, 525 nm, 3.8 W) for 6 h or with blue light ([Ru(bpy)\_3]Cl\_2·6H\_2O, LED, 450 nm, 3.8 W) for 1 h. After the irradiation was discontinued, water (5 mL) was added to give an emulsion which was extracted with diethylether (3×5 mL). The organic phases were washed with brine (5 mL) and dried over MgSO<sub>4</sub>. Solvents were evaporated in vacuo, and the residue was purified by flash column chromatography (SiO<sub>2</sub>, pentane/ethyl acetate from 5/0 to 5/1).

(4-Methoxyphenyl)(trifluoromethyl)sulfane: Colourless oil. Yield: 70%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ, ppm: 7.57 (d, 8.8 Hz, 2H), 6.93 (d, 8.9 Hz, 2H), 3.84 (s, 3H). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ, ppm: 161.9, 138.3, 134.8, 129.6 (q, 308 Hz), 115.0, 55.4. <sup>19</sup>F-NMR (282 MHz, CDCl<sub>3</sub>): δ, ppm: -44.43. LRMS (EI, 70 eV, m/z): 208 [M<sup>+</sup>].

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**Keywords:** aromatic substitutions • photoredox • radical reactions • fluorinations • thiols

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COMMUNICATION

## **Entry for the Table of Contents**

# COMMUNICATION

The radical trifluoromethylthiolation of arenediazonium salts with commercial bis(trifluoromethyl) disulfide was studied under base-mediated dark and photoredox-catalytic conditions. While the operationally simple base protocol afforded the sulfides in moderate yields, photoredox catalysis with only 0.5 mol% [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> gave up to 90% yield within 3 h.



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