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Selective oxidation and chlorination of trifluoromethylsulfide using trichloroisocyanuric acid in ionic liquid

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Abstract

A route to chemoselective oxidation and chlorination of aryltrifluoromethylsulfide using trichloroisocyanuric acid (TCCA) in ionic liquid, an efficiently *O*-methylation reaction and a reduction of nitro- to amido- in excellent yields have been developed.

Keywords: Trifluoromethylsulfide; Trifluoromethylsulfoxide; Selective oxidation; Trichloroisocyanuric acid

1. Introduction

Aryltrifluoromethylsulfoxides are used as precursors of trifluoromethylating reagents [1]. Trifluoromethyltrimethylsilane [2] (a useful nucleophilic trifluoromethylating agent) and *S*-(trifluoromethyl)-diphenyl-sulfonium triflates [3–5] (an interesting electrophilic trifluoromethylating agent) are prepared from aryltrifluoromethylsulfoxides. The trifluoromethanesulfinyl substituent is also present in the structure of the potent insecticide fipronil [6,7]. However, there are few examples about the synthesis of aryltrifluoromethylsulfoxide. The first method is the classical oxidation of the corresponding sulfides [3,4,8]. This oxidation is very sensitive to temperature; a mixture of sulfoxide, sulfone and initial sulfide is often obtained. The second method is the direct trifluoromethylation using trifluoromethyltrimethylsilane. However, the reaction involves the use of the expensive tri(dimethylamino)sulfonium difluorotrimethylsilicate as a fluoride anion source, and require very low temperature [9,10]. Direct sulfinylation reaction of aromatic compounds is another interesting alternative path. However, it suffers from some drawbacks. For example, electrophilic reaction of substrates with the poorly stable trifluoromethanesulfinate/phosphoryl chloride mixture was limited to electron-rich heterocyclic compounds [11,12]. Expensive triflic acid and triflic anhydride are wasted in the reaction of simple aromatic compounds by triflinate salts [13]. Obviously, to develop a simple and efficient route to synthesis of aryltrifluoromethylsulfoxide under neutral conditions is still a goal. Herein, we wish to report a route to *O*-methylation under mild conditions and a route to chemoselective oxidation and chlorination of aryltrifluoromethylsulfides using trichloroisocyanuric acid in ionic liquid at room temperature.

2. Results and discussion

There are many methods about the synthesis of aryltrifluoromethylsulfides [14–33]. Thereinto, the reaction of aryl disulfide with trifluoromethyl bromide in the presence of sulfoxylate anion radical precursors developed by Wakselman et al. [23,24] constitute an important method of synthesis. It is widely used in experiment and industry during a long time. We used this synthetic method to prepare aryltrifluoromethylsulfides **1a**, **1b**, **1c** and **1f** (see Section 4).

Compound **1e** is a useful building block for constructing various *N*-heterocyclic compounds. Herein, iron powder was used for the reduction of compounds **1a** to **1e** (Scheme 1). This reaction proceeded smoothly under mild conditions. It required 1 h and gave product in excellent yield.

Compound **1f** is another potential synthetic building block for the production of fragrances, cosmetics, pharmaceuticals, and dyestuffs. Herein, the reaction of compound **1f** with methyl iodide in ionic liquid at room temperature was studied. Potassium carbonate was used as alkali. After 10-min reaction, high-yielding product **1d** was obtained (Scheme 2).

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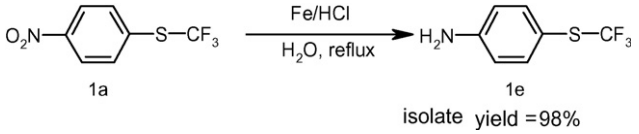
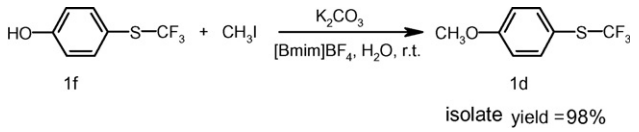
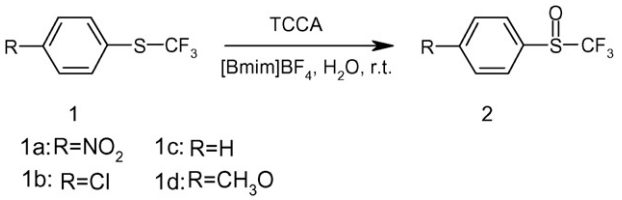


Scheme 1.



Scheme 2.



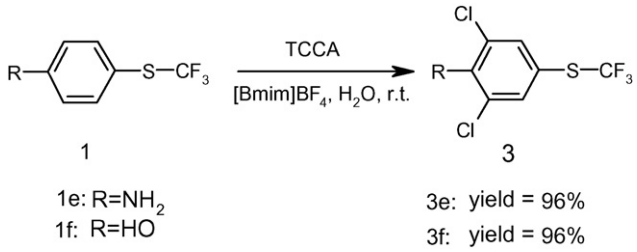
Scheme 3.

At present, the completely chemoselective oxidation of aryltrifluoromethylsulfide to sulfoxide has not yet been reported. Recently, although one example was reported, we have developed a selective oxidation of arylpyrazolyl trifluoromethyl thioether to sulfoxide using trichloroisocyanuric acid [34]. In this paper, we systematically evaluated the chemoselective oxidation of aryltrifluoromethylsulfides with the most representative functional group using trichloroisocyanuric acid in ionic liquid at room temperature (Scheme 3). It was found that the chemoselectivity was very high, no sulfone was detected (determined by the ^{13}C NMR and ^{19}F NMR) and high-yielding products were obtained (Table 1, entries 1–4). The reactions generally required short time for oxidation. However, it required 1 day for **2a** and 6 h for **2b** when using acetonitrile as solvent. Interestingly, both the reactions of compound **1e** and **1f** with trichloroisocyanuric acid produced high-yielding chlorinated products instead of sulfoxide (Scheme 4). Although altered the solvent or added slowly the solution of trichloroisocyanuric acid in acetonitrile by syringe, it still got the same chlorinated products **3e** and **3f**. Although excessive trichloroisocyanuric acid was used, no corresponding sulfoxide can be found in the reactions. It was said that trichloroisocyanuric acid can act not only as an oxidant

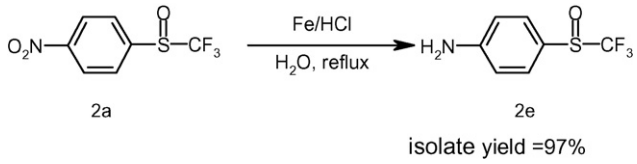
Table 1
Synthesis of compound **2**[a]

Entry	Product	R	Time	Yield (%)[b]
1	**2a**	NO_2	3.5 h	95
2	**2b**	Cl	1 h	98
3	**2c**	H	10 min	98
4	**2d**	CH_3O	10 min	98

[a] Reaction conditions: [Bmim]BF_4 (2 mL), TCCA (2 equiv.), H_2O (cat.), room temperature.
[b] Isolate yield based on sulfide **1**.



Scheme 4. Reaction conditions: TCCA (1 equiv.), H_2O (cat.), [Bmim]BF_4 (2 mL), room temperature, reaction time: 5 min; isolate yield based on sulfide.



Scheme 5.

but a chlorinating reagent [35]. Juenge et al. [36] have observed that the chlorination of aromatic systems using trichloroisocyanuric acid, with electron-rich groups, occurred easily; with electron-withdrawing groups, did not occur. The chlorinated compounds were either *ortho*-isomers or *para*-isomers. Therefore, the chlorinated products **3e** and **3f** should be the *ortho*-isomers. Although compounds **3e** and **3f** were unexpected products, they are useful synthetic building blocks (due to trifluoromethyl anilines are valuable intermediates for synthesizing active compounds in the pharmaceutical and plant-protection fields [37,38]), especially the product **3e**, which has the very similar configuration to 2,6-dichloro-4-trifluoromethyl-aniline (an important initial material for potent insecticide fipronil [39,40]).

The reduction method (Scheme 2) was also applied efficiently to reduction of compounds **2a** to **2e**. This reduction reaction was selective when using suitable quantity of iron powder, no corresponding sulfide was found in the reduction of **2a**. It gave product **2e** in excellent yield (Scheme 5).

3. Conclusion

In summary, an efficient and high chemoselective oxidation or chlorination of aryltrifluoromethylsulfides using trichloroisocyanuric acid in ionic liquid and an efficient route to nucleophilic reaction of **2f** with methyl iodide in ionic liquid have been developed. These strategies have advantages of high atom-efficiency, mild reaction conditions and high selectivity.

4. Experimental

All the melting points were uncorrected. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a FT-Bruker AT-300 instrument using $CDCl_3$ as a solvent with tetramethylsilane (TMS) as the internal standard. *J*-values are given in Hz. Compounds were properly characterized by elemental analyses using a Carlo-Erba EA-1112 instrument. IR spectra were measured on a

Bruker VECTOR55 instrument. Silica gel 60 GF254 was used for analytical and preparative TLC.

4.1. General procedure for the synthesis of aryltrifluoromethylsulfides (1)

A solution of aryl disulfide (4 mmol) in dimethylformamide (40 mL) and a solution of Na_2HPO_4 powder (1.7 g, 12 mmol) in water (5 mL) were introduced into a 100-mL autoclave, followed by $HOCH_2SO_2Na$ (1.9 g, 16 mmol; $Na_2S_2O_4$ for **1b**). The autoclave was then closed and degassed by vacuum pump. CF_3Br was slowly introduced at a pressure of 12 bar (autogenous pressure) with fast stirring. After 2.5 h of good stirring at room temperature, water (200 mL) was then poured into the reactant. The latter mixture was subjected to a careful extraction with ethyl ether (3× 50 mL). The ether phase was collected and eluted by water (2× 50 mL). The ether phase was dried over $MgSO_4$. After removing the solvent, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (7:3) as eluent to give yellow oil.

4.1.1. 4-Nitrophenyl trifluoromethylsulfide (1a)

Yellow liquid; yield: 68%. IR (KBr) (cm^{-1}): 1571, 1501, 1332, 1106, 833, 726, 620. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.37, J = 2.12, 2H, aromatic); 8.28 (dd, J = 8.37, J = 2.12, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.3 (2C), 128.9 (q, J = 306.9, 1C), 132.6 (1C), 136.1 (2C), 149.1 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −41.3 (s, 3F, SCF_3). Anal. calcd for $C_7H_4F_3NO_2S$: C, 37.67%; H, 1.81%. Found: C, 37.46%; H, 1.68%.

4.1.2. 4-Chlorophenyl trifluoromethylsulfide (1b)

Colorless liquid; yield: 83%. IR (KBr) (cm^{-1}): 3062, 1615, 1466, 1421, 1112, 812, 724. ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, J = 8.15, 2H, aromatic); 7.60 (d, J = 8.15, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.3 (2C), 129.5 (q, J = 306.7, 1C), 130.8 (1C), 137.6 (2C), 140.1 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −42.8 (s, 3F, SCF_3). Anal. calcd for $C_7H_4ClF_3S$: C, 39.54%; H, 1.90%. Found: C, 39.28%; H, 1.71%.

4.1.3. Phenyl trifluoromethylsulfide (1c)

Colorless liquid; yield: 91%. IR (KBr) (cm^{-1}): 3047, 1593, 1489, 1440, 1137, 826, 738, 691. ^1H NMR (300 MHz, $CDCl_3$): δ 7.41–7.51 (m, 3H, aromatic); 7.68 (d, J = 7.12, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.4 (1C), 129.6 (q, J = 306.0, 1C), 129.4 (2C), 130.8 (2C), 136.3 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −42.7 (s, 3F, SCF_3). Anal. calcd for $C_7H_5F_3S$: C, 47.19%; H, 2.83%. Found: C, 47.01%; H, 2.64%.

4.1.4. 4-Hydroxylphenyl trifluoromethylsulfide (1f)

Yellow liquid; yield: 86%. IR (KBr) (cm^{-1}): 3651, 3041, 1592, 1526, 1455, 1369, 1208, 1110, 821, 753. ^1H NMR (300 MHz, $CDCl_3$): δ 5.46 (s, 1H, OH); 6.88 (dd, J = 8.63, J = 1.87, 2H, aromatic); 7.54 (d, J = 8.63, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.0 (1C), 116.5 (2C), 129.6 (q, J = 306.7, 1C), 138.5 (2C), 158.2 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −43.6 (s, 3F, SCF_3). Anal. calcd for $C_7H_5F_3OS$: C, 43.30%; H, 2.60%. Found: C, 43.12%; H, 2.41%.

4.2. Procedure for the synthesis of compound 1e and 2e

In a 25-mL flask was placed with **1a** (0.223 g, 1 mmol), iron powder (0.2 g, 3.5 mmol; 2.5 mmol for **2a**), H_2O (1.5 mL). The reaction mixture was heated to 90 °C. HCl (0.5 mL, 36%) was added drop by drop. After 1-h reaction, reactant was cooled to room temperature and neutralized by saturated solution of Na_2CO_3 in water until pH 8. The precipitate was removed by filtration and washed with CH_2Cl_2. The filtrate was extracted with CH_2Cl_2 (3× 3 mL), organic phase was collected and dried over $MgSO_4$. After removing the solvent, the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (3:1) as eluent to give colorless oil.

4.2.1. 4-Aminophenyl trifluoromethylsulfide (1e)

Brown liquid. IR (KBr) (cm^{-1}): 3507, 3396, 3056, 1605, 1561, 1489, 1394, 1113, 814, 760. ^1H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 2H, NH_2); 6.66 (dd, J = 8.30, J = 1.90, 2H, aromatic); 7.42 (d, J = 8.30, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.3 (1C), 115.3 (2C), 126.7 (q, J = 306.3, 1C), 138.2 (2C), 149.1 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −44.4 (s, 3F, SCF_3). Anal. calcd for $C_7H_6F_3NS$: C, 43.52%; H, 3.13%. Found: C, 43.35%; H, 2.96%.

4.2.2. 4-Aminophenyl trifluoromethylsulfoxide (2e)

Colorless solid; mp: 69–71 °C. IR (KBr) (cm^{-1}): 3521, 3405, 3052, 1595, 1483, 1397, 1196, 1140, 1092, 825, 734, 580. ^1H NMR (300 MHz, $CDCl_3$): δ 4.27 (s, 2H, NH_2); 6.78 (d, J = 8.58, 2H, aromatic); 7.56 (d, J = 8.58, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.8 (2C), 122.2 (1C), 124.7 (q, J = 333.0, 1C), 128.3 (2C), 151.8 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −76.7 (s, 3F, $OSCF_3$). Anal. calcd for $C_7H_6F_3NOS$: C, 40.19%; H, 2.89%. Found: C, 40.13%; H, 2.77%.

4.3. Procedure for the synthesis of compound 1d

In a 25-mL flask was placed with K_2CO_3 (0.22 g, 1 mmol) and H_2O (0.5 mL). Ionic liquid [Bmim]BF_4 (2 mL) then was added into the flask, followed by **1f** (0.097 g, 0.5 mmol). The mixture was allowed to stir for 5 min. CH_3I (33.3 μL, 0.6 mmol) was added to the flask. After stirring for 10 min at room temperature, reactant was neutralized by a HCl (5%) solution until pH 6.5. H_2O (10 mL) was added. The mixture of solution was extracted with diethyl ether (3× 5 mL), the ether phase was collected and dried over $MgSO_4$. After removing the solvent, the crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as eluent to give yellow oil (ionic liquid can be recovered).

4.3.1. 4-Methoxylphenyl trifluoromethylsulfide (1d)

Yellow liquid. IR (KBr) (cm^{-1}): 3042, 2967, 2853, 1588, 1545, 1432, 1302, 1109, 860. ^1H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H, OCH_3); 6.94 (d, J = 8.78, 2H, aromatic); 7.59 (d, J = 8.78, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4

(1C), 114.9 (2C), 129.6 (q, J = 306.0, 1C), 132.7 (1C), 138.3 (2C), 161.8 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −44.1 (s, 3F, SCF_3). Anal. calcd for $C_8H_7F_3OS$: C, 46.15%; H, 3.39%. Found: C, 45.91%; H, 3.24%.

4.4. Typical procedure for the synthesis of compound **2** and chlorinated compound **3**

In a 25-mL flask was placed with **1a** (0.112 g, 0.5 mmol), ionic liquid [Bmim]BF_4 (2 mL) and water (two drops). TCCA (0.233 g, 1 mmol) was added. After stirring for 3.5 h, excessive TCCA was destroyed by the slow addition of saturated solution of $NaHSO_3$. During this process, wet iodide-starch test paper was used to periodically test for the presence of oxidizing agents. The precipitate was removed by filtration and washed with diethyl ether. Filtrate was extracted with diethylether (3× 5 mL), ether phase was collected and washed with saturated solution of NaCl (4 mL), and then was dried over $MgSO_4$. After removing the solvent, the crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (6:1) as eluent to give colorless solid (part ionic liquid can be recovered).

4.4.1. 4-Nitrophenyl trifluoromethylsulfoxide (**2a**)

Colorless solid; mp: 55 °C. IR (KBr) (cm^{-1}): 3110, 1608, 1533, 1345, 1207, 1138, 1086, 850, 804, 722, 682, 621. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (dd, J = 8.80, J = 1.91, 2H, aromatic); 8.49 (dd, J = 8.80, J = 1.91, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.3 (q, J = 333.8, 1C), 125.5 (2C), 127.9 (2C), 143.5 (1C), 151.9 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −73.18 (s, 3F, $OSCF_3$). Anal. calcd for $C_7H_4F_3NO_3S$: C, 35.15%; H, 1.69%. Found: C, 34.98%; H, 1.47%.

4.4.2. 4-Chlorophenyl trifluoromethylsulfoxide (**2b**)

Colorless liquid. IR (KBr) (cm^{-1}): 3087, 1575, 1476, 1393, 1188, 1140, 1088, 826, 744. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J = 8.48, 2H, aromatic); 7.76 (d, J = 8.48, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.5 (q, J = 333.2, 1C), 127.3 (2C), 130.0 (2C), 134.2 (1C), 140.3 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −74.41 (s, 3F, $OSCF_3$). Anal. calcd for $C_7H_4ClF_3OS$: C, 36.78%; H, 1.76%. Found: C, 36.54%; H, 1.61%.

4.4.3. Phenyl trifluoromethylsulfoxide (**2c**)

Colorless liquid. IR (KBr) (cm^{-1}): 3071, 1593, 1452, 1370, 1195, 1143, 1096, 688, 606. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–8.06 (m, 5H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.6 (q, J = 333.4, 1C), 126.5 (1C), 130.2 (2C), 131.3 (2C), 133.9 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −74.45 (s, 3F, $OSCF_3$). Anal. calcd for $C_7H_5F_3OS$: C, 43.30%; H, 2.60%. Found: C, 43.13%; H, 2.46%.

4.4.4. 4-Methoxylphenyl trifluoromethylsulfoxide (**2d**)

Light-yellow liquid. IR (KBr) (cm^{-1}): 3062, 2961, 2855, 1582, 1484, 1398, 1195, 1145, 1091, 1013, 819, 736. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H, CH_3); 7.11 (d, J = 8.37, 2H, aromatic); 7.75 (d, J = 8.37, 2H, aromatic) ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7 (1C), 115.2 (2C), 124.1 (q, J = 333.6, 1C), 128.1 (2C), 130.8 (1C), 164.0 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −75.1 (s, 3F, $OSCF_3$). Anal. calcd for $C_8H_7F_3O_2S$: C, 42.86%; H, 3.15%. Found: C, 42.67%; H, 2.97%.

4.4.5. 2,6-Dichloro-5-aminophenyl trifluoromethylsulfide (**3e**)

Colorless solid; mp: 49–50 °C. IR (KBr) (cm^{-1}): 3491, 3388, 1608, 1550, 1473, 1389, 1301, 1109, 875, 784, 719, 597. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.80 (s, 2H, NH_2); 7.49 (s, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.3 (1C), 119.2 (2C), 129.2 (q, J = 306.8, 1C), 135.8 (2C), 142.7 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −43.9 (s, 3F, SCF_3). Anal. calcd for $C_7H_4Cl_2F_3NS$: C, 32.08%; H, 1.54%. Found: C, 31.91%; H, 1.32%.

4.4.6. 2,6-Dichloro-5-hydroxylphenyl trifluoromethylsulfide (**3f**)

Yellow liquid. IR (KBr) (cm^{-1}): 3611, 1602, 1548, 1475, 1377, 1217, 1103, 866, 773. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.23 (s, 1H, OH); 7.60 (s, 2H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.2 (1C), 121.8 (2C), 129.3 (q, J = 306.7, 1C), 136.2 (2C), 150.5 (1C). ^{19}F NMR (220 MHz, $CDCl_3$): δ −43.2 (s, 3F, SCF_3). Anal. calcd for $C_7H_3Cl_2F_3OS$: C, 31.96%; H, 1.15%. Found: C, 31.75%; H, 0.97%.

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