Green Chemistry

Conversion of thiols into sulfonyl halogenides under aerobic and metal-free conditions†‡

Marjan Jereb * and Luka Hribernik

An environmentally benign, metal-free synthesis of sulfonyl chlorides and bromides from thiols in the presence of ammonium nitrate, an aqueous solution of HCl and HBr and oxygen as a terminal oxidant was developed. The reactivity of various substituted thiophenols, benzyl-, aliphatic- and heteroaromatic thiols was examined. Ammonium nitrate served as a source of nitrogen oxides (NO/NO₂), which are the crucial players in a redox-catalytic cycle. Sulfonyl chlorides and bromides were isolated without extraction and "filtered" over a short pad of silica gel; the use of solvents was greatly reduced in comparison with traditional isolation and purification. A "one-pot" protocol for the conversion of thiol into sulfonylamine is also demonstrated. Scale-up experiments on the preparation of sulfonyl chloride and bromide are shown. A possible reaction pathway is discussed.

Introduction

Green chemistry has become an increasingly important subject in organic chemistry.¹ In an era of serious climate changes, humanity will be forced to strengthen endeavors in the direction of sustainable development. Reducing the use of hazardous reagents and solvents, minimizing the production of harmful waste, and enhancing safety, cost- and atom efficiency, with renewable resources in operationally simple processes are the prime targets in this regard.² Oxidation reactions are common chemical transformations employing a vast number of oxidizing agents. Several metal- and halogen-based oxidants are toxic and hazardous; moreover, they produce considerable amounts of hazardous waste. Although often efficient, such reagents need safer and nontoxic replacements. Environmentally benign oxidants, such as an aqueous solution of hydrogen peroxide³ and air or oxygen, are "green" alternatives that produce no dangerous waste, and are welcome from an economic point of view.⁴ Hence, aerobic transformation is a current hot topic in chemistry.⁵ Organic sulfonyl halogenides are versatile intermediates in chemical, agrochemical, and medicinal chemistry. They can be converted into numerous different sulfonyl derivatives i.e. amides, hydrazides, azides, cyanides, sulfonates, sulfimates, sulfoami de nitrogen oxides (NO/NO₂), which are the crucial players in a redox-catalytic cycle. Sulfonyl chlorides and bromides were isolated without extraction and "filtered" over a short pad of silica gel; the use of solvents was greatly reduced in comparison with traditional isolation and purification. A "one-pot" protocol for the conversion of thiol into sulfonylamine is also demonstrated. Scale-up experiments on the preparation of sulfonyl chloride and bromide are shown. A possible reaction pathway is discussed.

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Dedicated to Professor Emeritus Marko Zupan on the occasion of his 70th anniversary.

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the sole oxidants may play a dual role also as a source of chloride i.e. NaOCl·5H2O,39 NCS,40 DCDMH,41 and ClO2.42 There are several methods for the synthesis of sulfonyl chlorides from miscellaneous reactants. These include chlorination of sodium sulfonates with Ph3P·Cl2,43 or cyanuric chloride,44 chlorination of sulfonic acids with cyanuric chloride,39 1,3,5-triazoo-2,4,6-triphosphorine 2,2,4,4,6,6-hexachloride (TAPC),45 and Cl3CCN/PPh3.46 It can be achieved by reaction of disulfides with NCS,47 oxidation of the biologically relevant sulfides48 with chlorine on an industrial scale,49 and transformation of S-alkylisothioureaisaltswithNaClO2,50NaClO51 and NCS.52 In addition, sulfonic chlorides can be prepared from other different sulfur functionalities,53–55 by oxidation of triisopropylsilanylsulfanyls with KNO3/SO2Cl2,56 oxidation/chlorination of thioacetates,57 reaction of the Grignard reagents with SO258 and DABSO,59 and transformation of the lithiated aromatics with SO2 and NCS60 and others. Meerwein’s batch approach61 was successfully modified by chlorosulfonation with SO2/CuCl2 of an in situ generated diazonium salt by using a continuous flow reactor.62

Chlorosulfonation of aeren can also be performed directly by reacting with ClSO3H, SO4Cl2, or a mixture of SO2 and Cl2; however, these reagents are extremely hazardous, irritant, and highly reactive. Reagents like ClSO3H, PCl3 or SO2Cl2 can convert sulfonic acid into sulfonyl chlorides; however, these agents are noxious and their use may be dangerous due to the possible internal pressure.63 Phenyl chlorosulfate was found to be an excellent source of [SO2Cl]+ species in a Pd-catalyzed Suzuki–Miyaura cross-coupling reaction.64 Several other halogenating agents and oxidants, i.e. NCS, 1,3-dichloro-5,5-dimethylhydantoin (DCDMH), cyanuric chloride, trichloroisocyanuric acid (TCCA), 1,3,5-triazoo-2,4,6-triphosphorine 2,2,4,4,6,6-hexachloride (TAPC), oxone and Ph3P·Cl2 are efficient reagents; however, they are associated with a generation of a considerable amount of waste. A sustainable synthetic method for the preparation of sulfonyl halogenides embracing an environmentally benign oxidant and the natural form of the halogen is therefore highly desired. Here, we report on a metal-free synthesis of sulfonyl halogenides from thiols in the presence of ammonium nitrate, an aqueous solution of HCl or HBr and oxygen as a terminal oxidizer.

Results and discussion

4-Methylthiophenol 1a was selected as a model substrate to optimize the reaction conditions. It was allowed to react in a selected solvent in the presence of HBr (48% aqueous solution, 1.1 equiv.) and NH4NO3 (0.2 equiv.) at 60 °C for 1.25 h. The results of the solvent screening experiments are summarized in Table 1 and briefly discussed as follows. Whereas compound 1a remained completely unreacted in water (entry 1), a 7% conversion into disulfide 3a was observed in methanol (entry 2). Aprotic and rather non-polar DCM was also found to be ineffective (entry 3). The full conversion of 1a and encouraging selectivity was noted in acetic acid, affording 33% of disulfide 3a and 67% of sulfonyl bromide 2a (entry 4). Finally, the reaction in acetonitrile took place with a quantitative conversion of 1a, yielding exclusively and in excellent isolated yield the desired sulfonyl bromide 2a (entry 5).

With acetonitrile as the solvent of choice, we examined the effect of the reaction temperature. The experiments were conducted at three different temperatures under otherwise identical reaction conditions, and the results are summarized in Table 2. At room temperature and 40 °C, a modest 6% and 24% conversion of thiophenol 1a into disulfide 3a was noted (entries 1 and 2). Interestingly, raising the temperature to 60 °C resulted in a full conversion into the target sulfonyl bromide 2a, which could be isolated in 93% yield, setting 60 °C as the temperature of choice (entry 3) for further experiments.

Next, we examined the effect of concentration of thiophenol 1a in the reaction mixture, and the results are collected in

![Table 1: The effect of solvent on the product distribution](https://example.com/table1)

| Entry | Solvent | T (°C) | 2a (%) | 3a (%) | Conv. (%) |
|-------|---------|--------|--------|--------|-----------|
| 1     | H2O     | 60     | 0      | 0      | 0         |
| 2     | MeOH    | 60     | 0      | 7      | 7         |
| 3     | DCM     | 40     | 0      | 6      | 6         |
| 4     | AcOH    | 60     | 67     | 33     | 100       |
| 5     | MeCN    | 60     | 100    | 0      | 100 (93)%|

* Reaction conditions: 1a (124 mg, 1 mmol), solvent (5 mL), NH4NO3 (16 mg, 0.2 mmol), HBr (48% aqueous solution, 186 mg, 1.1 mmol), 1.25 h, balloon of O2. Relative distribution of products determined by 1H NMR. |
The role of ammonium nitrate (AN) was also examined, and the results are summarized in Table 5. To demonstrate its role, the functionalization of 1a was performed under the optimized reaction conditions as indicated above in the presence of different amounts of AN. The increasing amount of AN, ranging between 0 and 0.1 equiv. relative to 1a, increased the conversion into disulfide 3a (entries 1–3). Surprisingly, a complete turn in selectivity was observed when using 0.2 equiv. of AN, affording full conversion of thiophenol 1a into sulfonyl bromide 2a (entry 4).

In principle, one equiv. of HBr should be a sufficient amount for the complete conversion of 1a into 2a. The experimental work, however, demonstrated that a small excess of acid is beneficial and that 1.1 equiv. of 48% aqueous solution of HBr provided an optimal performance. The above screening through the reaction conditions revealed the optimal concentration and solvent (0.2 M of 1a in MeCN), temperature (60 °C), atmosphere (O2 balloon) and additives (0.2 equiv. of AN and 1.1 equiv. of 48% HBr), which were used in the subsequent experiments.

Having optimized parameters for aerobic bromination of thiophenol 1a, the experiments were directed towards aerobic chlorination with HCl. For this reaction, the amounts of AN and HCl were reoptimized, and the results are summarized in Table 6. An optimal (100%) conversion into the desired sulfonyl chloride 5a was achieved by using 1.0 equiv. of AN and 1.8 equiv. of 37% aqueous solution of HCl. Here again, in the absence of AN only trace amounts of 1a reacted to form disulfide 3a, confirming the importance of AN (entry 1).

Due to the higher oxidation potential, the chloride ion is expected to be less reactive compared to the bromide ion; explaining higher amounts of HCl and AN required for the transformation (compare Tables 5 and 6). However, although by employing 0.5 equiv. of AN and 2.0 equiv. of HCl full conversion of 1a could be achieved, the selectivity was disappointing with sulfonyl chloride 5a, disulfide 3a and thiosulfonate 4a in the ratio 64 : 10 : 26 (entry 2). It appeared that a larger excess

### Table 3  The effect of the concentration of 1a on the selectivity of the bromination

| Entry | V (mL) | 2a | 3a | Conv. (%) |
|-------|--------|----|----|-----------|
| 1     | 1      | 0  | 26 | 26        |
| 2     | 20     | 100| 0  | 100       |
| 3     | 5      | 100| 0  | 100       |

* Reaction conditions: 1a (124 mg, 1 mmol), MeCN (5 mL), NH4NO3 (16 mg, 0.2 mmol), HBr (48% aqueous solution, 186 mg, 1.1 mmol), 1.25 h, balloon of O2.

### Table 4  The role of the reaction atmosphere in the functionalization of 1a

| Entry | Atmosphere | 2a | 3a | Conv. (%) |
|-------|------------|----|----|-----------|
| 1     | O2         | 100| 0  | 100       |
| 2     | Air        | 0  | 46 | 46        |
| 3     | N2         | 23 | 23 |           |

* Reaction conditions: 1a (124 mg, 1 mmol), MeCN (5 mL), NH4NO3 (16 mg, 0.2 mmol), HBr (48% aqueous solution, 186 mg, 1.1 mmol), 1.25 h, balloon of gas. Relative distribution of products determined by 1H NMR.

### Table 5  The role of AN in the transformation of 1a with HBr under aerobic conditions

| Entry | AN (equiv.) | 2a | 3a | Conv. (%) |
|-------|-------------|----|----|-----------|
| 1     | 0           | 0  | 0  | 100       |
| 2     | 0.05        | 0  | 27 | 27        |
| 3     | 0.1         | 0  | 57 | 57        |
| 4     | 0.2         | 100| 0  | 100       |

* Reaction conditions: 1a (124 mg, 1 mmol), MeCN (5 mL), NH4NO3 (16 mg, 0.2 mmol), HBr (48% aqueous solution, 186 mg, 1.1 mmol), 1.25 h, balloon of O2. Relative distribution of products determined by 1H NMR.
of HCl could not compensate for the lower amount of AN. An additional optimization finally returned the optimal reaction conditions for the selective formation of sulfonyl chloride 5a (entries 3 and 4).

In the next step, we explored the substrate scope. Several aromatic and aliphatic thiols were subjected to the reaction conditions, optimized for the preparation of sulfonyl bromides, and the results are summarized in Table 7. Thiophenols 1a–1d bearing electron-donating groups yielded the corresponding sulfonyl bromides 2a–2d in moderate to high yield (entries 1–4). Transformation proceeded well with electron-deficient thiophenols also (entries 5–13) furnishing the related sulfonyl bromides in good to high yields. No significant substituent effect could be observed.

**Table 6** Optimization of amounts of AN and HCl in the aerobic transformation of 1a

| Entry | AN (equiv.) | HCl (equiv.) | 5a<sup>b</sup> | 3a<sup>b</sup> | 4a<sup>b</sup> | Conv.<sup>b</sup> (%) |
|-------|-------------|--------------|--------------|--------------|--------------|------------------|
| 1     | 0           | 1.8          | 0            | 4            | 0            | 4                |
| 2     | 0.5         | 2.0          | 64           | 10           | 26           | 100              |
| 3     | 1.0         | 1.5          | 89           | 0            | 11           | 100              |
| 4     | 1.0         | 1.8          | 100          | 0            | 0            | 100 (84)<sup>c</sup> |

<sup>a</sup> Reaction conditions: 1a (124 mg, 1 mmol), MeCN (5 mL), NH<sub>4</sub>No<sub>3</sub> (up to 80 mg, 1.0 mmol), HCl (37% aqueous solution, up to 197 mg, 2.0 mmol), 1 h, balloon of O<sub>2</sub>.<sup>b</sup> Isolated yield.

## Scheme 1

**Scheme 1** Aerobic functionalization of coumarine derivative 1r.
electron rich as well as aromatic and aliphatic substrates afforded the desired sulfonyl chlorides 5 in good yields. The results suggest that chlorination and bromination reaction pathways are similar.

Unlike aromatic and aliphatic thiols, benzylic thiols turned out to be somehow more specific substrates in the transformation with HBr/AN, exhibiting considerably higher reactivity.

For this reason, the reactions were performed under slightly modified conditions, at 40 °C with 0.4 equiv. of AN and 2.2 equiv. of HBr. Higher temperatures and lower amounts of reagents gave rise to complex reaction mixtures. Nevertheless, 4-methoxybenzyl thiol 6a was transformed into two unexpected products, 7a and 8a. Apparently, oxidation into aldehyde 8a and ipso-substitution into 7a is accompanied by an electrophilic aromatic substitution ortho to the activating methoxy group. In contrast, 4-chlorobenzyl thiol 6b yielded the corresponding disulfide 7b, and only 3-(trifluoromethyl)benzyl thiol 6c furnished the expected sulfonyl bromide 7c in a moderate 22% yield.

As discussed above, under certain conditions, oxidative halogenation of thiol 1a gave rise to disulfide 3a and thiosulfonate 4a (Tables 1–6). To shed light on the reaction mechanism, the above-mentioned presence of disulfide 3a and thiosulfonate 4a prompted us to prepare and react three disulfides 3a–g and thiosulfonate 4g. As shown in Schemes 3 and 4, upon reaction with HCl or HBr in the presence of AN both types of the substrates afforded the corresponding sulfon halogenides, with no other products being detected. This suggested that disulfides 3 and/or thiosulfonates 4 are potential intermediates in the reaction pathway from 1 to 2 or 5.

The transformation of 1a under the optimized reaction conditions was then carried out with HBr/AN in the presence of various inhibitors and traps, including 2,2,6,6-tetramethylpiperidine oxil (TEMPO), 2,6-di-tert-butyl-4-methylphenol (BHT) and o-dinitrobenzene (o-DNB) in equimolar amounts. The results are presented in Table 9.

The reaction course in the presence of TEMPO (entry 2) was noticeably different from a reaction without TEMPO (entry 1). Full conversion of 1a was noted, and only 36% of the targeted product 2a was formed, signifying that radical intermediates play one of the key roles in this transformation. In addition, 64% of an unknown product was observed, which was transformed into thiosulfonate 4a during the attempt of isolation. A potential explanation is presented in Scheme 5. Although the effect of BHT was less pronounced, it significantly modified the distribution of the products (Table 9, entry 3). o-DNB as an electron scavenger made little impact, but its influence on the
course of the reaction was in favor of the involvement of single-electron transfer and radical intermediates (Table 9, entry 4).

As established earlier, it is reasonable to expect that vic-disulfoxide (A) decomposes to a sulfinyl radical (B), and the latter recombines into OS-sulfenyl sulfinate (C). The unstable species (C) fragments into sulfenyl- (D) and sulfonyl radical (E) that recombine into thiosulfonate (F), Scheme 5.

One of the potential pathways for the formation of disulfide 3a from 1a could be via sulfinyl halogenide (RSX), a source of RS+. As compounds RSX are highly reactive and difficult to isolate, experiments were performed to test their presence in the reaction mixture. Thus, thiol 1a was treated with HBr/AN under the optimized reaction conditions in the presence of 1 equiv. of 1,1-diphenylethene (DPE), a potential scavenger of electrophilic species.

When TLC noted the complete consumption of 1a, the reaction was quenched and the crude reaction mixture was analyzed by $^1$H NMR spectroscopy. It revealed the full conversion of DPE, and the presence of three compounds. One of those, exhibiting a singlet resonance in the aliphatic region at approximately $\delta$ 4.5 ppm (minor component in the spectrum), was tentatively assigned to the addition product (G). The other two compounds, having singlet resonances in the olefinic region at $\delta$ 6.8 ppm were assigned to the addition–elimination products (H) (major component) and (I) (Scheme 6). Sulfonyl bromide 2a could only be detected in trace amounts. To reduce the complexity of the above crude reaction mixture, it was allowed to react with potassium carbonate in refluxing DCM for 6 h. Subsequent $^1$H NMR analysis showed the disappearance of the resonance belonging to (G), whereas those

### Table 9 The role of inhibitors in the aerobic transformation of 1a

| Entry | Inhibitor | 2a | 3a | 4a | Conv. (%) |
|-------|-----------|----|----|----|-----------|
| 1     | —         | 100| 0  | 0  | 100       |
| 2     | TEMPO     | 36 | 0  | 0  | 100$^c$   |
| 3     | BHT       | 71 | 17 | 12 | 100       |
| 4     | o-DNB     | 94 | 0  | 6  | 100       |

$^a$ Reaction conditions: 1a (37 mg, 0.3 mmol), MeCN (2.5 mL), inhibitor (0.3 mmol), NH$_4$NO$_3$ (5 mg, 0.06 mmol), HBr (48% aqueous solution, 36 mg, 0.33 mmol), 1.25 h, balloon of O$_2$. $^b$ Relative distribution of products determined by $^1$H NMR.$^c$ 64% of an unknown product was observed, and it was transformed into 4a during column chromatography on silica gel.
to (H) and (I) remained present. GC-MS analysis revealed the presence of the main product (H) with m/z 302, and two minor products, 1-bromo-2,2-diphenylethene (I) (m/z 258) and disulfide 3a (m/z 246). Detection of product (H) gives a strong indication of the presence of electrophilic sulfenyl bromide. Product (I) confirmed the formation of electrophilic bromine species. Another positive indication of the electrophilic bromonium species is the above-mentioned aromatic ring bromination of 6a into 7a and 8a (Scheme 2).

In bromination of thiol 1a into sulfenyl bromide 2a, p-tolyl-sulfenyl bromide is likely an intermediate. To confirm this hypothesis, in independent experiments, 1a was upon treatment with NBS and NCS transformed into p-tolylsulfenyl bromide and chloride, respectively, which were then further treated with oxygen in the presence of ammonium nitrate at 60 °C. p-Tolylsulfenyl bromide was completely converted into sulfonyl chloride 5a, whereas the oxidation of p-tolylsulfenyl chloride into sulfonil chloride 5a proceeded with lower conversion and selectivity. It could be concluded that RSX may play a role as an intermediate in this transformation.

A potential reaction cycle, proposed in Scheme 7 is similar to the one proposed by Madabhushi.38 Ammonium nitrate decomposition in the acidic medium yielded NO/NO2, which are the key players in the catalytic cycle. Indeed, during the experiments it was possible to observe several consecutive appearances and disappearances of brown gas.

NO2 served as an oxidizer for halogenide ions into the electrophilic halogen species, and the latter might be involved in oxidation processes to give the final sulfonil halogenides. Oxidation of NO into NO2 took place with oxygen as the terminal oxidizer. Thiol probably reacted first with the electrophilic halogen species that is formed from HX, thus giving RSX.

Thiol could react with RSX, yielding disulfide and HX. A direct formation of disulfide from thiols and without RSX could not be completely ruled out,68 however, the reaction could in part take place directly and partly over RSX formation. Disulfide is further likely oxidized into thiosulfonate with the involvement of the potential intermediates as shown in Scheme 5. An experiment in favor of these intermediates may possibly be seen in Table 9, entry 2, where an unknown product was transformed into thiosulfonate 4a during column chromatography.

Thiosulfonate is finally transformed into the target sulfonil halogenide by attack of halogenide ions, while the concomitantly formed RSH enters a new cycle.

Sulfonyl halogenides are versatile synthons for the preparation of sulfonil amides, which are very useful in pharmacy and human and veterinary medicine. One of our goals was a “one-pot” transformation of thiols into sulfonamides, Scheme 8.

4-Methylthiophenol 1a and 4-chlorothiophenol 1g were transformed into the corresponding sulfonil bromides 2a and 2g and sulfonil chlorides 5a and 5g, and were treated further
without isolation with the aqueous solution of ammonia. Sulfonamides \(9a\) and \(9g\) were successfully isolated; however, the yields of sulfonamides from sulfonyl bromides were appreciably higher (Scheme 8).

Finally, we explored the reaction scale-up with HBr and HCl systems. Thiol \(1a\) (20 mmol) was solubilized in 20 mL of MeCN and stirred at 60 °C in the presence of 0.2 equiv. of AN (4 mmol) and 1.1 equiv. of 48% aqueous solution of HBr. The reaction was complete in 3 h as judged by TLC. Reactions on a one mmol scale were conducted with higher amounts of MeCN (5 mL) in order to assure relatively short reaction times. In the case of scale-up, we decided to reduce the amount of solvent at the cost of a reasonably longer reaction time. We were pleased to see that the reaction was complete in 3 h in comparison with 1.25 h on a one mmol scale. Several cycles of NO\(_2\) were observed with appearances and disappearances of brown gas. The balloon was replaced with a new balloon of oxygen when the cycling ceased. Two replacements of balloons with oxygen were made. The solvent was removed under reduced pressure, and 40 mL of water was added and solid filtered. The air-dried solid was “filtered” over a short pad of silica gel, and 56% of \(2a\) was isolated.

Scale-up in the case with HCl/AN was also carried out on 20 mmol of \(1a\) in 20 mL of MeCN with 1.8 equiv. of 36% aqueous solution of HCl and 1.5 equiv. of AN. Similarly as in the case of HBr, the lower amount of solvent was used, and the reaction was complete in 4.5 h. On a one mmol scale, the reaction was complete in 1 h. The reaction course was similar to the previous example. Two replacements of balloons with oxygen were made. The solvent was evaporated, and 20 mL of methyl-t-butyl ether (MTBE) and a few drops of water were added. The resulting mixture was cooled in an ice-bath, carefully neutralized with solid NaHCO\(_3\), dried with anhydrous sodium sulfate and filtered. The filtrate was concentrated, and “filtered” over a short pad of silica gel. Sulfonyl chloride \(5a\) was isolated in 52% yield.

**Conclusion**

Environmentally benign, metal-free aerobic oxidation of thiols into sulfonyl bromides and chlorides with the aqueous solutions of HBr and HCl in the presence of AN was developed. Inorganic reactants were used in their natural form – bromide, chloride, nitrate and oxygen. Halogenated solvents were not used. The reacting system consisted of NO\(_2\) gases, a crucial actor, while oxygen was the terminal oxidizer. The HBr/AN system exhibited higher reactivity than the HCl/AN system due to the more favorable oxidation potential of the bromide ion. Consequently, transformations in the case of HBr/AN required lower amounts of reactants: 0.2 equivalents of AN and 1.1 equivalents of HBr, thus contributing noticeably to the atom economy. The transformations produced low amounts of non-hazardous inorganic waste, while there was practically no organic waste in contrast to the numerous known methods for the preparation of sulfonyl halogenides. Acetonitrile was removed by distillation and could be reused. Aryl- and alkyl-substituted thiols furnished the corresponding sulfonyl halogenides as sole products, whereas benzyl thiols exhibited higher reactivity and products with different selectivity. An important contribution to green chemistry principles was made by isolation and purification. Sulfonyl halogenides were isolated without extraction and column chromatography. Owing to the excellent reaction selectivity and the purity of the crude products, “filtration” over a short pad of silica gel was done. Avoidance of both classic operations saved considerable amounts of solvents. The reaction pathways were examined and a catalytic cycle was proposed. Disulfides and thiosulfoxides as potential intermediates could yield the sulfonyl halogenides under the studied reaction conditions. Electrophilic sulfur species RS\(^{+}\) and HOX were also the likely intermediates according to the isolated products. Radicals are likely to be important intermediates in this transformation, and the substituents have a rather low influence on the reactivity of the aryl-substituted thiols. Comparison of the reactivity of alkyl- and aryl thiols may be an indication that nucleophilicity was not the main factor governing the reactivity. Little differences in the reactivity of aryl thiols indicated that acidity was not the decisive factor determining the reactivity. It appears that stabilization of the thiophenoxy radical is a more important parameter. “One-pot” transformation of thiol into sulfonamide via sulfonyl bromide and chloride was demonstrated. Scale-up preparation of sulfonyl bromide and chloride was also carried out.

**Scheme 8** “One-pot” conversion of thiols to sulfonamides.
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