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Iron(III)-Catalyzed Radical Cross-Coupling of Thiols with Sodium Sulfinates: A Facile Access to Thiosulfonates

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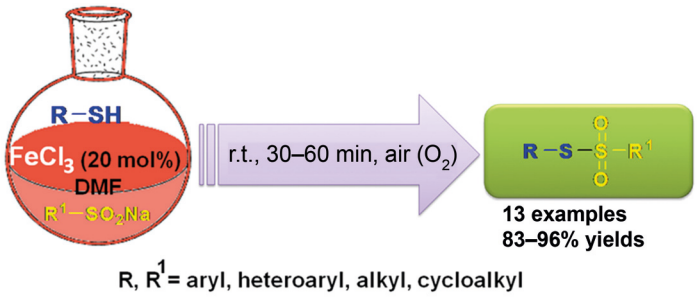

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Abstract A convenient and efficient synthesis of symmetrical and asymmetric thiosulfonates from thiols and sodium sulfinates is reported. The protocol involves iron(III)-catalyzed formation of sulfenyl and sulfonyl radicals in situ under aerobic conditions and their subsequent cross-coupling to afford thiosulfonates in 83–96% yield. The utilization of readily available, nontoxic, and inexpensive iron(III) as a catalyst and atmospheric oxygen as an oxidant is within the confines of green and sustainable chemistry.

Key words sulfonates, thiols, thiosulfonates, iron, catalysis, oxidation

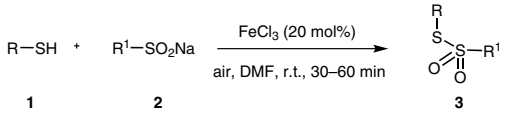
Free-radical chemistry has played a crucial role in shaping modern organic synthesis, including polymer synthesis.[1,2] Free-radical reactions generally require demanding conditions, such as an inert atmosphere and anhydrous degassed solvents, which make such reactions less economical and contrary to the requirements of green chemistry. Consequently, any research directed to overcoming this situation would be warmly welcomed. One way of working within the boundaries of green and sustainable chemistry involves the use of inexpensive, readily available, and nontoxic aerial dioxygen in synthetically useful free-radical reactions.[3,4] There are numerous reports in the literature on the activation of molecular oxygen by employing various transition metals.[5]

The broad spectrum of biological activities and the wide range of synthetic and industrial uses of thiosulfonates have led to their identification as interesting organosulfur compounds.[6–9] Thiosulfonates exhibit antimicrobial and fungicidal activities; their mode of action involves the blocking the normal metabolism of the microorganism through sulfenylation of thiol groups in enzymes.[6] Because of their greater stability and greater ease of handling compared with sulfenyl chlorides and their stronger sulfenylating power compared with disulfides, thiosulfonates have been used extensively as sulfenylating reagents in organic synthesis.[9] Thiosulfonates have also found a wide range of industrial applications in polymer production and in photographic processes.[8]

Many methods for the synthesis of thiosulfonates have been reported in the literature.[10,11] Most of these transformations involve the direct oxidation of disulfides or thiols to afford symmetrical thiosulfonates.[12] These methods often require an excess of the oxidant, and they are not suitable for the synthesis of asymmetric thiosulfonates, as they give mixtures of isomeric products in such cases. The synthesis of asymmetrical thiosulfonates generally involves formation of an S–S bond by sulfenylation of a sulfinic acid or a sulfenic acid derivative.[13–16] Alternatively, thiosulfonates can be obtained by thiosulfonate exchange reactions of sulfenamides,[17] by the reduction of sulfonyl chlorides,[18] by oxidation of thiosulfinates,[19] by the reaction of potassium thiosulfonates with diaryliodonium salts,[20] or by spontaneous desulfurization of sulfenic sulfonic thioanhydrides.[21] However, these methods are limited because they demand toxic and unstable sulfenylating reagents and/or require cautious handling.

The literature records only a few methods that are applicable to the synthesis of either symmetric or asymmetric thiosulfonates.[15a,b,22] Two of these methods start from either disulfides[15a] or *N*-(organolithio)succinimides,[15b] rather than from thiols,[22] and they require an additional step. A recently reported method starts from thiols and utilizes CuI with 1,10-phenanthroline as a ligand and water as a catalyst, but it requires ten equivalents (with respect to the catalyst) of NH_4BF_4 as an additive, which makes the method less economical.[22]

After a careful consideration of these points, and as part of our continuing efforts to develop synthetically useful radical reactions,[23] we hypothesized that an iron(III)-catalyzed radical cross-coupling of thiols with sodium sulfinates under aerobic conditions might be a convenient and economical method for preparing symmetric and asymmetric thiosulfonates (Scheme 1).

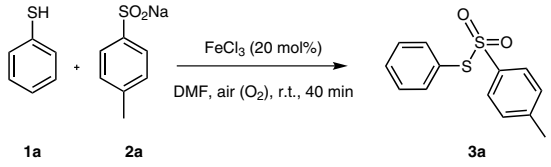


Scheme 1 Oxidative sulfonylation of thiols

To realize our hypothesis and to optimize the reaction conditions, we chose benzenethiol (**1a**) and sodium 4-toluenesulfinate (**2a**) as model coupling partners, and their reaction was conducted in DMF at r.t. in the presence of $FeCl_3$ as a catalyst under an atmosphere of air (Table 1). Interestingly, the reaction delivered the desired product *S*-phenyl 4-toluenethiosulfonate (**3a**) in an excellent yield of 96%.

Next, we probed the reaction in various solvents, and we found that DMF was the best solvent, whereas CH_2Cl_2, THF, MeCN, 1,4-dioxane, and DMSO were not suitable (Table 1, entry 1 versus entries 2–6). Complete conversion of benzenethiol (**1a**) into the thiosulfonate **3a** in high yield was observed in DMF (Table 1, entry 1). No byproduct was obtained during the reaction, indicating that the reaction has excellent chemoselectivity. When the reaction was carried out in DMSO, the major product was the disulfide instead of the thiosulfonate (entry 5).

Table 1 Oxidation of Benzenethiol with Iron(III) Chloride in Various Solvents at Room Temperature[a]

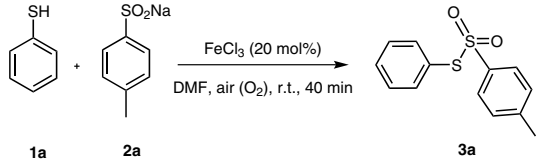


Entry	Solvent	Time	Yield[b] (%)
1	DMF	40 min	96
2	THF	1 h	0
3	MeCN	1 h	0
4	1,4-dioxane	1 h	0
5	DMSO	1 h	5[c]
6	CH_2Cl_2	1 h	0

[a] Reaction conditions: PhSH (**1**; 0.5 mmol), 4-TolSO_2Na (**2**; 1 mmol), $FeCl_3$ (20 mol%), solvent (3 mL), stirring, r.t., air atmosphere.
[b] Isolated yield of pure product **3a**.
[c] PhSSPh was produced in 86% yield

Next, we assessed the reaction in the presence of various transition-metal catalysts [CuI, $ZnCl_2$, CuBr, $CuCl_2$, $Mn(OAc)_2$, and $FeCl_3$] in DMF, and we found that $FeCl_3$ was the best catalyst at r.t. in terms of yield and reaction time (Table 2, entries 1–6). The variation in the efficiency of the transition-metal catalysts might be attributable to their various oxidizing powers under the present reaction conditions. Moreover, the order of catalytic efficiency of CuI, CuBr, and $CuCl_2$ agreed with that reported by Taniguchi.[22] When the loading of the catalyst was reduced from 20 mol% to 15 mol%, the yield fell to 76% (entries 6 and 7). Note that no thiosulfonate **3a** was obtained in the absence of $FeCl_3$ under air, even at a higher temperatures; instead, the disulfide was produced in 86% yield (entry 8).

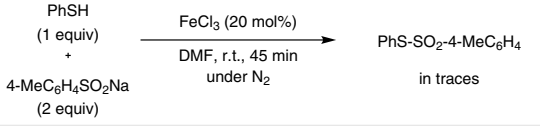
Table 2 Oxidation of Benzenethiol with Iron(III) Chloride in the Presence of Various Catalysts at Room Temperature[a]



Entry	Catalyst (mol%)	Time	Yield (%)[b]
1	CuI (20)	1 h	0
2	$ZnCl_2$ (20)	1 h	0
3	CuBr (20)	1 h	32
4	$CuCl_2$ (20)	1 h	49
5	$Mn(OAc)_2$ (20)	1 h	42
6	$FeCl_3$ (20)	40 min	96
7	$FeCl_3$ (15)	4 h	76
8	–	1 h	0[c]

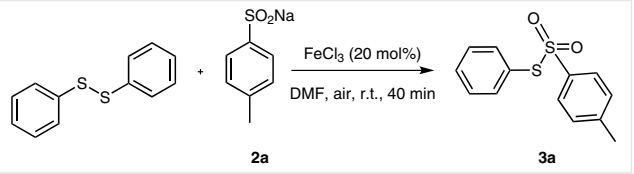
[a] Reaction conditions: PhSH (**1a**; 0.5 mmol), 4-TolSO_2Na (**2**; 1 mmol), catalyst (20 mol%), DMF (3 mL), stirring, r.t., air.
[b] Isolated yield of pure product.
[c] PhSSPh was produced in 86% yield at 80 °C.

Furthermore, only traces of product **3a** were obtained under a nitrogen atmosphere, which emphasizes the need to perform the reaction under air (Scheme 2).



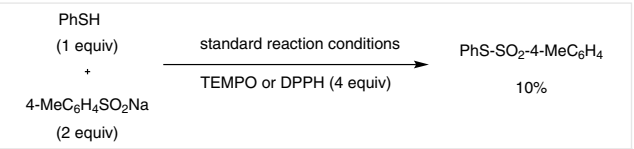
Scheme 2 Reaction conducted in the absence of air

The reaction also gave a 94% yield of *S*-phenyl 4-toluenethiosulfonate (**3a**) when diphenyl disulfide was used instead of benzenethiol (Scheme 3).



Scheme 3 Reaction with diphenyl disulfide

Next, we examined the effect of the ratio of the coupling partners benzenethiol (**1a**) and sodium 4-toluenesulfinate (**2a**). When the ratio of **1a** to **2a** was varied from 1:2 to 1:1 (equivalents), the yield of the desired product **3a** decreased considerably due to oxidation of benzenethiol (**1a**) to diphenyl disulfide in the presence of $FeCl_3$. This demonstrates that two equivalents of sodium thiosulfinate is the optimal amount for complete conversion of thiols into thiosulfonates. Moreover, the reaction was quenched by the radical scavengers TEMPO and 2,2-diphenyl-1-picrylhydrazyl (DPPH), indicating that it involves a radical intermediate (Scheme 4).

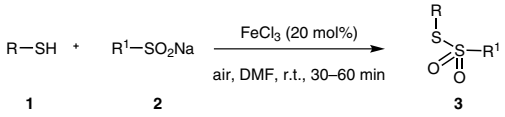


Scheme 4 Evidence in support of the involvement of a radical intermediate

With the optimized conditions in hand, various combinations of the thiols and sodium sulfinates were surveyed (Table 3).[28] The reaction of benzenethiols **1** substituted with electron-donating or electron-withdrawing groups proceeded well and gave the corresponding thiosulfonates **3** in excellent yields (Table 3, entries 2–8). These results indicate that an existing group on the aromatic ring has no obvious effect on the yield of the reaction products. The reactions of the heterocyclic thiols pyridine-2-thiol and 1,3-benzoxazole-2-thiol also delivered the desired products in excellent yields (entries 9 and 10). The method also worked well for the selective oxidation of aliphatic and cycloaliphatic thiols to the corresponding thiosulfonates (entries 11–13).

On the basis of our investigations and precedents in the literature,[3f,h] we propose the plausible reaction pathway for the formation of thiosulfonates **3** that is shown in Scheme 5. Sulfinate anion **1** undergoes single-electron transfer with dioxygen to form an oxygen-centered radical **II**, which resonates with the sulfonyl radical **III**.[3f] Similarly, the thiol **2** undergoes Fe^{3+}-catalyzed oxidation to form the thiyl radical **5**. Cross-coupling of radicals **III** and **5** affords the desired thiosulfonate **3**.

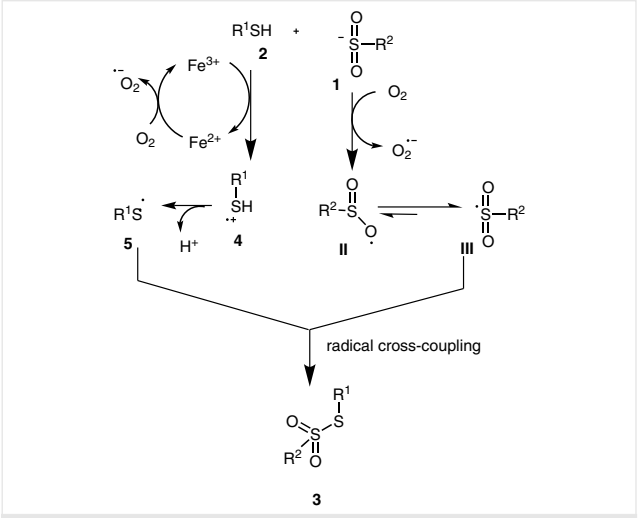
Table 3 Substrate Scope for the Synthesis of Thiosulfonates[a]



Entry	R	R^1	Time (min)	Yield[b,c] (%)
1	Ph	4-MeC_6H_4	40	96
2	4-MeC_6H_4	4-MeC_6H_4	40	89
3	4-FC_6H_4	4-FC_6H_4	45	92
4	4-FC_6H_4	4-MeC_6H_4	30	95
5	3-$O_2NC_6H_4$	4-MeC_6H_4	50	90
6	4-HOC_6H_4	4-HOC_6H_4	45	92
7	4-ClC_6H_4	4-ClC_6H_4	50	94
8	4-$O_2NC_6H_4$	4-ClC_6H_4	60	91
9	2-pyridyl	2-pyridyl	40	89
10	1,3-benzoxazol-2-yl	1,3-benzoxazol-2-yl	60	93
11	*s*-Bu	*s*-Bu	40	83
12	Bu	Bu	40	85
13	Cy	Cy	30	88

[a] Reaction conditions: thiol **1** (0.5 mmol), sodium sulfinate **2** (1 mmol), $FeCl_3$ (20 mol%), DMF (3 mL), stirring, r.t., air atmosphere.
[b] Isolated yield after flash chromatography.
[c] All products **3** are known and were characterized by comparison of their spectral data with those reported in the literature.22·24–27

In summary, we have developed a convenient and cost-effective one-pot method for the synthesis of a variety of symmetrical and asymmetric thiosulfonates by a radical cross-coupling of aryl, hetaryl, alkyl, or cycloaliphatic thiols



Scheme 5 A plausible reaction pathway for the formation of thiosulfonate **3**

with sodium sulfinates. The protocol efficiently uses Fe(III) as an inexpensive and green catalyst to induce a radical process, and it offers many desirable features, such as utilization of air (O_2) as a sustainable oxidant, room-temperature reaction, operational simplicity, short reaction times, and high yields.

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(28) **Thiosulfonates 3; General Procedure**
A mixture of the appropriate thiol **1** (0.5 mmol), sodium thiosulfinate **2** (1.0 mmol), and $FeCl_3$ (20 mol%) in DMF (3 mL) was stirred at r.t. for 30–60 min under air in a round-bottomed flask. When the reaction was complete (TLC), H_2O (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient mixture of hexane and EtOAc as eluent.

***S*-Phenyl 4-Toluenethiosulfonate (Table 3, Entry 1)**
Colorless solid; yield: 126 mg (96%); mp 74–75 °C. IR (KBr): 1130, 1315 (SO_2) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.40 (s, 3 H) 7.31 (t, 2 H, *J* = 6.8 Hz), 7.34 (t, 2 H, *J* = 6.8 Hz), 7.40–7.44 (m, 2 H), 7.58 (d, 2 H, *J* = 8.4 Hz), 7.48 (d, 1 H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 28.3, 127.4, 127.9, 128.8, 129.3, 131.5, 133.5, 136.6, 143.0. EIMS: *m*/*z* = 264 [M^+]. Anal. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58. Found: C, 59.28; H, 4.45.

***S*-(4-Fluorophenyl) 4-Fluorobenzenethiosulfonate (Table 3, Entry 3)**
Colorless crystal; yield: 132 mg (92%); mp 68–70 °C. IR (KBr): 1229, 1330 (SO_2) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.10 (d, 2 H, *J* = 8.4 Hz), 7.16 (t, 2 H, *J* = 8.4 Hz), 7.35 (dd, 2 H, *J* = 5.2 Hz, *J* = 9.0 Hz), 7.63 (dd, 2 H, *J* = 4.8 Hz, *J* = 9.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 116.4, 117.0, 123.2, 123.7, 130.1, 138.7, 163.9, 166.1. EIMS: *m*/*z* = 286 [M^+]. Anal. Calcd for $C_{12}H_8F_2O_2S_2$: C, 50.34; H, 2.82. Found: C, 50.54; H, 2.76.

***S*-(3-Nitrophenyl) 4-Toluenethiosulfonate (Table 3, Entry 5)**
Colorless crystal; yield: 139 mg (90%); mp 97–99 °C. IR (KBr): 1140, 1331 (SO_2) cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.39 (s, 3 H), 7.24–7.28 (m, 2 H), 7.40–7.49 (m, 2 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 7.83–7.86 (m, 1 H), 8.02 (s, 1 H), 8.32–8.39 (m, 1 H).
^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.2, 125.6, 127.4, 129.8, 130.4, 130.5, 131.0, 139.5, 142.0, 145.7, 148.3. EIMS: *m*/*z* = 309 [M^+]. Anal. Calcd for $C_{13}H_{11}NO_4S_2$: C, 50.47; H, 3.38; N, 4.53. Found: C, 50.26; H, 3.49; N, 4.80.

***S*-(4-Chlorophenyl) 4-Chlorobenzenethiosulfonate (Table 3, Entry 7)**
Colorless crystal; yield: 149 mg (94%); mp 134–136 °C. IR (KBr): 1140, 1330 (SO_2) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.35 (d, 2 H, *J* = 8.4 Hz), 7.39 (d, 2 H, *J* = 8.8 Hz), 7.46 (d, 2 H, *J* = 9.2 Hz), 7.52 (d, 2 H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 128.8, 129.3, 130.0, 130.4, 137.7, 138.5, 140.5, 141.2. EIMS: *m*/*z* = 318 [M^+], 320 [M + 2]$^+$, 322 [M + 4]$^+$. Anal. Calcd for $C_{12}H_8Cl_2O_2S_2$: C, 45.15; H, 2.53. Found: C, 45.00; H, 2.75.