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ARTICLE

Electrochemical Synthesis of Methyl Sulfoxides from Thiophenols / Thiols and Dimethyl Sulfoxide

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A new route for one-pot synthesis of methyl sulfoxides using electrochemical technique from thiophenols / thiols and dimethyl sulfoxide was developed. This protocol proceeded smoothly by employing electron and hydrogen peroxide as clean oxidants, and a wide range of aromatic and aliphatic sulfoxides were synthesized in moderate to good yields.

Introduction

Methyl sulfoxides are one group of organosulfur compounds which are important as intermediates in the generation of natural products and biologically active compounds, and as ligands in transition-metal catalysis.^[1] The most straightforward method for the synthesis of methyl sulfoxides is the methylation of thiophenols / thiols followed by chemo-selective oxidation of methyl sulfides. Typically, methyl iodide,^[2] dimethyl sulfate,^[3] and dimethyl carbonate^[4] are employed for the methylation of thiophenols / thiols. In recent years, dimethyl sulfoxide (DMSO) has been used as a methyl source in organic synthesis due to its rather low cost and low toxicity.^[5] C_{sp}²-H methylation,^[6] N-H methylation,^[7] as well as COO-H methylation^[8] have been documented. However, S-H methylation from DMSO has not been reported.

In addition, selective oxidation of sulphides to sulfoxides still remains a major challenge since most reported protocols involved over oxidation to sulfones.^[9] Electroorganic synthesis has been recognized as an environmentally friendly methodology and has gained extensive interest in modern synthetic chemistry. Especially, the anodic electrochemistry can provide a powerful and high selective means for making and modifying organic molecules.^[10] In continuation of our interest in the application of electrochemical methods to organic synthesis,^[11] herein we reported the first highly efficient and selective synthesis of sulfoxides from thiophenols / thiols and dimethyl sulfoxide through an electrochemical method.

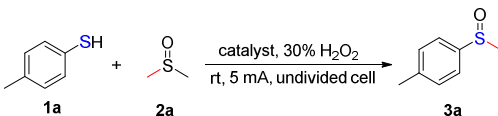
Results and discussion

We began our investigation by using 4-methyl thiophenol (**1a**) and dimethyl sulfoxide (**2a**) as model substrates to find out the optimized conditions. A constant current electrolysis was performed at 5 mA in an undivided cell using NH₄ClO₄ as conducting salt and platinum plates (1.0 × 1.5 cm²) as electrodes. The yield of

the desired product methyl 4-methylphenyl sulfoxide (**3a**) was only 11% in the presence of 30% aqueous H₂O₂ (Table 1, entry 1). When 10 mol% of FeCl₂ was added, the yield increased to 55% (Table 1, entry 2). The yield of **3a** increased to 82% when 20 mol% of FeCl₂ was employed (Table 1, entry 3). Further increasing the dosage of FeCl₂ resulted in a lower yield at 77% (Table 1, entry 4). Other iron salts, for instance, FeSO₄, Fe(acac)₃ and FeCl₃ also showed activities in this reaction (Table 1, entries 5-7), but they were inferior to FeCl₂ in terms of yields. Among the electrolytes that were tested, NH₄ClO₄ was found to be optimal (Table 1, entries 3 and 8-10). Studies on the effect of current revealed that an increase or decrease of the current led to the yield decrease (Table 1, entries 11 and 12). When RVC or nickel was used as an anode, the yields decreased (Table 1, entries 13 and 14). Reaction carried out under a nitrogen or an oxygen balloon had little effect on the yield (Table 1, entries 15 and 16). Poor productivity of **3a** was observed when the reaction was performed in the absence of current (Table 1, entry 17). Hence, the best conditions were shown in entry 3, Table 1.

With the optimal conditions in hand, we then examined the substrate scope (Table 2). As shown in Table 2, a broad scope of thiophenols with different substituents could afford the corresponding sulfoxides in moderate to good yields. Generally, the ortho substitutions on the phenyl of the thiophenols disfavored this reaction in comparison with the para substitutions (**3a** vs **3b**, **3j** vs **3k**, **3n** vs **3o**). The electron-rich thiophenols were more reactive than electron-deficient ones (**3d**, **3g** vs **3q**, **3r**), while weak electron-withdrawing groups (**3j**, **3l**, **3n**) had little influence on the yields. It was also noteworthy that the halide substituents could be well tolerated under the electrochemical conditions and could thus provide an opportunity for further transformations at the halide position. It was interesting to find that the hydroxyl substituted thiophenols (**1h** and **1i**) were highly selectively methylated on the sulfhydryl to produce the desired product in 67% (**3h**) and 69% (**3i**) yields, respectively. Besides, aliphatic thiols were also applicable for this method. The primary thiols, 2-phenylethanethiol and 1-hexanethiol, could be transformed smoothly to the corresponding products (**3u** and **3v**) in 82% and 74% yields, respectively. The

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Table 1. Optimization of reaction conditions.^[a]


Entry	Catalyst (equiv)	Electrolyte	Yields (%) ^[b]
1	—	NH ₄ ClO ₄	11%
2	FeCl ₂ (0.1)	NH ₄ ClO ₄	55%
3	FeCl ₂ (0.2)	NH ₄ ClO ₄	82%
4	FeCl ₂ (0.3)	NH ₄ ClO ₄	77%
5	FeSO ₄ (0.2)	NH ₄ ClO ₄	67%
6	Fe(acac) ₃ (0.2)	NH ₄ ClO ₄	31%
7	FeCl ₃ (0.2)	NH ₄ ClO ₄	61%
8	FeCl ₂ (0.2)	LiClO ₄	56%
9	FeCl ₂ (0.2)	<i>t</i> Bu ₄ NBF ₄	27%
10	FeCl ₂ (0.2)	NH ₄ Cl	33%
11 ^[c]	FeCl ₂ (0.2)	NH ₄ ClO ₄	55%
12 ^[d]	FeCl ₂ (0.2)	NH ₄ ClO ₄	67%
13 ^[e]	FeCl ₂ (0.2)	NH ₄ ClO ₄	59%
14 ^[f]	FeCl ₂ (0.2)	NH ₄ ClO ₄	63%
15 ^[g]	FeCl ₂ (0.2)	NH ₄ ClO ₄	80%
16 ^[h]	FeCl ₂ (0.2)	NH ₄ ClO ₄	83%
17 ^[i]	FeCl ₂ (0.2)	NH ₄ ClO ₄	19%

^[a] Reaction conditions: the mixture of **1a** (0.3 mmol), cat. FeCl₂, 30% aqueous H₂O₂ (0.4 mL, 3.6 mmol), in DMSO (5 mL) with 0.2 M electrolyte was electrolyzed at constant current (5 mA) in an undivided cell for 7.5 hours at room temperature. Anode: Pt foil (1.0 × 1.5 cm²), cathode: Pt foil (1.0 × 1.5 cm²).

^[b] Isolated yield.

^[c] The current was 3 mA.

^[d] The current was 8 mA.

^[e] Anode: reticulated vitreous carbon (RVC, 1.0 × 1.5 × 0.2 cm³), cathode: Pt foil (1.0 × 1.5 cm²).

^[f] Anode: Ni foil (1.0 × 1.5 cm²), cathode: Pt foil (1.0 × 1.5 cm²).

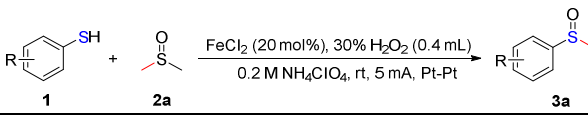
^[g] Reaction was performed under N₂.

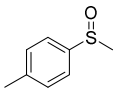
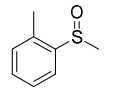
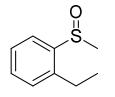
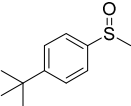
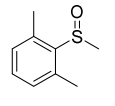
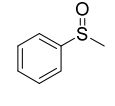
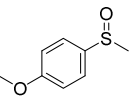
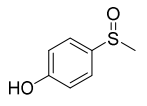
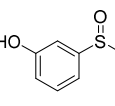
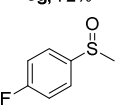
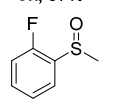
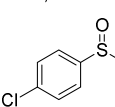
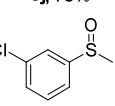
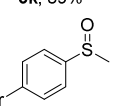
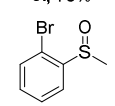
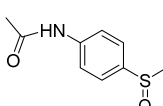
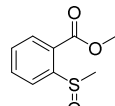
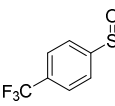
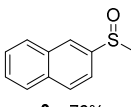
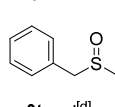
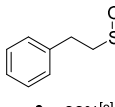
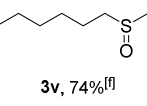
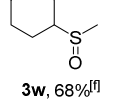
^[h] Reaction was performed under O₂.

^[i] No current.

secondary thiol, i.e. cyclohexanethiol gave the product (**3w**) in a yield of 68% at a prolonged reaction time. Unfortunately, the mixture of benzyl disulfide and benzaldehyde was obtained, instead of methyl benzyl sulfoxide (**3t**) when benzyl mercaptan was used as the reactant.

We evaluated the scalability of this electrocatalytic transformation by performing the reactions on a 3 mmol scale (10 eqv). The reaction furnished smoothly the desired product (**3a**) in a 78% yield (Scheme 1a). Similarly, a gram-scale reaction between **1d** and DMSO afforded the desired product (**3d**) in a 67% yield. When

Table 2. Substrate scope of thiophenols / thiols.^[a,b]


		
3a, 82%	3b, 80%	3c, 71%
		
3d, 81%	3e, 52%	3f, 52%^[c]
		
3g, 72%	3h, 67%	3i, 69%
		
3j, 75%	3k, 59%	3l, 73%
		
3m, 58%	3n, 74%	3o, 42%
		
3p, 75%	3q, 34%	3r, 42%
		
3s, 76%	3t, n.d.^[d]	3u, 82%^[e]
		
3v, 74%^[f]	3w, 68%^[f]	

^[a] Reaction conditions: **1a** (0.3 mmol), **2a** (5 mL), FeCl₂ (20 mol%, 7.5 mg), 30% H₂O₂ (0.4 mL), NH₄ClO₄ (0.2 M). Anode: Pt foil (1.0 × 1.5 cm²), cathode: Pt foil (1.0 × 1.5 cm²). The electrolysis was conducted at a constant current of 5 mA for 7.5 hours in an undivided cell at room temperature.

^[b] Isolated yields.

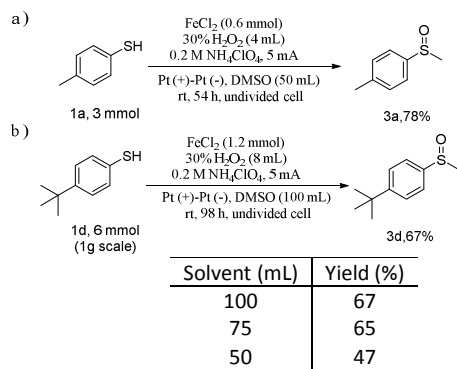
^[c] Phenyl disulfide as a substrate.

^[d] Not detected.

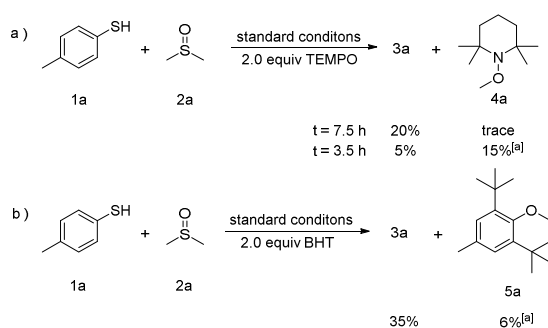
^[e] Reaction time: 9.5 h.

^[f] Reaction time: 12 h.

the amount of solvent was reduced from 100 mL to 75 mL, the reaction proceeded smoothly without a notable change in terms of



Scheme 1. Scale-up experiment.



[a] NMR yield based on TEMPO or BHT

Scheme 2. Radical trapping experiments.

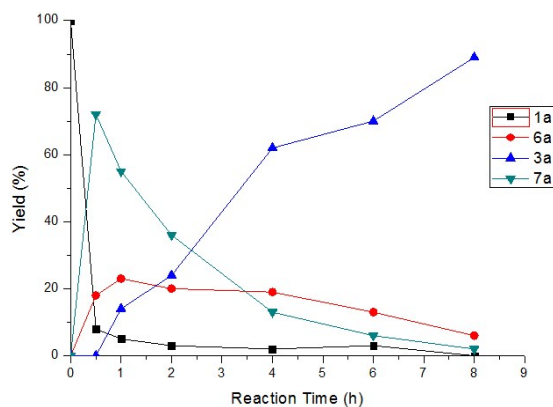
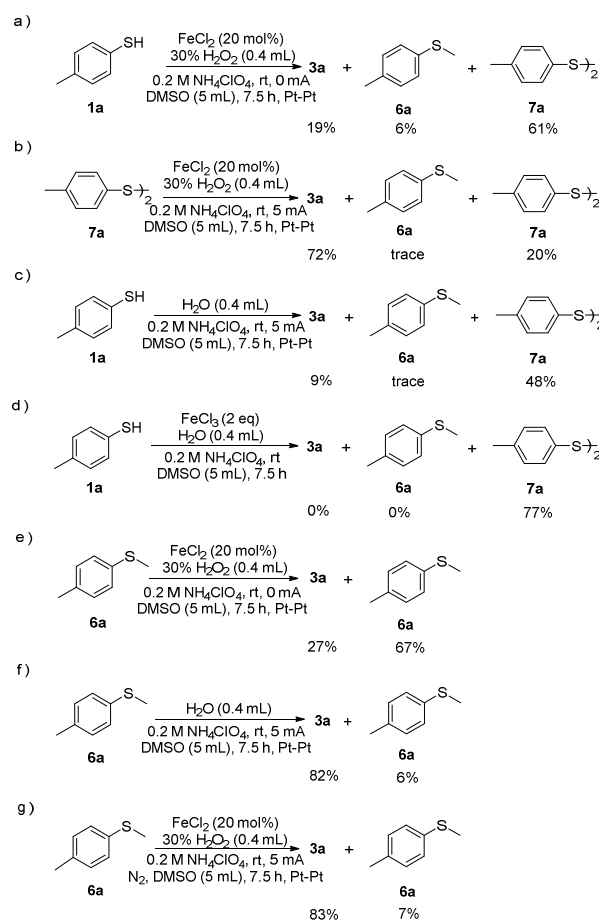


Figure 1. Monitoring of the reaction composition by GC-MS

the yield. However, the yield decreased to 47% when the amount of solvent was reduced to 50 mL. (Scheme 1. More details, please refer to the Supporting Information). These results showed the great potential of this electrochemical reaction in practical synthesis.

To gain an understanding of the reaction mechanism, 2 equivalent of 2,2,6,6-tetramethylpiperidin-1-yl-oxy (TEMPO) was added into the reaction mixture under the standard conditions (Scheme 2a). 20% of product **3a** with trace of 1-methoxy-2,2,6,6-tetra-methylpiperidine (**4a**) were detected by NMR analysis. If this reaction was stopped at 3.5 h, 15% of **4a** could be collected. Another radical scavenger, butylated hydroxytoluene (BHT) was also tested and it was found that 35% of **3a** was afforded and 6% of 3,5-di-tert-butyl-4-methoxytoluene (**5a**) was collected (Scheme 2b). These results suggested that a radical pathway was involved and methyl radical might be generated as a radical intermediate in this reaction.

Next, GC-MS analysis was employed to monitor the reaction process. It had shown that **1a** was consumed rapidly and the corresponding bis(*p*-tolyl)disulfide **7a** was generated in a 76% yield in the first 0.5 hour. The yield was then decreased gradually during the reaction. Control experiment showed that when the standard reaction was performed with **7a** as the starting material, **3a** was obtained in 72% (Scheme 3b). Meanwhile, methyl *p*-tolyl sulphide



Scheme 3. Control experiments.

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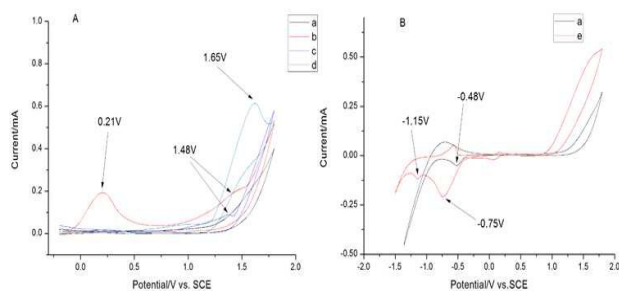


Figure 2. Cyclic voltammogram of 0.2 M NH_4ClO_4 solution in DMSO at rt. a) none, b) **1a** (0.05 M), c) **7a** (0.05 M), d) **6a** (0.05 M), e) FeCl_3 (0.02M). The voltammogram was obtained with Pt wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The scan rate was 0.1 V/s on a platinum disk electrode ($d = 2$ mm).

6a was also observed in the reaction mixture by GC-MS analysis. The yield of **6a** reached highest at 23% at 1 hour and then decreased slowly to 6% at the end of the reaction. When **6a** was subjected to the standard reaction conditions, **3a** was collected in a yield of 86%. Hence, it was proposed that **6a** was formed followed by the oxidation to produce the final product.

In a control experiment in the absence of current, **7a** was obtained as a major product in a 61% yield and **3a** was produced in a 19% yield (Scheme 3a). It was also found that the reaction in the absence FeCl_2 and H_2O_2 could produce **3a** in a 9% yield (Scheme 3c). When FeCl_2 and H_2O_2 were replaced by FeCl_3 (2 eq) no desired product was observed in the absence of electricity (Scheme 3d). This indicated that both the chemical oxidants and the anode oxidation had played roles in the generation of methyl free radicals. The oxidation of **6a** to **3a** was then studied. A low yield (27%) of **3a** was obtained in the absence of the electricity (Scheme 3e), while a 82% yield was achieved in the absence of H_2O_2 and iron salt (Scheme 3f). Moreover, the approximate yield (83%) was obtained when the control reaction was carried out under a nitrogen atmosphere (Scheme 3g), suggesting that the air was not crucial for

the process. Hence it was speculated that anode oxidation might be crucial for the transformation of **6a** to **3a**.

Cyclic voltammetry (CV) experiments (Figure 2. More details please refer to the Supporting Information) revealed the oxidation peak of 4-methyl thiophenol(**1a**) at a potential of 0.21V and 1.48V vs. SCE, bis(*p*-tolyl)disulfide (**7a**) at a potential of 1.48V vs. SCE and methyl *p*-tolyl sulfide (**6a**) at a potential of 1.65V vs. SCE; the reduction potential of Fe^{3+} to Fe^{2+} was -0.75V vs. SCE.

On the basis of the above experimental results and previous reports,^[6,8,12,13] a plausible mechanism for the reaction between **1a** and **2a** was shown in Scheme 4. First, sulfur radicals A, which was formed by oxidation of **1a**, underwent rapid dimerization to generate a **7a**. Meanwhile, DMSO was oxidized to generate a methyl radical intermediate and it could undergo either radical substitution with the generated **7a** or direct coupling with the sulfur radical A to afford **6a**. **6a** was then oxidized on the anode to give product **3a**. Concomitantly, cathodic reduction of Fe^{3+} lead to the formation of Fe^{2+} .

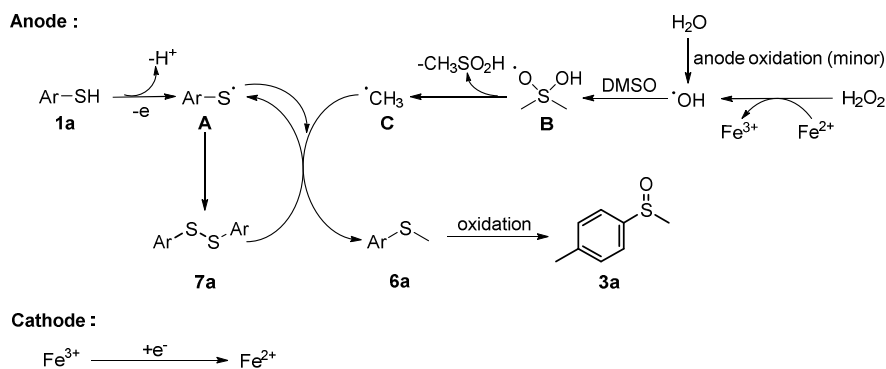
Experimental

General Information

Unless otherwise noted, all the chemicals were purchased commercially, and used without further purification. Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance III-400 spectrometers (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR). Cyclic voltammetry (CV) analysis was performed on CHI660D chenhua Shanghai (<http://www.Chinstr.com/>) with a conventional three-electrode cell, using a platinum electrode ($d = 2$ mm) as working electrode, a Pt wire as counter electrode and saturated calomel electrode (SCE) as a reference electrode. Cyclic voltammograms were recorded at 0.1 V/s scan rate.

General Procedure for the Electrochemical Synthesis of Sulfoxides

A round-bottomed flask (5 mL) was added thiophenols /thiols **1a** (0.3 mmol), FeCl_2 (0.06 mmol), DMSO **2a** (5 mL), NH_4ClO_4 (0.2 M) and 0.4 mL 30% H_2O_2 . The reaction flask was equipped with Pt foils



Scheme 4. Proposed mechanism.

as anode and cathode ($1.0 \times 1.5 \text{ cm}^2$). The solution was electrolyzed at a constant current (5 mA) at ambient temperature for 7.5 h (4.7 F/mol). After electrolysis, the mixture was quenched by water and extracted with ethyl acetate ($3 \times 15 \text{ mL}$). The combined organic layer was washed with brine (10 mL) and dried over MgSO_4 . Purified product **3a** was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.

Spectroscopic Data of Products

Methyl 4-methylphenyl sulfoxide (3a):^[14] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3a** as colorless oil (37.8 mg, 82%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.54 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.70 (s, 3H), 2.41 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 142.3, 141.3, 129.9, 123.4, 43.8, 21.2.

2-Methylphenyl methyl sulfoxide (3b):^[15] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3b** as colorless oil (37.1 mg, 80%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.95 (d, J = 7.7 Hz, 1H), 7.46-7.37 (m, 2H), 7.20 (d, J = 7.4 Hz, 1H), 2.69 (s, 3H), 2.38 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 143.7, 133.7, 130.5, 130.4, 127.2, 122.7, 41.8, 17.8.

Methyl 2-ethylphenyl sulfoxide (3c):^[15] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give **3c** as colorless oil (35.8 mg, 71%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.98 (d, J = 9.0 Hz, 1H), 7.44 (d, J = 7.5 Hz, 2H), 7.31-7.21 (m, 1H), 2.80-2.62 (m, 5H), 1.28 (t, J = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 143.5, 140.5, 131.1, 128.7, 127.6, 123.1, 43.2, 24.6, 15.3.

Methyl 4-tert-butylphenyl sulfoxide (3d):^[16] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give **3d** as white solid (47.7 mg, 81%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.54 (q, J = 8.5 Hz, 4H), 2.70 (s, 3H), 1.33 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 154.7, 142.4, 126.4, 123.4, 43.8, 35.0, 31.2.

2,6-Dimethylphenyl methyl sulfoxide (3e):^[15] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give **3e** as colorless oil (26.3 mg, 52%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.20 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 7.6 Hz, 2H), 2.85 (s, 3H), 2.57 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 139.0, 137.8, 130.7, 130.2, 38.2, 18.9.

Methyl phenyl sulfoxide (3f):^[17] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give **3f** as colorless oil (21.8 mg, 52%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.65-7.63 (m, 2H), 7.52-7.50 (m, 3H), 2.72 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 145.7, 131.1, 129.4, 123.5, 43.9.

Methyl 4-methoxyphenyl sulfoxide (3g):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3g** as brown solid (36.7 mg, 72%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.54 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 2.65 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 161.9, 136.5, 125.4, 114.8, 55.4, 43.9.

4-Hydroxyphenyl methyl sulfoxide (3h):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:4) to give **3h** as white solid (31.4 mg, 67%);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 9.14 (s, 1H), 7.50 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 2.76 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 160.6, 133.2, 126.1, 116.9, 43.1.

3-Hydroxyphenyl methyl sulfoxide (3i):^[19] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:4) to give **3i** as colorless oil (32.3 mg, 69%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 9.12 (s, 1H), 7.54 (s, 1H), 7.29 (t, J = 7.9 Hz, 1H), 6.97 (dd, J = 2.2, 8.1 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 2.75 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 158.6, 144.9, 130.5, 119.2, 114.6, 110.2, 43.3.

4-Fluorophenyl methyl sulfoxide (3j):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3j** as light yellow oil (35.6 mg, 75%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.65 (m, 2H), 7.23 (m, 2H), 2.71 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 164.0 (d, J = 250.0 Hz), 141.0 (d, J = 3.0 Hz), 125.6 (d, J = 9.0 Hz), 116.4 (d, J = 23.0 Hz), 44.0.

2-Fluorophenyl methyl sulfoxide (3k):^[20] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3k** as light yellow oil (28.0 mg, 59%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.87-7.83 (t, J = 7.5 Hz, 1H), 7.49-7.47 (m, 1H), 7.40-7.36 (t, J = 7.5 Hz, 1H), 7.13-7.08 (t, J = 9.0 Hz, 1H), 2.81 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 157.7 (d, J = 250.0 Hz), 132.7, 132.6, 125.4, 115.8, 115.7, 42.0.

4-Chlorophenyl methyl sulfoxide (3l):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3l** as light yellow oil (38.2 mg, 73%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.58 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 2.70 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 144.2, 137.3, 129.7, 125.0, 44.0.

3-Chlorophenyl methyl sulfoxide (3m):^[20] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3m** as colorless oil (30.4 mg, 58%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.66 (s, 1H), 7.50-7.46 (m, 3H), 2.74 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 147.5, 135.6, 131.8, 131.5, 123.5, 121.5, 43.8.

4-Bromophenyl methyl sulfoxide (3n):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **3n** as light yellow oil (48.6 mg, 74%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.66 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 6.8 Hz, 2H), 2.70 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 144.9, 132.6, 125.5, 125.2, 44.0.

2-Bromophenyl methyl sulfoxide (3o):^[20] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give **3o** as colorless oil (27.6 mg, 42%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.93-7.91 (d, J = 7.7 Hz, 1H), 7.58-7.53 (m, 2H), 7.37-7.33 (m, 1H), 2.80 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 145.4, 132.9, 132.2, 128.8, 125.7, 118.4, 41.9.

4-Acetoamidophenyl methyl sulfoxide (3p):^[21] The crude product was purified by column chromatography on silica gel (methanol/ethyl acetate = 1:10) to give **3p** as white solid (44.4 mg, 75%); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.16 (bs, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 2.71 (s, 3H), 2.18 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 169.2, 141.3, 139.5, 124.7, 120.4, 43.8, 24.5.

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2-(Methylsulfinyl)methyl benzoate (3q):^[20] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give 3q as white solid (20.3 mg, 34%); ¹H NMR (400 MHz, CDCl₃): δ = 8.32 (d, *J* = 7.9 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 2.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.6, 150.2, 133.9, 130.6, 130.1, 126.3, 124.0, 52.5, 43.9.

4-(Trifluoromethyl)phenyl methylsulfoxide (3r):^[22] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give 3r as white oil (26.2 mg, 42%); ¹H NMR (400 MHz, CDCl₃): δ = 7.85-7.69 (m, 4H), 2.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 150.0, 133.2 (q, *J* = 31.3 Hz), 126.3 (q, *J* = 3.6 Hz), 124.0, 123.5 (q, *J* = 274.0 Hz), 43.8.

2-(Methylsulfinyl)naphthalene (3s):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give 3s as white solid (43.3 mg, 76%); ¹H NMR (400 MHz, CDCl₃): δ = 8.17 (s, 1H), 7.94-7.86 (m, 3H), 7.57-7.53 (m, 3H), 2.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 142.7, 134.3, 132.8, 129.5, 128.4, 127.9, 127.7, 127.3, 123.9, 119.4, 43.7.

2-(Methylsulfinyl)ethylbenzene (3u):^[23] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give 3u as white solid (41.3 mg, 82%); ¹H NMR (400 MHz, CDCl₃): δ = 7.34-7.32 (m, 2H), 7.30-7.25 (m, 3H), 3.13-3.09 (m, 2H), 2.96 (dd, *J* = 8.0, 17.2 Hz, 2H), 2.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.7, 128.8, 128.5, 126.8, 56.0, 38.5, 28.7.

n-Hexyl methyl sulfoxide (3v):^[24] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give 3v as colorless oil (32.9 mg, 74%); ¹H NMR (400 MHz, CDCl₃): δ = 2.70-2.60 (m, 2H), 2.52 (s, 3H), 1.75-1.68 (m, 2H), 1.45-1.40 (m, 2H), 1.30-1.28 (m, 4H), 0.85 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 54.7, 38.5, 31.3, 28.4, 22.5, 22.4, 13.9.

Cyclohexyl methyl sulfoxide (3w):^[18] The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give 3w as colorless oil (29.8 mg, 68%); ¹H NMR (400 MHz, CDCl₃): δ = 2.52-2.44 (m, 1H), 2.48 (s, 3H), 2.12-2.09 (d, *J* = 12.7 Hz, 1H), 1.88-1.83 (m, 3H), 1.70-1.67 (d, *J* = 12.0 Hz, 1H), 1.42-1.18 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 60.8, 35.1, 26.0, 25.5, 25.3, 25.1, 24.8.

Conclusions

In summary, an electrochemical synthesis of sulfoxides from thiophenols / thiols and dimethyl sulfoxide has been developed. A series of sulfoxides were prepared by this method. Thiophenols, primary and secondary aliphatic thiols are suitable substrates for this transformation to afford desired products in moderate to good yields. The reaction is selective, mild and environmentally friendly. Further investigation to determine the mechanism of this reaction and to expand its scope is underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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Paper

Electrochemical Synthesis of Methyl Sulfoxides from Thiophenols / Thiols and Dimethyl Sulfoxide

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A new route for one-pot synthesis of methyl sulfoxides using electrochemical technique from thiophenols / thiols and dimethyl sulfoxide was developed.

