Electrochemical Synthesis of Methyl Sulfoxides from Thiophenols /

Thiols and Dimethyl Sulfoxide

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Supporting Information

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General information

Unless otherwise noted, all the chemicals were purchased commercially, and used without further purification. Dimethyl sulfoxide (DMSO, $H_2O \le 0.2\%$) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Analytical thin layer chromatography (TLC) plates and the silica gel (300-400 mesh) for column chromatography were purchased from Qingdao Haiyang Chemical and Special Silica Gel Co., Ltd.

Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectroscopy were performed on Bruker Advance III-400 spectrometers (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR). The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ¹H), CDCl₃ (δ 7.26 ppm for ¹H NMR and δ 77.1 ppm for ¹³C). Multiplicities were given as: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplets), etc. The number of protons (n) for a given resonance was indicated by nH.

GC-MS analyses were obtained on a Thermo Scientific Trace GC Ultra Gas Chromatograph equipped with a TG-5MS 30 m \times 0.25 mm ID \times 0.25 μ m capillary column (Thermo Scientific). The GC was directly interfaced to a Thermo Scientific DSQ single quadrupole mass spectrometer (EI, 70 eV). The following GC oven temperature programs were used: 80 °C hold for 2 min, ramp 25 °C/min to a final temperature of 280 °C, and hold for 3 min. Helium was used as a carrier gas, with a constant column flow of 1.0 mL/min. The injector temperature was held constant at 260 °C.

Electrolysis reactions were conducted using a Model QJ3003T (32 V) power supply purchased from Qiujing Instruments (Shenzhen) Co., Ltd. The current was recorded with a Model UT33D digital multimeter purchased from Uni-Trend GroupCo., Ltd.

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 100 mV/s scan rate.

Experimental Procedure

A round-bottomed flask (5 mL) was added thiophenols **1a** (0.3 mmol), FeCl₂ (0.06 mmol), DMSO **2a** (5 mL), 30% aqueous H₂O₂ (0.4 mL, 3.6mmol), and NH₄ClO₄ (0.2 M). The reaction flask was equipped with Pt foils as anode and cathode ($1.0 \times 1.5 \text{ cm}^2$). The solution was electrolyzed at a constant current (5 mA) for 7.5 h (4.7 F/mol) at ambient temperature. After electrolysis, the mixture was quenched by water and extracted with ethyl acetate (3×15 mL). The combined organic layer was washed with brine (10 mL) and dried over MgSO₄. Purified product **3a** was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.

Procedure for scale-up experiments



A round-bottomed flask (100 mL) was added **1a** (3 mmol), FeCl₂ (0.6 mmol), DMSO **2a** (50 mL), 30% aqueous H_2O_2 (4 mL) and NH_4ClO_4 (0.2 M). The reaction flask was equipped with Pt foils as anode and cathode (1.0 × 1.5 cm²). The solution was electrolyzed at a constant current (5 mA) at ambient temperature for 54 h (3.4 F/mol). After electrolysis, the mixture was quenched by water and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was washed with brine (50 mL) and dried over MgSO₄. Purified product **3a** was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.



A round-bottomed flask (100 mL) was added 1d (6 mmol), FeCl₂ (1.2 mmol), DMSO 2a (100 mL), 30% aqueous H₂O₂ (8.0 mL) and NH₄ClO₄ (0.2 M). The reaction flask was equipped with Pt foils 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 98 h (3.0 F/mol). After electrolysis, the mixture was quenched by water and extracted with ethyl acetate ($3 \times 100 \text{ mL}$). The combined organic layer was washed with brine (50 mL) and dried over MgSO₄. Purified product 3d was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.

Cyclic Voltammograms

a

b



Figure S1. Cyclic voltammograms of the relevant compounds in DMSO (0.2 M NH_4CIO_4 as electrolyte), using platinum electrode as working electrode (d = 2 mm), a Pt wire as counter electrode

and a saturated calomel electrode (SCE) as a reference electrode, at a scan rate of 0.1 V/s: (a) none. (b) **3a** (0.05 M). (c) **6a** (0.05 M). (d) **7a** (0.05 M). (e) FeCl₃ (0.020 M). (f) H_2O_2 (0.200 M). (g) FeCl₂ (0.005 M) + H_2O_2 (0.200 M). (h) a+e.

Detection of the reaction intermediates by GC-MS experiment

The reaction conditions were the same as the general procedure as shown in page S2. For the GC-MS analysis of the reaction mixture, sample was taken with a syringe and was then diluted with EtOAc.

Retention time for intermediates and product:

4-methyl thiophenol **1a** (t = 2.63 min), methyl *p*-tolyl sulphide **6a** (t = 3.56 min), methyl *p*-methylphenyl sulfoxide **3a** (t = 5.16 min), bis(*p*-tolyl)disulfide **7a** (t = 7.90 min), internal standard: *n*-dodecane (t = 3.66 min).



















200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

















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$\begin{array}{c} & 2.7157\\ & 2.6829\\ & 2.6829\\ & 2.6209\\ & 2.5207\\$



-7.2602





-7.2596

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0