Facile One-Pot Synthesis of α-Chloro Sulfoxides from Sulfides

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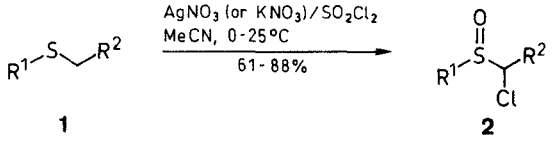
Various sulfides **1** reacted with sulfuryl chloride in the presence of metal nitrates in acetonitrile under mild conditions to give the corresponding α-chloro sulfoxides **2** in good yields.

α-Halo sulfoxides have become useful in organic syntheses[1] and consequently a number of methods have appeared for their synthesis. Both the direct chlorination of sulfoxides with chlorination reagents[1-4] and oxidation of a α-chloro sulfides[5] have been the main procedures. It was reported that sulfuryl chloride acts as a chlorination agent for the chlorination of sulfoxides[6-7] or as an oxidizing agent for the oxidation of sulfides to sulfoxides in the presence of wet silica gel.[8] It was also reported that organic nitrates such as acyl nitrate[9] and nitronium hexafluorophosphate[10] oxidized the sulfides to sulfoxides. In the course of a study on α-chloro sulfoxides, it was found that a mixture of sulfuryl chloride and metal nitrate can be a useful reagent for the direct preparation of α-chloro sulfoxides from sulfides.

In this paper, we report a convenient one-pot synthesis of α-chloro sulfoxides from sulfides using sulfuryl chloride and silver nitrate or potassium nitrate. Various sulfides **1** were allowed to react with an equimolar amount of sulfuryl chloride and silver nitrate (or potassium nitrate) in acetonitrile under mild conditions to yield the corresponding α-chloro sulfoxides **2** together with quantitative precipitation of silver chloride (Scheme 1). The oxidation and chlorination reactions may proceed through an intermediate sulfuryl chloride nitrate.[11] α-Chloro sulfoxides **2** were isolated in good yields by chromatography and identified by comparing their ^{1}H NMR, IR, mass spectra, and mp with those of authentic samples (Table 1).

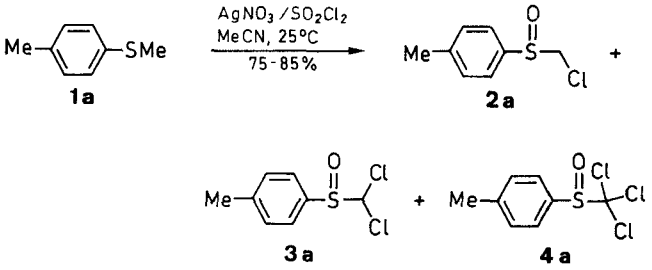


1 **2**

	R^1	R^2		R^1	R^2
a	4-Me-C_6H_4	H	**e**	4-Br-C_6H_4	H
b	Ph	H	**f**	4-Me-C_6H_4	Me
c	Ph	Me	**g**	Me	H
d	4-Cl-C_6H_4				

Scheme 1

When one equivalent amount of methyl *p*-tolyl sulfide **(1a)** was reacted with sulfuryl chloride and silver nitrate, α-chloromethyl *p*-tolyl sulfoxide **(2a)** was obtained as a major product in high yield (85%). However, when an excess of sulfuryl chloride and silver nitrate were used,



1a **2a** **3a** **4a**

Scheme 2

Table 1. Preparation of α-Chloro Sulfoxides **2**

Product	Reaction Time (min)	Yield[a] (%)	mp (°C) or bp (°C)/Torr found	mp (°C) or bp (°C)/Torr reported	IR (neat/KBr) $\nu_{S=O}$ (cm^{-1})	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) m/z (%)
2a	50 (80)[b]	85 (86)[b]	60–61	61.5–62[14]	1046	2.4 (s, 3H), 4.4 (s, 2H), 7.2–7.7 (m, 4H)	188 (M^+, 18.7), 139 (100)
2b	60 (90)[b]	84 (82)[b]	38–39	78–79/0.02[12]	1048	4.4 (s, 2H), 7.3–7.8 (m, 5H)	174 (M^+, 15.2)
2c	80	88	96/0.1	82/0.03[13]	1058	1.7 (d, 3H, J = 7), 4.8 (q, 1H, J = 7), 7.7 (m, 5H)	190 (M^+, 0.5)
2d	100	72	86–87	85.5–87[13]	1056	4.5 (s, 2H), 7.5–7.7 (m, 4H)	208 (M^+, 7.1)
2e	70	81	91–92	$C_7H_6BrClOS$[d] (253.5)	1045	4.4 (s, 2H), 7.5–7.8 (m, 4H)	252 (M^+, 10.7), 203 (100)
2f	50	88	91/0.1	oil[16]	1046	1.6 (d, 3H), 2.4 (s, 3H), 4.7 (q, 1H, J = 7.2), 7.2–7.7 (m, 4H)	202 (M^+, 4.8)
2g	120	61[c]	74/0.1	65/0.05[13]	1042	2.0 (s, 3H), 4.7 (s, 2H)	96 (M^+, 10.5)

[a] Isolated yields using sulfuryl chloride and silver nitrate.
[b] Refers to the method using KNO_3.
[c] Determined by GC.
[d] calc. C 33.16 H 2.38 Cl 13.98
found 33.18 2.33 13.55

Table 2. Preparation of Chloro Sulfoxides from Sulfide (**1a**)

Amount of Reagents (equiv.)			Product	Reaction Time (min)	Yield[a] (%)	mp (°C)	mp (°C) or Molecular Formula	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)
1a	$AgNO_3$	SO_2Cl_2						
1	1	1	**2a**	50	85	60–61	61.5–62[14]	2.4 (s, 3H), 4.4 (s, 2H), 7.2–7.7 (m, 4H)
1	1.2	2	**3a**	80	76	67–68	68[14]	2.4 (s, 3H), 6.1 (s, 1H), 7.2–7.7 (q, 4H, J = 8)
1	1.2	3	**4a**	120	75	84–85	$C_8H_7Cl_3OS$[b] (257.6)	2.4 (s, 3H), 7.3–7.7 (q, 4H, J = 8)

[a] Isolated yield.
[b] IR (KBr): ν = 1048 cm^{-1} (S=O).
MS: m/z (%) = 256 (M^+, 1.7), 139 (100).
[c] calc. C 37.30 H 2.74 Cl 41.29
found 37.24 2.71 41.85

α,α-dichloromethyl *p*-tolyl sulfoxide (**3a**) and α,α,α-trichloromethyl *p*-tolyl sulfoxide (**4a**) were obtained as shown in Scheme 2. Thus, the formation of the products **2a**, **3a**, and **4a** can be controlled by the amount of the reagents (Table 2).

The oxidation mechanism is not yet clear. The oxygen has probably originated from sulfuryl chloride nitrate,[11] which is formed by the treatment of sulfuryl chloride with metal nitrate. Work on the scope and the interesting mechanism is in progress and will be reported in due course.

Melting points were measured on an Electrothermal melting point apparatus. ^{1}H NMR spectra were determined on Varian T-60A or FT-80A spectrometer. IR spectra were recorded on a Perkin-Elmer model 283B and Bomem MB-100 FT-IR spectrophotometers. Mass spectra were obtained on a Hewlett-Packard GC/MS system 5985A. Analytical TLC plates and silica gel 60 (70–230 mesh) were purchased from Merck. Starting sulfides were prepared by literature procedures.[15]

Chloromethyl *p*-Tolyl Sulfoxide (2a); Typical Procedure:
A solution of sulfuryl chloride (80 μL, 1 mmol) in MeCN (5 mL) was added dropwise to a solution of $AgNO_3$ (167 mg, 1 mmol) and methyl *p*-tolyl sulfide (**1a**; 138 mg, 1 mmol) in MeCN (10 mL) over a period of 50 min at 0 °C with good stirring. The reaction was monitored by TLC (Et_2O/hexane, 1 : 1). After the reaction was complete, the mixture was treated with water (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was separated, dried ($MgSO_4$), and concentrated under reduced pressure. The product was isolated by preparative TLC (silica gel, Et_2O/hexane, 1 : 1) and identified by comparing their ^{1}H NMR and mp with those of an authentic sample; mp 60–61 °C (Lit.[12] mp 60–62 °C).

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(11) The formation of **5** was observed by IR (asym. NO_2: 1670 cm^{-1}, sym. NO_2: 1375 cm^{-1}) of an equimolar mixture of SO_2Cl_2 and $AgNO_3$ after removing AgCl by filteration (almost quantitative formation of AgCl was observed). Methyl *p*-tolyl sulfide was only chlorinated, but not oxidized to sulfoxide in the absence of $AgNO_3$. The intermediate **5** may act as an oxidizing agent like acyl nitrate[6] and also as a chlorinating agent.

$$SO_2Cl_2 \xrightarrow{MNO_3} \left[ClSO_3NO_2\right] + MCl$$

Sulfuryl chloride nitrate (**5**)

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