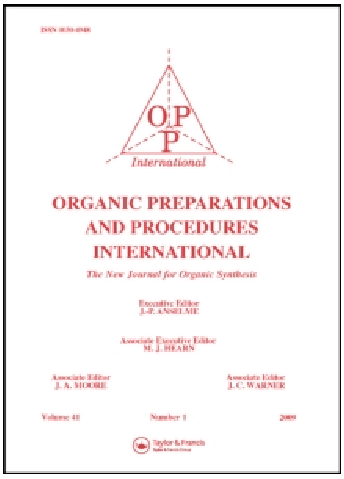

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AN EFFICIENT OXIDATION OF LONG CHAIN ALKYL METHYL SULFIDES TO SULFOXIDES

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6b, mp 222°. IR (KBr): 3035, 3008, 2877, 1774, 1454, 1365, 1334, 1268, 1168, 1122 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.54 (s, 4H), 4.57 (m, 2H), 4.83 (m, 2H), 5.09 (s, 2H), 5.50 (m, 2H), 7.30-7.38 (m, 10H) ppm. ^{13}C NMR (DMSO-d_6): δ 60.05, 69.95, 79.51, 81.04, 82.25, 85.22, 127.66, 127.83, 128.21, 137.25, 171.82 ppm.

Anal. Calcd for $C_{26}H_{22}O_8$: C, 67.53; H, 4.79. Found C, 67.24; H, 4.91

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AN EFFICIENT OXIDATION OF LONG CHAIN ALKYL METHYL SULFIDES TO SULFOXIDES

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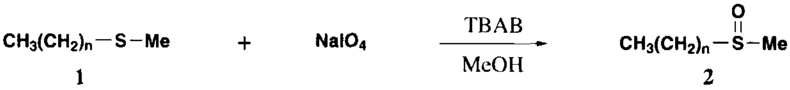
The oxidation of sulfides with sodium periodate in water[1] or in aqueous methanol[2] affords sulfoxides selectively and in high yields. On the other hand, the oxidation of sulfides which are poorly soluble or insoluble in these solvent systems does not lead to good results. We now report that long chain alkyl methyl sulfoxides (LCAMSO), which exhibit molecular alignment similar to those of surfactants,[3] have been obtained efficiently by oxidation of the corresponding sulfides (LCAMS) using a phase-transfer system.



$$\underset{\mathbf{1}}{CH_3(CH_2)_n-S-Me} + NaIO_4 \xrightarrow[MeOH]{TBAB} \underset{\mathbf{2}}{CH_3(CH_2)_n-\overset{O}{\overset{\|}{S}}-Me}$$

a) n = 7 b) n = 13 c) n = 15 d) n = 17 e) n = 21

TBAB: tetra-(*n*-butyl)ammonium bromide

The oxidations of methyl n-octyl sulfide (**1a**) with sodium periodate in the commonly used systems, MeOH-H$_2$O[2] (Entry 1) and MeOH (Entry 2) at room temperature for 24 hr, gave the corresponding sulfoxide (**2a**) in 92% (with 0.2% of sulfone **3a**) and 34% conversion by NMR, respectively. The oxidation of **1a** in MeOH in the presence of tetrabutylammonium bromide (TBAB) under the same conditions afforded **2a** as the sole product in 92-97% conversions (Entries 5-7).

Table 1. The Results of the Oxidation of LCAMS **1** with NaIO$_4$[a]

Entry	LCAMS	NaIO$_4$ / **1** (mol / mol)	TBAB / **1** (mol / mol)	Solvent	% Conversion[b] **2**	% Conversion[b] **3**[c]
1	**1a**	1.1	------	MeOH-H$_2$O	92	0.2
2	**1a**	1.1	------	MeOH	34	~0
3	**1a**	1.1	0.05	CH$_2$Cl$_2$	7	~0
4	**1a**	1.1	0.05	Me$_2$CO	9	~0
5	**1a**	1.1	0.05	MeOH	94	~0
6	**1a**	1.1	0.10	MeOH	97	~0
7	**1a**	1.1	0.01	MeOH	92	~0
8	**1c**	1.1		MeOH-H$_2$O	12	~0
9	**1c**	1.1	0.10	MeOH	95	~0

a) Conditions: rt, 24 hr. b) The values were determined by ^{1}H NMR. c) Alkyl methyl sulfones.

In the oxidation of a longer alkyl methyl sulfide (n-hexadecyl methyl sulfide **1c**) in the two systems, NaIO$_4$-MeOH-H$_2$O (Entry 8) and NaIO$_4$-MeOH-TBAB (Entry 9), the conversion to a sulfoxide (**2c**) were 12% and 95%, respectively. Such a large difference with the oxidation of the longer alkyl methyl sulfide **lb** between the two systems seems to be attributable to the action of tetrabutylammonium ion.

These results of the preparation (isolation) of LCAMSOs **2a-e** from **1a-e**, are listed in Table 2. Regardless of the alkyl length, the corresponding sulfoxides **2** were obtained in high yields without formation of sulfones. Furthermore, the present oxidation system has the merit that the pure LCAMSOs are obtained by simpe washing of the products (**2** containing 2-5% of **1**) with small amounts of *n*-hexane two or three times.

Table 2. Preparation of LCAMSOs **2** using $NaIO_4$-TBAB in MeOH[a]

LCAMS	$NaIO_4$ / **1** (mmol / mmol)	Temp / Time (°C / h)	**2** mp (°C) (*lit.* mp)	Yield (%)
1a	1.1	rt / 24	38-39 (40-40.5)[b]	84
1b	1.1	rt / 24	68-69	96
1c	1.1	rt / 24	76.0-76.5 (75)[b]	90
1d	1.1	rt / 24	81.0-81.8 (84-86)[c]	92
1e	1.1	rt / 24	91.0-92.0	88

a) Molar ratio of TBAB to **1**: 0.10. b) Reference No. 7. c) Reference No.8.

EXPERIMENTAL SECTION

All melting points are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8100A spectrophotometer and ^{1}H-NMR spectra on a JEOL JNM-GSX270 spectrometer using TMS as the internal standard in $CDCl_3$. High-resolution mass data were obtained by JEOL JMS-AX505W. Octyl methyl sulfide and all 1-chloroalkanes (Tokyo Kasei Kogyo Co., Ltd) were used after purification.

Preparation of Sulfides 1. General Procedure.- To a stirred solution of 5.0 mmol of 1-chloroalkane in 20-30 mL of EtOH was added 10.0 mmol of sodium methylmercaptide in water (15% aqueous solution) at room temperature. After refluxing for 10-20 hrs, the solvent EtOH and water from the reaction mixture were removed by distillation under reduced pressure. The resulting residue was extracted with 25 mL of ether. The ethereal extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to give an oily or semi-solid residue of **1**. The residue was purified by distillation or recrystallization from hexane, and the structures of **1** was confirmed by IR, NMR and mass spectra.

Methyl *n*-Tetradecyl Sulfide (1b).- (92% yield), bp. 132-135° / 5 mmHg. *lit.*[4] 134-140° / 0.35-0.5 mmHg. ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.6 Hz), 1.26 (s, 20H), 1.31-1.45 (m, 2H), 1.53-1.64 (m, 2H), 2.09 (s, 3H), 2.49 (t, 2H, J = 7.3 Hz). MS (EI) : 244 (M^+, 70%), 229 (M^+-15, 100%).

Methyl *n*-Hexadecyl Sulfide (1c).- (87% yield), bp. 141-143° / 3 mmHg. *lit.*[5] 163-165° / 19 mmHg. ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.7 Hz), 1.26 (s, 24H), 1.27-1.43 (m, 2H), 1.53-1.63 (m, 2H), 2.10 (s, 3H), 2.49 (t, 2H, J = 7.3 Hz). MS (EI) : 272 (M^+, 67%), 257 (M^+-15, 100%).

Methyl *n*-Octadecyl Sulfide (1d).- (88% yield), bp. 171-173° / 3 mmHg. *lit.*[6] 386° / 760 mmHg. ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.6 Hz), 1.26 (s, 28H), 1.27-1.43 (m, 2H), 1.53-1.65 (m, 2H), 2.09 (s, 3H), 2.49 (t, 2H, J = 7.3 Hz).

MS (EI) : 300 (M^+, 60%), 285 (M^+-15, 100%).

Methyl *n*-Docosyl Sulfide (1e).- (89% yield), mp. 45.0-45.8° (from hexane). ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.6 Hz), 1.25 (s, 36H), 1.27-1.42 (m, 2H), 1.53-1.65 (m, 2H), 2.10 (s, 3H), 2.49 (t, 2H, J = 7.6 Hz). HRMS (EI) calcd for $C_{23}H_{48}S$ (M^+) : 356.3489, found: 356.3483.

Oxidation of Sulfides

(a) *Oxidation in $NaIO_4$-MeOH-H_2O System*.- To a mixture of 5.00 mmol of sulfide **1** in 30 mL of MeOH was added 5.50 mmol of $NaIO_4$ in 25 mL of water. After stirring at room temperature (22±2°) for 24 hrs, the *solid* or *semisolid matter* precipitated. In the case of the reaction mixture containing the *solid precipitate*, the solid was collected by filtration, while the filtrate was mixed with 15 mL of saturated sodium chloride solution, followed by extraction with three 20-mL portions of CH_2Cl_2. The collected *solid* was dissolved in the combined extract and the resulting solution was washed twice with 20 mL of 10% NaCl aq. and 20 mL of water, and dried over anhydrous sodium sulfate. In the case of the reaction mixture containing the *semisolid precipitate*, the mixture was mixed with 15 mL of saturated sodium chloride solution, and then treated in a similar maner to the *solid precipitate*. The dried solutions were evaporated to dryness, respectively. To determine the composition of the organosulfer compounds in the residue, the ^{1}H NMR spectrum was recorded.

(b) *Oxidation in $NaIO_4$-MeOH System*.- To a suspended solution containing 5.50 mmol of $NaIO_4$ in 30 mL of MeOH was added 5.00 mmol of sullfide **1** in 5 mL of MeOH. After stirring at room temperature (20-25°) for 24 hrs, the solvent MeOH in the reaction mixture was removed by distillation under reduced pressure below room temperature. The residue was treated twice with 20 mL of CH_2Cl_2 to extract organic materials. The subsequent procedure for the dichloromethane extract was carried out in a similar manner to (a).

(c) *Oxidation in $NaIO_4$-TBAB-MeOH System*.- To a suspended solution containing 5.00 mmol of sulfide **1** and 5.50 mmol of $NaIO_4$ in 25 mL of MeOH was added 0.5 mmol of tetrabutylammonium bromide in 5 mL of MeOH. After stirring at room temperature (20-24°) for 24 hrs, the solvent MeOH in the reaction mixture was removed by distillation under reduced pressure below room temperature. The subsequent procedure for the residue was carried out in a similar manner to (b).

Preparation of Sulfoxides 2. General Procedure.- The sulfides were oxidized according to the procedure (c) and the resulting reaction mixtures worked up. After examination by ^{1}H NMR spectra, the crude sulfoxides were purified by washing with 5 mL of *n*-hexane two or three times.

Methyl *n*-Octyl Sulfoxide (2a).- IR: 1031 cm^{-1} (S=O). ^{1}H-NMR: δ 0.88 (s, 3H, J = 6.7 Hz), 1.23-1.38 (m, 8H), 1,36-1.56 (m, 2H), 1.70-1.82 (m, 2H), 2.56 (s, 3H), 2.59- 2.77 (m, 2H).

Methyl *n*-Tetradecyl Sulfoxide (2b).- IR: 1020 cm^{-1} (S=O) . ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.8 Hz), 1.24 (s, 20H), 1.45-1.55 (m, 2H), 1.70-1.83 (m, 2H), 2.56 (s, 3H), 2.60-2.82 (m, 2H). HRMS (CI): Calcd for $C_{15}H_{32}OS$ (M^+ + H) 261.2252; found 261.2257.

Methyl *n*-Hexadecyl Sulfoxide (2c).- IR: 1027 cm^{-1} (S=O) . ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.6 Hz), 1.26 (bs, 24H), 1.45-1.55 (m, 2H), 1.70-1.82 (m, 2H), 2.56 (s, 3H), 2.62-2.82 (m, 2H).

Methyl *n*-Octadecyl Sulfoxide (2d).- IR: 1012 cm^{-1} (S=O). ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.8 Hz), 1.25 (s, 28H), 1.38-1.52 (m, 2H), 1.69-1.83 (m, 2H), 2.56 (s, 3H), 2.60-2.82 (m, 2H). HRMS (CI): Calcd for $C_{19}H_{40}OS$ (M^+ + H) 317.2878; found 317.2871.

Methyl *n*-Docosyl Sulfoxide (2e).- IR: 1026 cm^{-1} (S=O). ^{1}H-NMR: δ 0.88 (t, 3H, J = 6.6 Hz), 1.25 (s, 36H), 1.38-1.52 (m, 2H), 1.68-1.82 (m, 2H), 2.56 (s, 3H), 2.60-2.82 (m, 2H). HRMS (CI): Calcd for $C_{23}H_{48}OS$ (M^+ + H) 373.3504; found 373.3506.

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