This article was downloaded by: [134.117.10.200]
On: 16 June 2014, At: 07:12
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Organic Preparations and Procedures International: The New Journal for Organic Synthesis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

AN EFFICIENT OXIDATION OF LONG CHAIN ALKYL METHYL SULFIDES TO SULFOXIDES

Tamotsu Yamamoto [a] , Tetsushi Hayakawa [a] , Mugi Yoshino [a] , Soh-Ichiroh Hata [a] & Yorinobu Hirayama [a]
[a] Department of Industrial Chemistry, Faculty of Engineering , Kanto Gakuin University , Mutsuura Kanazawa-ku, Yokohama, 236-0032, JAPAN
Published online: 12 Feb 2009.

To cite this article: Tamotsu Yamamoto , Tetsushi Hayakawa , Mugi Yoshino , Soh-Ichiroh Hata & Yorinobu Hirayama (2000) AN EFFICIENT OXIDATION OF LONG CHAIN ALKYL METHYL SULFIDES TO SULFOXIDES, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 32:2, 192-196, DOI: 10.1080/00304940009356286

To link to this article: http://dx.doi.org/10.1080/00304940009356286

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [134.117.10.200] at 07:12 16 June 2014

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

REFERENCES

1. M. Sander, E. V. Dehmlow, B. Neumann and H.-G. Stammler, *Tetrahedron* **55**, 13395 (1999).
2. O. Diels and K. Alder, *Ann.*, **490**, 243 (1931).
3. J. Kallos and P. Deslongchamps, *Can. J. Chem.*, **44**, 1239 (1966).
4. For the use of trifluoroacetic acid anhydride to generate anhydride units in cyclic furan derivatives see J. A. Moore and J. E. Kelly, *Org. Prep. Proced. Int.* **6**, 255 (1974).
5. R. N. Warrener, S. Wang, L. Maksimovic, P. M. Tepperman and D. N. Butler, *Tetrahedron Lett.*, **36**, 6141 (1995).
6. P. F. Ranken, B. J. Harty, L. Kapicak and M. A. Battiste, *Synth. Commun.*, **3**, 311 (1973).
7. Compound **6a** has been mentioned by J. B. Hendrickson and V. Singh, *Tetrahedron Lett.*, **24**, 431 (1983).

Downloaded by [134.117.10.200] at 07:12 16 June 2014

****

AN EFFICIENT OXIDATION OF LONG CHAIN ALKYL METHYL SULFIDES TO SULFOXIDES

Submitted by (12/16/99)
Tamotsu Yamamoto,* Tetsushi Hayakawa, Mugi Yoshino,
Soh-ichiroh Hata, and Yorinobu Hirayama

Department of Industrial Chemistry, Faculty of Engineering
Kanto Gakuin University
Mutsuura, Kanazawa-ku, Yokohama 236-0032, JAPAN

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

Downloaded by [134.117.10.200] at 07:12 16 June 2014

surfactants,[3] have been obtained efficiently by oxidation of the corresponding sulfides (LCAMS) using a phase-transfer system.

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

1 2

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_2O[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_2O	92	0.2
2	**1a**	1.1	------	MeOH	34	~0
3	**1a**	1.1	0.05	CH_2Cl_2	7	~0
4	**1a**	1.1	0.05	Me_2CO	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_2O	12	~0
9	**1c**	1.1	0.10	MeOH	95	~0

a) Conditions: rt, 24 hr. b) The values were determined by ^1H 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_2O (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.

Downloaded by [134.117.10.200] at 07:12 16 June 2014

Downloaded by [134.117.10.200] at 07:12 16 June 2014

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.

REFERENCES

1. C. R. Johnson and J. E. Keiser, *Org. Syn.*, Coll. Vol. **V**, 791, John Wiley & Sons, New York, NY (1973).

2. L. L. Replogle and J. R. Maynard, *J. Org. Chem.*, **32**, 1909 (1967).

3. a) T. Yamamoto, M. Yoshino, S. Ueda and T. Watanabe, *70th Annual Meeting of Chem. Soc. Jpn, Preprint,* **II**, 1365 (1996); b) M. Yoshino, K. Kataoka, H. Kuroki and T. Yamamoto, *71st Annual Meeting of Chem. Soc. Jpn, Preprint,* 386 (1996).

4. D. M. Burness, *J. Org. Chem.*, **24**, 849 (1959).

5. R. Kuhn and O. Dann, *Ber.*, **73B** 1092 (1940).

6. *Beilstein,* **1** EIV, 1894.

7. D. Jerchel, L. Dippelhofer and D. Renner, *Chem. Ber.*, **87**, 947 (1954): The oxidation of sulfides was carried out with 30% H_2O_2 in acetone or acetic acid, and **2a** and **2c** were obtained in 75 and 83% yields, respectively.

8. C. George, T. J. Lewis, J. P. Llewellyn, S. Salvagno, D. M. Taylar, C. J. Stirling and V. Vogel, *J. Chem. Soc., Faraday Trans., I,* **84**, 1531 (1988): **2d** was obtained in a18% yield by oxidation with *m*-chloroperbenzoic acid followed by column-chromatographic separation from a mixture containing sulfide and sulfone.

Downloaded by [134.117.10.200] at 07:12 16 June 2014