  Bull. Chem. Soc. Jpn., 54, 1443—1447 (1981)

Selective Oxidation of Unsymmetrical Thiosulfinic *S*-Esters to the Corresponding Thiosulfonic *S*-Esters with $NaIO_4$[1]

Toshikazu TAKATA, Yong Hae KIM,[2] and Shigeru OAE*

Department of Chemistry, The University of Tsukuba, Sakura, Ibaraki 305

(Received October 17, 1980)

Unsymmetrical thiosulfinic *S*-esters were oxidized with sodium metaperiodate in aqueous media to the corresponding unsymmetrical thiosulfonic *S*-esters nearly quantitatively. The oxidation was accelerated by addition of a catalytic amount of inorganic and organic acids or halogen. Sulfinic esters were produced competitively along with the thiosulfonic *S*-esters in the oxidation of thiosulfinic *S*-esters in aqueous alcohol. However, unsymmetrical disulfides were not oxidized selectively to the corresponding unsymmetrical thiosulfonic *S*-esters but a mixture of both symmetrical and unsymmetrical thiosulfonic *S*-esters was obtained.

We have recently reported that oxidations of unsymmetrical thiosulfinic *S*-esters with peroxy acid[3] or dinitrogen tetraoxide[4] afforded the corresponding symmetrical thiosulfonic *S*-esters which were undoubtedly derived by the cleavage of sulfur-sulfur bond. A few previous studies[3,5] on the oxidations of thiosulfinic S-esters with some peroxy acids or peroxides revealed that none of these oxidations resulted in the selective oxidation of unsymmetrical thiosulfinic *S*-ester to the corresponding unsymmetrical thiosulfonic *S*-ester with no apparent cleavage of sulfur-sulfur bond. The oxidation of linear unsymmetrical thiosulfinic *S*-ester generally afforded both symmetrical and unsymmetrical thiosulfonic *S*-esters (Eq. 1). Only the oxidation of a six-membered cyclic thiosulfinic *S*-ester with peroxy acid was found to proceed without any apparent cleavage of sulfur-sulfur linkage to afford two unsymmetrical thiosulfonic *S*-esters in good yields.[6a]

$$\mathrm{RSSR'} \xrightarrow{[O]} \mathrm{RS(O)SR'} + \mathrm{RSS(O)R'} + \mathrm{RS(O)SR} + \mathrm{R'S(O)SR'} \qquad (1)$$

In attempts to detect imaginary "α-disulfoxide (RS(O)S(O)R')" which is considered to be formed initially in the oxidation of thiosulfinic *S*-ester but too unstable to be observed, Barnard[5a] and Kice *et al.*[5c] have carried out the oxidation of unsymmetrical thiosulfinic *S*-esters and obtained a mixture of thiosulfonic *S*-esters, resulting from the initial oxidation, subsequent cleavage of the disulfide linkage, and the recombination.

However, surprisingly, when sodium metaperiodate ($NaIO_4$) was used as an oxidant, many unsymmetrical thiosulfinic *S*-esters were found to be oxidized selectively to the corresponding unsymmetrical thiosulfonic *S*-esters in aqueous media such as dioxane–water under mild conditions, with no apparent cleavage of sulfur-sulfur bond. This paper describes this new selective oxidation in detail.

Results and Discussion

$NaIO_4$ Oxidation. When an unsymmetrical thiosulfinic *S*-ester **1** was treated with an equimolar amount of sodium metaperiodate, only one product, *i. e.* the corresponding unsymmetrical thiosulfonic *S*-ester **2**, was found to be obtained. The reaction was also found to be accelerated by addition of a catalytic amount of inorganic or organic acid as well as iodine. Selected results are listed in Table 1.

$$\mathrm{R\text{-}S(O)\text{-}S\text{-}R'} \xrightarrow[\text{aqueous solvent, r.t., Cat.}]{NaIO_4} \mathrm{R\text{-}S(O)_2\text{-}S\text{-}R'} \qquad (2)$$

1 → **2** ≈100%

1a	R=Ph, R'=Ph	**1f**	R=Et, R'=Ph
1b	R=Ph, R'=*p*-Tol	**1g**	R=Ph, R'=Pr
1c	R=*p*-Tol, R'=Ph	**1h**	R=Me, R'= 
1d	R=Ph, R'=Me	**1i**	*p*-Tol, R'=Me
1e	R=Me, R'=Ph	**1j**	*p*-ClC_6H_4, R'=Me

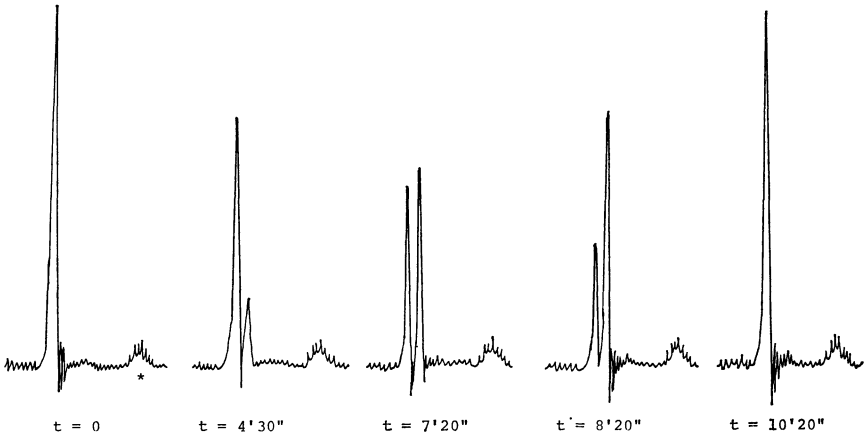
Following is a typical run. A solution of $NaIO_4$ (1.2 mmol) in water (2.0 ml) was added into a dioxane solution (3.5 ml) containing thiosulfinic *S*-ester (**1**, 1.0 mmol) at room temperature. To the resulting mixture a small amount of a catalyst (*e. g.* concd HCl, 1 or 2 drop) was added. After stirring the mixture for *ca.* 30 min at the room temperature or until the solution turned to dark brown, the highly pure unsymmetrical thiosulfonic *S*-ester **2** was obtained nearly quantitatively by extraction of the reaction mixture. The product generally showed only one component on GC, LC, TLC, or NMR. The yield of the product was determined by isolation through column chromatography or GC. New products were identified by comparing their IR and NMR spectra with those of authentic samples prepared by a known method[7] which is the condensation of sulfinic acids and sulfenyl chlorides in the presence of a tertiary amine. The starting thiosulfinic *S*-ester **1** were prepared by the condensation of the corresponding sulfinyl chlorides and thiols in the presence of pyridine in carbon tetrachloride at a temperature lower than 0 °C, according to the method of Backer *et al.*[8] The purification of **1** was carried out by recrystallization or column chromatography, while the identification was performed by several spectra and elemental analysis, as described in "Experimental Section."

As shown in Table 1, thiosulfinic *S*-esters of various types were oxidized to the corresponding thiosulfonic *S*-esters without cleavage of sulfur-sulfur linkage. Electrophilic catalysts highly accelerated the reaction while the reaction usually had a long induction period without any catalyst. Yields of the unsymmetrical thiosulfonic *S*-esters were nearly quantitative regardless

TABLE 1. SELECTIVE OXIDATION OF UNSYMMETRICAL THIOSULFINIC *S*-ESTER WITH $NaIO_4$ AT 20 °C

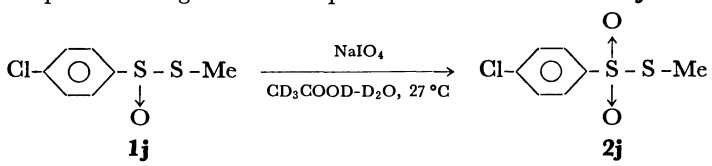
Substrate	Solvent	Catalyst	Time/h	Yield of products/%	
1a	dioxane	no	26.0	**2a**	quant.[a]
1b	CH_3CN	concd HCl	<1.0	**2b**	quant.[a]
1c	CH_3CN	I_2	0.5	**2c**	quant.[a]
1d	dioxane	dioxane	<2.0	**2d**	quant.[a]
1e	dioxane	dioxane	8.0	**2e**	98[b]
1f	dioxane	concd HCl	1.0	**2f**	90[b]
1g	dioxane	dioxane	1.0	**2g**	85[b]
1h	dioxane	concd HCl	0.5	**2h**	90[c]
1i	CD_3COOD[d]	no	0.5	**2i**	quant.[a]
1j	CD_3COOD[d]	no	0.5	**2j**	quant.[a]

a) No other product was observed in GC and NMR. b) Isolated yield. c) The yield was determined by GC and NMR. d) The reaction was carried out in NMR sample tube; substrate: 0.1 mmol.



* Signals due to undeuterized proton of acetic acid-d_4.

Fig. 1. Spectral change in NMR spectra in the oxidation of **1j** with $NaIO_4$.



1j **2j**

of the substituent.

No detectable intermediate was observed in the NMR study of the oxidation of thiosulfinic *S*-ester **1j** with $NaIO_4$ in CD_3COOD–D_2O as shown in the following Fig. 1. Methyl signal at 2.33 ppm (from external TMS) of **1j** gradually changed to the signal at 2.26 ppm which is identical to that of **2j**. No other peak of methyl group was observed in the NMR spectra throughout the reaction. An interesting relationship found between the two unusual chemical shifts of **1** and **2** in which the chemical shift of **1j** is lower than that of **2j**, has been re-confirmed.[9]

Effects of Catalyst and Solvent. The oxidation was found to be accelerated by addition of a catalytic amount of organic or inorganic acid or halogen. While weaker acids such as acetic and formic acids than trifluoroacetic acid (pK_a 1.0) did show little catalytic ability, the oxidation was accelerated in acetic acid as solvent even without catalyst. Catalysts effective in the oxidation are the following: CF_3COOH, H_2SO_4, HIO_4, $HClO_4$, HCl, I_2, and Br_2, as shown partially in Table 2. The catalytic activity of iodine found in this reaction was already noticed in the oxidation of cyclic disulfide to the corresponding thiosulfonic *S*-ester with KIO_4 by Field and Kim.[10] Solvents used were dioxane, acetonitrile, and acetone, all of which can mix freely with water. Acetic acid was effective not only as a solvent but also as a catalyst and hence the best system for the oxidation. Alcohols were not effective because the competitive reaction of **1** with the alcohols took place, as described later.

If no catalyst was used, the reaction occurred suddenly with coloring by iodine derived from $NaIO_4$ after a long induction period (5—10 h) and finished within 1 h as in the case with catalyst, due mainly to the catalytic action of iodine accumulated. Figure 2 indicates the rate of disappearance of **1c** in the oxidation with $NaIO_4$ as monitored by LC. Appearance of color of iodine was in accordance with the initiation of the reaction. The reaction is presumed to be an auto-catalyzed reaction with iodine formed since iodine increases as the reaction proceeds.

Table 2. Effects of catalyst and solvent (20 °C)

Substrate	Solvent	Catalyst	Time/h	Yield of products/%[a]	
1d	dioxane	no	6.0	**2d**	92
1d	CH_3CN	no	5.0	**2d**	92
1d	acetone	no	27.0	—	—[b]
1c	CH_3CN	HCOOH	6.0	**2c**	90
1d	dioxane	CH_3COOH	6.0	**2d**	90
1d	acetone	I_2	3.0	**2d**	quant.[c]
1d	dioxane	concd HCl	1.0	**2d**	93
1d	dioxane	CH_3COOH	2.0	**2d**	quant.[c]
1d	CH_3COOH	no	0.5	**2d**	95[d]
1c	CH_3CN	Br_2	0.5	**2c**	95[e]
1c	CH_3CN	H_2SO_4	1.0	**2c**	quant.[c,e]
1c	CH_3CN	HIO_4	1.0	**2c**	quant.[c,e]
1c	CH_3CN	CH_3CN	1.0	**2c**	quant.[c,e]

a) The yield was determined by GC and NMR. b) Starting material was recovered. c) No other product was observed in GC and NMR. d) Solvent ratio: $CH_3COOH/H_2O=7/4$ (v/v). e) The yield was determined by LC.

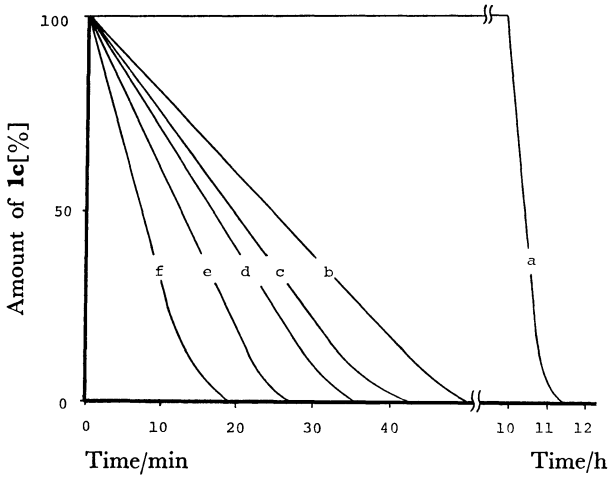
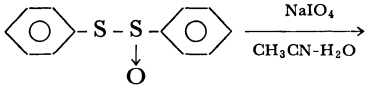
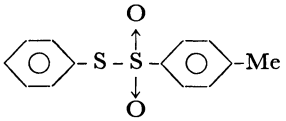


Fig. 2. Oxidation of thiosulfinic *S*-ester **1c** with $NaIO_4$ either with or without catalyst.
a: Reaction at 17 °C without catalyst, b: reaction at 0—4 °C with iodine as a catalyst, c: reaction at 20 °C with HIO_4, d: reaction at 20 °C with H_2SO_4, e: reaction at 20 °C with $HClO_4$, f: reaction at 20 °C with iodine or bromine.

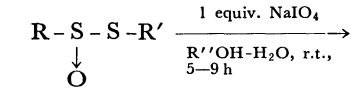


1c



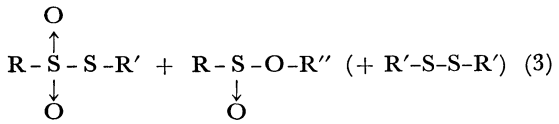
2c

Reaction in Aqueous Alcohol. The oxidation of **1d** with $NaIO_4$ in aqueous alcohol resulted in the competitive formation of the sulfinic ester of the alcohol along with that of the usual oxidation product of thiosulfonic *S*-ester **2d** (Eq. 3). When three different alcohols of varying bulkiness, *i.e.* ethanol, isopropyl alcohol and *t*-butyl alcohol were used as solvents, the amount of the sulfinic ester **3** produced was found



1

1d (R=Ph, R′=Me), R″=Et
R″=*i*-Pr,
R″=*t*-Bu



(3)

2 **3** **4**

42% (44)* 39% (47)*
67% 27%
82% 7%

* Reaction catalyzed by concd HCl within 1 h.

to decrease in the following order: ethanol>isopropyl alcohol>*t*-butyl alcohol, which is the order of bulkiness as well as the nucleophilicity of the alcohols used. The distribution of products changed little in the acid-catalyzed reaction (parentheses). Sulfinic esters (**3**) were not oxidized at all under these conditions. GC analysis confirmed that the symmetrical disulfide is derived only from the sulfenyl part. The disulfide was considered to be produced from the thiol formed during the reaction involving nucleophilic attack of alcohol to **1**. The thiol thus formed should be oxidized immediately to the corresponding disulfide under the conditions.

Reaction of Disulfide with $NaIO_4$. When an unsymmetrical disulfide, methyl phenyl disulfide **5**, was treated with two molar amount of $NaIO_4$ under the same conditions, the following two symmetrical thiosulfonic *S*-esters (**6** and **7**) were obtained as major products which are undoubtedly derived by the cleavage of sulfur-sulfur bond, along with $PhSSO_2Me$ (**8**) (Eq. 4). By direct observation of NMR spectral change in the reaction of **5** with 2 equiv. $NaIO_4$ in CD_3COOD–D_2O at 27 °C, the cleavage of sulfur-sulfur bond was found to occur at the beginning of the reaction and is competitive with the oxidation

$$\underset{\mathbf{5}}{\text{Ph-S-S-Me}} \xrightarrow[\text{dioxane-}H_2O,\ \text{r.t.}]{\text{2 equiv. } NaIO_4} \underset{\mathbf{6}\ 27\%}{PhSSO_2Ph} + \underset{\mathbf{7}\ 25\%}{MeSSO_2Me} + \underset{\mathbf{8}\ 31\%}{PhSSO_2Me} \quad (4)$$

of sulfur atom, since all the methyl signals of dimethyl disulfide and the starting disulfide and those attached to sulfinyl and sulfonyl groups were observed simultaneously during the reaction. Meanwhile, oxidation of a mixture of diphenyl disulfide and dimethyl disulfide with $NaIO_4$ under the same conditions as in the above NMR study, also afforded an unsymmetrical and two symmetrical thiosulfonic *S*-esters (Eq. 5).

$$\left.\begin{matrix}\text{PhSSPh}\ \ \mathbf{9}\\ \text{MeSSMe}\ \ \mathbf{10}\end{matrix}\right\} \xrightarrow[\substack{CD_3COOD\text{-}D_2O\\ 27\ ^\circ C\ (NMR)}]{\text{4 equiv. } NaIO_4} \underset{\mathbf{8}}{PhSSO_2Me} + \underset{\mathbf{7}}{MeSSO_2Me}\ (+\ \underset{\mathbf{6}}{PhSSO_2Ph}) \quad (5)$$

Thus, any unsymmetrical thiosulfinic *S*-ester can be selectively oxidized to the corresponding unsymmetrical thiosulfonic *S*-ester nearly quantitatively in this oxidation with $NaIO_4$.

Obviously the oxidation of thiosulfinic *S*-ester with $NaIO_4$ is entirely different from that with peracetic acid which proceeds *via* formation of "α-disulfoxide,"[3] which is so unstable to collapse immediately yielding the corresponding four symmetrical and unsymmetrical thiosulfonic *S*-esters by the cleavage of sulfur-sulfur bond. In fact, in order to confirm the difference, the oxidations of 3-methyl-1,2-dithiane 1-oxide, a six-membered unsymmetrical thiosulfinic *S*-ester, were carried out with both $NaIO_4$ and peroxy acid, and the clear difference between products of two oxidations was confirmed.[6] This new selective oxidation of thiosulfinic *S*-ester with $NaIO_4$ appears to proceed by the nucleophilic attack of the periodate on the sulfinyl sulfur atom to form the corresponding thiosulfonic *S*-ester.

Experimental

General. Chemicals were of reagent grade unless otherwise specified. All melting points were measured by Yanaco instrument and were uncorrected. IR spectra were taken on a Hitachi 215 spectrophotometer. NMR spectra of the compounds were taken with a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ using TMS as an internal standard. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Shimadzu GC-6A instrument was used for gas chromatography using N_2 gas as a carrier gas. High pressure liquid chromatography was carried out with Yanaco L-1030 instrument using methanol as an eluent. Elemental analyses were carried out by the Chemical Analysis Center at this university.

Preparation of Thiosulfinic S-*Ester.* Both symmetrical and unsymmetrical thiosulfinic *S*-esters were prepared by the method reported by Backer and Kloosterziel[8] with rather little modification. Namely, addition of a thiol into a distilled sulfinyl chloride in CCl_4 under cooling at a temperature lower than 0 °C gave thiosulfinic *S*-ester (85—90%). The thiosulfinic *S*-ester was identified by comparing melting point with that reported previously, IR spectrum, and NMR spectrum, and elemental analysis.

S-*Phenyl Benzenethiosulfinate* **1a**: Pale yellow crystals; mp 69—70 °C (lit,[11] 69—70 °C); IR ($CHCl_3$, cm^{-1}) 3055, 1577, 1475, 1093, and 1060 (S=O).

S-p-*Tolyl Benzenethiosulfinate* **1b**: Pale yellow crystals; mp 70—71 °C (lit,[11] 68 °C); IR ($CHCl_3$, cm^{-1}) 3050, 1590, 1470, 1095, and 1055 (S=O).

S-*Phenyl* p-*Toluenethiosulfinate* **1c**: Pale yellow crystals; mp 82 °C (lit,[11] 83—84 °C); IR ($CHCl_3$, cm^{-1}) 3050, 1590, 1470, 1095, and 1065 (S=O).

S-*Methyl Benzenethiosulfinate* **1d**: Colorless crystals; mp 26—28 °C; IR (neat, cm^{-1}) 3050, 2975, 2900, 1570, 1470, 1095, and 1060 (S=O) (lit,[12] 1104 (in CCl_4)).

S-*Phenyl Methanethiosulfinate* **1e**: Colorless oil; IR (neat, cm^{-1}) 3050, 2980, 2900, 1570, 1470, and 1090 (S=O), (lit,[12] 1101 (in CCl_4)).

S-*Phenyl Ethanethiosulfinate* **1f**: Pale yellow oil; IR (neat, cm^{-1}) 3050, 1575, 1473, 1440, and 1085 (S=O); NMR ($CDCl_3$, δ) 1.41 (3H, t, $-CH_3$, J=7.5 Hz), 3.10 (2H, q, $-CH_2-$, J=7.5 Hz), 7.20—7.73 (5H, m, arom.). Found: C, 51.53; H, 5.50%. Calcd for $C_8H_{10}OS_2$: C, 51.58; H, 5.41%.

S-*Propyl Benzenethiosulfinate* **1g**: Colorless oil; IR (neat, cm^{-1}) 3050, 2950, 1575, 1470, 1090, and 1060 (S=O); NMR ($CDCl_3$, δ) 1.03 (6H, t, $-CH_3$, J=7.5 Hz), 1.80 (2H, m, $-C\underline{H}_2-$ CH_3), 3.09 (1H, t, $-S-CH_2-$, H_A or H_B, J=6.0 Hz), 3.12 (1H, t, H_A or H_B, J=7.4 Hz), 7.33—7.75 (5H, m, arom.). Found: C, 54.08; H, 5.98%. Calcd for $C_9H_{12}OS_2$: C, 53.96; H, 6.03%.

S-*Cyclohexyl Methanethiosulfinate* **1h**: Colorless oil; IR (neat, cm^{-1}) 2970, 2905, 2840, 1440, and 1080 (S=O); NMR ($CDCl_3$, δ) 1.05—2.35 (10H, m, ring protons), 2.95 (3H, s, $-CH_3$), 3.28 (1H, broad s, $-S-CH\langle$). Found: C, 47.15; H, 7.85%. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91%.

S-*Methyl* p-*Toluenethiosulfinate* **1i**: Pale yellow oil; IR (neat, cm^{-1}) 3000, 2900, 1590, 1490, 1085, and 1062 (S=O); NMR ($CDCl_3$, δ) 2.38 (3H, s, Ar-$C\underline{H}_3$), 2.52 (3H, s, $-S-CH_3$), 7.23 (2H, d, arom., J=8.3 Hz), 7.54 (2H, d, arom., J=8.3 Hz). Found: C, 51.60; H, 5.35%. Calcd for $C_8H_{10}OS_2$: C, 51.58; H, 5.41%.

S-*Methyl* p-*Chlorobenzenethiosulfinate* **1j**: Colorless oil; IR (neat, cm^{-1}) 3070, 2970, 1573, 1470, and 1080 (S=O); NMR ($CDCl_3$, δ) 2.53 (3H, s, $-CH_3$), 7.41 (2H, d, arom., J=8.9 Hz), 7.63 (2H, d, arom., J=8.9 Hz). Found: C, 41.03; H, 3.19%. Calcd for $C_7H_7ClOS_2$: C, 40.67; H, 3.41%.

Oxidation of Thiosulfinic S-*Ester* **1** *with* $NaIO_4$. All the reactions were carried out at room temperature (*ca.* 20 °C).

To a stirred solution of thiosulfinic *S*-ester (**1**, 1.0 mmol) in organic solvent (acetone, acetonitrile, or dioxane, 3.5 ml) a solution of sodium metaperiodate ($NaIO_4$, 1.2 mmol) in 2.0 ml of water was added. A small amount of one of catalysts (H_2SO_4, HCl, HIO_4, CF_3COOH, I_2, or Br_2, one or two drop(s) of liquid catalyst, or 3—10 mg of solid catalyst) was added to the mixture. Within 1.0 h the solution turned to light yellow and gradually changed to dark brown. The solution became usually homogeneous but sometimes remained heterogeneous. After disappearance of the starting material was confirmed by TLC, the reaction mixture was poured into water and extracted three times with chloroform (*ca.* 100 ml) and then organic layer was washed with an aqueous sodium thiosulfate solution (sat. 10 ml) and water. When chloroform was removed *in vacuo* after drying the organic layer with $MgSO_4$, the residue was highly pure thiosulfonic *S*-ester. Usually GC, LC, and NMR spectra showed only one component. Products were identified by comparing their IR and NMR spectra with those of authentic samples prepared by another method and the structures

of new compounds were confirmed by elemental analyses besides IR and NMR spectra.

If no catalyst was used, the oxidation was very slow and had a long induction period (*ca.* 5—10 h). However, the reaction after the long induction period was nearly as fast as the reaction with catalyst and completed within 1.0 h after the start of the reaction.

When acetic acid was used as a solvent, the oxidation proceeded as fast as the reaction with catalyst, although the catalytic amount of acetic acid did not accelerated the oxidation. In order to remove acetic acid from organic extract, the solution was washed with $NaHCO_3$ solution before washing with a sodium thiosulfate solution.

The reaction in alcohol as solvent was performed as in the above-mentioned oxidation procedure. The whole feature of the reaction was similar to the ordinary oxidation and the reaction was also accelerated by addition of catalyst. However, the distribution of products, *i. e.* thiosulfonic *S*-ester (**2**) and sulfinate (**3**), was affected rather little. Yields of both **2** and **3** were easily determined by measuring NMR spectra of the reaction mixture. The structures of the sulfinates obtained as side products were identified by comparison of their IR (S=O) and NMR spectra[13] with those of authentic samples which were prepared by the reaction of sulfinyl chloride and excess alcohol according to the known method.[14]

The reaction of disulfide with $NaIO_4$ was carried out using acetic acid as a solvent. The reaction procedure was also the same as the usual oxidation method mentioned above. The amount of $NaIO_4$ used was two equivalent to disulfide. After the disappearance of unsymmetrical disulfide **5** or the mixture of symmetrical disulfides **9** and **10** was confirmed, the usual work-up gave a mixture of both symmetrical and unsymmetrical thiosulfonic *S*-esters which were identified by comparing their retention times in GC charts and chemical shifts of methyl groups in NMR spectra with those of authentic samples.

S-*Phenyl Benzenethiosulfonate* ***2a***: Pink crystals; mp 44—45 °C (lit,[15] 44—45 °C); IR (KBr, cm^{-1}) 3050, 1578, 1471, 1440, 1325, and 1310 (SO_2), 1147 (S=O); MS (70 eV) *m/e* 250 (M^+, 39%), 125 (M^+—PhSO, 100%).

S-p-*Tolyl Benzenethiosulfonate* ***2b***: Colorless crystal; mp 52 °C (lit,[15] 54 °C); IR ($CHCl_3$, cm^{-1}) 3030, 1598, 1450, and 1330 (SO_2), 1145 (S=O); MS (70 eV) *m/e* 264 (M^+, 39%), 139 (M^+—PhSO, 100%).

S-*Phenyl* p-*Toluenethiosulfonate* ***2c***: Colorless crystals; mp 78—80 °C (lit,[15] 78 °C); IR ($CHCl_3$, cm^{-1}) 3025, 1597, 1443, 1335 (SO_2), 1145 (S=O); MS (70 eV) *m/e* 264 (M^+, 68%), 155 (M^+—PhS, 100%).

S-*Methyl Benzenethiosulfonate* ***2d***: Colorless oil; IR (neat, cm^{-1}) 3050, 3000, 2920, 1580, 1475, 1445, 1330, and 1302 (SO_2), 1142 (S=O); NMR ($CDCl_3$, δ) 2.48 (3H, s, $-CH_3$), 7.21—8.08 (5H, m, arom.). Found: C, 44.92; H, 4.18%. Calcd for $C_7H_8O_2S_2$: C, 44.66; H, 4.28%.

S-*Phenyl Methanethiosulfonate* ***2e***: Colorless crystals; mp 85—86.5 °C, IR (KBr, cm^{-1}) 3050, 3000, 2905, 1565, 1465, and 1310 (SO_2), 1130 (S=O); NMR ($CDCl_3$, δ) 3.12 (3H, s, $-CH_3$), 7.30—7.83 (5H, m, arom.). Found: C, 44.87; H, 4.25%. Calcd for $C_7H_8O_2S_2$: C, 44.66; H, 4.28%.

S-*Phenyl Ethanethiosulfonate* ***2f***: Colorless crystals; mp 52 °C (lit,[16] 50—52 °C); IR ($CHCl_3$, cm^{-1}) 3055, 2975, 2930, 1575, 1472, and 1326 (SO_2), 1128 (S=O); NMR ($CDCl_3$, δ) 1.41 (3H, t, $-CH_3$, J=7.4 Hz), 3.16 (2H, q, $-CH_2-$, J=7.4 Hz), 7.18—7.75 (5H, m, arom.).

S-*Propyl Benzenethiosulfonate* ***2g***: Colorless oil; IR (neat, cm^{-1}) 3065, 2970, 2930, 2875, 1580, 1330, and (SO_2), 1150 (S=O); NMR ($CDCl_3$, δ) 0.90 (3H, t, $-CH_3$, J=6.6 Hz), 1.62 (2H, m, $-CH_2-CH_3$), 2.97 (2H, t, $-S-CH_2-$, J=6.4 Hz), 7.26—8.00 (5H, m, arom.). Found: C, 49.69; H, 5.38%. Calcd for $C_9H_{12}O_2S_2$: C, 49.97; H, 5.59%.

S-*Cyclohexyl Methanethiosulfonate* ***2h***: Colorless oil; IR (neat, cm^{-1}) 2925, 2850, and 1321 (SO_2), 1132 (S=O); NMR ($CDCl_3$, δ) 1.10—2.35 (10H, m, ring protons), 3.32 (3H, s, $-CH_3$), 3.48 (1H, broad s, $-CH<$). Found: C, 43.10; H, 7.31%. Calcd for $C_7H_{14}O_2S_2$: C, 43.27; H, 7.26%.

S-*Methyl* p-*Toluenethiosulfonate* ***2i***: Colorless crystals; mp 59—61 °C; IR ($CHCl_3$, cm^{-1}) 3050, 2915, 1592, 1493, 1335, and 1305 (SO_2), 1142 (S=O); NMR (CD_3COOD–D_2O (3:1), δ, external TMS) 2.13 (3H, s, Ar–CH_3), 2.21 (3H, s, –S–CH_3), 7.08 (2H, d, arom.), 7.48 (2H, d, arom.). Found: C, 47.80; H, 4.99%. Calcd for $C_7H_{10}O_2S_2$: C, 47.50; H, 4.98%.

S-*Methyl* p-*Chlorobenzenethiosulfonate* ***2j***: Colorless crystals; mp 35—37 °C; IR ($CHCl_3$, cm^{-1}) 3080, 3020, 2920, 1578, 1475, and 1335 (SO_2), 1145 (S=O); NMR (CD_3COOD–D_2O (3:1), δ, external TMS) 2.32 (3H, s, $-CH_3$), 7.40 (2H, d, arom.), 7.70 (2H, d, arom.). Found: C, 38.01; H, 3.15%. Calcd for $C_7H_7ClO_2S_2$: C, 37.75; H, 3.16%.

References

1) Y. H. Kim, T. Takata, and S. Oae, *Tetrahedron Lett.*, **21**, 2305 (1980).

2) Address correspondence to Department of Chemistry, The Korea Advanced Institute of Science, P. O. Box 150, Chongyangni, Seoul, Korea.

3) S. Oae, Y. H. Kim, T. Takata, and D. Fukushima, *Tetrahedron Lett.*, **1977**, 1195.

4) S. Oae, D. Fukushima, and Y. H. Kim, *Chem. Lett.*, **1978**, 279.

5) a) D. Barnard and E. J. Percy, *Chem. Ind. (London)*, **1960**, 1332; b) U. Marangeli, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 681 (1960); c) M. M. Chau and J. L. Kice, *J. Am. Chem. Soc.*, **98**, 7711 (1976); d) B. C. Gilbert, B. Gill, and M. J. Ramsden, *Chem. Ind. (London)*, **1979**, 283.

6) a) S. Oae and T. Takata, *Tetrahedron Lett.*, **21**, 3213 (1980); b) N. Isenberg and H. F. Herbrandson, *Int. J. Sulfur Chem.*, **A1**, 179 (1971).

7) C. J. M. Stirling, *J. Chem. Soc.*, **1957**, 3579.

8) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **73**, 129 (1954).

9) T. Takata, Y. H. Kim, and S. Oae, *Tetrahedron Lett.*, **1978**, 4303.

10) L. Field and Y. H. Kim, *J. Org. Chem.*, **37**, 2710 (1972).

11) S. Oae, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Jpn.*, **42**, 2899 (1969).

12) G. Ghesetti and G. Modena, *Spectrochim. Acta*, **19**, 1809 (1963).

13) J. W. Wilt and W. J. Wagner, *Chem. Ind. (London)*, **1964**, 1389.

14) H. F. Herbrandson and K. T. Dickerson, Jr., *J. Am. Chem. Soc.*, **81**, 4120 (1959).

15) S. Oae, R. Nomura, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Jpn.*, **42**, 2903 (1969).

16) A. K. Bhattacharya and A. G. Hortman, *J. Org. Chem.*, **43**, 2728 (1978).