Tetrahedron Vol. 41, No. 11, pp. 2133 to 2137, 1985
Printed in Great Britain.

0040–4020/85 $3.00 + .00

NEW SYNTHETIC UTILITY OF SINGLET OXYGEN IN SULPHIDE PHOTO-OXIDATION

SELECTIVE AND STEREOSPECIFIC HYDROXYLATION α TO SULPHUR OF 4-SUBSTITUTED 3-BENZOYL-2,2-DIMETHYLTHIAZOLIDINES†

TOSHIKAZU TAKATA, YOSHIHARU TAMURA and WATARU ANDO*
Department of Chemistry, The University of Tsukuba, Sakura, Ibaraki 305, Japan

(*Received in Japan* 5 *April* 1984)

Abstract—Direct hydroxylation α to sulphur was accomplished in singlet oxygenation of thiazolidine derivatives. Photo-oxidation of 4-substituted 3-benzoyl-2,2-dimethylthiazolidines in aprotic solvents below 0° gave the corresponding 5-hydroxy derivatives quantitatively by subsequent treatment of dimethyl sulphide or triphenyl phosphine. The alcohols were stereospecifically formed with 4,5-*trans* configuration. Protic solvent, such as methanol, inefficiently afforded a mixture of 5-hydroxide and S-oxide. The photo-oxidation of optically active 4-methoxycarbonyl derivative gave the optically active alcohol as only one diastereomer.

Direct α-functionalization of sulphides has been an important synthetic procedure. In addition to halogenation[2] at the α-C of sulphides, direct introduction of oxy-function has high utility. The Kharasch–Sosnovsky reaction[3] is a useful method of introducing an acyl group to an allylic C or a C adjacent to hetero atoms using diacyl peroxide or perester. This process has been applied to synthesis[4] and functionalization of β-lactum compounds bearing cyclic sulphide groups, although the yields of desired products have not been satisfactory.

Meanwhile, Woodward *et al.*[6] previously utilized azodicarbonyl compounds‡ for the introduction of an OH group α to the S of a thiazolidine derivative in the course of cephalosporin C synthesis. Our recent studies[8] on the similarity of azodicarbonyl compounds with singlet oxygen in their reactivity toward sulphides as well as olefins,[9] prompted us to investigate the possibility of direct oxy-functionalization of thiazolidines with singlet oxygen, although singlet oxygenation of sulphides affords only S-oxidation products[10] except for benzylic sulphides.[8,11] In this paper the exclusive and stereospecific hydroxylation of thiazolidine derivatives with singlet oxygen, is described.

RESULTS AND DISCUSSION

Photo-oxidation of thiazolidines

Thiazolidine (**1**, 1 mmol) prepared from L-cysteine methyl ester as shown in Eq. (1),§ was photoirradiated with 500 W halogen lamp in the presence of a sensitizer and with O_2 bubbling through. After disappearance of the starting material, excess dimethyl sulphide (DMS) or equimolar triphenyl phosphine was added. Separation by column chromatography gave the corresponding 5-hydroxy thiazoliding (**2**) in a quantitative yield (Eq. 2). The alcohol, **2**, had the 4,5-*trans* configuration found by examination of spectroscopic analyses as described later in detail. Small amounts of S-oxide **4** were obtained in the case of **1b**. The results are summarized in Table 1. Optically active **1a** (100% e.e.) was similarly converted to the optically active alcohol (100% e.e.).

When dimethyl sulphoxide (DMSO, *ca* 20 equivalents), as a weak reducing agent having low reactivity toward singlet oxygen, was used as part of the solvent, the alcohol was produced in 50–60% yield with ketone **3** and sulphoxide **4** in low yields (5–15%), and also dimethyl sulphone ($DMSO_2$) (runs 4, 5 and 7).

Effects of solvent, temperature, sensitizer and concentration

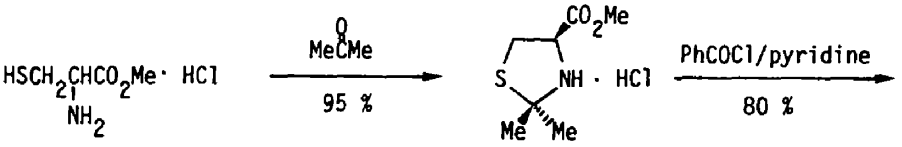
Various solvents were used in the photo-oxidation of the thioazolidines. THF was the best solvent used (Table 2). Benzene was also a useful solvent (run 2), but needed a little longer reaction time. The other aprotic solvents gave mainly the alcohol but with low conversions. The sulphoxide, **4**, was mainly produced in methanol, but slowly (run 11).

There is, therefore a clear contrast in the photo-oxidation of linear sulphides, with methanol being the most effective solvent and aprotic solvents, such as benzene and acetonitrile, being very inefficient.[10] Polymer-supported Rose Bengal is synthetically useful due to the simple work-up and easy purification of the products, although its effectiveness is low enough to take more time in completing the reaction, presumably owing to the heterogeneous conditions (runs 4–7). TPP (tetraphenylporphyrin) is a comparable sensitizer to MB (methylene blue) (runs 8 and 10). A lower temperature (−45°) seems to yield **2** in slightly better yield than at 0° (run 14). As indicated in runs 8 and 9, favourable formation of **2** at lower concentration, especially in the presence of methanol, is in accordance with the intermolecular formation of sulphoxide.[10]

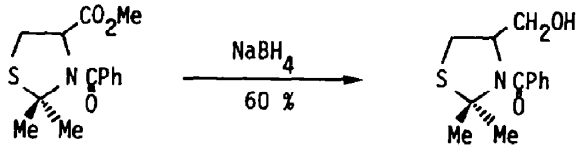
† Part of this work has appeared in other publications.[1]

‡ For reactions of sulphides with azodicarbonyl compounds see lit.[7]

§ While synthesis of chiral **1a** was carried out by the literature method,[12] achiral **1a** and **1b** were prepared according to Eq. (1). In the modified method (Eq. 1), use of benzene as a solvent in the acylation made the work-up easy in only having to filter the heterogeneous mixture to remove the pyridine hydrochloride formed, although this procedure always caused racemization.

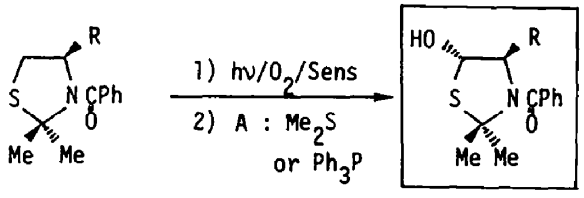


L-cysteine methyl ester



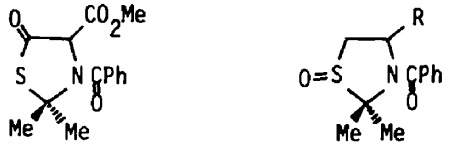
(1)

1a **1b**



(2)

1 **2** quant.



3 **4**

Table 1. Photo-oxidation of thiazolidine derivatives

Run	Compound	Reaction conditions[a,b]	Conversion (%)	A	Isolated yield (%)[c] 2	3	4	AO
1	**1a**	THF/TPP/0/90	100	Ph_3P	90	0	0	97
2		THF/TPP/0/100	100	Me_2S	91	0	0	ND[d]
3		THF/TPP/0/150	95	[e]	81	0	0	100
4		CH_3CN/MB/0/360	100	Me_2SO[f]	52	13	3.4	[g]
5		CH_3CN/MB/RT/150	100	Me_2SO[f]	63	9	13	[g]
6	**1b**	THF/TPP/0/95	100	Ph_3P	84	0	12	ND
7		CH_3CN/MB/−40/180	100	Me_2SO[f]	15	0	21	[g]
8		THF/TPP/−45/60	95	Me_2S	88[h]	0	10[h]	85

[a] Solvent/sensitizer/temperature (°)/time (min).
[b] Abbreviations: TPP, tetraphenylporphyrin; MB, methylene blue; P-RB, polymer-supported Rose Bengal.
[c] The given yields are those divided by the conversions.
[d] Not determined.
[e] 4-(*p*-Chlorophenyl)thiane.
[f] Added at the beginning of the reaction.
[g] Dimethyl sulphone was isolated in more than 100% yield, since the direct photo-oxidation of dimethyl sulphoxide took place.
[h] NMR yield.

Table 2. Effects of solvent, sensitizer, temperature and concentration on the photo-oxidation of thiazolidine derivatives

Run	Compound	Reaction conditions[a,b]	Conversion (%)	Isolated yield (%)[c] A	2	4	AO
1	**1a**	THF/TPP/0/90	100	Ph_3P	90	0	97
2		Benzene/TPP/5/180	98	Me_2S	97	0	68
3		$CHCl_3$/TPP/−45/240	46	Me_2S	81	19	72[e]
4		CH_2Cl_2/P-RB/−45/180	29	Me_2S	69	31	59[e]
5		Acetone/P-RB/−45/180	29	Me_2S	72	24	62[e]
6		THF/P-RB/−45/360	57	Me_2S	90	Trace	68[e]
7		$CHCl_3$/P-RB/−45/180	31	Me_2S	68	32	61[e]
8		THF–MeOH[f]/TPP/0/120	88	Me_2S	25	42	32
9		THF–MeOH[f,g]/TPP/0/215	70	Me_2S	73	26	68[h]
10		THF–MeOH[f]/MB/0/180	71	Me_2S	44	52	ND[i]
11		MeOH/MB/0/570	88	Ph_3P	8.0	55	ND
12	**1b**	THF/TPP/0/95	100	Ph_3P	84	12	ND
13		MeOH/MB/−45/180	79	Me_2S	14	86	32
14	**1a**	THF/TPP/−45/100	100	Me_2S	100	0	100
15		THF/none/0/180	0	Me_2S	Trace	0	0
16		THF/TPP/0/180	0	Me_2S	0	0	0[j]

[a] Solvent/sensitizer/temperature (°)/time (min).
[b] Abbreviations: TPP, tetraphenylporphyrin; MB, methylene blue; P-RB, polymer-supported Rose Bengal.
[c] The given yields are those divided by the conversions.
[d] Some loss of dimethyl sulphoxide due to chromatographic separation.
[e] NMR yield.
[f] MeOH–THF, 1 : 1.
[g] 0.037 M.
[h] Sulphone 3.1%.
[i] Not determined.
[j] DABCO (1.0 equivalent) was added at the beginning of the reaction.

Structure determination of the products

The structures of the products **2–4** were tentatively assigned by IR, ^{1}H- and ^{13}C-NMRs, mass spectra and elemental analysis data. For **2a**, IR absorption of the OH group at 3360 cm^{-1} and CO groups at 1740 and 1630 cm^{-1} revealed the alcohol without changing the original CO functional groups of **1a**. Two singlet methine protons (Fig. 1) indicated a 4,5-*trans* configuration where the dihedral angle of both protons is nearly 90°. Two doublet signals in ^{13}C-NMR were observed at δ 78.6 and 75.7 which support structure **2a**. Woodward *et al.*,[6] Baldwin *et al.*[4] and Iwakawa *et al.*[12] showed the 4,5-*trans* relationship in introductions of 5-hydroxy and 5-benzoyloxy groups into similar thiazolidine derivatives. Chemical shifts and zero coupling of 4- and 5-methine protons in ^{1}H-NMR spectra of 5-benzoyloxy derivatives of **1a** and **2a** were approximately consistent with those of the similar derivatives reported by Baldwin *et al.*[4] and Iwakawa *et al.*[12] and was completely coincident with an authentic sample of **2a** synthesized according to the method of Woodward.[13] The structure of **2b** was also found to have the same configuration. As for the ketone, **3**, new absorption at 1700 cm^{-1} and ^{13}C-NMR resonance at δ

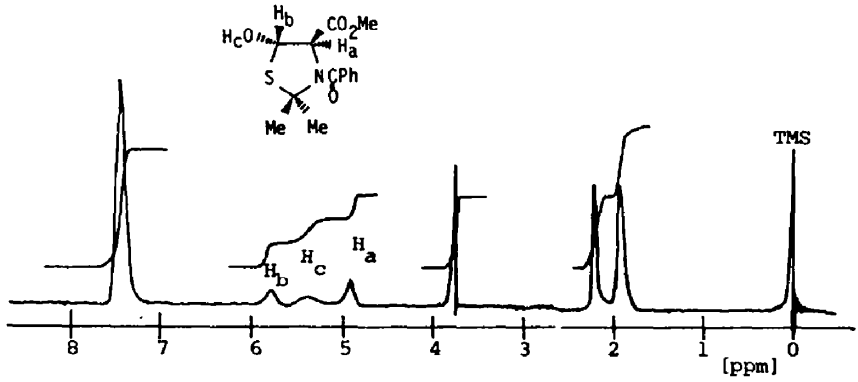


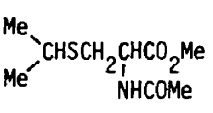
Fig. 1. ^{1}H-NMR (60 MHz) spectrum of **2a** in deuterochloroform.

191.2 corresponding to a thioester group, strongly suggested a 5-oxo structure. This was also supported by mass and ^{1}H-NMR spectra, and elemental analysis.

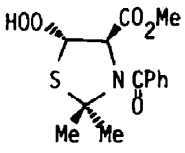
SUMMARY AND DISCUSSION

A linear sulphide, **5**, related to **1** underwent photo-oxidation to produce a mixture of sulphoxide and sulphone only.[1a] However, in the photo-oxidation of benzylic sulphides, fragmentation products resulted from C—S bond cleavage competing with S-oxidation.[11] On the other hand, the photo-oxidation of the simplest five-membered cyclic sulphide is reported to give a mixture of C—S cleavage and S-oxidation products, while a few six-membered cyclic sulphides in turn are only oxidized to sulphoxides and sulphones.[1a] From these results Takata *et al.*[1a] concluded that this hydroxylation may be limited to five-membered ring sulphides.

Singlet oxygen may be an active species in this reaction because of complete quenching by the addition of DABCO (1,4-diazabicyclo(2.2.2)octane) (run 16) and no product formation in the absence of sensitizer (run 15).



5



6

Formation of the alcohol, **2**, and the ketone, **3**, is quite interesting and both have never been obtained yet in the photo-oxidation of sulphides.[10] Although details on the formation of these products are under investigation, α-hydroperoxy sulphide (**6**) should be a precursor of **2** and **3**.[1a] DMS and triphenyl phosphine, therefore, reduce the hydroperoxide to the alcohol, **2**. The hydroperoxidation is considered to be derived by the Pummerer type rearrangement[13] of a persulphoxide intermediate, usually formed during singlet oxygenation of sulphides.[1a,10] Treatment of **4** with acetic anhydride under Pummerer reaction conditions, has been reported to yield ring a expansion product (thiazine derivative) without any Pummerer product.[12]

The stereospecific formation of the 4,5-*trans* isomer, **2**, may be accounted for by the steric demand for Pummerer type rearrangement as suggested by Nozaki.[14] Synthetic utility of this hydroxylation may be found in, for example, synthesis of a part of the penem skeleton via dehydration of the alcohol, **2**. Application of this hydroxylation is also in active progress.

EXPERIMENTAL

M.ps were measured with a Yamato Scientific m.p. apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-50 IR spectrometer. ^{1}H-NMR spectra at 60 MHz and ^{13}C-NMR spectra at 15.09 MHz were obtained on a Varian EM-360A and a JEOL FX 90Q, respectively, in deuterochloroform with tetramethylsilane as an internal standard. Optical rotations were determined with a JASCO DIP-140 polarimeter using a 5 cm (length) quartz cell.

Thin layer and column chromatographies were performed over silica gel (Merck silica gel 60, PF_{254}) and alumina (Merck alumina 60).

All solvents used were dried over appropriate drying agents after distillation. Commercial grade reagents were used without any further purifications: L-cysteine and L-cysteine methyl ester (Nippon Rikagaku Yakuhin), methylene blue (Kanto Chemicals), tetraphenyl porphyrin (Tokyo Kasei Kogyo), and pyridine, DABCO, benzoyl chloride, NaOAc and sodium borohydride (Wako Pure Chemicals). Lead tetra-acetate (Wako Pure Chemicals) was recrystallized from HOAc. Polymer-supported Rose Bengal was prepared from the styrene monomer and Rose Bengal was prepared from the styrene monomer and Rose Bengal (Wako Pure Chemicals) according to the lit.[15]

Preparation of 2,2-dimethyl-4(R)-methoxycarbonylthiazolidine hydrochloride. A suspension of L-cysteine methyl ester hydrochloride (15 g, 0.087 mol) in dry acetone (*ca* 300 ml) was refluxed for 0.5 hr. The mixture, cooled in an ice–water bath, was filtered. Solid material was washed with cold acetone and dried for 15–20 min with a sucker. The fairly dry colourless solid was dissolved in dry acetone (*ca* 200 ml) and the mixture refluxed for 15 min. It was then cooled in an ice–water bath. The creamy mass was filtered and the colourless ppts washed with cold acetone and well dried with a sucker. The pure crude product had an m.p. of 152–155° (lit.[16] 152–154°). Yield 95%. IR ν_{max}^{nujol}, 3000–2300, 2040, 1750, 1590 cm^{-1}.

Preparation of 3 - benzoyl - 2,2 - dimethyl - 4 - methoxycarbonylthiazolidine (**1a**). To a heterogeneous mixture of 2,2-dimethyl-4(*R*)-methoxycarbonylthiazolidine hydrochloride (10 g, 0.047 mol) and benzoyl chloride (1.2 equivalents, 8.0 g, 0.057 mol) in dry benzene (200 ml, 0.05 g/ml) was added dry pyridine (2.4 equivalents, 9.0 g, 0.11 mol) dropwise with syringe. The mixture was stirred at 60° until the hydrochloride disappeared on TLC (R_f 0.5, silica gel/benzene–EtOAc, 4:1). Adding EtOAc (50 ml), the mixture was cooled with an ice–water bath and filtered off. The filtrate was evaporated, then triturated with EtOAc and the insoluble material filtered off. The resulting clean filtrate was concentrated under reduced pressure and the residue recrystallized from a small amount of benzene–EtOAc. Colourless needles (80%), m.p. 105–106° (lit.[12] 105–106.5°). IR ν_{max}^{KBr} 1735, 1630 cm^{-1} (C=O); ^{1}H-NMR δ ($CDCl_3$) 7.42 (5H, s), 4.81 (1H, m), 3.66 (3H, s), 3.25 (2H, m), 1.99 (3H, s), 1.95 (3H, s).

Preparation of optically active **1a**. This was obtained by reaction of 2,2-dimethyl-4(*R*)-methoxycarbonylthiazolidine with benzoyl chloride in dry pyridine according to the lit.[12] giving a yield of 88%. Physical and spectroscopic data were identical to those of achiral **1a**. $[\alpha]_D^{21} - 179.6°$ ($c = 0.92$, chloroform) (lit.[12] $[\alpha]_D^{21} - 180°$), e.e. 99.8%.

General procedure of photo-oxidation. A dry THF soln (5.4 ml) of **1** (1.0 mmol, 0.185 M) in the presence of a photosensitizer (10–15 mg for MB or TPP and 20–30 mg for P-RB), was irradiated with a 500 W halogen lamp whilst bubbling O_2 through [Pyrex reaction tube (10 × 200 mm) was immersed in MeOH as a refrigerant in a Dewar with a slit for irradiation]. Temp. control was performed by an immersion cooler (Cryocool, NESLAB) in the range from −50 to 0° with a temp. controller. The reaction was monitored by both silica gel and alumina TLC. Reaction time and temp. are shown in Tables 1 and 2. When the starting material disappeared, Me_2S (1.0 ml) or triphenyl phosphine (262 mg, 1.0 mmol) was added to the mixture at that temp. and the resulting mixture was then allowed to stand at room temp. for 1 hr. Concentration of the mixture was carried out under reduced pressure and this was chromatographed on silica gel using a solvent system of benzene–EtOAc–MeOH. After elution of TPP, starting material, alcohol and sulphoxide were eluted in that order. DMSO was eluted last while triphenyl phosphine oxide was separated following the alcohol.

When P-RB was used, the heterogeneous mixture was filtered to remove solid P-RB, and the colourless clean soln

was concentrated under reduced pressure. Unless any starting material remained, the residue contained the nearly pure alcohol together with DMSO or triphenyl phosphine oxide. Conditions and the yields are summarized in Tables 1 and 2.

Photo-oxidation without sensitizer. Irradiation of **1a** in THF for 3 hr without the photosensitizer was carried out. Only a trace of the alcohol, **2a**, was observed on TLC, and most of **1a** was recovered (Table 2, run 15).

Photo-oxidation in the presence of DABCO. DABCO (112 mg, 1.0 mmol) was added to the reaction system (**1a**, THF and TPP at 0°) and irradiation for 3 hr afforded no oxidation products (Table 2, run 16).

Photo-oxidation in acetonitrile in the presence of dimethyl sulphoxide. A mixture of the substrate (**1**, 5.0 mmol) and sensitizer (TPP or MB, 50–60 mg) was irradiated in DMSO (20 equivalents, 7.0 ml)–dry acetonitrile (20 ml, 0.185 M) in a similar manner. On disappearance of **1** for TLC, dilute brine and CH_2Cl_2 were added and the mixture was extracted three times with CH_2Cl_2 (total 200 ml). The organic layer was dried over $MgSO_4$ and evaporated. Remaining DMSO was removed *in vacuo* and the residue chromatographed on silica gel. Yields of the products are shown in Table 1.

3 - *Benzoyl* - 2,2 - *dimethyl* - 5 - *hydroxy* - 4 - *methoxycarbonylthiazolidine* (**2a**). M.p. 170–171° (dec.); IR ν_{max}^{KBr} 3360 (OH), 1740 (C=O), 1630 cm^{-1} (C=O); ^{1}H-NMR δ ($CDCl_3$) 7.48 (5H, s), 5.53 (1H, s, H_b), 4.96 (1H, s, H_a), 3.85 (1H, s, H_c) [this chemical shift value due to the OH group varied in the range δ 3–7 (see Fig. 1, H_c); coupling (J = 3.2 Hz) of H_b and H_c was sometimes observed depending on the conditions], 3.69 (3H, s), 2.09 (3H, s), 1.98 (3H, s); ^{13}C-NMR δ ($CDCl_3$) 170.7 (s), 168.7 (s), 138.1 (s), 129.4 (d), 128.9 (d), 125.8 (d), 77.6 (d), 75.7 (d), 52.8 (q), 32.4 (q), 28.7 (q); MS *m/z* 267 $[M]^+$. (Found: C, 56.92; H, 5.80; N, 4.69; S, 10.93%. Calc for $C_{14}H_{17}O_4NS$: C, 56.93; H, 5.80; N, 4.74; S, 10.85%.)

3 - *Benzoyl* - 2,2 - *dimethyl* - 5 - *hydroxy* - 4 - *hydroxymethylthiazolidine* (**2b**). IR ν_{max}^{KBr} 3400 (OH), 3150 (OH), 1590 cm^{-1} (C=O); ^{1}H-NMR δ ($CDCl_3$) 7.44 (5H, s), 6.40 (1H, br s), 5.24 (1H, br s), 4.94 (1H, t), 4.19 (1H, q), 3.20 (2H, m), 1.96 (3H, s), 1.86 (3H, s); ^{13}C-NMR δ (DMSO-d_6) 169.0 (s), 139.0 (s), 129.1 (d), 128.4 (d), 126.3 (d), 77.9 (d), 75.0 (d), 72.1 (s), 62.4 (t), 31.6 (q), 30.4 (q). (Found: C, 58.51; H, 6.41; N, 5.24%. Calc for $C_{13}H_{17}O_3NS$: C, 58.41; H, 6.41; N, 5.24%.)

3 - *Benzoyl* - 2,2 - *dimethyl* - 4 - *methoxycarbonyl* - 5 - *oxothiazolidine* (**3**). Oil; IR $\nu_{max}^{CHCl_3}$ 1745 (C=O), 1700 (C=O), 1655 cm^{-1} (C=O); ^{1}H-NMR δ ($CDCl_3$) 7.43 (5H, s), 5.21 (5H, s), 3.60 (3H, s), 2.22 (6H, s); ^{13}C-NMR δ ($CDCl_3$) 191.2 (s), 169.7 (s), 165.7 (s), 136.4 (s), 130.3 (d), 129.9 (d), 126.2 (d), 76.1 (s), 73.8 (d), 53.5 (q), 30.4 (q), 29.8 (q); MS *m/z* 365 $[M]^+$.

3 - *Benzoyl* - 2,2 - *dimethyl* - 4 - *methoxycarbonylthiazolidine* S-*oxide*. Both *cis*- and *trans*-S-oxides were identical to those reported[12] in spectroscopic studies.

3 - *Benzoyl* - 4 - *hydroxy* - 2,2 - *dimethylthiazolidine* S-*oxide*. *Cis*: ^{1}H-NMR δ ($CDCl_3$) 7.55 (5H, s), 5.13 (1H, m), 3.38 (4H, m), 1.63 (6H, s); IR ν_{max}^{KBr} 3230 (OH), 1590 (C=O), 1055 cm^{-1} (S=O). *Trans*: ^{1}H-NMR δ ($CDCl_3$) 7.48 (5H, s), 4.75 (1H, m), 3.39 (4H, m), 2.01 (3H, s), 1.78 (3H, s); IR ν_{max}^{KBr} 3350 (OH), 1630 (C=O), 1045 cm^{-1} (S=O).

3 - *Benzoyl* - 5 - *benzoyloxy* - 2,2 - *dimethyl* - *methoxycarbonylthiazoldine*. The reaction of **1a** with benzoyl peroxide was carried our according to the lit.[12] The title compound was obtained in 10% yield by chromatography on silica gel. The chemical shifts and coupling constants were compared with those reported[12] and of **2a** obtained in the photo-oxidation.

Preparation of an authentic sample of **2a**. A mixture of **1a** (1.5 g, 5 mmol) and excess diethylazodicarboxylate (2.0 ml, 19 mmol)[17] was heated at 120–140° for 20 hr. The mixture was chromatographed over silica gel (benzene–EtOAc, 4 : 1) and a yellow clear resin (1.0 g, 51%) was separated. The product was slightly impure due to contamination with hydrazo compound from NMR and was used in the following procedure with no further purification.

The product thus obtained (1.0 g, 2.6 mmol) was dissolved in dry benzene (8 ml). Lead tetra-acetate (2.2 equivalents, 2.5 g, 5.6 mmol) was added to the soln, which was then refluxed overnight. After substitution of solvent benzene with dry MeOH (15 ml), NaOAc (2.3 g, 28 mmol) was added to the mixture and the resulting mixture was refluxed for 10 hr. Dirty mixture was chromatographed over silica gel using benzene–EtOAc (2 : 1) as an eluent. The product (30 mg, 4%) showed the same ^{1}H-NMR spectrum and R_f value as those of **2a** obtained by photo-oxidation.

REFERENCES

[1a] T. Takata, K. Hoshino, T. Takeuchi, Y. Tamura and W. Ando, submitted for publication; [b] K. Hoshino, Ms thesis, The University of Tsukuba (1983); [c] *The 11th Symposium on Organic Sulfur and Phosphorus Chemistry*, Abstract p. 1, Tsukuba, Japan (1983).

[2] G. E. Wilson Jr. and R. Albert, *J. Org. Chem.* **38**, 2159, 2160 (1973).

[3] D. J. Rawlinson and G. Sosnovsky, *Synthesis* 1 (1972).

[4] J. E. Baldwin, A. Au, M. Christie, S. B. Haber and D. Hesson, *J. Am. Chem. Soc.* **97**, 5957 (1975).

[5] H. Matsumura, T. Yano, M. Ueyama, K. Tori and W. Nagata, *J. Chem. Soc. Chem. Commun.* 485 (1979).

[6] R. B. Woodward, K. Hensler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan and H. Vorbrüggen, *J. Am. Chem. Soc.* **88**, 852 (1966).

[7a] G. Ahlgren, *Tetrahedron Letters* 2779 (1974); [b] G. E. Wilson Jr. and J. H. Martin, *J. Org. Chem.* **37**, 2510 (1972); [c] E. E. Smissman and A. Makriyannis, *J. Org. Chem.* **38**, 1652 (1973).

[8] W. Ando, K. Ito and T. Takata, *Tetrahedron Letters* **23**, 3909 (1982).

[9] W. Adam and O. De Lucchi, *Tetrahedron Letters* **22**, 929 (1981).

[10a] W. Ando, *Sulfur Report* **1**, 143 (1981); [b] W. Ando and T. Takata, in *Singlet O_2* (Edited by A. A. Frimer), Vol. 3, Chap. 1. Chemical Rubber Publishing Co., Cleveland, Ohio (1984), in press.

[11a] E. J. Corey and C. Quannès, *Tetrahedron Letters* 4263 (1976); [b] W. Ando, T. Nagashima, K. Saito and S. Kohmoto, *J. Chem. Soc. Chem Commun.* 154 (1979).

[12] M. Iwakawa, B. M. Pinto and W. A. Szarek, *Can. J. Chem.* **56**, 326 (1978).

[13] S. Oae and T. Numata, in *Isotopes in Organic Chemistry, Pummerer and Pummerer Type of Reactions* (Edited by E. Buncel and C. C. Lee), Chap. 2. Elsevier, New York (1980).

[14] H. Nozaki, *Hoshiimonodake Tsukuru Kagaku*, p. 217. (Japanese) Shōkabo, Tokyo (1982).

[15] A. P. Schaap, A. L. Thayer, E. C. Blossey and D. C. Neckers, *J. Am. Chem. Soc.* **97**, 3741 (1975).

[16] A. H. Cook and I. M. Heilbron, in *Chemistry of Penicillin* (Edited by H. T. Clark, J. R. Johnson and R. Robinson), p. 921. Princeton University Press, Princeton, New Jersey (1949).

[17] N. Rabjohn (Editor), *Org. Synth. Coll.* Vol. 4, p. 411. Wiley, New York (1963).