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Stereochemistry of Alkylation of Cyclic β-Ketosulfoxides. I. Alkylations of 3-Methylisothiochroman-4-one 2-Oxide and 2-Methylthian-3-one 1-Oxide

YASUMITSU TAMURA,* JUN-ICHI UENISHI,
and HIROYUKI ISHIBASHI

*Faculty of Pharmaceutical Sciences, Osaka University,
1-6, Yamada-oka, Suita, Osaka 565, Japan*

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Alkylation of the carbanions derived from six-membered β-ketosulfoxides, 3-methylisothiochroman-4-one 2-oxide (**1**) and 2-methylthian-3-one 1-oxide (**8**), with alkyl halide was found to occur *trans* to the S–O bond with high stereoselectivity. The mechanism of the stereoselective alkylation is discussed.

Keywords——alkylation; carbanion; isothiochroman-4-one 2-oxide; β-ketosulfoxide; cyclic sulfoxide stereochemistry; thian-3-one 1-oxide

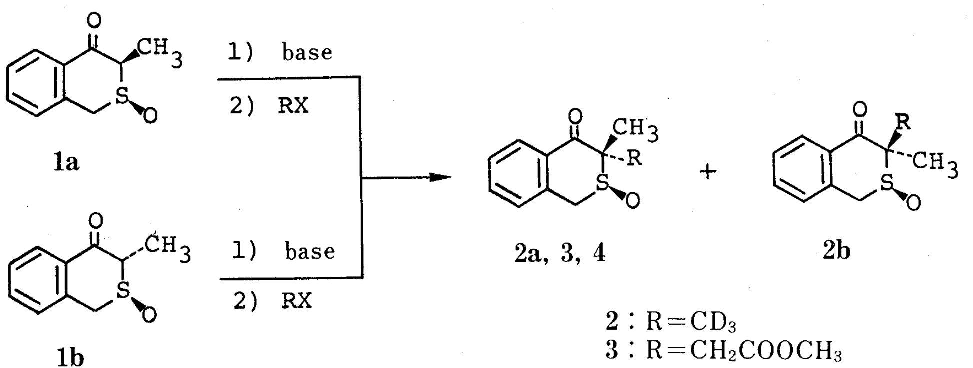
Alkylation of the α-carbanion of a β-ketosulfoxide has been widely used for carbon–carbon bond formation in organic synthesis.[1)] Since the β-ketosulfoxide has an asymmetric center at its sulfur atom, it is of interest to examine whether the alkyl group is introduced *cis* (*syn*) or *trans* (*anti*) to the S–O bond. It was reported that the alkylation of β-ketosulfoxide bearing no substituent at the α-position gave a mixture of two diastereoisomers.[1b,c)] However, in this case, it is difficult to discuss the exact stereochemistry of the alkylation, because the primarily alkylated product may be epimerized under the basic conditions. We have now examined the stereochemistry of the α-alkylation of α-substituted cyclic β-ketosulfoxides, 3-methylisothiochroman-4-one 2-oxide (**1**) and 2-methylthian-3-one 1-oxide (**8**), and found that the alkylation occurs *trans* to the S–O bond with high stereoselectivity.

Alkylation of 3-Methylisothiochroman-4-one 2-Oxide (1)

Oxidation of 3-methylisothiochroman-4-one[2)] with sodium metaperiodate gave a mixture of *cis*-[3)] (**1a**) and *trans*-3-methylisothiochroman-4-one 2-oxide (**1b**). Treatment of **1a** with *n*-butyllithium (*n*-BuLi) (1 eq) in tetrahydrofuran (THF) followed by alkylation with trideuteriomethyl iodide (CD_3I) gave a 9:1 mixture of *trans*-3-trideuteriomethyl-*cis*-3-methyl-(**2a**) and *cis*-3-trideuteriomethyl-*trans*-3-methyl-isothiochroman-4-one 2-oxide (**2b**), whose ratio was determined from the areas of the signals due to the methyl protons in the proton nuclear magnetic resonance (^1H-NMR) spectrum (*vide infra*). A similar trideuteriomethylation of **1b** with CD_3I gave a mixture of **2a** and **2b** in a ratio of 91:9. In these alkylations, it was observed that the use of sodium hydride (NaH) or potassium hydride (KH) as a base did not affect the product distribution of **2a** and **2b**, and the use of methyl bromoacetate or benzyl bromide as an alkylating agent caused the exclusive formation of the *trans* alkylated product (**3** or **4**), as shown in Table I.

Stereochemical assignment for **1a**, **b**, **2a**, **b**, **3**, and **4** was made on the basis of their ^1H-NMR spectra [with the use of a shift reagent, $Eu(fod)_3$] and their carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra. The spectral data are listed in Table II, and the lanthanide induced shifts (LIS) *vs.* weight of the added $Eu(fod)_3$ are plotted in Fig. 1.

The isothiochroman-4-one 2-oxide derivatives (**1**—**4**) were proved to have a pseudo chair

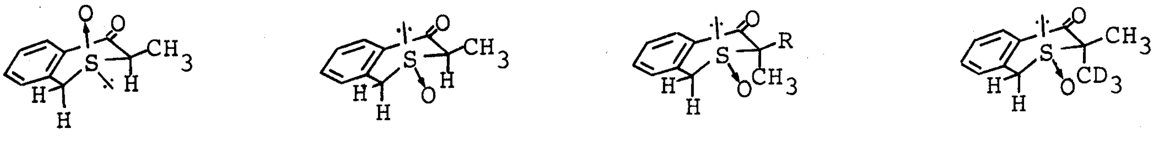


2 : R=CD_3
3 : R=CH_2COOCH_3
4 : R=$CH_2C_6H_5$

Chart 1

TABLE I. Alkylations of **1a, b** with Alkyl Halides

Substrate	Base	RX	Product	Selectivity (*trans* : *cis*)	Yield (%)
1a	*n*-BuLi	CD_3I	**2a**+**2b**	90:10	55
1b	*n*-BuLi	CD_3I	**2a**+**2b**	91: 9	51
1a	NaH	CD_3I	**2a**+**2b**	90:10	61
1b	NaH	CD_3I	**2a**+**2b**	89:11	59
1a	KH	CD_3I	**2a**+**2b**	89:11	75
1b	KH	CD_3I	**2a**+**2b**	90:10	79
1a+**1b**	NaH	$BrCH_2COOCH_3$	**3**	100: 0	69
1a+**1b**	NaH	$BrCH_2C_6H_5$	**4**	100: 0	75



2a : R=CD_3
3 : R=CH_2COOCH_3
4 : R=$CH_2C_6H_5$

Chart 2

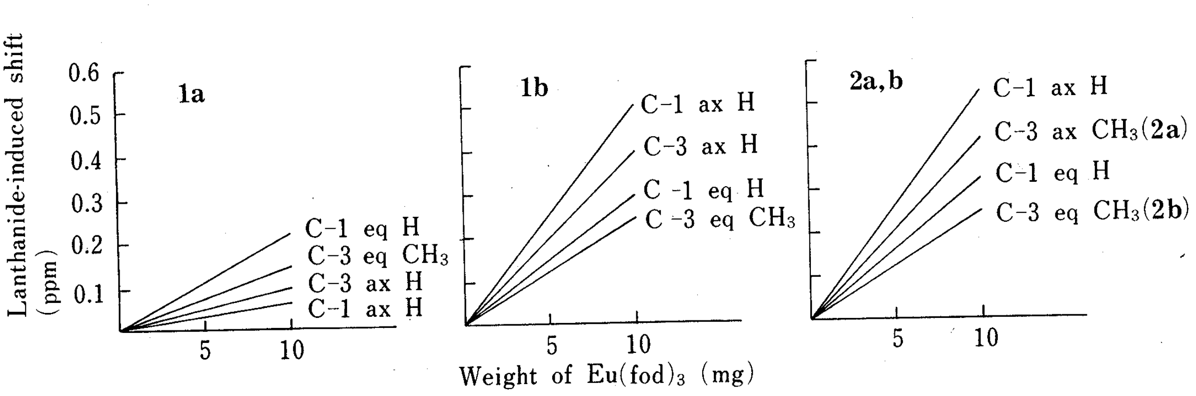


Fig. 1. Plot of $\Delta\delta$ against Weight of $Eu(fod)_3$ for **1a, b** and **2a, b** (0.2 mmol in 0.4 ml of $CDCl_3$)

TABLE II. ^{1}H- and ^{13}C-NMR Spectral Data for **1a**, **b**, **2a**, **b**, **3**, and **4**

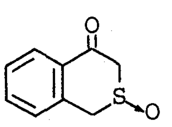
Compound	^{1}H-NMR[a]					^{13}C-NMR[b]			
	C-1 ax.	C-1 eq.	C-3 ax.	C-3 eq.	Others	C-1	C-3	Substituent on C-3	
								ax.	eq.
1a	H 4.26 (s) (Δ0.38)	H 4.26 (s) (Δ0.75)	H 3.76 (q)[c] (Δ0.26)	CH_3 1.69 (d)[c] (Δ0.48)	7.2—7.8 (3H, m) 8.0—8.2 (1H, m)	49.6	59.5	—	CH_3 10.3
1b	H 4.25 (d)[d] (Δ1.28)	H 4.48 (d)[d] (Δ0.88)	H 3.81 (q)[c] (Δ1.66)	CH_3 1.66 (d)[c] (Δ0.81)	7.2—7.7 (3H, m) 7.85—8.0 (1H, m)	53.9	67.6	—	CH_3 9.5
2a	H 4.18 (d)[e] (Δ1.42)	H 4.32 (d)[e] (Δ1.07)	CH_3 1.59 (s) (Δ1.26)	—	7.2—7.7 (3H, m) 8.0—8.2 (1H, m)	46.8	61.6	CH_3 16.8	—
2b	H 4.18 (d)[e] (Δ1.42)	H 4.32 (d)[e] (Δ1.07)	—	CH_3 1.57 (s) (Δ0.83)	7.2—7.7 (3H, m) 8.0—8.2 (1H, m)	46.8	61.6	—	CH_3 19.9
3	H 4.22 (d)[d] (Δ1.15)	H 4.35 (d)[d] (Δ0.76)	CH_3 1.55 (s) (Δ0.95)	CH_2 3.03 (d)[f] (Δ0.91) 3.32 (d)[f] (Δ0.58)	3.63 (3H, s) 7.2—7.8 (3H, m) 8.0—8.15 (1H, m)	48.1	64.1	CH_3 13.6	CH_2 38.1
4	H 4.19 (d)[e] (Δ1.12)	H 4.21 (d)[e] (Δ0.81)	CH_3 1.56 (s) (Δ0.88)	CH_2 3.12 (d)[g] (Δ0.79) 3.55 (d)[g] (Δ0.50)	7.1—7.65 (8H, m) 8.0—8.15 (1H, m)	46.8	67.4	CH_3 15.7	CH_2 39.0

a) Chemical shifts in ppm relative to tetramethylsilane; solvent, $CDCl_3$; values in parentheses are the LIS values obtained by adding 0.15 molar eq of Eu(fod)$_3$ to the sulfoxide solution.
b) Chemical shifts in ppm relative to tetramethylsilane; solvent $CDCl_3$; diagnostic data only.
c) $J=7$ Hz. *d)* $J=15$ Hz. *e)* $J=17.5$ Hz. *f)* $J=17.5$ Hz. *g)* $J=14$ Hz.

form, as depicted in Chart 2, by the following evidence: i) in the ^{1}H-NMR spectra of **3** and **4** irradiation of the signal due to the C-3 methyl protons brought about 20% enhancement of the signal intensity (n.O.e.) for the C-1 axial protons. ii) in the ^{13}C-NMR spectra of the 3,3-disubstituted compounds (**2**—**4**), steric shift[4)] was observed at the C-1 carbon atom (5.8—7.1 ppm high field shift compared to the corresponding carbon of **1b**).

Configurational assignments for the C-3 substituent and the S–O bond of **1**—**4** were made as follows. As can be seen from Fig. 1, **1a** and **1b** showed quite different LIS slopes for the C-1 equatorial and axial protons, indicating that **1a** and **1b** are stereoisomeric with respect to the S–O bond. It is generally accepted that the magnitude of the deshielding effect is proportional to the distance between the proton and the sulfinyl oxygen,[5)] and hence the difference of the LIS slopes for **1a** and **1b** can be explained only if the S–O bond is axial for **1a** and equatorial for **1b**. Similarity of the LIS slope of the C-3 proton of **1a** to that of the C-1 axial proton of **1a** indicates the axial configuration of the C-1 proton of **1a**. Thus, **1a** is assigned as a *cis* isomer having an axial S–O bond and an equatorial methyl group, and **1b** as a *trans* isomer having a diequatorial S–O bond and methyl group. Similarity of the LIS slope of **2b** to that of **1b** due to C-1 protons and C-3 methyl protons shows that **2b** has a diequatorial S–O bond and C-3 methyl group, and hence **2a** has an equatorial S–O bond and an axial C-3 methyl group. The stereochemistry of **3** and **4** was similarly deduced from their LIS values (see Table II).

Next, we attempted to clarify the structure of the lithium or sodium salt of **1a**, **b** by measuring the ^{13}C-NMR spectrum, but failed because of its poor solubility in THF-d_8. Then, we measured the spectra of the lithium and sodium salts (**6** and **7**) of isothiochroman-4-one 2-oxide (**5**) to get information on the structure. The spectra of **6** and **7** showed the signals due to C-3 carbons at δ 110 and 108 ppm, respectively, indicating the enolate structure of the carbanions **6** and **7**.[6)] If the salt derived from **1a**, **b** has such an enolate structure, the stereoselective alkylation of **1a**, **b** can be rationalized as follows. Two conformers A and B shown in Chart 4 can be considered for the enolate structures of **1a**, **b**. Taking into account the repulsive interaction between the sulfinyl lone pair and perpendicular anion lobe of the neighboring carbanion,[7)] the conformer A is expected to be preferred to the alternative B. The alkylation is presumed to proceed by a preferential axial attack[8)] of an alkyl halide on the carbanion A from the face opposite to the S–O bond, giving the *trans* alkylated product **2a**, **3**, or **4** *via* a favorable pseudo chair transition state.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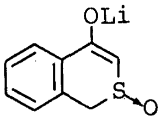
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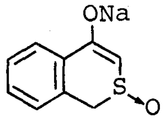
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Chart 3

Chart 4

Alkylation of 2-Methylthian-3-one 1-Oxide (8)

Oxidation of 2-methylthian-3-one[9)] with *m*-chloroperbenzoic acid (*m*CPBA) gave *cis*-(**8a**) and *trans*-2-methylthian-3-one 1-oxide (**8b**). Trideuteriomethylation of **8a** by almost the same procedure as described above for **1a**, **b** afforded a 77:23 mixture of the two stereoisomers, **9a** and **9b**. Similarly, the reaction of a mixture of **8a** and **8b** (2:3) with CD_3I gave **9a** and **9b** in the ratio 79:21. The ratios of **9a** and **9b** were determined from the peak heights of the signals due to the methyl carbons on C-2 in the ^{13}C-NMR spectra.

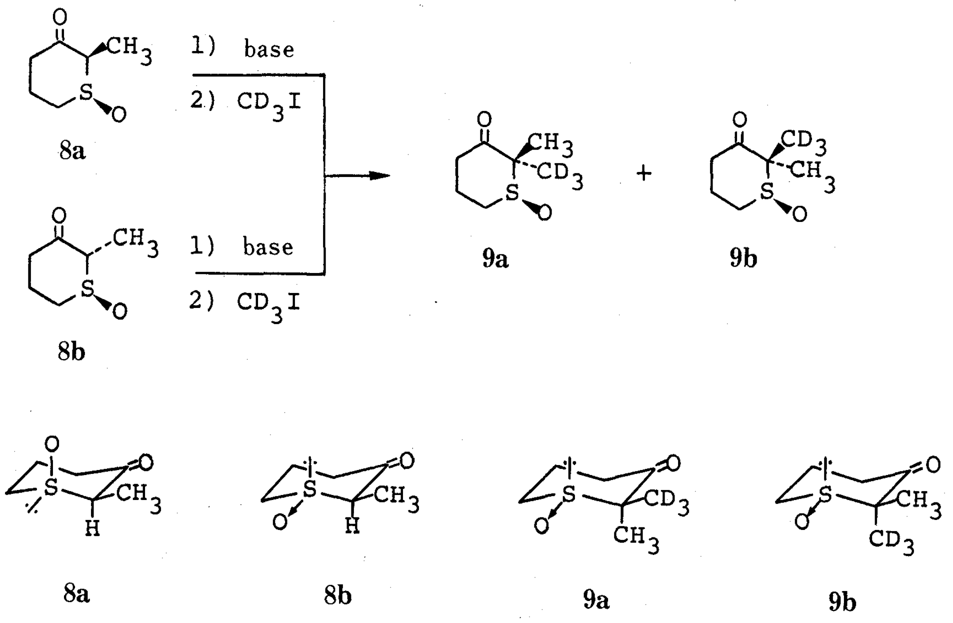

Chart 5

Table III. ^{1}H- and ^{13}C-NMR Spectral Data for **8a, b** and **9a, b**

Compound	^{1}H-NMR[a)] C-2 ax.	^{1}H-NMR[a)] C-2 eq.	^{13}C-NMR[b)] Substituent on C-2 ax.	^{13}C-NMR[b)] Substituent on C-2 eq.	C-2	C-4	C-6
8a	H 3.57 (q)[c)] (Δ0.04)	CH_3 1.45 (d)[c)] (Δ0.39)	—	CH_3 9.8	61.5	46.6	42.0
8b	H 3.63 (q)[c)] (Δ1.45)	CH_3 1.34 (d)[c)] (Δ0.68)	—	CH_3 9.5	69.3	49.3	39.8
9a	CH_3 1.50 (s) (Δ1.27)	—	CH_3 18.6	—	64.3	42.3	36.9
9b	—	CH_3 1.47 (s) (Δ0.94)	—	CH_3 20.1			

a) Chemical shifts in ppm relative to tetramethylsilane; solvent, $CDCl_3$; values in parentheses are the LIS values obtained by adding 0.15 molar eq of $Eu(fod)_3$ to the sulfoxide solution; diagnostic data only.
b) Chemical shifts in ppm relative to tetramethylsilane; solvent, $CDCl_3$ for **8a, b** and DMSO-d_6 for **9a, b**; diagnostic data only.
c) $J=7$ Hz.

The structures **8a, b** and **9a, b** were confirmed by the same method as described for **1**—**4**. Table III summarizes the ^{1}H- and ^{13}C-NMR spectral data for **8a, b** and **9a, b**. The *cis* isomer **8a** has already been proved to exist as a chair conformation having an axial S–O bond and an equatorial C-2 methyl group.[9] The *trans* isomer **8b** was shown to have a diequatorial S–O bond and methyl group by the finding that the LIS value (Δ 0.68) of the methyl protons on C-2 of **8b** is larger than that (Δ 0.04) of the proton on C-2 of **8a**. If the S–O bond and methyl group were both axial, the LIS value of the methyl protons of **8b** would be smaller than that of the proton on C-2 of **8a**. The LIS value (Δ 1.27) of the methyl protons of **9a** was larger than that (Δ 0.94) of **9b**, indicating that the methyl group of **9a** is *cis* and that of **9b** is *trans* to the S–O bond. The S–O bonds of **9a**, **b** must be equatorial, because if the S–O bonds were axial, the LIS value (Δ 0.94) of the methyl protons of **9b** would be smaller than that (Δ 0.04) of the axial proton on C-2 of **8a**.

In conclusion, the α-alkylations of β-ketosulfoxides employed herein were found to occur always *trans* to the S–O bond with high stereoselectivity. It was suggested that the geometry of the S–O bond in the intermediary carbanion plays an important role in deciding the stereochemical course of the alkylation.

Experimental[10]

***cis*- (1a) and *trans*-3-Methylisothiochroman-4-one 2-Oxide (1b)**——A solution of sodium metaperiodate (2.14 g, 10 mmol) in water (25 ml) was added dropwise to a stirred solution of 3-methylisothiochroman-4-one[2] (1.78 g, 10 mmol) in methanol (25 ml) during 15 min at room temperature. The stirring was continued for an additional 2 h at the same temperature and the precipitated salt was filtered off. The filtrate was extracted with CH_2Cl_2 (25 ml × 3) and the combined organic layer was washed with water, and dried ($MgSO_4$). Evaporation of the solvent gave a mixture of **1a** and **1b** as colorless needles (1.6 g, 80%). Two recrystallizations of the mixture from benzene and AcOEt (1 : 1) gave **1a** in a pure form, mp 147—148 °C. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1680 (C=O), 1050 (SO). MS *m/e*: 194 (M^+). *Anal.* Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 62.13; H, 5.22. The mother liquor was concentrated and the residue was triturated with benzene and *n*-hexane (1 : 1) to afford a mixture of **1a** and **1b** (1 : 2). Further evaporation of the mother liquor gave **1b** in a pure form, mp 103—105 °C. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1685 (C=O), 1045 (SO). MS *m/e*: 194 (M^+). *Anal.* Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 61.97; H, 5.20. Compound **1a** or **1b** epimerized easily in a protic solvent or in the presence of acid or base to give an equilibrium mixture of **1a** and **1b** (3 : 2), but no epimerization was observed in an aprotic solvent such as benzene, $CHCl_3$, or THF even under refluxing conditions.

***trans*-3-Trideuteriomethyl-*cis*-3-methyl- (2a) and *cis*-3-Trideuteriomethyl-*trans*-3-methyl-isothiochroman-4-one 2-Oxide (2b)**——Sodium hydride (NaH) (105 mg, 2.15 mmol, 50% dispersion in mineral oil) was washed twice with dry light petroleum (1 ml) in order to remove the mineral oil. A solution of **1a** or **1b** (388 mg, 2 mmol) in anhydrous THF (70 ml) was added to the flask containing NaH at room temperature under an argon atmosphere and the mixture was stirred until the evolution of hydrogen ceased. CD_3I (300 μl, 4.8 mmol) was added and the mixture was stirred for 4 h at room temperature. The reaction was quenched by the addition of silica gel (5 g, Merck silica gel 60), which was then removed by filtration. The solvent was evaporated off and the residue was chromatographed on silica gel with AcOEt as an eluent to give a mixture of **2a** and **2b** (316—333 mg, 75—79%) as an oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1670 (C=O), 1150 (SO). *Anal.* Calcd for $C_{11}H_9D_3O_3S$: C, 62.53; H+D, 7.15. Found: C, 62.40; H+D, 7.01. When KH (1.05 eq, 24% dispersion in mineral oil) was used as a base in the above reaction, the metallation of **1** was performed at 0—5 °C, and when *n*-BuLi was used (1.05 eq, 15% solution in *n*-hexane), it was added to the solution of **1** in THF at −20 °C in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.05 eq). The yields and the ratios of **2a** and **2b** are given in Table I.

***trans*-3-Methoxycarbonylmethyl-*cis*-3-methylisothiochroman-4-one 2-Oxide (3)**——A mixture of **1a** and **1b** was metallated with NaH by the same method as described above, and then methyl bromoacetate (1.2 eq) was added to the solution at room temperature. The reaction mixture was stirred for 4 h at 50 °C and worked up to give **3** in 69% yield, mp 131—132 °C (from benzene and *n*-hexane, 1 : 1). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1735 (CO), 1675 (CO), 1045 (SO). MS *m/e*: 266 (M^+). *Anal.* Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30. Found: C, 58.80; H, 5.33.

***trans*-3-Benzyl-*cis*-3-methylisothiochroman-4-one 2-Oxide (4)**——By the same procedure as described above for the preparation of **3**, compound **4** was obtained from a mixture of **1a** and **1b** and benzyl bromide (1.2 eq) in 75% yield, mp 97—98 °C (from benzene and *n*-hexane, 1 : 1). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1670 (C=O), 1035 (SO). MS *m/e*: 284 (M^+). *Anal.* Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.62; H, 5.62.

Measurement of ^{13}C-NMR Spectra of the Salts 6 and 7——*n*-BuLi (0.27 mmol) in *n*-hexane or sodium methoxide (0.27 mmol) in methanol was added (*via* a syringe) to a solution of **5** (50 mg, 0.27 mmol) in anhydrous THF (4 ml). The mixture was stirred for 5—10 min at room temperature, then the solvent was evaporated off. The residual solid **6** or **7** was dissolved in THF-d_8 (1 ml) and the supernatant was placed in a sample tube for measurement of the ^{13}C-NMR spectrum.

***cis*- (8a) and *trans*-2-Methylthian-3-one 1-Oxide (8b)**——*m*-Chloroperbenzoic acid (1.57 g, 7.7 mmol, 85%) was added to a stirred solution of 2-methylthian-3-one[9] (1 g, 7.7 mmol) in $CHCl_3$ (120 ml) during 15 min at 0—5 °C. The mixture was stirred for 1 h at room temperature, then washed with 5% $NaHCO_3$ and brine, and dried ($MgSO_4$). Removal of the solvent gave a mixture of **8a** and **8b** as an oil (900 mg, 80%). The mixture was triturated with benzene and *n*-hexane (7 : 1) to give **8a** as pure crystals, mp 95—97 °C (from *n*-hexane). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1710 (CO), 1040 (SO). MS *m*/*e*: 146 (M^+). *Anal.* Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89. Found: C, 49.07; H, 6.94. The mother liquor contained **8a** and **8b** in a ratio of 2 : 3.

***trans*-2-Trideuteriomethyl-*cis*-2-methyl- (9a) and *cis*-2-Trideuteriomethyl-*trans*-2-methyl-thian-3-one 1-Oxide (9b)**——*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (530 μl, 3.27 mmol) was added to a stirred solution of **8a** or a mixture of **8a** and **8b** (478 mg, 3.27 mmol) in anhydrous THF (40 ml) under an argon atmosphere at room temperature, and then *n*-BuLi (2.1 ml, 3.27 mmol, 15% in *n*-hexane) was added to the solution with stirring at −40 °C. The mixture was warmed to room temperature, and CD_3I (1 ml, 15.8 mmol) was added. Stirring was continued for 20 min at room temperature and for 1 h at 60—70 °C. The reaction mixture was then cooled and the salt was filtered off. After removal of the solvent, the residue was chromatographed on silica gel with methanol–AcOEt mixture (1 : 2) as an eluent to give a mixture of **9a** and **9b** (360 mg, 67%), mp 160—162 °C (from benzene). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1670 (CO), 1040 (SO). MS *m*/*e*: 163 (M^+). High MS calcd for $C_7H_9D_3O_2S$: 162.992. Found: 162.991.

References and Notes

1) *a*) P. G. Gassman and G. D. Richmond, *J. Org. Chem.*, **31**, 2355 (1966); *b*) G. A. Russel, E. Sabourin, and G. J. Mikol, *ibid.*, **31**, 2854 (1966); *c*) P. A. Bartlett, *J. Am. Chem. Soc.*, **98**, 3305 (1976) and references cited therein.
2) P. Cagniant and M. P. Cagniant, *Bull. Soc. Chim. Fr.*, **1959**, 1998.
3) The terms *cis* and *trans* used here refer to the relationship to the S–O bond.
4) E. Breimaier and W. Voelter, "^{13}C-NMR Spectroscopy," Verlag Chemie, Weinheim, New York, 1978, pp. 74—75.
5) R. R. Fraser, T. Durst, M. R. McClory, R. Viau, and Y. Y. Wigfield, *Int. J. Sulfur Chem.* (*A*), **1**, 133 (1971).
6) It is well known that the ^{13}C-NMR spectrum exhibits signals due to methylene carbons α to a carbonyl group at δ 35—65 ppm, and those of the corresponding carbons in the enolate forms at δ 90—120 ppm.[11] The signal due to the C-3 carbon of **5** appeared at δ 60.2 ppm as a triplet.
7) U. Folli, D. Larossi, I. Moretti, F. Taddei, and G. Torre, *J. Chem. Soc.*, *Perkin Trans. 2*, **1974**, 1655.
8) H. O. House, "Modern Synthetic Reactions," 2nd ed., W. A. Benjamin, Inc., Menlo Park, Calif., 1972, p. 586; D. Caine, "Carbon–Carbon Bond Formation," ed. by R. L. Augustine, Marcel Dekker, New York, 1979, p. 220.
9) K. Bergesen, B. M. Carden, and M. J. Cook, *J. Chem. Soc.*, *Perkin Trans. 2*, **1978**, 1001.
10) All melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. The infrared (IR) spectra were recorded with a JASCO IRA-1 spectrophotometer. The ^{1}H-NMR spectra were measured on a Hitachi R-22 (90 MHz) spectrometer with tetramethylsilane as an internal standard, and the ^{13}C-NMR spectra were measured by Fourier transformation carried out on a Hitachi R-900 spectrometer at 22.6 MHz. Mass spectra (MS) were obtained with a JMS D-300 instrument with a direct inlet system operating at 70 eV.
11) G. A. Olah, J. L. Grant, and P. W. Westerman, *J. Org. Chem.*, **40**, 2102 (1975); H. O. House, A. V. Prabhu, and W. V. Phillips, *ibid.*, **41**, 1209 (1976).