[Chem. Pharm. Bull. 30(11)4069—4074(1982)]

Synthesis, Stereochemistry, and Rearrangement of *N*-Tosylsulfilimines and (Bismethoxycarbonyl)methylides of 1,4-Dimethylthioxanthene and Its 9-Alkyl Derivatives

YASUMITSU TAMURA,* CHISATO MUKAI, and MASAZUMI IKEDA

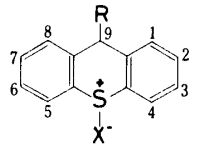
Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka 565, Japan

(Received May 22, 1982)

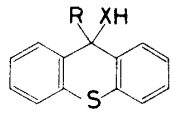
The *N*-tosylsulfilimines and (bismethoxycarbonyl)methylides of 1,4-dimethylthioxanthene and its 9-alkyl derivatives were synthesized, and their stereochemistry was assigned on the basis of nuclear magnetic resonance spectral comparison with the corresponding 2,4-dimethylthioxanthene derivatives. Treatment of 1,4-dimethylthioxanthene *N*-tosylsulfilimine and 1,4-dimethylthioxanthenium (bismethoxycarbonyl)methylide with base gave the rearranged products, 9-tosylamino- and 9-(bismethoxycarbonyl)methyl-1,4-dimethylthioxanthenes, respectively, but the 9-alkyl derivatives did not undergo this rearrangement.

Keywords——chloramine-T; *O*-mesitylenesulfonylhydroxylamine; thioxanthene *N*-tosylsulfilimine; sulfilimine; thioxanthenium (bismethoxycarbonyl)methylide; ylide; stereochemistry; rearrangement

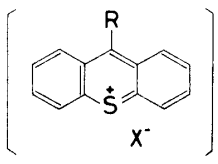
The chemistry of thioxanthene derivatives has attracted particular attention, because it provides an opportunity to explore the unique stereochemical problem of a six-membered ring held in a boat conformation. A variety of derivatives including sulfoxides (**1**),[1,2] *N*-tosylsulfilimines (**2**),[3] and sulfonium methylides (**3**)[4,5] has been investigated. Among them, **2** and **3** have been shown to undergo a base-promoted rearrangement to 9-tosylamino- and 9-(bismethoxycarbonyl)methyl-thioxanthenes, **4** and **5**, by way of a mechanism which involves thioxanthylium ions (**6**).[3] The rate of the rearrangement is markedly influenced by the stereochemistry of the starting ylides as well as by the steric bulk of the 9-alkyl group. We have now prepared the *N*-tosylsulfilimines and (bismethoxycarbonyl)methylides of 1,4-dimethylthioxanthene and its 9-alkyl derivatives, in order to see how the steric crowding affects the stereochemistry and rearrangement of these thioxanthene derivatives.



1 : X=O
2 : X=NTs
3 : X=C(CO$_2$Me)$_2$



4 : X=NTs
5 : X=C(CO$_2$Me)$_2$



6

Chart 1

Synthesis

The synthetic routes to the 1,4-dimethylthioxanthene derivatives **8a**—**c** and **12a**—**c** are illustrated in Chart 2. 1,4-Dimethylthioxanthene *N*-tosylsulfilimine (**8a**) was prepared in 38% yield by the reaction of **7a** with chloramine-T. This reaction was accompanied by the formation of **9** (40%).[3a] When **7b** and **7c** were treated with chloramine-T, only a complex mixture was obtained. The sulfilimines **8b**, **c** were prepared by a two-step procedure involving tosylation of the corresponding *S*-amine salts **10** and **11**, which in turn were synthesized by the reaction of **7b**, **c** with *O*-mesitylenesulfonylhydroxylamine (MSH).[3b] This procedure gave

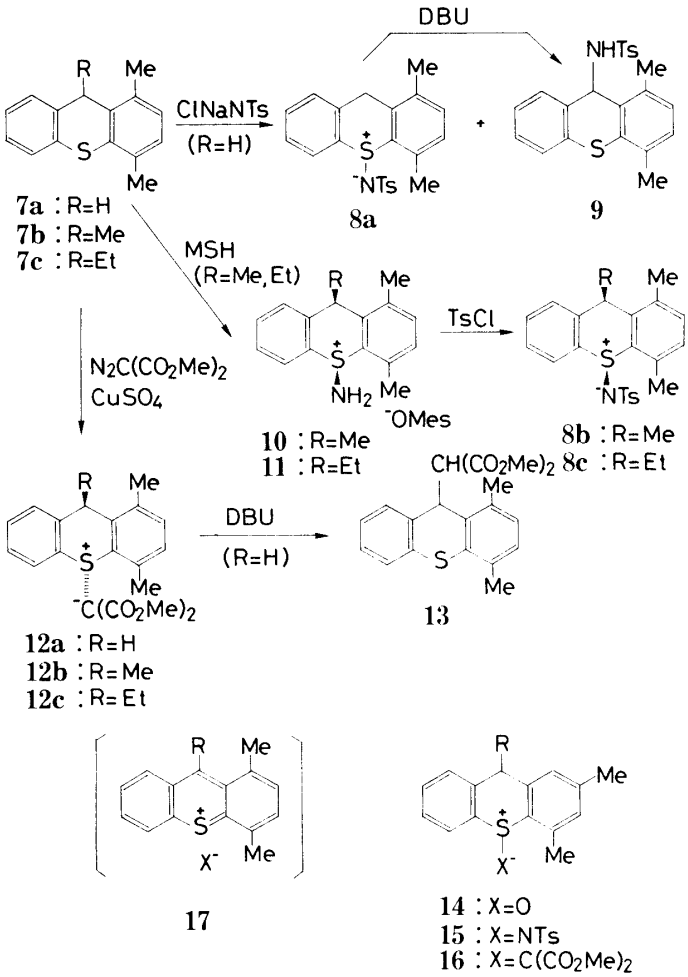


Chart 2

only the *cis*-isomers. The (bismethoxycarbonyl)methylides **12a**—**c** were synthesized by heating **7a**—**c** with dimethyl diazomalonate in the presence of cupric sulfate in 65, 79, and 62% yields, respectively.[4b] In the cases of **7b**, **c** only the *trans*-isomers were obtained. Since the products **8b**, **c** and **12b**, **c** did not thermally epimerize,[6] they are considered to be the most stable isomers.

Stereochemistry

The stereochemistry of **8a**—**c** and **12a**—**c** was assigned on the basis of a comparison of the ^{1}H-nuclear magnetic resonance (NMR) spectra with those of the corresponding 2,4-dimethylthioxanthene derivatives **15**[3d] and **16**.[4b]

The H-9 protons of **8a** and **12a** appear as an AB quartet at δ 4.10 and 4.58 with $J=18$ Hz (for **8a**) and δ 4.00 and 4.66 with $J=20$ Hz (for **12a**), the lower doublet (axial proton) of which is broadened due to allylic coupling with the H-8 proton. This result is in good agreement with that for the corresponding 2,4-dimethylthioxanthene derivatives in which the S^+–N^-Ts and S^+–$C^-(CO_2Me)_2$ groups are axial to avoid the interaction between these groups and the 4-methyl group.[1d,4b] The assignment was finally confirmed by an X-ray analysis of **12a**.[7]

The chemical shifts of H-9 and the 9-alkyl group of **8b**, **c** and **12b**, **c** are in accordance with those of the corresponding **15** and **16** except for the downfield shift (0.12—0.25 ppm) of the H-9 (equatorial) signal in the 1,4-dimethylthioxanthene series. This shift is attributed to a van der Waal's effect[8] caused by the presence of a methyl group at the 1-position. The results are summarized in Table I. The structure of **12b** has been confirmed by its X-ray analysis.[9]

TABLE I. NMR Data for the *N*-Tosylsulfilimines and (Bismethoxycarbonyl)-methylides derived from 1,4-Dimethylthioxanthene and Its 9-Alkyl Derivatives

Compd.	X	R	Preferred conformn.	H-9	9-R
8a	NTs	H	ax-X	4.10 4.58[a] (ABq)	—
15a	NTs	H	ax-X	3.86 4.80[a] (ABq)	—
8b	NTs	Me	D	4.34 (q)	1.88 (3, d)
cis-**15b**	NTs	Me	D	4.15 (q)	1.89 (3, d)
trans-**15b**[b]	NTs	Me	B	5.14 (q)	1.81 (3, d)
8c	NTs	Et	D	4.00 (dd)	2.25 (2, quintet) 0.98 (3, t)
cis-**15c**	NTs	Et	D	3.78 (t)	2.35 (2, quintet) 0.98 (3, t)
trans-**15c**	NTs	Et	B	4.51 (t)	2.02 (2, quintet) 1.00 (3, t)
12a	C $(CO_2Me)_2$	H	ax-X	4.00 4.66[a] (ABq)	—
16a[b]	C $(CO_2Me)_2$	H	ax-X	3.96 5.03[a] (ABq)	—
12b[b]	C $(CO_2Me)_2$	Me	A	4.51 (q)	1.30 (3, d)
cis-**16b**	C $(CO_2Me)_2$	Me	C or D[c]	4.11 (q)	1.99 (3, d)
trans-**16b**	C $(CO_2Me)_2$	Me	A	4.39 (q)	1.39 (3, d)
12c	C $(CO_2Me)_2$	Et	A	4.38 (t)	1.60 (2, quintet) 0.76 (3, t)
trans-**16c**[b]	C $(CO_2Me)_2$	Et	A	4.13 (t)	1.60 (2, quintet) 0.76 (3, t)

a) Broadened by allylic coupling with C_8–H (and C_1–H).
b) Stereochemistry has been confirmed by an X-ray analysis. [*trans*-**15b**, ref. 13; **16a**, ref. 7; **12b**, ref. 8; *trans*-**16c**, ref. 4b].
c) Probably C.

In principle, the 9-alkylthioxanthene derivatives (*e.g.*, **1**—**3**, R≠H) can exist in four possible configurational and conformational structures, *i.e.*, A—D. The preferred conformations of these derivatives are determined by a combination of the following three factors: (1) the steric interference between the equatorial S^+–X^- group and the peri-hydrogens (H-4 and H-5) and/or 4-methyl group (see structures A and C), (2) the steric interference between the equatorial 9-alkyl group and the peri-hydrogens (H-1 and H-8) and/or 1-methyl group (see structures B and C), and (3) the non-bonded interaction between two boat-axial substituents in structure D.

Previous studies indicated that the orders of stability of the sulfoxides and *N*-tosylsulfilimines are very similar, and in the 2,4-dimethylthioxanthene series (**14** and **15**), D>B>A or C when R=Me and Et,[3d,10] and D>A>B or C when R=iso-Pr.[11] The present work showed that the most stable structure of 1,4-dimethyl-9-alkylthioxanthene *N*-tosylsulfilimines **8b**, **c** is also D: the factors 1 and 2 become very important, making the structures A, B, and C unfavorable.

On the other hand, the most stable structure of the methylides *trans*-**16** (R=Me,[4b] Et,[4b] iso-Pr[11]) and **12b**, **c** is always structure A, in which the (bismethoxycarbonyl)methylide group is equatorial, in spite of the fact that unfavorable interaction between this and the 4-methyl group (factor 1) can be expected. Such a preference for the equatorial position of S^+–C^--$(CO_2Me)_2$ group[12] has been rationalized by Ternay *et al.*[5b]: the axial conformer would be destabilized either by steric interaction between one of the ester group and the axial 9-substituent (see structure E) or by electron-electron repulsion between the sulfur lone pair and the *p*-orbital of the methylide carbon (see structure F). Such interactions are not present in the sulfoxides and *N*-tosylsulfilimines. In addition, the longer bond length of S^+–C^- (*ca.* 1.74

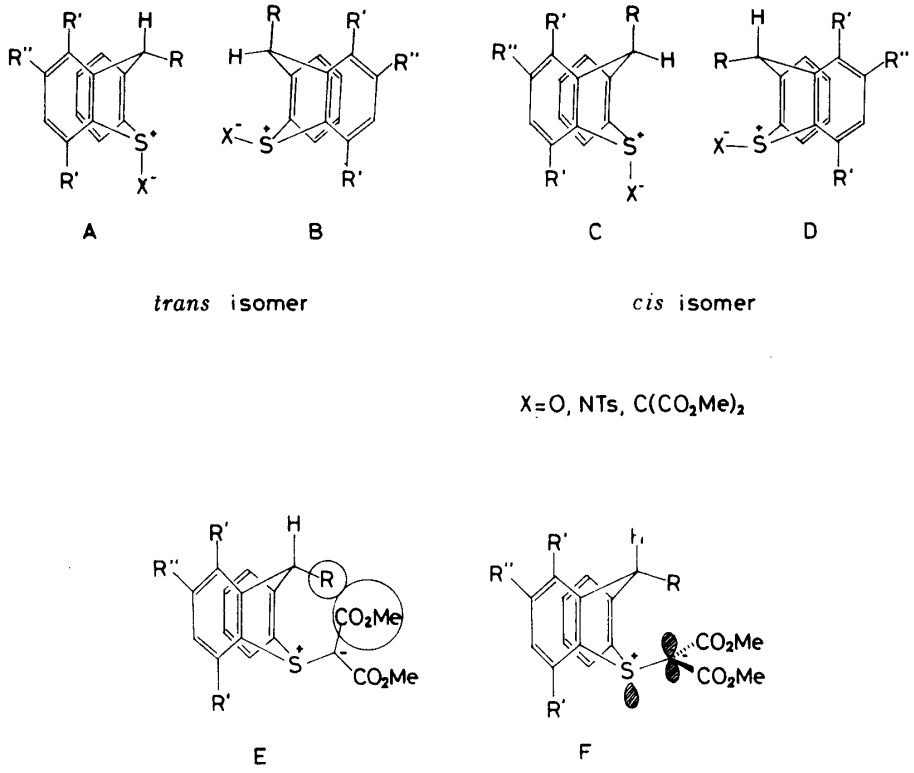


Chart 3

Å)[4b,5b] than of S^+–O^- (*ca.* 1.50 Å)[10] and S^+–N^- (*ca.* 1.64 Å)[13] may also contribute to the decrease of the unfavorable interaction between the equatorial S^+–$C^-(CO_2Me)_2$ and 4-methyl group.

Of particular interest is the signal of the two methoxyl groups in the NMR spectra (Table II): *trans*-**3** (R=Me) and *trans*-**16** (R=Me, Et) show a sharp singlet, whereas *trans*-**3** (R=Et, iso-Pr), *trans*-**16** (R=iso-Pr),[12] and **12b**, **c** show a broad signal or split signals.[14] This means that rotation about the S^+–C^- bond is free for the first three compounds but hindered for the latter five compounds. The presence of a bulky 9-alkyl group and/or introduction of a 1-methyl group appear to increase the energy barrier for rotation, but the 4-methyl group does not have a significant influence. The change of the dihedral angle between the planes of the two benzene rings might be responsible for these phenomena. However, a precise conclusion must await a more detailed investigation, particularly by X-ray studies.

Table II. Splitting Pattern of the equatorial-Methoxycarbonyl Group of 9-Alkylthioxanthenium (Bismethoxycarbonyl)methylides at 34°C

Compd.	9-R		
	Me	Et	iso-Pr
trans-**3**	3.59 (6H, sharp s)	3.59 (6H, br s)	3.82 (3H, s)
trans-**16**	3.64 (6H, sharp s)	3.54 (6H, sharp s)	3.26 (3H, s)
trans-**12**	4.1—3.1 (6H, br)	3.86 (3H, s)	4.1—2.9 (6H, br)
		3.26 (3H, s)	—

s = singlet; br = broad.

Rearrangement

Treatment of **8a** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene at room temperature gave the rearranged product **9** in 71% yield. The structure of **9** was apparent

from its spectral data (see "Experimental"). Refluxing of **12a** in toluene in the presence of DBU for 2 h afforded the rearranged product **13** in 81% yield. However, **8b, c** and **12b, c** were stable under the reaction conditions which we used for the rearrangement of **8a** and **12a**. Prolonged refluxing of **12b** in toluene (for more than 20 h) resulted in decomposition. Non-bonded interaction between the 9-alkyl group and 1-methyl group in the transition state leading to the thioxanthylium ion **17** may increase the activation energy of the rearrangement.[15]

Experimental[16]

1,4-Dimethylthioxanthene *N*-Tosylsulfilimine (8a) and 9-(*N*-Tosylamino)-1,4-dimethylthioxanthene (9)——Chloramine-T·$3H_2O$ (1.4 g, (5 mmol) was added all at once to a stirred solution of **7a** (1.13 g, 5 mmol) in methanol (25 ml) and methylene chloride (12 ml) containing AcOH (0.05 ml) at room temperature. After 30 min, $CHCl_3$ (30 ml) was added to the reaction mixture and the solution was washed with a saturated $NaHCO_3$ solution and H_2O, then dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel with benzene–AcOH (5: 1) to give **9** (745 mg, 38%) and **8a** (785 mg, 40%).

Compound **9** gave mp 163—164°C (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3370 (NH), 1340, and 1160 (SO_2). NMR ($CDCl_3$) δ: 7.4—6.8 (m, 10H, aromatic protons), 5.90 (d, 1H, $J=8$ Hz, H-9), 5.16 (br d, 1H, $J=8$ Hz, NH), 2.47 (s, 3H, CH_3), and 2.30 (s, 6H, $2\times CH_3$). *Anal.* Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.80; H, 5.35; N, 3.54. Found: C, 67.10; H, 5.25; N, 3.60.

Compound **8a** gave mp 153—157°C (from MeOH–AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1290, 1140, 1095 (SO_2), and 960 (S^+–N^-). NMR ($CDCl_3$) δ: 7.7—6.9 (m, 10H, aromatic protons), 4.58, 4.10 (ABq, 1H each, $J=18$ Hz, H-9), and 2.42, 2.39, 2.33 (all s, 3H each, $3\times CH_3$). *Anal.* Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.80; H, 5.35; N, 3.54. Found: C, 66.87; H, 5.23; N, 3.58.

General Procedure for the Preparation of 10-Amino-9-alkyl-1,4-dimethylthioxanthenium Mesitylenesulfonates (10 and 11)——A solution of MSH (4.2 mmol) in CH_2Cl_2 (15 ml) was added to an ice-cooled solution of **7b** or **7c** (4 mmol) in CH_2Cl_2 (15 ml) with stirring. The reaction mixture was stirred at room temperature for 2.5 h and then ether (30 ml) was added. The precipitated crystals were collected by filtration and recrystallized from MeOH–AcOEt.

Compound **10** (85%) gave mp 171—173°C. *Anal.* Calcd for $C_{25}H_{29}NO_3S_2$: C, 65.90; H, 6.42; N, 3.07. Found: C, 65.53; H, 6.49; N, 3.35.

Compound **11** (89%) gave mp 191—193°C. *Anal.* Calcd for $C_{26}H_{31}NO_3S_2\cdot 1/2H_2O$: C, 65.24; H, 6.74; N, 2.93. Found: C, 65.04; H, 6.91; N, 2.87.

General Procedure for the Preparation of *cis*-9-Alkyl-1,4-dimethylthioxanthene *N*-Tosylsulfilimines (8b, c)——Tosyl chloride (2 mmol) and K_2CO_3 (2.5 mmol) were added all at once to a solution of **10** or **11** (2 mmol) in dimethylformamide (DMF) (20 ml) at 0°C. The reaction mixture was stirred at room temperature for 3 h, then concentrated *in vacuo* at below 30°C, and $CHCl_3$ (30 ml) was added to the residue. The solution was washed with H_2O, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel with benzene–AcOEt (4: 1).

Compound **8b** (31%) gave mp 247.5—248.5°C (from $CHCl_3$–MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1290, 1140, 1090 (SO_2), and 950 (S^+–N^-). NMR ($CDCl_3$) δ: 7.8—7.0 (m, 10H, aromatic protons), 4.34 (q, 1H, $J=7.5$ Hz, H-9), 2.43, 2.41, 2.36 (s each, 3H each, $3\times CH_3$), and 1.88 (d, 3H, $J=7.5$ Hz, 9-CH_3). MS *m/z*: 409 (M^+). *Anal.* Calcd for $C_{23}H_{23}NO_2S_2$: C, 67.45; H, 5.66; N, 3.42. Found: C, 67.24; H, 5.57; N, 3.44.

Compound **8c** (45%) gave mp 223—224°C (from benzene). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1290, 1140, 1090 (SO_2), and 950 (S^+–N^-). NMR ($CDCl_3$) δ: 7.8—6.9 (m, 10H, aromatic protons), 4.00 (dd, 1H, $J=11$ and 6 Hz, H-9), 2.25 (m, 2H, $C\underline{H}_2CH_3$), 2.40 (s, 6H, $2\times CH_3$), 2.35 (s, 3H, CH_3), and 0.98 (t, 3H, $J=7$ Hz, $CH_2C\underline{H}_3$). MS *m/z*: 423 (M^+). *Anal.* Calcd for $C_{24}H_{25}NO_2S_2$: C, 68.05; H, 5.95; N, 3.31. Found: C, 67.91; H, 5.86; N, 3.32.

General Procedure for the Preparation of 1,4-Dimethylthioxanthenium and *trans*-9-Alkyl-1,4-dimethylthioxanthenium (Bismethoxycarbonyl)methylides (12a—c)——A mixture of **7a—c** (5 mmol), dimethyl diazomalonate (5.5 mmol), and anhydrous cupric sulfate (50 mg) was heated with vigorous stirring at 90°C for 3 h, then cooled. $CHCl_3$ (50 ml) was added to the reaction mixture and the whole was filtered and concentrated to give a yellow oil, which was chromatographed on silica gel with benzene–AcOEt (1: 1).

Compound **12a** (65%) gave mp 184—185°C (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 and 1640 (C=O). NMR ($CDCl_3$) δ: 7.8—6.9 (m, 6H, aromatic protons), 4.66, 4.00 (ABq, 1H each, $J=20$ Hz), 3.61 (s, 6H, $2\times OCH_3$), and 2.53, 2.39 (s each, 3H each, $2\times CH_3$). *Anal.* Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66. Found: C, 67.35; H, 5.65.

Compound **12b** (79%) gave mp 178—179°C (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 (C=O); NMR ($CDCl_3$) δ: 7.8—6.9 (m, 6H, aromatic protons), 4.51 (q, 1H, $J=7.5$ Hz, H-9), 3.9—3.1 (br, 6H, $2\times OCH_3$), 2.51, 2.47 (s each, 3H each, $2\times CH_3$), and 1.30 (d, 3H, $J=7.5$ Hz, 9-CH_3). MS *m/z*: 370 (M^+). *Anal.* Calcd for $C_{21}H_{22}O_4S$: C, 68.08; H, 5.99. Found: C, 67.91; H, 6.05.

Compound **12c** (62%) gave mp 175—176°C (from AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 (C=O). NMR ($CDCl_3$) δ: 7.8—6.9 (m, 6H, aromatic protons), 4.38 (t, 1H, $J=7$ Hz, H-9), 3.86, 3.26 (s each, 3H each, $2\times OCH_3$), 2.52, 2.48 (s each, 3H each, $2\times CH_3$), 1.60 (quint, 2H, $J=7$ and 7 Hz, $C\underline{H}_2CH_3$), and 0.76 (t, 3H, $J=7$ Hz, $CH_2C\underline{H}_3$). MS *m/z*: 384 (M^+). *Anal.* Calcd for $C_{22}H_{24}O_4S$: C, 68.73; H, 6.29. Found: C, 68.65; H, 6.32.

Rearrangement of 8a to 9——A solution of **8a** (100 mg, 0.25 mmol) and DBU (20 mg, 0.13 mmol) in benzene (8 ml) was stirred at room temperature for 30 min. Benzene (10 ml) was added to the reaction mixture and the benzene solution was washed with 10% HCl and H_2O, then dried ($MgSO_4$), and concentrated. The residual solid was recrystallized from benzene–*n*-hexane to give **9** (71 mg, 71%), mp 163—164°C.

Rearrangement of 12a to 13——A solution of **12a** (120 mg, 0.34 mmol) and DBU (50 mg, 0.33 mmol) in toluene (9 ml) was refluxed for 2 h and then benzene (20 ml) was added. The reaction mixture was washed with 10% HCl and H_2O, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel with benzene to give **13** (97 mg, 81%), mp 122—122.5°C (from MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750 and 1730 C=O). NMR ($CDCl_3$) δ: 7.6—6.9 (m, 6H, aromatic protons), 5.23 (d, 1H, $J=11$ Hz), 4.34 (d, 1H, $J=11$ Hz), 3.50, 3.34 (both s, 3H each, $2\times OCH_3$), and 2.48, 2.41 (both s, 3H each, $2\times CH_3$). *Anal.* Calcd for $C_{20}H_{20}O_4S$: C, 67.40; H, 5.66. Found: C, 67.25; H, 5.58.

References and Notes

1) *a*) A.L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969); *b*) A.L. Ternay, Jr. and S.A. Evans, *ibid.*, **39**, 2941 (1974); *c*) S.A. Evans and A.L. Ternay, Jr., *ibid.*, **40**, 2993 (1975); **43**, 5026 (1978); *d*) A.L. Ternay, Jr., J. Herrmann, B.R. Hayes, and P. Joseph-Nathan, *ibid.*, **45**, 189 (1980).
2) M. Hori, T. Kataoka, and H. Shimizu, *Chem. Lett.*, **1974**, 1073.
3) *a*) Y. Tamura, Y. Nishikawa, K. Sumoto, M. Ikeda, M. Murase, and M. Kise, *J. Org. Chem.*, **42**, 3226 (1977); *b*) Y. Tamura, Y. Nishikawa, C. Mukai, K. Sumoto, M. Ikeda, and M. Kise, *ibid.*, **44**, 1684 (1979); *c*) Y. Tamura, C. Mukai, Y. Nishikawa, and M. Ikeda, *ibid.*, **44**, 3296 (1979); *d*) Y. Tamura, C. Mukai, N. Nakajima, and M. Ikeda, *ibid.*, **45**, 2972 (1980).
4) *a*) Y. Tamura, C. Mukai, and M. Ikeda, *Heterocycles*, **12**, 1179 (1979); *b*) Y. Tamura, C. Mukai, N. Nakajima, M. Ikeda, and M. Kido, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 212.
5) *a*) A.L. Ternay, Jr., D. Craig, and H.R. O'Neal, *J. Org. Chem.*, **45**, 1520 (1980); *b*) M.A. Abbady, D. Craig, A.L. Ternay, Jr., G.E. Martin, J. Galloy, and W.H. Watson, *ibid.*, **46**, 1793 (1981).
6) On being refluxed in either benzene or toluene for 4 h, **8b**, **c** and **12b**, **c** were recovered unchanged.
7) *a*) A private communication from A.L. Ternay, Jr.; *b*) Y. Tamura, C. Mukai, M. Ikeda, and M. Kido unpublished data.
8) L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Ed., Pergamon Press, Oxford, 1969, p. 71.
9) A private communication from A.L. Ternay, Jr.
10) *a*) S.S.C. Chu, R. Rosenstein, and A.L. Ternay, Jr., *Acta Cryst.*, **B35**, 2430 (1979); *b*) S.S.C. Chu, W.K. Grant, V. Napoleone, A.L. Ternay, Jr., and F. Massah, *ibid.*, **B37**, 1948 (1981); *c*) S.S.C. Chu, V. Napolenone, F. Massah, and A.L. Ternay, Jr., *ibid.*, **B37**, 775 (1981).
11) Y. Tamura, C. Mukai, and M. Ikeda, unpublished results.
12) It has been demonstrated by X-ray studies[4b,5b] that the (bismethoxycarbonyl)methyl group is planar.
13) Y. Tamura, C. Mukai, M. Ikeda, and M. Kido, *Chem. Lett.*, **1981**, 619.
14) Such broadening of the methoxyl signal has been observed with some thioxanthonium (bismethoxycarbonyl)methylides.[5b]
15) For detailed mechanistic discussions, see refs. 3*d* and 4*b*.
16) All melting points are uncorrected. The infrared (IR) spectra were determined with a JASCO IRA-1 spectrophotometer and NMR spectra with a Hitachi R-22 spectrometer (90 MHz) with tetramethylsilane as an internal standard. Mass spectra were obtained with a JMS-D-300 instrument at 70 eV.