concentrated. The residue was chromatographed on silica gel with AcOEt-*n*-hexane (1:2) to give *S*-oxo-9-ethylidenethioxanthene (**6a**; 330 mg, 31%) as colorless crystals: mp 134–135 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 1070 (SO) cm^{-1}; NMR ($CDCl_3$) δ 7.1–8.1 (m, 8, aromatic protons), 6.27 (q, 1, J = 8 Hz, vinylic proton), 2.10 (d, 3, J = 8 Hz, CH_3).

Anal. Calcd for $C_{15}H_{12}OS$: C, 74.96; H, 5.03. Found: C, 74.97; H, 4.89.

Further elution with the same solvent afforded 9-ethylidenethioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (**5a**; 950 mg, 58%) as colorless crystals: mp 190–191 °C (from AcOEt-*n*-hexane); IR ($CHCl_3$) 1300, 1140, 1090 (SO_2), 960 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.2–8.0 (m, 12, aromatic protons), 6.35 (q, 1, J = 8 Hz, vinylic proton), 2.42 (s, 3, toluene ring CH_3), 2.11 (d, 3, J = 8 Hz, CH_3).

Anal. Calcd for $C_{22}H_{19}NO_2S_2$: C, 67.14; H, 4.86; N, 3.56. Found: C, 67.23; H, 4.72; N, 3.57.

Reaction of 4b with Chloramine T. To a stirred solution of **4b** (840 mg, 3.5 mmol) in methanol (24 mL) and methylene chloride (12 mL) containing a catalytic amount of acetic acid (0.05 mL) was added chloramine T trihydrate (1.90 g, 6.7 mmol) at room temperature. Workup as described above gave *S*-oxo-9-*n*-propylidenethioxanthene (**6b**; 250 mg, 28%) and 9-*n*-propylidenethioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (**5b**; 770 mg, 53%).

Compound **6b** was an oil: IR ($CHCl_3$) 1040 (SO) cm^{-1}; NMR ($CDCl_3$) δ 7.3–8.1 (m, 8, aromatic protons), 6.17 (t, 1, J = 8 Hz, vinylic proton), 2.55 (quintet, 2, J = 8 Hz, CH_2CH_3), 1.16 (t, 3, J = 8 Hz, CH_2CH_3); mass spectrum, m/e 254 (M^+).

Compound **5b** had the following: mp 111–112 °C (from AcOEt-*n*-hexane); IR ($CHCl_3$) 1300, 1140, 1085 (SO_2), 960 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.1–8.0 (m, 12, aromatic protons), 6.18 (t, 1, J = 8 Hz, vinylic proton), 2.50 (quintet, 2, CH_2CH_3), 2.40 (s, 3, toluene ring CH_3), 1.15 (t, 3, J = 8 Hz, CH_2CH_3).

Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.30; H, 5.33; N, 3.44.

Reaction of 4c with Chloramine T. To a stirred solution of **4c** (490 mg, 2 mmol) in methanol (12 mL) and methylene chloride (6 mL) containing a catalytic amount of acetic acid (0.03 mL) was added chloramine T trihydrate (1.13 g, 4 mmol) at room temperature. Workup as described above and column chromatography of the resulting oil on silica gel with AcOEt-*n*-hexane (1:2) gave *S*-oxo-9-isopropylidenethioxanthene (**6c**; 140 mg, 26%) and 9-isopropylidenethioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (**5c**; 635 mg, 74%).

Compound **6c** had the following: mp 125–126 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 1095 (SO) cm^{-1}; NMR ($CDCl_3$) δ 7.2–8.0 (m, 8, aromatic protons), 2.09 (s, 6, 2 CH_3).

Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55. Found: C, 75.23; H, 5.46.

Compound **5c** had the following: mp 207–208 °C (from AcOEt-*n*-hexane); IR ($CHCl_3$) 1300, 1140, 1080 (SO_2), 960 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.2–8.1 (m, 12, aromatic protons), 2.39 (s, 3, toluene ring CH_3), 2.04 (s, 6, 2 CH_3).

Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.72; H, 5.19; N, 3.44. Found: C, 67.82; H, 5.19; N, 3.44.

Base-Catalyzed Rearrangement of 5a. A solution of **5a** (203 mg, 0.52 mmol) in benzene (10 mL) containing DBU (200 mg, 1.3 mmol) was stirred at room temperature for 19 h. The solution was washed with 10% hydrochloric acid and water, dried ($MgSO_4$), and concentrated to give 9-(*N*-*p*-toluenesulfonamido)-9-vinylthioxanthene (**8a**; 190 mg, 94%) as colorless crystals: mp 179–180 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 3240 (NH), 1320 and 1160 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.3 (m, 12, aromatic protons), 5.6–6.6 (m, 3, vinylic protons), 4.69 (br s, 1, NH), 2.33 (s, 3, toluene ring CH_3).

Anal. Calcd for $C_{22}H_{19}NO_2S_2$: C, 67.14; H, 4.87; N, 3.56. Found: C, 67.06; H, 4.73; N, 3.65.

Base-Catalyzed Rearrangement of 5b. A solution of **5b** (30 mg, 0.13 mmol) in benzene (3 mL) containing DBU (60 mg, 0.4 mmol) was stirred at room temperature for 48 h. Workup as described above gave 9-(1-propenyl)-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**8b**, 23 mg, 75%) as colorless crystals: mp 164–165 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 3380 (NH), 1325, 1150 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.8 (m, 12, aromatic protons), 5.9–6.25 (m, 1, vinylic proton), 5.75 (d, 1, J = 16 Hz, vinylic proton), (4.72 (br s, 1, NH), 2.35 (s, toluene ring CH_3), 1.95 (d, 3, J = 6 Hz, CH_3).

Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.61; H, 5.12; N, 3.62.

Base-Catalyzed Rearrangement of 5c. A solution of **5c** (254 mg, 0.6 mmol) in benzene (10 mL) containing DBU (500 mg, 3 mmol) was refluxed for 7 h. After cooling, the benzene solution was washed with 10% hydrochloric acid and water, dried ($MgSO_4$), and concentrated to give 9-isopropenyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**8c**; 248 mg, 95%) as colorless crystals: mp 173–174 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 3350 (NH), 1320 and 1150 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.7–7.6 (m, 12, aromatic protons), 5.84 (s, 1, vinylic proton), 5.43 (br s, 1, vinylic proton), 5.05 (br s, 1, NH), 2.30 (s, 3, toluene ring CH_3), 1.49 (s, 3, $CH_3C{=}CH_2$).

Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44. Found: C, 67.71; H, 5.16; N, 3.52.

Registry No. **4a**, 73872-48-7; **4b**, 73872-49-8; **4c**, 40102-95-2; **5a**, 73872-50-1; **5b**, 73872-51-2; **5c**, 73872-52-3; **6a**, 73872-53-4; **6b**, 73872-54-5; **6c**, 73872-55-6; **8a**, 73872-56-7; **8b**, 73872-57-8; **8c**, 73872-58-9; thioxanthone, 492-22-8; ethyl iodide, 75-03-6; *n*-propyltriphenylphosphonium bromide, 6228-47-3; isopropyltriphenylphosphonium iodide, 24470-78-8; chloramine T, 127-65-1.

Synthesis, Stereochemistry, and Base-Catalyzed Rearrangement of 9-Alkyl-2,4-dimethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines

Yasumitsu Tamura,* Chisato Mukai, Noriko Nakajima, and Masazumi Ikeda

Faculty of Pharmaceutical Sciences, Osaka University, 133-1, Yamada-kami, Suita, Osaka, Japan

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trans-2,4,9-trimethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (**5a**) and *trans*-9-ethyl-2,4-dimethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (**5b**) were synthesized by reaction of the corresponding thioxanthenes with chloramine T. The cis isomers were obtained by thermal isomerization of the trans isomers. The stereochemistry of the sulfilimines was determined by examination of the NMR spectra. When treated with base, *trans*-**5a,b** rearranged rapidly to 9-methyl- and 9-ethyl-9-(*N*-*p*-toluenesulfonamido)-2,4-dimethylthioxanthenes (**9a,b**), respectively. Under the same conditions, *cis*-**5b** rearranged much more slowly to **9b**. A mechanistic interpretation of these results is advanced.

The mechanism of the base-catalyzed rearrangement of thioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines **1** to 9-(*N*-*p*-toluenesulfonamido)thioxanthenes **3** has been investigated recently.[1-3] This rearrangement was formulated as

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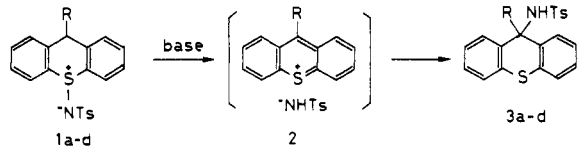


a, R=Me; b, R=Et; c, R=Ph; d, R=H

proceeding via thioxanthylium ions **2** which collapsed to **3**. Interestingly, the more stable *trans*-**1a–c** rearranged significantly faster than *cis*-**1a–c**.[2,3] To account for this observation, we suggested a mechanism involving a concerted syn 1,4-elimination from the trans isomers. If this mechanism operates, *trans*-**1a–c**, which exist in conformer A, must preequilibrate with the less stable conformer B, the presence of which has never been demonstrated. In order to test our hypothesis, we have prepared the stereoisomers of conformers *trans*-**5** and have evaluated their reactivities.

Results and Discussion

Synthesis. Reaction of 9-methyl- and 9-ethyl-2,4-dimethylthioxanthenes (**4a,b**) with 2 equiv of chloramine T, analogous to the procedure used to synthesize **1a,b**,[2] afforded exclusively *trans*-**5a,b** in 79 and 67% yields, respectively (Scheme I). The cis isomers were obtained by thermal isomerization of the trans isomers. Thus, refluxing *trans*-**5a** in benzene for 4 h gave an equilibrium mixture consisting of *cis*- and *trans*-**5a** in a ratio of ~3:2 (by ^{1}H NMR spectroscopy, Table I). Unfortunately, the mixture could not be separated by conventional means. On the other hand, *trans*-**5b** was completely isomerized to *cis*-**5b** under the same conditions. It is interesting to note that only the less stable trans isomers were formed in the reaction of **4a,b** with chloramine T. For comparison purposes, 9-unsubstituted derivative **6** was also prepared. Treatment of **4c** with 1 equiv of chloramine T[1] gave two products, which were separated by column chromatography to give **6** (38%) and **7** (50%).[4]

The structures of thus obtained sulfilimines were apparent from the spectral evidence (see Experimental Section). Final confirmation of these structures was given by the NMR spectra, which will be discussed in detail.

Stereochemistry. Before the stereochemistry of **5a,b** is discussed, the preferred conformation of 9-unsubstituted sulfilimine **6** should be mentioned. In the ^{1}H NMR spectrum of **6** the H-9 atoms appear as an AB quartet at δ 3.86 and 4.80 with J = 18 Hz in which the downfield doublet is broadened relative to the upfield doublet. This is in contrast to the case of *S*-oxothioxanthene[5] and thioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (**1d**),[1] in which the upfield doublet is broadened. Ternay and co-workers,[5] in their investigation of the stereochemistry of *S*-oxo-9-alkylthioxanthene, showed that such broadening of the H-9 signal results from allylic coupling with the peri hydrogens (H-1 and H-8) and occurs when H-9 is axial. They also showed that the chemical shifts of H-9 depend upon the conformation of the sulfinyl group: if the sulfinyl group is equatorial, the equatorial H-9 appears at lower field than the axial H-9 mainly because the former is deshielded by the two benzene rings of the thioxanthene molecule, and if the sulfinyl group is axial, the axial H-9 shifts to lower field due to the deshielding effect of the axial sulfinyl group. Analogy to the sulfoxides suggests that the S^+–N^-Ts group in sulfilimine **6** occupies an axial position. Attainment of this particular conformation is aided by relief of the nonbonding interaction between the S^+–N^-Ts and 4-methyl groups.

The stereochemical assignments of **5a,b** were also made by examination of the ^{1}H NMR spectra. The distinguishing feature of the ^{1}H NMR spectrum of *trans*-**5a,b** is the signal of H-9 which shows broadening and a large downfield shift (δ 5.14 and 4.51, respectively). This is consistent with the assigned conformation in which both the H-9 and S^+-N^-Ts groups are axial (i.e., conformer B). The H-9 of *cis*-**5a** appears as a sharp quartet and is assigned to be equatorial; in comparison, the H-9 (axial) of *cis*-**1a** (conformer C) occurs as a broadened quartet. In addition, the 9-methyl signal (axial) of *cis*-**5a** occurs at δ 1.89,[6] which is shifted 0.46 ppm to lower field than that (δ 1.43) of *trans*-**1a**, in which the S^+–N^-Ts group is equatorial. This downfield shift can be attributed to the deshielding effect of the axial S^+–N^-Ts group, and thus *cis*-**5a** exists in conformer D. In *cis*-**5b** the signals of both the

Scheme I

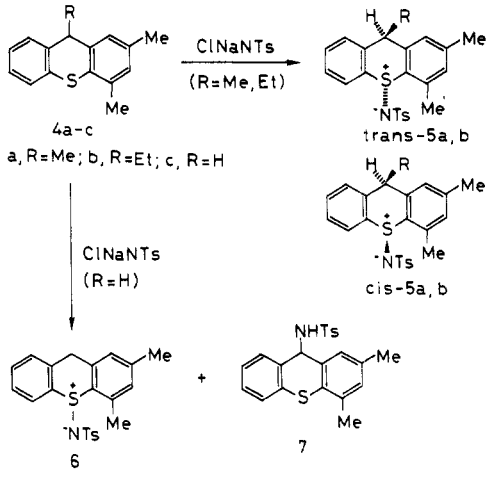
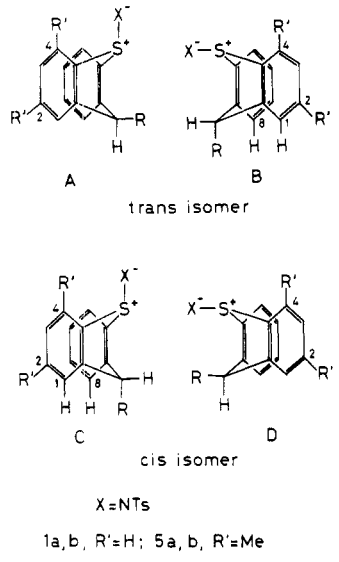


Table I. ^{1}H NMR Spectral Data for 9-Alkylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines

compd	preferred conformn	chemical shift, δ H-9	chemical shift, δ 9-R
cis-1a	C	3.86 (q)[a]	1.90 (3, d)
trans-1a	A	4.35 (q)	1.43 (3, d)
cis-5a	D	4.15 (q)	1.89 (3, d)
trans-5a	B	5.14 (q)[a]	1.81 (3, d)
cis-1b	D	3.80 (t)	2.28 (2, quintet), 1.04 (3, t)
trans-1b	A	4.06 (t)	1.69 (2, m), 0.87 (3, t)
cis-5b	D	3.78 (t)	2.35 (2, quintet), 0.98 (3, t)
trans-5b	B	4.51 (t)[a]	2.02 (2, quintet), 1.00 (3, t)

[a] Broadened by allylic coupling with H-1 and H-8. This was confirmed by decoupling experiments.

(1) Tamura, Y.; Nishikawa, Y.; Sumoto, K.; Ikeda, M.; Murase, M.; Kise, M. *J. Org. Chem.* **1977**, *42*, 3226.
(2) Tamura, Y.; Nishikawa, Y.; Mukai, C.; Sumoto, K.; Ikeda, M.; Kise, M. *J. Org. Chem.* **1979**, *44*, 1684.
(3) Tamura, Y.; Mukai, C.; Nishikawa, Y.; Ikeda, M. *J. Org. Chem.* **1979**, *44*, 3296.
(4) Compound **7** could also be obtained by base-catalyzed rearrangement of **6**.
(5) Ternay, A. L., Jr.; Ens, L.; Herrmann, J.; Evans, S. *J. Org. Chem.* **1969**, *34*, 940.
(6) The methyl group (equatorial) in *cis*-**1a** occurs at essentially the same position (δ 1.90) as that of *cis*-**5a**. However, the downfield shift in the former is due to the deshielding effect of the benzene rings of the thioxanthene molecule.



H-9 and the 9-methylene protons occur at almost the same positions as those of *cis*-**1b** (conformer D), suggesting that both compounds have the same stereochemistry.

It appeared to be of interest to see if the ^{13}C NMR spectra can be used for the stereochemical assignments. Some representative examples are listed in Table II. It was found that the effect of the stereochemistry of the 9-alkyl group is significant; the chemical shifts of the C-9 and 9-methyl or methylene carbons in the isomers with the equatorial alkyl group (conformer B or C) appear at higher field (5–8 ppm for the C-9 carbon and 10–16 ppm for the 9-methyl or methylene carbon) than those in the isomers with the axial alkyl group (conformer A or D). The upfield shifts of the C-9 and 9-methyl or methylene carbons in the former are of diagnostic value and can be attributed to the steric compression[7] between the equatorial 9-alkyl group and the perihydrogens at the 1 and 8 positions. On the other hand, the effect of the stereochemistry of the S^+–N^-Ts group is minor.

In considering the preferred conformations of **5a,b**, one needs to take into account the following three factors: (i) the steric interaction between the equatorial S^+–N^-Ts and 4-methyl groups (present in conformers A and C), (ii) the steric interference between the equatorial alkyl group and the perihydrogens at the 1 and 8 positions (present in conformers B and C), and (iii) the nonbonded interaction between two boat–axial substituents in conformer D. However, the last factor appears to be less important than the second one, particularly in 9-ethyl derivatives, as suggested by the fact that *cis*-**1b** exists as conformer D rather than as conformer C.[2] As described earlier, when refluxed in benzene, *trans*-**5b** (conformer B) isomerized completely to *cis*-**5b** (conformer D), whereas *trans*-**5a** (conformer B) gave an equilibrium mixture consisting of *cis*-**5a** (conformer D) and *trans*-**5a** in a ratio of ~3:2. These results together with consideration of the above three factors indicate that the stability of the possible four conformers, at least in **5b**, decreases in the order D ≫ B > A > C; in **5a**, the difference in the stability between conformers D and B becomes smaller mainly because of the decrease of the interaction between the equatorial 9-methyl group and the perihydrogens in conformer B. In conclusion, the steric interaction between the equatorial S^+–N^-Ts and 4-methyl groups is the most important factor which governs the conformations of **5a,b**. Recently a similar conclusion has been obtained by an X-ray crystallographic study of *cis*-2,4,9-trimethyl-*S*-oxothioxanthene.[8]

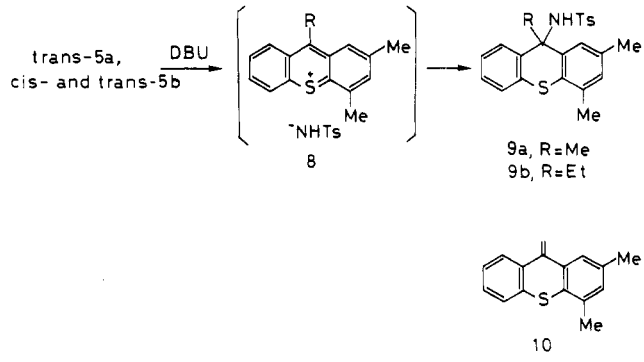
(7) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315.

Table II. ^{13}C NMR Spectral Data for 9-Alkylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines[a]

compd	preferred conformn	chemical shift[b] C-9	chemical shift[b] 9-R
cis-**1a**	C	37.63	10.99
trans-**1a**	A	42.60	24.14
cis-**5a**	D	42.75	29.48
trans-**5a**	B	34.66	13.06
cis-**1b**	D	48.57	33.23, 13.12
trans-**1b**	A	50.07	30.79, 12.55
cis-**5b**	D	50.34	35.80, 13.26
trans-**5b**	B	44.97	25.25, 11.80

[a] Run at 90 MHz in $CDCl_3$ solution; chemical shifts are given in parts per million from internal Me_4Si. [b] Resonances of the 2- and 4-methyls, the toluene ring methyl, and the aromatic carbons are as follows: 21.39, 139.78, 139.66, 132.85, 131.39, 129.47, 127.64, 127.37, 126.56, 126.42, and 126.27 for *cis*-**1a**; 21.42, 142.05, 141.21, 138.40, 132.50, 131.33, 129.44, 128.12, 127.94, 126.38, and 125.78 for *trans*-**1a**; 21.39, 21.30, and 19.05 for *cis*-**5a** (aromatic carbons were overlapped by those of *trans*-**5a**); 21.66, 21.36, 19.29, 146.16, 145.71, 142.86, 141.34, 139.39, 132.41, 130.10, 129.98, 129.77, 129.35, 128.93, 126.92, 126.62, 126.44, 125.93, and 124.71 for *trans*-**5a**; 21.39, 143.28, 141.46, 131.99, 130.19, 129.62, 129.05, 127.70, and 126.56 for *cis*-**1b**; 21.42, 142.02, 141.28, 136.96, 132.77, 130.88, 129.44, 128.84, 127.88, 126.35, and 125.55 for *trans*-**1b**; 21.33, 19.17, 145.41, 144.69, 142.81, 141.88, 141.25, 140.23, 132.08, 131.33, 130.43, 130.37, 129.80, 129.41, 129.17, 128.84, 126.53, and 126.29 for *cis*-**5b**; 21.33, 20.25, 142.00, 141.88, 141.52, 141.10, 139.51, 132.71, 131.60, 131.00, 129.02, 128.81, 127.19, 126.95, and 126.38 for *trans*-**5b**.

Scheme II



Rearrangement. Treatment of the sulfilimine *trans*-**5a** with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in benzene at room temperature gave the rearranged product **9a** (Scheme II), which was found to be sensitive to acid or alumina. Thus, attempts to obtain a pure sample of **9a** by chromatography on silica gel or alumina were unsuccessful, but treatment of the crude **9a** with silica gel gave 9-methylenethioxanthene **10**. On the other hand, treatment of *cis*- and *trans*-**5b** with DBU gave the stable rearranged product **9b**. The structures of **9a,b** were elucidated by the spectral evidence (see Experimental Section).

Crossover experiments[2] and a study on the rearrangement of 9-alkylidenethioxanthene-*N*-(*p*-toluenesulfonyl)-sulfilimines[9] firmly established that this rearrangement involves thioxanthylium ions **8** as intermediates. The intriguing question is how such intermediates may arise. As

(8) Chu, S. S. C.; Rosenstein, R. D.; Terney, A. L., Jr. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2430.

(9) Tamura, Y.; Takebe, Y.; Mukai, C.; Ikeda, M. *J. Org. Chem.*, in press.

Scheme III

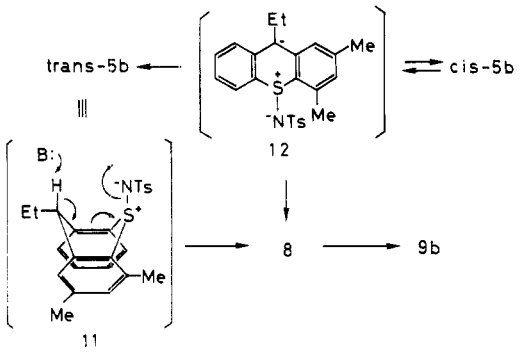


Table III. Half-Lives of 9-Ethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines in $CDCl_3$ Containing Piperidine as Base at 34 °C

compd	conformer	$t_{1/2}$	compd	conformer	$t_{1/2}$
trans-**1b**	A	~5 min	*cis*-**1b**	D	*b*
trans-**5b**	B	<30 s[a]	*cis*-**5b**	D	*b*

[a] After 30 s, *trans*-**5b** completely disappeared. [b] No reaction. This compound rearranged with DBU as base at toom temperature.

described in previous papers,[2,3] the thermodynamically more stable trans isomers (conformer A) rearranged significantly faster than the cis isomers (conformer C or D) in 9-alkylthioxanthenesulfilimines **1a,b**. These results could not be rationalized by an E1cB mechanism alone.[10] As an alternative mechanism, we suggested a concerted syn 1,4-elimination[11,12] from the trans isomers which involves a transition state such as **11** (Scheme III). This mechanism, however, requires the postulation that *trans*-**1a,b** preequilibrate with the less stable conformer B. This conformer is now in hand, and the rates of the rearrangements of *cis*- and *trans*-**5b** were measured. As expected, *trans*-**5b** (conformer B) ($t_{1/2}$ < 30 s) rearranged much more rapidly than *trans*-**1b** (conformer A) ($t_{1/2} \simeq$ 5 min), but *cis*-**5b** (conformer D) did not rearrange under the conditions used (see Table III).

Although the above data are in good agreement with our hypothesis, the faster rearrangement of *trans*-**5b** might also be explained as a reflection of the high ground-state energy level of the starting material. However, this explanation, of course, cannot be applied to the cases of **1a,b**, because *trans*-**1a,b** are more stable than *cis*-**1a,b**.

The conformation of *cis*-**5b** (conformer D) is unfavorable for such a concerted pathway, and the reaction may proceed via carbanion intermediate **12** (an E1cB mechanism) which induces either the S–N bond cleavage to give **8** or undergoes isomerization to the trans isomers and then rearranges.

Experimental Section

Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were determined with Hitachi R-22 and R-900 spectrometers, respectively, using tetramethylsilane as an internal standard. IR spectra were recorded with a Hitachi EPI-G2 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6D instrument with a direct-inlet system operating at 70 eV.

2,4,9-Trimethylthioxanthene (4a). The procedure of Price and co-workers[13] was employed. To a stirred solution of methylmagnesium iodide [prepared from methyl iodide (8.5 g, 60 mmol) and magnesium (1.5 g, 60 mmol)] in dry ether (100 mL) was added dropwise under an argon atmosphere a solution of 2,4-dimethylthioxanthone (7.2 g, 30 mmol) in dry ether (100 mL). The mixture was refluxed for 5 h. After cooling, the mixture was poured into a saturated ammonium chloride solution, and the ethereal layer was separated. The water layer was extracted with ether. The combined organic layer was washed with water, dried ($MgSO_4$), and concentrated. The residue was dissolved in ether (130 mL), and 70% perchloric acid (7 mL) was added dropwise with stirring to the ether solution at 0 °C, and stirring was continued for 1 h. A red precipitate was collected and dried. The perchlorate (8.2 g) was added portionwise to a stirred solution of $NaBH_4$ (7 g) in tetrahydrofuran (200 mL) over a 15-min period, and the reaction mixture was stirred at room temperature for 1 h. Evaporation of solvent gave a yellow solid which was dissolved in $CHCl_3$, and the solution was washed with water, dried ($MgSO_4$), and concentrated. The residual solid was recrystallized from $CHCl_3$–methanol to give **4a** (5.2 g, 73%) as colorless needles, mp 100–100.5 °C.

Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71. Found: C, 79.62; H, 6.63.

9-Ethyl-2,4-dimethylthioxanthene (4b). The procedure of Ternay[14] was employed. To a solution of **4c** (2.5 g, 11 mmol) in dry ether (75 mL) was added *n*-butyllithium in *n*-hexane solution (8 mL, 12 mmol) at 0 °C over a 10-min period. The solution gradually turned to red. After 15 min, a solution of ethyl iodide (1.8 g, 12 mmol) in dry ether (8 mL) was added to the reaction mixture. The mixture was stirred at room temperature for 24 h and diluted with water. The organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel with *n*-hexane to give **4b** (2.5 g, 89%) as colorless needles, mp 48–50 °C (from methanol).

Anal. Calcd for $C_{17}H_{18}S$: C, 80.27; H, 7.13. Found: C, 79.86; H, 7.24.

***trans*-2,4,9-Trimethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (*trans*-5a).** To a stirred solution of methanol (30 mL) and methylene chloride (15 mL) containing acetic acid (0.04 mL) was added all at once **4a** (960 mg, 4 mmol) and chloramine T trihydrate (2.26 g, 8 mmol) at room temperature. After 30 min, $CHCl_3$ (50 mL) was added to the reaction mixture, and the solution was washed with a saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residual solid was recrystallized from $CHCl_3$–*n*-hexane to give *trans*-**5a** (966 mg, 79%) as colorless plates: mp 165–167 °C; IR ($CHCl_3$) 1280, 1135, 1085 (SO_2), 945 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.8 (m, 10, aromatic protons), 5.14 (br q, 1, J = 6 Hz, H-9), 2.45, 2.36, 2.34 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 1.81 (d, 3, J = 6 Hz, 9-CH_3); mass spectrum, m/e (relative intensity) 409 (0.4, M^+), 394 (0.1), 239 (26), 238 (100), 225 (49).

Anal. Calcd for $C_{23}H_{23}NO_2S_2$: C, 67.45; H, 5.66; N, 3.42. Found: C, 67.13; H, 5.62; N, 3.44.

***trans*-9-Ethyl-2,4-dimethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (*trans*-5b).** Treatment of **4b** (254 mg, 1 mmol) with chloramine T trihydrate (564 mg, 2 mmol) in methanol (5 mL) and methylene chloride (2.5 mL) containing acetic acid (0.01 mL) afforded, after workup and column chromatography on silica gel with benzene–AcOEt (5:1), *trans*-**5b** (284 mg, 67%) as a pale yellow solid: IR ($CHCl_3$) 1285, 1160, 1090 (SO_2), 955 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.9 (m, 10, aromatic protons), 4.51 (br t, 1, J = 7 Hz, 9-H), 2.52, 2.38, 2.32 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 2.02 (quintet, 2, J = 7 Hz, 9-CH_2CH_3), 1.00 (t, 3, 9-CH_2CH_3).

This compound was thermally unstable and isomerized to *cis*-**5b** upon being heated in benzene.

2,4-Dimethylthioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimine (6) and 2,4-Dimethyl-9-(*N*-*p*-toluenesulfonamido)-thioxanthene (7). To a stirred solution of methanol (25 mL) and methylene chloride (12.5 mL) containing acetic acid (0.025 mL) was added all at once **4c** (565 mg, 2.5 mmol) and chloramine

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T trihydrate (700 mg, 2.5 mmol) at room temperature. Workup and chromatography of the resulting oil on silica gel with benzene–AcOEt (5:1) gave **7** (497 mg, 50%) as colorless crystals: mp 132.5–134 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 3350 (NH), 1330 and 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.5 (m, 10, aromatic protons), 5.52, 5.15 (AB q, 1 each, J = 8 Hz, benzylic proton and NH, respectively), 2.33, 2.29, 2.18 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3).

Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.90; H, 5.38; N, 3.56.

Further elution with the same solvent afforded **6** (377 mg, 38%) as colorless needles: mp 138–144 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 1282, 1140, 1090 (SO_2), 950 (S^+–N^-) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.7 (m, 10, aromatic protons), 4.80, 3.86 (AB q, 1 each, J = 18 Hz, benzylic protons), 2.40, 2.34, 2.30 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3); mass spectrum, m/e (relative intensity) 395 (3.9, M^+), 239 (48), 225 (100), 224 (2.0), 211 (8.6).

Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.76; H, 5.28; N, 3.59.

Thermal Isomerization of *trans*-5a. A solution of *trans*-**5a** (100 mg) in benzene (5 mL) was refluxed for 4 h and concentrated to give an equilibrium mixture of *cis*- and *trans*-**5a** in a ratio of ~3:2 by ^1H NMR spectroscopy. For the ^1H NMR spectral data of *cis*-**5a**, see Table I.

Thermal Isomerization of *trans*-5b. A solution of *trans*-**5b** (100 mg) in benzene (5 mL) was refluxed for 30 min and concentrated to give *cis*-**5b**: mp 118–120 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 1280, 1160, 1080 (SO_2), 940 (S^+–N^-) cm^{-1}; ^1H NMR ($CHCl_3$) δ 6.8–7.9 (m, 10, aromatic protons), 3.78 (t, 1, J = 7.5 Hz, 9-H), 2.39, 2.36, 2.35 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 2.35 (quintet, 2, J = 7.5 Hz, 9-CH_2CH_3), 0.98 (t, 3, J = 7.5 Hz, 9-CH_2CH_3); mass spectrum, m/e (relative intensity) 423 (1.1, M^+), 394 (4.2), 253 (57), 252 (23), 225 (100).

Anal. Calcd for $C_{24}H_{25}NO_2S_2$: C, 68.05; H, 5.95; N, 3.31. Found: C, 67.78; H, 5.91; N, 3.39.

Base-Catalyzed Rearrangement of 6 with DBU. A solution of **6** (100 mg, 0.25 mmol) and DBU (40 mg, 0.25 mmol) in benzene (8 mL) was stirred at room temperature for 30 min. The mixture was diluted with benzene (10 mL), washed with 10% HCl and water, dried ($MgSO_4$), and concentrated to give a yellow solid which was recrystallized from benzene–*n*-hexane, affording **7** (90 mg, 90%).

Base-Catalyzed Rearrangement of *trans*-5a with DBU. By using a procedure similar to that described above, 2,4,9-trimethyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**9a**) was obtained as a yellow oil from **5a** (100 mg, 0.25 mmol) and DBU (40 mg, 0.25 mmol). Because **9a** was sensitive to silica gel or alumina, the structure was based on the NMR spectrum of the crude sample of **9a** which was transformed to **10**: ^1H NMR ($CDCl_3$) δ 6.7–7.7 (m, 10, aromatic protons), 5.14 (s, 1, NH), 2.36, 2.30, 2.26 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 2.12 (s, 3, 9-CH_3).

2,4-Dimethyl-9-methylenethioxanthene (10). Crude **9a** obtained from **5a** (100 mg) was dissolved in benzene (5 mL), and silica gel (2 g) was added to the benzene solution. The reaction mixture was stirred at room temperature for 30 min. The silica gel was filtered off, and the filtrate was concentrated and chromatographed on silica gel with *n*-hexane to give **10** (38 mg, 65% from **5a**) as a light yellow oil: IR ($CHCl_3$) 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.2 (m, 6, aromatic protons), 5.41 (s, 2, vinyl protons), 2.35, 2.31 (2 s, 3 each, 2- and 4-CH_3); mass spectrum, m/e 238 (M^+).

Base-Catalyzed Rearrangement of *trans*-5b. A solution of *trans*-**5b** (120 mg, 0.28 mmol) and DBU (45 mg, 0.28 mmol) in benzene (9 mL) was stirred at room temperature for 1 h. Workup and chromatography on silica gel with benzene–AcOEt (5:1) gave 9-ethyl-2,4-dimethyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**12b**; 108 mg, 90%) as colorless crystals: mp 135–137 °C (from methanol); IR ($CHCl_3$) 3350 (NH), 1330 and 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.7–7.7 (m, 10, aromatic protons), 5.77 (s, 1, NH), 2.32, 2.23, 2.05 (3 s, 3 each, 2-CH_3, 4-CH_3, and toluene ring CH_3), 0.60 (s, 3, J = 7.5 Hz, 9-CH_2CH_3). The resonance signal for the 9-methylene was masked by the three methyl signals.

Anal. Calcd for $C_{24}H_{25}NO_2S_2$: C, 68.05; H, 5.95; N, 3.31. Found: C, 68.01; H, 5.93; N, 3.31.

Base-Catalyzed Rearrangement of *cis*-5b with DBU. A solution of *cis*-**5b** (80 mg, 0.19 mmol) and DBU (30 mg, 0.19 mmol) in benzene (8 mL) was refluxed for 4.5 h. Workup gave a yellow solid which was recrystallized from methanol, giving **12b** (71 mg, 89%).

Determination of the Half-Life of 5b in $CDCl_3$ in the Presence of Piperidine as Base at 34 °C. The sample (0.25 M in substrate) was made up in NMR tubes from weighed amounts of **5b** in $CDCl_3$ with tetramethylsilane as internal standard. The NMR spectrum was then recorded, and piperidine (8.5 mg) was added. The spectrum was immediately recorded again at intervals, the temperature being held at 34 °C. The reaction was followed by electronic integration of H-9 signals.

Registry No. *cis*-**1a**, 73839-26-6; *trans*-**1a**, 73839-27-7; *cis*-**1b**, 73839-28-8; *trans*-**1b**, 73839-29-9; **4a**, 73839-30-2; **4b**, 73839-31-3; **4c**, 17394-12-6; *cis*-**5a**, 73839-32-4; *trans*-**5a**, 73839-33-5; *cis*-**5b**, 73839-34-6; *trans*-**5b**, 73839-35-7; **6**, 73839-36-8; **7**, 73839-37-9; **9a**, 73839-38-0; **10**, 73839-39-1; **12b**, 73839-40-4; methyl iodide, 74-88-4; ethyl iodide, 75-03-6.

Molecular Rearrangements. 13.[1a] Kinetics and Mechanism of Rearrangements of Some Ring-Substituted α-Chlorostyrene Oxides and *trans*-β-Chlorostyrene Oxides

Richard N. McDonald* and Raymond C. Cousins[1b]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

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The synthesis of certain phenyl-substituted derivatives of the isomeric *trans*-β-chlorostyrene oxides (**6**) and α-chlorostyrene oxides (**7**) are reported. The kinetics of rearrangement of **6** (X = *p*-CH_3, H, *p*-Br, *m*-Cl, *p*-NO_2) to phenylchloroacetaldehydes (**12**) in CCl_4 buffered by Na_2HPO_4 and **7** (X = *p*-CH_3, H, *p*-NO_2) to ω-chloroacetophenones in CCl_4 were determined by following the rates of disappearance of the α-chloro epoxide and formation of the α-chloro carbonyl product. These substituent effects at 130 °C were correlated with σ^+ constants, yielding ρ values of −3.5 and −0.57 for the rearrangements of **6** and **7**, respectively. In nitrobenzene solvent, the $k_{C_6H_5NO_2}/k_{CCl_4}$ for **6** was 180 and for **7** was 1740, the latter solvent effect attributed to nucleophilic solvent participation. It was concluded that these thermal rearrangements of **6** and **7** occur by disrotatory C_β–O bond heterolysis to yield the corresponding α-keto carbonium–chloride ion pairs.

Early in our studies of the molecular rearrangements of α-substituted epoxides where the substituent is an electronegative atom or group, we decided to deal primarily with chlorine as that substituent. Our goal was to develop

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