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Synthesis, Stereochemistry, and Rearrangement of 9-Alkylthioxanthene *N*-(*p*-Toluenesulfonyl)sulfilimines

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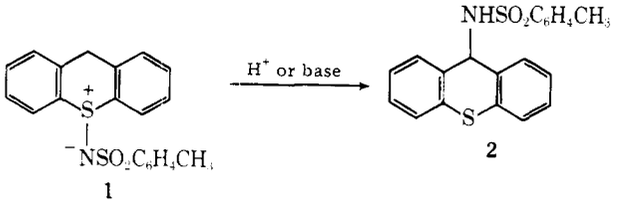
cis- and *trans*-9-Methyl- (**6a**), *cis*- and *trans*-9-ethyl- (**6b**), and *trans*-9-isopropylthioxanthene *N*-(*p*-toluenesulfonyl)sulfilimines (**6c**) were synthesized by two routes: (i) tosylation of 10-aminothioxanthenium mesitylenesulfonates, which were prepared by the reaction of the corresponding thioxanthenes with *O*-mesitylenesulfonylhydroxylamine; and (ii) reaction of the thioxanthenes with chloramine T. The stereochemistry of the sulfilimines **6a–c** was ascertained by a comparison of the NMR spectra of **6a–c** with those of the corresponding sulfoxides, whose stereochemistry has been well established, and by the thermal equilibration of **6a–c**. When refluxed in dioxane containing small amounts of concentrated hydrochloric acid, **6a–c** were reduced to the corresponding thioxanthenes. Upon treatment with DBU in benzene *cis*- and *trans*-**6a,b** and *trans*-**6c** rearranged to the corresponding 9-alkyl-9-(*N*-*p*-toluenesulfonamido)thioxanthenes. The rates of the rearrangement decreased in the order *trans*-**6a** > *trans*-**6b** > *cis*-**6a** > *cis*-**6b** > *trans*-**6c**.

Thioxanthene *N*-(*p*-toluenesulfonyl)sulfilimine (**1**) undergoes acid- and base-catalyzed rearrangement to 9-*N*-(*p*-toluenesulfonamido)thioxanthene (**2**).[1,2] We have now examined the effect of the 9-alkyl substituents on this rearrangement. In this paper the synthesis and stereochemistry of 9-alkylthioxanthene *N*-(*p*-toluenesulfonyl)sulfilimines (**6a–c**), and their behavior toward acid and base, are described.



Results and Discussion

Synthesis. 9-Alkylthioxanthene *N*-(*p*-toluenesulfonyl)-sulfilimines (**6a–c**) were synthesized by two routes as shown in Scheme I: (method A) tosylation of 10-aminothioxanthenium mesitylenesulfonates (**4a–c**),[3] which were prepared by the reaction of the thioxanthenes **3a–c** with *O*-mesitylenesulfonylhydroxylamine (MSH);[4] and (method B) reaction of **3a–c** with chloramine T.

Treatment of the thioxanthenes **3a–c** with 1 equiv of MSH in methylene chloride at room temperature gave the corresponding *S*-amine salts **4a–c**. Thus, 9-methylthioxanthene (**3a**) afforded two isomeric *S*-amine salts **4a** in a cis/trans ratio of ~3:5 (by NMR spectroscopy), which could be separated by fractional recrystallization. Tosylation of each isomer gave pure *cis*- and *trans*-**6a** in 8 and 19% overall yields, respectively. 9-Ethylthioxanthene (**3b**) also gave a mixture of cis and trans isomers of the *S*-amine salts **4b**. This mixture was directly converted into two isomeric *N*-(*p*-toluenesulfonyl)-sulfimines **6b**, which were separated by column chromatography to give pure *cis*- and *trans*-**6b** in 9 and 31% overall yields, respectively. 9-Isopropylthioxanthene (**3c**) produced exclusively the trans isomer of the *S*-amine salt **4c** in 73% yield. Passing an ethanolic solution of *trans*-**4c** through a

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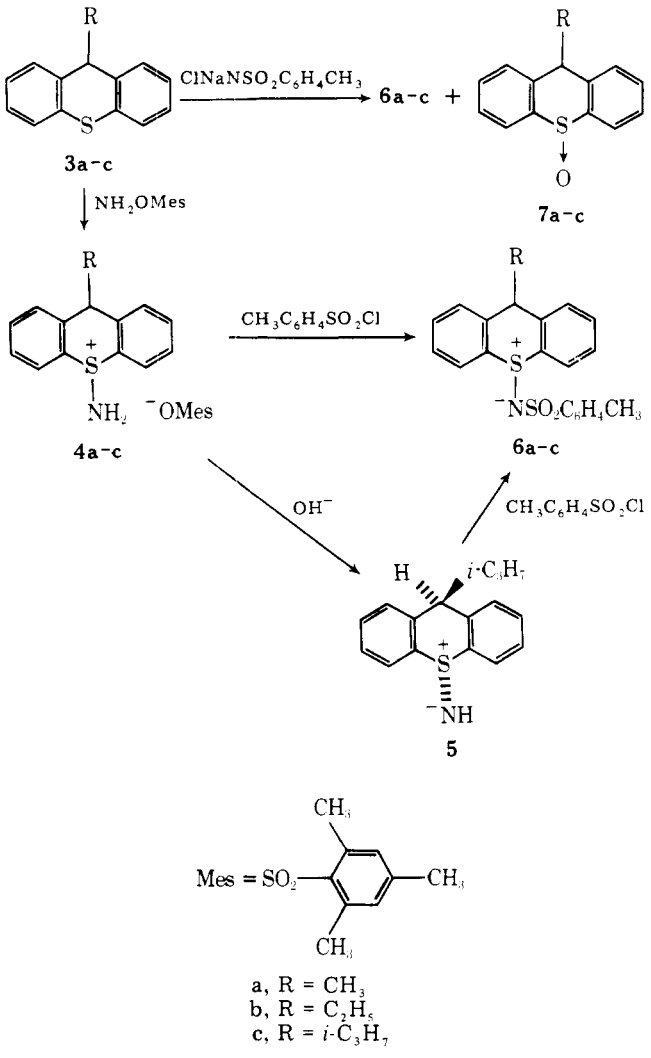
Scheme I



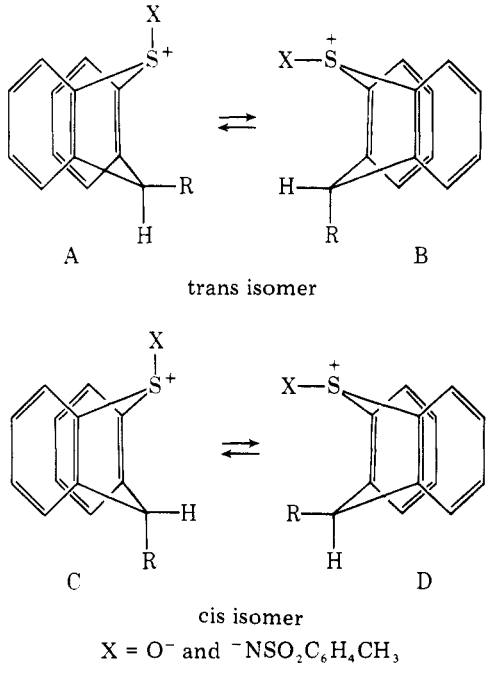
column of ion-exchange resin IRA-410 (OH^- form) gave stable free sulfilimine **5**. Tosylation of either *trans*-**4c** or **5** gave *trans*-**6c** in 35 and 64% yields, respectively.

The reaction of **3a** with 1 equiv of chloramine T gave a mixture of two isomeric sulfilimines **6a** (cis/trans ~1:5) and two isomeric sulfoxides **7a** (cis/trans ~1:5), from which *trans*-**6a** was isolated as a pure compound by a combination of column chromatography and recrystallization. Similarly, **3b,c** gave mixtures of sulfilimines **6b,c** and sulfoxides **7b,c**, respectively, but the reaction proceeded in a stereospecific manner to give the trans isomers only. The formation of the sulfoxides **7a–c**, however, was markedly suppressed by the use of 2 equiv of chloramine T, as shown in Table I. The last method was used for the synthesis of *trans*-**6a–c**.

The structures of **6a–c** were apparent from the spectral data. The mass spectra of all the sulfilimines showed the molecular ion peak and four diagnostically important fragment ions due to $(M - R)^+$, $(M - CH_3C_6H_4SO_2NH)^+$, $(M - CH_3C_6H_4SO_2NH_2)^+$, and $(M - CH_3C_6H_4SO_2NR)^+$. The IR spectra showed strong absorption at 1284–1302 (with splitting), 1142–1146, and 1085–1088 cm^{-1}, typical of an SO_2 group, and at 940–975 cm^{-1}, a characteristic band for an $S^+–N^-$ group.[6] The final confirmation of these structures was given by the NMR spectra, which will be discussed in detail (vide infra).

Stereochemistry. The stereochemical relationship between the 9-alkyl and $S^+–N^-SO_2C_6H_4CH_3$ groups in the sulfilimines **6a–c** was ascertained by a comparison of the NMR spectra with those of the corresponding sulfoxides **7a–c**, whose stereochemistry has been well established.[7–12]

Ternay and co-workers,[7–9] in their extensive investigation of the stereochemistry of 9-alkylthioxanthene 10-oxides **7a–c**, showed that the S–O group prefers the equatorial conformations (A and C) and governs the conformation of the stereoisomers in the 9-methyl derivative, while the 9-alkyl group prefers the axial conformations (A and D) and governs the



conformation of the isomers in the derivatives with the 9-alkyl group larger than methyl. This generalization was found to be valid in the sulfilimines **6a–c**.

The chemical shifts of C_9–H and C_9–alkyl group in the NMR spectra of each pair of **6a–c** and **7a–c** were markedly similar (Table II). Although this alone defines the stereochemistry of **6a–c**, the following simple analyses of the NMR spectra also provided a firm basis for the assignments of the stereochemistry. The equatorial C_9–H signal in *trans*-**6a** and **-7a** (conformer A) occurs at 0.49–0.57 ppm lower field than

Table I. Product Distribution in the Reaction of 3a–c with Chloramine T

thioxanthene	R	registry no.	chloramine T, mol	% *trans*-**6**[a,d]	% *trans*-**7**[a,e]
3a	CH_3	16860-11-0	1	44[b]	37[b]
			2	53[b]	19[c]
3b	C_2H_5	28612-38-6	1	52	44
			2	68	2
3c	i-C_3H_7	28612-39-7	1	43	32
			2	68	2

[a] Isolated yield. [b] Containing ~20% of the cis isomer (by NMR spectroscopy). [c] Interestingly, the cis isomer was not detected (on the NMR spectrum). [d] Registry no.: *trans*-**6a**, 69381-65-3; *trans*-**6b**, 69381-66-4; *trans*-**6c**, 69381-67-5. [e] Registry no.: *trans*-**7a**, 19018-81-6; *trans*-**7b**, 56195-78-9; *trans*-**7c**, 56195-79-0.

Table II. NMR Spectra (60 MHz, in $CDCl_3$) of 9-Alkylthioxanthene *N*-(*p*-Toluenesulfonyl)sulfilimines (6a–c) and 9-Alkylthioxanthene 10-Oxides (7a–c)

compd	registry no.	preferred conformation	chemical shift	
			C_9–H	R
cis-**6a**	69381-68-6	C	3.86 (q)	1.90 (3, d)
trans-**6a**		A	4.35 (q)	1.43 (3, d)
cis-**7a**	19018-80-5	C	3.68 (q)	1.90 (3, d)[a]
trans-**7a**		A	4.25 (q)	1.36 (3, d)[a]
cis-**6b**	69381-69-7	D	3.80 (t)	2.28 (2, m), 1.04 (3, t)
trans-**6b**		A	4.06 (t)	1.69 (2, m), 0.87 (3, t)
cis-**7b**	56195-77-8	D	3.78 (t)	2.28 (2, m), 1.08 (3, t)[b]
trans-**7b**		A	3.98 (t)	1.62 (2, m), 0.88 (3, t)[b]
trans-**6c**		A	3.72 (d)	1.75 (1, m), 0.82 (6, d)
cis-**7c**	55235-94-4	D	3.49 (d)	2.70 (1, m), 0.93 (6, d)[b]
trans-**7c**		A	3.64 (d)	1.61 (1, m), 0.80 (6, d)[b]

[a] Taken from ref 7. [b] A private communication from Professor A. L. Ternay, Jr., to whom we are indebted.

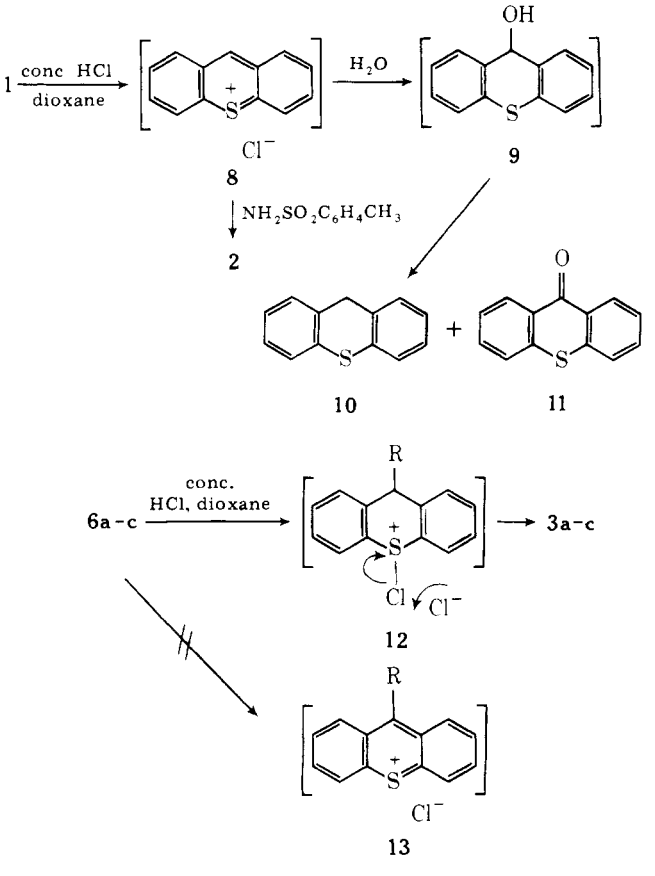
the axial C_9–H signal in *cis*-**6a** and -**7a** (conformer C), and the axial C_9–CH_3 signal in *trans*-**6a** and -**7a** appears at 0.47–0.54 ppm higher field than the equatorial C_9–CH_3 signal in *cis*-**6a** and -**7a**. The chemical shifts of these protons are affected mainly by the diamagnetic anisotropy of the benzene rings of the thioxanthene molecule; the equatorial C_9–H or –CH_3 should experience deshielding and the axial C_9–H or –CH_3 experience shielding. On the other hand, the difference (0.20–0.26 ppm) between the chemical shifts of the C_9–H in *cis*- (conformer D) and *trans*- (conformer A) -**6b** or -**7b** is smaller than that observed in the 9-methyl derivatives, in accordance with the assigned structures in which the C_9–H of both the isomers occupies an equatorial position. In addition, the signal of the methylene protons of the 9-ethyl group in *cis*-**6b** and -**7b** appears at 0.59–0.66 ppm lower field than the same protons in the corresponding trans isomers, a consequence of the former being in proximity to the axial S^+–$N^-SO_2C_6H_4CH_3$ or S^+–O^- group. Similar relationships were found in the 9-isopropyl derivatives **6c** and **7c**. The preferred conformations of the stereoisomers of the sulfilimines and sulfoxides are summarized in Table II.

Further support for these stereochemical assignments was obtained by the thermal equilibration of the sulfilimines **6a–c**. It is well known that optically active sulfilimines racemize upon heating in various solvents at 80–100 °C.[13] Thus, when refluxed in benzene for 10 h, both *cis*- and *trans*-**6a** gave an equilibrium mixture consisting of *cis*- and *trans*-**6a** in a ratio of ~1:2, and *cis*-**6b** isomerized completely to the thermodynamically more stable *trans*-**6b**. On the other hand, *trans*-**6b** and *trans*-**6c** were stable under these conditions. Apparently, the driving force for the complete isomerization of *cis*-**6b** to *trans*-**6b** is derived from the relief of the steric repulsion between two boat-axial substituents in *cis*-**6b**.

Acid-Catalyzed Rearrangement. As noted previously, thioxanthene *N*-(*p*-toluenesulfonyl)sulfilimine (**1**) undergoes ready rearrangement to 9-(*N*-*p*-toluenesulfonamido)thioxanthene (**2**) by refluxing in benzene containing small amounts of concentrated hydrochloric acid.[2] When the reaction was carried out in dioxane containing concentrated hydrochloric acid (homogeneous system), **1** gave not only **2** (19%) but also essentially equal amounts of thioxanthene (**10**; 35%) and thioxanthone (**11**; 40%). A mechanistic rationalization involves the assumption that **1** is first converted to thioxanthylium salt **8**, which is attacked competitively by *p*-toluenesulfonamide and water to give **2** and 9-thioxanthenol (**9**). Disproportionation of the latter gives **10** and **11**.[14]

Upon refluxing in dioxane containing concentrated hydrochloric acid, the sulfilimines **6a–c** were reduced in quantitative yields to the corresponding thioxanthenes **3a–c**. No obvious differences were found in reactivity of the two isomeric series.[15] These results suggest that the acid-catalyzed

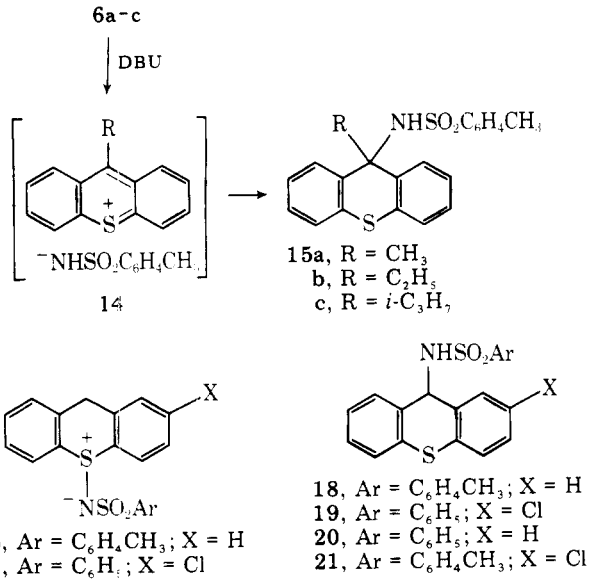
Scheme II



rearrangement of thioxanthene *N*-(*p*-toluenesulfonyl)sulfilimines is subjected to pronounced steric rate retardation. Because the presence of the 9-alkyl substituents is expected to retard significantly the rate of the transformation process to thioxanthylium ion[13] due to nonbonded interaction between the 9-alkyl group and two peri-hydrogen atoms in the transition state in its production, reduction of the sulfilimines would become the kinetically favored reaction pathway. Reduction of **6a–c** may proceed via intermediates **12**.[16]

Base-Catalyzed Rearrangement. The sulfilimine **1** undergoes almost quantitative conversion to **2** upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene at room temperature.[2] The sulfilimines *cis*- and *trans*-**6a,b** were found to behave analogously to give the corresponding rearranged products **15a,b** in high yields (Scheme III). Similar treatment of *trans*-**6c** led to no reaction, but at refluxing temperature it was converted to the rearranged product **15c**. The structures of **15a–c** were elucidated by spectral evidence (see Experimental Section).

Scheme III



Interestingly, the rate of the rearrangement was found to be markedly affected by both the steric bulk and stereochemistry of the 9-substituent. The reaction was monitored using ^1H NMR in deuteriochloroform in the presence of piperidine as base. The results summarized in Table III indicate that (i) the more stable trans-isomers rearrange significantly faster than the cis isomers with the exception of 9-isopropyl derivative **6c**, and (ii) the increase of the steric bulk of the 9-alkyl group decreases the rate of the rearrangement.

Previously we suggested that the base-catalyzed rearrangement (**1** → **2**) is explained in terms of the intermediacy of thioxanthylium ion **14** (R = H).[2] This is based on the fact that added benzenesulfonamide anion is partially incorporated into the rearranged product **2** when the reaction of **1** was carried out in the presence of sodium benzenesulfonamide in dimethylformamide.[17] This was confirmed by a crossover experiment with a mixture of thioxanthene *N*-(*p*-toluenesulfonyl)sulfilimine (**16**) and 2-chlorothioxanthene *N*-(benzenesulfonyl)sulfilimine (**17**) in dimethylformamide in the presence of DBU, which gave crossover products **18–21**, along with the corresponding thioxanthones. However, the reaction in benzene gave no crossover products; only **18** and **19** were obtained. These observations clearly indicate that the reaction mechanism shifts from intramolecular to intermolecular by changing from nonpolar solvent to polar.

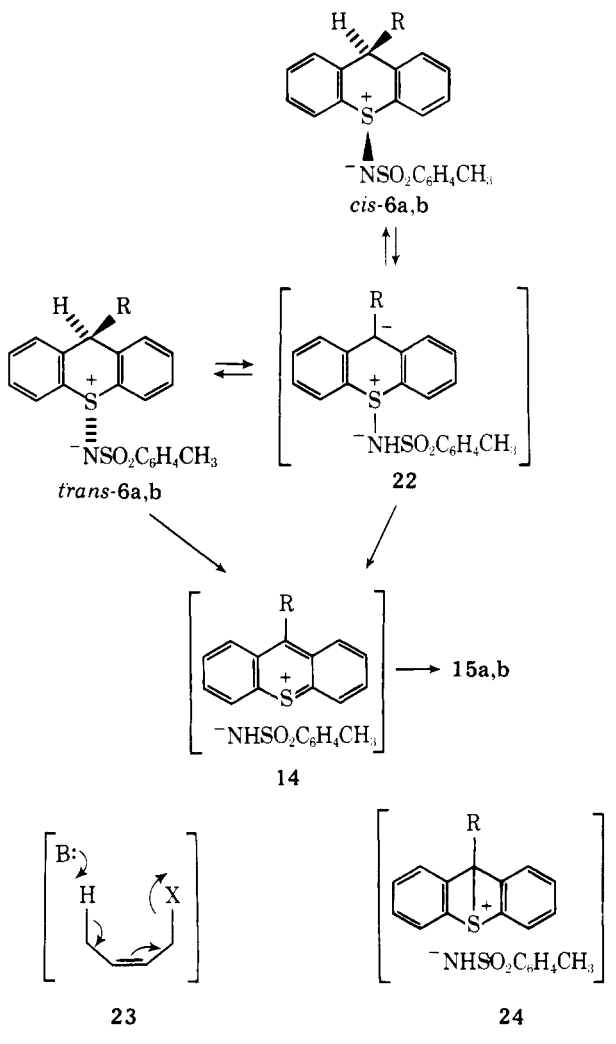
A simple mechanistic rationalization would involve an initial formation of carbanions **22**, which induce sulfur–nitrogen cleavage to give thioxanthylium ions **14**, followed by intra- or intermolecular recombination process to give **15**, depending upon the degree of dissociation of the ions in solvent used. If this mechanism is correct, some steric or stereoelectronic factors must operate before the formation of the carbanions **22**. The work of Cristol[18] on the elimination of *cis*- and *trans*-dihydroanthracene-9,10-diols demonstrated that the relative rates of elimination are interpreted in terms

Table III. The Half-lives of 6a-c in $CDCl_3$ Containing Piperidine as Base at 34 °C

compd	$t_{1/2}$	compd	$t_{1/2}$
trans-**6a**	<1 min	*cis*-**6a**	~85 min
trans-**6b**	~5 min	*cis*-**6b**	no reaction[a]
trans-**6c**	no reaction[b]		

[a] This compound rearranged by using DBU as base at room temperature. [b] This compound rearranged by using DBU as base in refluxing benzene.

Scheme IV



of preferred attack by base on the axial C_9 (or C_{10}) hydrogen. Unfortunately the relative rates of the reaction of *cis*- and *trans*-**6a,b** are difficult to rationalize on the basis of this mechanism alone; *trans*-**6a** (the preferred conformer has no axial hydrogen) rearranges more rapidly than does *cis*-**6a** (the preferred conformer has an axial hydrogen), and *trans*-**6b** rearranges significantly faster than *cis*-**6b** in spite of the fact that both the preferred conformations of *cis*- and *trans*-**6b** have only equatorial hydrogen.

An intriguing alternative to the initial cleavage of the C_9–H bond would involve a concerted process via a transition state such as **23**, which is analogous with one proposed for the S_N2' displacement reaction. This mechanism requires the postulation that *trans*-**6a,b** equilibrate with the less stable conformer B, which is favorable in a concerted syn process (but has higher energy due to a nonbonded interaction between the equatorial C_9–alkyl group and peri hydrogens). A similar process has been postulated by Cristol[19] in order to interprete the finding that the syn 1,4-elimination from dihydroanthracene-9,10-diols is more rapid than the corresponding anti (but later he presented evidence against this hypothesis[18]). Very recently Hill and Bock[20] have reported unambiguous examples of syn 1,4-elimination in cyclohexenyl systems. In the case of cis isomers, neither conformer C nor D is favorable for such concerted pathway and the reaction may proceed via carbanionic intermediates **22**, which induce S–N bond cleavage to give **14**, or undergo isomerization[21] to the more stable trans isomers, which can rearrange (Scheme IV). An entirely different pathway can be imagined in which anchimerically assisted decomposition of *trans*-**6a,b** would play

a key role. This mechanism would involve intramolecular S_N2 reaction on sulfur to form transient ions **24**, which may collapse to give **15**.

An increase of the steric bulk of the 9-alkyl group should increase the nonbonded interaction between the 9-alkyl group and peri-hydrogen atoms in the conformer B or in the transition state to thioxanthylium ion **14**. This steric interaction is responsible for the low reactivity of *trans*-**6c**.[22]

These mechanistic arguments are entirely speculative at this stage and many mechanistic questions still remain to be solved. We hope to pursue some of these problems in continuation of this work.

Experimental Section

Melting points are uncorrected. NMR spectra were determined with a Hitachi R-20A spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with a Hitachi EPI-G3 spectrophotometer. Low and high resolution mass spectra were obtained with a Hitachi RMU-6MG and JEOL-JMS-OISG instrument with a direct inlet system at 70 and 75 eV, respectively.

9-Methyl- (**3a**),[23] 9-ethyl- (**3b**),[7] and 9-isopropylthioxanthenes (**3c**)[7] were prepared following procedures reported in the literatures.

***cis*- and *trans*-10-Amino-9-methylthioxanthenium Mesitylenesulfonates (4a).** A solution of MSH (1.08 g) in CH_2Cl_2 (30 mL) was added to an ice-cooled and stirred solution of **3a** (1.06 g) in CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for 2 h and then ether (60 mL) was added. The precipitated crystals were collected and recrystallized from methanol–AcOEt to yield a mixture of *cis*- and *trans*-**4a** (1.96 g, 91%, cis/trans ~3:5 by NMR spectroscopy). CH_2Cl_2 (20 mL) was added to the mixture and the insoluble crystals were collected and recrystallized from methanol–acetone to afford pure *trans*-**4a** (1.12 g, 52%) as white crystals: mp 188–189 °C; NMR (Me_2SO-d_6) δ 7.5–8.1 (m, 8, aromatic protons), 7.85 (brs, 2, NH_2), 6.77 (s, 2, mesitylene ring protons), 4.70 (q, 1, C_9–H, J = 7.3 Hz), 2.52 (s, 6, mesitylene ring CH_3), 2.17 (s, 3, mesitylene ring CH_3), 1.38 (d, 3, 9-CH_3, J = 7.3 Hz).

Anal. Calcd for $C_{23}H_{25}NO_3S_2$: C, 64.62; H, 5.90; N, 3.28. Found: C, 64.46; H, 5.93; N, 3.28.

The CH_2Cl_2 mother liquor was evaporated and the residue was recrystallized from acetone–CH_2Cl_2 to afford pure *cis*-**4a** (0.42 g, 20%) as white crystals: mp 157–159 °C; NMR (Me_2SO-d_6) δ 7.5–8.1 (m, 8, aromatic protons), 7.85 (brs, 2, NH_2), 6.77 (s, 2, mesitylene ring protons), 4.29 (q, 1, C_9–H, J = 7.3 Hz), 2.52 (s, 6, mesitylene ring CH_3), 2.17 (s, 3, mesitylene ring CH_3), 1.81 (d, 3, 9-CH_3, J = 7.3 Hz).

Anal. Calcd for $C_{23}H_{25}NO_3S_2$: C, 64.62; H, 5.90; N, 3.28. Found: C, 64.61; H, 5.97; N, 3.30.

***cis*- and *trans*-10-Amino-9-ethylthioxanthenium Mesitylenesulfonates (4b).** By using the similar procedure as described above, **4b** (1.9 g, 76%) was obtained as a mixture of cis and trans isomers from **3b** (1.13 g) and MSH (1.08 g). The crude product was used for tosylation without further purification. A sample for microanalysis was obtained by two recrystallizations from methanol–AcOEt: mp 194–197 °C.

Anal. Calcd for $C_{24}H_{27}NO_3S_2$: C, 65.28; H, 6.16; N, 3.17. Found: C, 65.15; H, 6.13; N, 3.20.

***trans*-10-Amino-9-isopropylthioxanthenium Mesitylenesulfonate (4c).** By using the similar procedure as described for the preparation of **4a**, *trans*-**4c** (330 mg, 73%) was obtained from **3c** (240 mg) and MSH (215 mg): mp 218–220 °C (from methanol–AcOEt); NMR (Me_2SO-d_6) δ 7.1–8.3 (m, 10, aromatic protons and NH_2), 6.62 (s, 2, mesitylene ring protons), 3.80 (d, 1, C_9–H, J = 9 Hz), 2.35 (s, 6, mesitylene ring CH_3), 2.11 (s, 3, mesitylene ring CH_3), 1.4–2.0 [m, 1, C**H**(CH_3)$_2$], 0.81 [d, 6, CH(C**H**$_3$)$_2$, J = 6.8 Hz].

Anal. Calcd for $C_{25}H_{29}NO_3S_2$: C, 65.90; H, 6.42; N, 3.07. Found: C, 65.75; H, 6.36; N, 3.24.

***trans*-9-Isopropylthioxanthene Sulfilimine (5).** A solution of *trans*-**4c** (150 mg) in methanol was passed through a column of Amberite IRA-410 ion-exchange resin (strong base, OH^- form) followed by evaporation of the solvent to give stable **5** (80 mg, 95%): mp 77–79 °C (from benzene-*n*-hexane); IR (KCl) 912 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.9–8.2 (m, 2, aromatic protons), 7.6–7.2 (m, 6, aromatic protons), 3.63 (d, 1, C_9–H, J = 10 Hz), 1.84 (s, 1, NH), 1.5–2.1 [m, 1, C**H**(CH_3)$_2$], 0.83 [d, 6, CH(C**H**$_3$)$_2$, J = 7 Hz].

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{16}H_{17}NS$, 255.1081; found, 255.1034.

***cis*- and *trans*-9-Methylthioxanthene *N*-(*p*-Toluenesulfonylsulfilimines (6a). Method A.** To a stirred solution of *cis*-**4a** (100 mg) in dimethylformamide (5 mL) was added all at once *p*-toluenesulfonyl chloride (47 mg) and K_2CO_3 (47 mg). The mixture was stirred at room temperature for 2 h and concentrated in vacuo, and $CHCl_3$ (50 mL) was added to the residue. The solution was washed with water, dried ($MgSO_4$), and concentrated. The residual solid was purified by preparative TLC on silica gel with AcOEt–benzene (1:5) as solvent to give *cis*-**6a** (35 mg, 39%): mp 208–210 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 1301, 1143, 1088 (SO_2), 968 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.05–8.05 (m, 12, aromatic protons), 3.86 (q, 1, C_9–H, J = 7.3 Hz), 2.28 (s, 3, toluene ring CH_3), 1.90 (d, 3, 9-CH_3, J = 7.3 Hz); mass spectrum *m/e* (rel intensity) 381 (1.4, M^+), 366 (0.3), 211 (100), 210 (18), 197 (23).

Anal. Calcd for $C_{21}H_{19}NO_2S_2$: C, 66.11; H, 5.02; N, 3.67. Found: C, 66.06; H, 4.94; N, 3.70.

Similarly, *trans*-**6a** (33 mg, 37%) was obtained from *trans*-**4a** (100 mg): mp 172–173 °C (from methanol–benzene); IR ($CHCl_3$) 1300, 1142, 1085 (SO_2), 960, 975 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.1–8.15 (m, 12, aromatic protons), 4.35 (q, 1, C_9–H, J = 7.3 Hz), 2.38 (s, 3, toluene ring CH_3), 1.43 (d, 3, 9-CH_3, J = 7.3 Hz); mass spectrum *m/e* (rel intensity) 381 (1.1, M^+), 366 (0.4), 211 (78), 210 (100), 197 (49).

Anal. Calcd for $C_{21}H_{19}NO_2S_2$: C, 66.11; H, 5.02; N, 3.67. Found: C, 65.92; H, 5.21; N, 3.79.

Method B. To a stirred solution of methanol (5 mL) and CH_2Cl_2 (2.5 mL) containing acetic acid (0.01 mL) was added all at once **3a** (212 mg) and chloramine T·$3H_2O$ (564 mg) at room temperature. After 60 min, CH_2Cl_2 (20 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 oil was purified by preparative TLC on silica gel with benzene–AcOEt (5:1) as solvent to give **6a** (201 mg, 53%, cis/trans ~1:5 by NMR spectroscopy) and *trans*-9-methylthioxanthene 10-oxide (*trans*-**7a**; 43 mg, 19%). Two recrystallizations of the cis/trans mixture of **6a** from methanol gave pure *trans*-**6a**, mp 172–173 °C.

Reaction of **3a** (226 mg) with chloramine T·$3H_2O$ (282 mg) gave **6a** (168 mg, 44%, cis/trans ~1:5) and **7a** (84 mg, 37%, cis/trans ~1:5).

***cis*- and *trans*-9-Ethylthioxanthene *N*-(*p*-Toluenesulfonyl)-sulfilimines (6b). Method A.** Analogous treatment of **4b** (100 mg, as a mixture of cis and trans isomers) with *p*-toluenesulfonyl chloride (433 mg) and K_2CO_3 (313 mg) gave a mixture of *cis*- and *trans*-**6b**, which was separated by preparative TLC on silica gel with AcOEt–benzene (1:5) as solvent to give fast-moving *trans*-**6b** (356 mg, 41%) and slow-moving *cis*-**6b** (121 mg, 12%).

cis-**6b** had: mp 176–178 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 1284, 1142, 1088 (SO_2), and 955, 940 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.05–7.9 (m, 12, aromatic protons), 3.80 (t, 1, C_9–H, J = 7 Hz), 2.39 (s, 3, toluene ring CH_3), 2.28 (m, 2, 9-C**H**$_2$CH$_3$), 1.04 (t, 3, 9-CH_2C**H**$_3$, J = 7 Hz); mass spectrum *m/e* (rel intensity) 395 (1.1, M^+), 366 (5.6), 225 (100), 224 (9), 197 (46).

Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.63; H, 5.21; N, 3.49.

trans-**6b** had: mp 201–203 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 1300, 1145, 1088 (SO_2), 967 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.1–8.2 (m, 12, aromatic protons), 4.06 (t, 1, C_9–H, J = 10 Hz), 2.38 (s, 3, toluene ring CH_3), 1.69 (m, 2, 9-C**H**$_2$CH$_3$), 0.87 (t, 3, 9-CH_2C**H**$_3$, J = 9 Hz); mass spectrum *m/e* (rel intensity) 395 (1.2, M^+), 366 (6.1), 225 (100), 224 (22), 197 (49).

Anal. Calcd for $C_{22}H_{21}NO_2S_2$: C, 66.81; H, 5.35; N, 3.54. Found: C, 66.87; H, 5.36; N, 3.70.

Method B. Reaction of **3b** (226 mg) with chloramine T·$3H_2O$ (564 mg) gave *trans*-**6b** (267 mg, 68%), mp 201–203 °C, and *trans*-9-ethylthioxanthene 10-oxide (**7b**; 6 mg, 2%), mp 111.5–112 °C (lit.[9,10] 111.0–112.0 °C).

Reaction of **3b** (226 mg) with chloramine T·$3H_2O$ (282 mg) gave *trans*-**6b** (216 mg, 52%) and *trans*-**7b** (111 mg, 44%).

***trans*-9-Isopropylthioxanthene *N*-(*p*-Toluenesulfonyl)sulfilimine (6c). Method A. From *trans*-4c.** Analogous treatment of *trans*-**4c** (200 mg) with *p*-toluenesulfonyl chloride (88 mg) and K_2CO_3 (61 mg) gave *trans*-**6c** (62 mg, 35%): mp 190–192 °C (from benzene-*n*-hexane); IR ($CHCl_3$) 1302, 1146, 1088 (SO_2), 970 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.1–8.1 (m, 12, aromatic protons), 3.72 (d, 1, C_9–H, J = 7 Hz), 2.39 (s, 3, toluene ring CH_3), 1.75 [m, 1, 9-C**H**(CH_3)$_2$], 0.82 [d, 6, 9-CH(C**H**$_3$)$_2$, J = 10 Hz]; mass spectrum *m/e* (rel intensity) 409 (0.6, M^+), 366 (1), 239 (54), 238 (2.7), 197 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{23}H_{23}NO_2S_2$, 409.1170; found, 409.1144.

From 5. A solution of **5** (50 mg) and *p*-toluenesulfonyl chloride (39 mg) in methanol (5 mL) was stirred at room temperature for 1 h. The reaction mixture was concentrated and $CHCl_3$ (40 mL) was added to the residue. The solution was washed with a saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residual solid was pu-

rified by preparative TLC on silica gel with benzene–AcOEt (10:1) as solvent to give *trans*-**6c** (51 mg, 64%): mp 190–192 °C.

Method B. Reaction of **3c** (240 mg) with chloramine T·3H_2O (564 mg) gave *trans*-**6c** (277 mg, 68%), mp 190–192 °C, and *trans*-9-isopropylthioxanthene 10-oxide (**7c**) (6 mg, 2%), mp 98–99 °C (lit.[9,10] 101.0–102.5 °C).

Reaction of **3c** (240 mg) with chloramine T·3H_2O (282 mg) gave *trans*-**6c** (176 mg, 43%) and *trans*-**7c** (81 mg, 32%).

Thermal Isomerization of *cis*-6a and *trans*-6a. A solution of *cis*-**6a** (30 mg) in benzene (3 mL) was refluxed for 10 h and concentrated to give an equilibrium mixture of *cis*- and *trans*-**6a** in a ratio of ~1:2 by NMR spectroscopy.

Similar treatment of *trans*-**6a** gave an equilibrium mixture of *cis*- and *trans*-**6a** (ratio ~1:2).

Thermal isomerization of *cis*-6b and *trans*-6b. A solution of *cis*-**6b** (20 mg) in benzene (2 mL) was refluxed. Analysis by TLC showed that *cis*-**6b** was completely converted into *trans*-**6b** after 10 h. The benzene solution was concentrated and the residue was purified by preparative TLC on silica gel with benzene–AcOEt (5:1) to give *trans*-**6b** (12 mg).

Reaction of 1 with Concentrated HCl in Dioxane. A solution of **1** (100 mg) in dioxane (5 mL) containing concentrated HCl (0.1 mL) was refluxed for 2 h. The reaction mixture was concentrated, neutralized with a 5% NaOH solution, and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel. Elution with benzene gave thioxanthene (**10**; 19 mg, 35%) and thioxanthone (**11**) (23 mg, 40%). Further elution with the same solvent gave 9-(*N*-*p*-toluenesulfonylamido)thioxanthene (**2**; 19 mg, 19%).

Reaction of *trans*-6a with Concentrated HCl in Dioxane. A solution of *trans*-**6a** (50 mg) in dioxane (5 mL) containing concentrated HCl (0.1 mL) was refluxed for 2 h. The reaction mixture was concentrated, neutralized with a 5% NaOH solution, and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residual solid was chromatographed on silica gel with *n*-hexane to give 9-methylthioxanthene (**3a**; 24 mg, 86%). A similar result was obtained from *cis*-**6a**.

Reaction of *trans*-6b with Concentrated HCl in Dioxane. A solution of *trans*-**6b** (110 mg) in dioxane (5 mL) containing concentrated HCl (0.1 mL) was refluxed for 3.5 h. Workup as described above gave 9-ethylthioxanthene (**3b**; 53 mg, 84%). A similar result was obtained from *cis*-**6b**.

Reaction of *trans*-6c with Concentrated HCl in Dioxane. A solution of *trans*-**6c** (30 mg) in dioxane (3 mL) containing concentrated HCl (0.1 mL) was refluxed for 4 h. Workup as described above gave 9-isopropylthioxanthene (**3c**; 11 mg, 62%).

Reaction of *cis*- and *trans*-6a with Base in Benzene. A solution of *trans*-**6a** (100 mg) and DBU (40 mg) in benzene (5 mL) was stirred at room temperature for 10 min (the reaction was followed by TLC). The mixture was diluted with benzene (45 mL), washed with 5% HCl solution and water, dried ($MgSO_4$), and concentrated. The residue was purified by preparative TLC on silica gel with AcOEt–benzene (1:6) to give 9-methyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**15a**; 87 mg, 87%): mp 163–165 °C (from methanol); IR (KCl) 3250 (NH), 1322, 1162, 1088 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.5–7.55 (m, 12, aromatic protons), 4.90 (s, 1, NH), 2.32 (s, 3, toluene ring CH_3), 2.23 (s, 3, 9-CH_3); mass spectrum *m/e* 381 (M^+).

Anal. Calcd for $C_{21}H_{19}NO_2S_2$: C, 66.11; H, 5.02; N, 3.67. Found: C, 66.22; H, 5.08; N, 3.49.

Similar treatment of *cis*-**6a** (50 mg) gave **15a** (41 mg, 82%).

Reaction of *trans*-6a with Base in Methanol. A solution of *trans*-**6a** (100 mg) and DBU (40 mg) in methanol (5 mL) was stirred at room temperature for 10 min. Workup as described above gave 9-methoxy-9-methylthioxanthene (52 mg, 78%): mp 120–122 °C (from methanol); NMR ($CDCl_3$) δ 7.2–7.9 (m, 8, aromatic protons), 3.09 (s, 3, OCH_3), 1.55 (s, 3, 9-CH_3); mass spectrum *m/e* 242 (M^+).

Anal. Calcd for $C_{15}H_{14}OS$: C, 74.36; H, 5.83. Found: C, 74.32; H, 5.68.

Reaction of *cis*- and *trans*-6b with Base in Benzene. Treatment of *trans*-**6b** (100 mg) with DBU (38 mg) in benzene (5 mL) for 50 min at room temperature gave 9-ethyl-9-(*N*-*p*-toluenesulfonamido)-thioxanthene (**15b**; 95 mg, 95%): mp 126–128 °C (from methanol); IR (KCl) 3250 (NH), 1340, 1159, 1090 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.85–7.65 (m, 12, aromatic protons), 5.85 (s, 1, NH), 2.34 (s, 3, toluene ring CH_3), 2.33 (q, 2, 9-C**H**$_2$CH$_3$, J = 6.8 Hz), 0.61 (t, 3, 9-CH_2C**H**$_3$, J = 6.8 Hz).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{22}H_{21}NO_2S_2$, 395.1013; found, 395.0992.

Similar treatment of *cis*-**6b** (50 mg) with DBU (20 mg) in benzene (3 mL) for 50 min at room temperature gave **15b** (47 mg, 94%).

Reaction of *trans*-6c with Base in Benzene. A solution of *trans*-**6c** (20 mg) and DBU (9 mg) in benzene (2 mL) was refluxed and workup gave 9-isopropyl-9-(*N*-*p*-toluenesulfonamido)thioxanthene (**15c**; 17 mg): mp 214.5–215.5 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 3335 (NH), 1320, 1152, 1095 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.5 (m, 12, aromatic protons), 5.79 (s, 1, NH), 2.38 (s, 3, toluene ring CH_3), 1.9–2.4 [m, 1, 9-C**H**(CH_3)$_2$], 0.72 [d, 6, 9-CH(C**H**$_3$)$_2$, J = 6.8 Hz].

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{23}H_{23}NO_2S_2$, 409.1170; found, 409.1158.

Isomerization of *cis*-9-Ethylthioxanthene 10-Oxide (*cis*-7b) with DBU in Benzene. A solution of *cis*-**7b** (20 mg) and DBU (10 mg) in benzene (1 mL) was stirred at room temperature for 5 h. The reaction mixture was washed with 10% HCl and water, dried ($MgSO_4$), and concentrated. The residual solid was recrystallized from AcOEt to give *trans*-9-ethylthioxanthene 10-oxide (*trans*-**7b**; 17 mg, 85%).

Determination of the Half-Lives of 6a-c in $CDCl_3$ in the Presence of Piperidine as Base at 34 °C. The samples (0.25 M in substrate) were made up in NMR tubes from weighed amounts of the sulfilimine 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 C_9–H signals. The product was free of decomposition products or byproducts.

2-Chlorothioxanthene *N*-(Benzenesulfonyl)sulfilimine (17) and 2-Chloro-9-(*N*-benzenesulfonamido)thioxanthene (19). 2-Chlorothioxanthene (464 mg) and chloramine B·2H_2O (500 mg) were added all at once to a stirred solution of methanol (10 mL) and CH_2Cl_2 (5 mL) containing acetic acid (0.02 mL) and the mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with $CHCl_3$ (20 mL) and washed with a saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel with benzene–AcOEt (5:1) to give **19** (358 mg, 46%) as colorless needles: mp 157–158 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 3350 (NH), 1330, 1160, 1090 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 7.05–7.75 (m, 12, aromatic protons), 5.50, 5.30 (ABq, 1 each, J = 7.5 Hz, benzylic proton and NH, respectively).

Anal Calcd for $C_{19}H_{14}ClNO_2S_2$: C, 58.83; H, 3.64; N, 3.61. Found: C, 58.81; H, 3.70; N, 3.72.

Further elution with the same solvent gave **17** (257 mg, 33%) as colorless crystals: mp 130–134 °C (from benzene); IR ($CHCl_3$) 1310, 1150, 1090 (SO_2), 970 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.25–8.05 (m, 12, aromatic protons), 4.25, 3.85 (ABq, 1 each, J = 18 Hz, benzylic protons).

Anal. Calcd for $C_{19}H_{14}ClNO_2S_2$: C, 58.83; H, 3.64; N, 3.61. Found: C, 59.17; H, 3.64; N, 3.68.

2-Chlorothioxanthene *N*-(*p*-Toluenesulfonyl)sulfilimine and 2-Chloro-9-(*N*-*p*-toluenesulfonamido)thioxanthene (21). By using the similar procedure as described above, the *N*-(*p*-toluenesulfonyl)sulfilimine (453 mg, 38%) and **21** (480 mg, 40%) were obtained from 2-chlorothioxanthene (696 mg) and chloramine T·3H_2O (845 mg).

The sulfilimine had: mp 149–152 °C (from benzene); IR ($CHCl_3$) 1300, 1140, 1090 (SO_2), 960 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 7.1–8.0 (m, 11, aromatic protons), 4.28, 3.84 (ABq, 1 each, J = 17.5 Hz, benzylic protons), 2.40 (s, 3, CH_3).

Anal. Calcd for $C_{20}H_{16}ClNO_2S_2$: C, 59.76; H, 4.01; N, 3.49. Found: C, 60.05; H, 4.07; N, 3.49.

Compound **21** had: mp 148.5–149 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 3350 (NH), 1340, 1160, 1100 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.55 (m, 11, aromatic protons), 5.46, 5.25 (ABq, 1 each, J = 8.0 Hz, benzylic proton and NH, respectively), 2.35 (s, 3, CH_3).

Anal. Calcd for $C_{20}H_{16}ClNO_2S_2$: C, 59.76; H, 4.01; N, 3.49. Found: C, 59.81; H, 4.03; N, 3.59.

Crossover Experiments. A. In DMF. A mixture of **16** (95 mg) and **17** (100 mg) in DMF (15 mL) containing DBU (40 mg) was stirred at room temperature. The red solution was gradually decolorized. After 3 h, DMF was evaporated in vacuo below 30 °C. The reaction mixture was diluted with $CHCl_3$ and washed with 10% HCl, dried ($MgSO_4$), and concentrated. The residual oil was purified by preparative TLC on silica gel with benzene to give a mixture (41 mg) of **18** and **20** in a ratio of ~5:1 (by NMR spectroscopy) and a mixture of **19** and **21** (38 mg) in a ratio of ~5:1, along with 2-chlorothioxanthone (12 mg, 19%) and thioxanthone (10 mg, 18%).

B. In Benzene. A mixture of **16** (95 mg) and **17** (100 mg) in benzene (10 mL) containing DBU (40 mg) was stirred at room temperature. After 1 h, the reaction mixture was diluted with benzene (20 mL) and washed with 10% HCl, dried ($MgSO_4$), and concentrated. The residual

oil was chromatographed on silica gel with benzene to give **18** (40 mg, 40%) and **19** (31 mg, 33%).

Registry No.—**1**, 69381-70-0; **2**, 60914-90-1; *cis*-**4a**, 69381-72-2; *trans*-**4a**, 69381-74-4; *cis*-**4b**, 69381-76-6; *trans*-**4b**, 69381-78-8; *trans*-**4c**, 69381-80-2; **5**, 69381-81-3; **10**, 261-31-4; **11**, 492-22-8; **15a**, 69381-82-4; **15b**, 69381-83-5; **15c**, 69381-84-6; **16**, 69381-70-0; **17**, 69381-85-7; **18**, 60914-90-1; **19**, 69381-86-8; **20**, 63076-58-4; **21**, 69381-87-9; 9-methoxy-9-methylthioxanthene, 69381-88-0; 2-chlorothioxanthene *N*-(*p*-toluenesulfonyl)sulfilimine, 69381-89-1; 2-chlorothioxanthene, 92-38-6; MSH, 36016-40-7; chloramine T, 127-65-1.

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(10) The Experimental Section of ref 9 should be corrected as follows: page 2994, column 1, line 8. "*cis*-**5**" should be *trans*-**5**. Line 18. "*trans*-**5**" should be *cis*-**5**. Line 37. "*cis*-**6**" should be *trans*-**6**. Column 2, line 4. "*trans*-**8**" should be *cis*-**8**. (A private communication from Professor A. L. Ternay, Jr.).
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(17) Further evidence for the intermediacy of **14** was obtained from the reaction of **6a** in methanol in the presence of DBU, which afforded 9-methoxy-9-methylthioxanthene in 78% yield. Evidence for this structure was based on its elemental analysis and spectral data (see Experimental Section). Apparently attack of methanol to the thioxanthylium ion **14** (R = CH_3) can compete successfully with addition of *p*-toluenesulfonamide anion.
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(21) That cis–trans isomerization may occur with the *cis*-sulfilimines **6a,b** under the conditions used was suggested by the fact that *cis*-sulfoxide **7a** equilibrates with *trans*-**7a** on treatment with morpholine.[8] We have also observed the complete isomerization of *cis*-**7b** to *trans*-**7b** on treatment with DBU in benzene at room temperature.
(22) It should be noted here that *trans*-**6c** exchanged deuterium at C-9 upon treatment with potassium hydroxide in deuteriomethanol at room temperature. This implies the intervention of the carbanion **22** (R = *i*-C_3H_7) in the rearrangement of *trans*-**6c**.
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Optically Active Amines. 26.[1] Spectral Observations on Chiral Schiff Bases[2]

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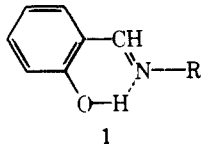
Examination of the isotropic electronic absorption (EA) and circular dichroism (CD) spectra of the Schiff base [*N*-benzylidene, *N*-(*o*-methoxybenzylidene), and *N*-salicylidene] derivatives of (*S*)-α-phenylethylamine, (*S*)-α-benzylethylamine, and 17β-amino-5α-androstan-3α-ol indicates that for the salicylidenimino chromophore, the lowest energy n → π* transition of the azomethine group occurs at about 275 nm. Although no absorption maximum can be observed in the EA spectrum for this transition, it gives rise to a moderately intense Cotton effect near 275 nm in the CD spectrum of the *N*-salicylidene derivatives of some amines. Since this Cotton effect occurs between those associated with absorption bands I and II at about 315 and 255 nm, respectively, and since it is generally opposite in sign to that of those associated with absorption bands I and II, its identification makes the application of the salicylidenimino chirality rule less ambiguous for the deduction of the absolute configuration of chiral primary amines.

The isotropic electronic absorption (EA) spectra of the *N*-salicylidene derivatives of chiral primary amines in hexane exhibit characteristic absorption bands at about 315 (log ϵ_{max} 3.68–3.73), 255 (4.12–4.21), and 215 nm (4.36–4.49), designated as bands I, II, and III, respectively,[4] which are assigned to transitions of the intramolecularly hydrogen-bonded salicylidenimino chromophore (**1**).[5] In polar solvents such as dioxane, ethanol, and methanol, a broad band at about 400 nm (log ϵ_{max} 1.32–1.89 in dioxane[6] and 3.06–3.38 in methanol[4] and ethanol[6]) and a shoulder near 280 nm (log ϵ_{max} 3.49–3.67 in ethanol[6]) become evident, and the other three bands show a slight decrease in intensity.[4,6] The two additional bands are attributed to the presence of a quinoid tautomer (**2**) in the polar solvents.[5] The corresponding circular dichroism (CD) spectra usually show for bands I and II corresponding Cotton effects of the same sign which can be correlated with the absolute configuration of the amine moiety by application of the salicylidenimino chirality rule.[4,7-11]



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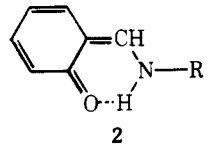

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In the course of these CD studies, we have noted the occasional appearance of an additional CD maximum, opposite in sign to that of bands I and II and centered at about 275 nm (cf. Figure 1 in ref 7). In the past, this band has been assigned to a transition of an aryl group of the amine moiety[7] or to the quinoid tautomer[4,9,11] or it has been unassigned.[10,11] Cotton effects near 280 and 400 nm can be assigned to the quinoid tautomer since these disappear using hexane as the solvent, but there are a few *N*-salicylidene derivatives for which the CD maximum near 275 nm persists in hexane and in which the chiral amine does not have a transition in the 275-nm region, notably the *N*-salicylidene derivatives of 1-alkyl-2-propynyl-

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