imine of a pyrrole was formed followed by isomerization to the pyrrole. We have already shown that the Dewar pyrrole **7a** does not thermally isomerize to the pyrrole **5a** and that cyclopropenyl *N*-phenyl imine does not isomerize to **5a**. Since we have observed that some amino compounds will add to the C–S bond of the thiirane ring of **9**, we tentatively propose the mechanism shown in Scheme III for this process.

Conclusion

Tetrakis(trifluoromethyl)(Dewar pyrroles) or cyclopropenyl imines did not give the corresponding pyrrole compounds thermally at the temperature at which photochemical transposition of pyrroles is observed, while Dewar pyrroles were transformed photochemically to the pyrroles. The *N*-phenylpyrrole compound was converted photochemically to the cyclobutindole compound, possibly through the Dewar form. The reaction of the Dewar thiophene **9** with aniline gave *N*-phenylpyrrole **5a**, possibly through the attack by the nitrogen atom of aniline on the carbon–sulfur bond of **9**.

Experimental Section

Reaction of Cyclopropenyl Imine Compounds 4. A solution of **4** in pentane was sealed in a 4-mm Pyrex tube and heated at 140–150 °C for several hours. As observed by ^{19}F NMR spectroscopy, **4** was not converted to pyrroles. Then, the solution was irradiated with a high-pressure mercury lamp, but **4** was still not changed to any other products.

Synthesis of *N*-Phenylcyclopropenyl Imine 4a and Its Reactions. A solution of cyclopropenyl ketone [5,6] **6** (340 mg, 1.0 mmol) in *n*-pentane (5 mL) was cooled at −78 °C under nitrogen, and titanium tetrachloride (0.06 mL, 0.5 mmol) was added to this cold solution. To this solution was added aniline (279 mg, 3.0 mmol) with stirring. The mixture was warmed to room temperature and further stirred overnight. The reaction mixture was filtered through Celite. The filtrate was concentrated, and the residue was distilled by a bulb-to-bulb distillation at 68–69 °C (13 mmHg) to give **4a** (136.8 mg, 33% yield) as a yellow oil: IR (CCl_4) 3060, 3020, 1905 (cyclopropenyl double bond), 1680, 1600, 1280, 1155; ^1H NMR (CCl_4) δ 6.6–7.5 (PhH, m); ^{19}F NMR (CCl_4)[9] for isomer A −3.6 (6 F, m), 3.6 (3 F, m), 7.2 (3 F, m) ppm; for isomer B −3.4 (6 F, m), −1.12 (3 F, m), 3.6 (3 F, m) ppm; mass spectrum, *m/e* 415 (M^+); high-resolution mass spectrum, calcd for $C_{14}H_5NF_{12}$ *m/e* 415.0230, found *m/e* 415.0258. In the ^{19}F NMR spectrum, **4a** showed two pairs of signals (A/B ratio of 1:2), which suggested that **4a** was a compound with two conformational isomers.

Thermolysis at 140 °C and photolysis (a high-pressure mercury lamp) of **4a** obtained by this method was followed by ^{19}F NMR analysis, but conversion of **4a** to *N*-phenylpyrrole **5a** was not observed.

Photolysis of *N*-Phenylpyrrole 5a. A solution of **5a** (11 mg, 0.0265 mmol) in pentane (0.2 mL) was sealed in a quartz tube under vacuum. After irradiation with a low-pressure mercury lamp, four new signals appeared in the ^{19}F NMR. At this time, GLC of the reaction mixture showed two peaks, one of which was starting material (**5a**) and another which was cyclobutindole **8**. Upon GLC/MS the later peak showed a parent peak at *m/e* 415. Photolysis of this mixture caused **5a** to isomerize to *N*-phenyl-(Dewar pyrrole) **7a** and **7a** was further transformed to cyclobutindole **8** by a [3.3] sigmatropic reaction.

Reaction of Dewar Thiophene 9 with Aniline. To a solution of Dewar thiophene **9** (135 mg, 0.379 mmol) in CCl_4 (0.3 mL) was added aniline (35 mg, 0.376 mmol). The solution was stirred at room temperature for 96 h. The reaction mixture was concentrated under vacuum, and the residue was purified through column chromatography (SiO_2, *n*-pentane) to give crystals. The crystals were recrystallized from *n*-pentane at dry ice–acetone temperature to give **5a** (29 mg, 18.7% yield) as colorless prisms: mp 98–99 °C; IR (KBr) 1600, 1160, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16–7.66 (PhH, m); ^{19}F NMR ($CDCl_3$) −9.6 (12F, m) ppm; mass spectrum, *m/e* 415 (M^+); high-resolution mass spectrum, calcd for $C_{14}H_5NF_{12}$ *m/e* 415.0230, found *m/e* 415.0210.

Registry No. 4a, 73679-96-6; **5a**, 73679-97-7; **6**, 67705-04-8; **7a**, 64747-39-3; **8**, 64747-38-2; **9**, 39091-73-1; aniline, 62-53-3.

(9) Benzotrifluoride (BTF) as internal standard.

Rearrangement of 9-Alkylidenethioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines to 9-(*N*-*p*-Toluenesulfonamido)-9-vinylthioxanthenes

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9-Ethylidene-, 9-propylidene-, and 9-isopropylidenethioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines were prepared by reaction of the corresponding thioxanthenes with chloramine T. Treatment of the sulfilimines with DBU in benzene gave the corresponding 9-(*N*-*p*-toluenesulfonamido)-9-vinylthioxanthenes. This rearrangement is rationalized in terms of the thioxanthylium ion intermediates.

In a series of papers[1-4] we have shown that thioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines **1** undergo base-catalyzed rearrangement to 9-(*N*-*p*-toluenesulfonamido)thioxanthenes **2**. The proposed mechanism for this rearrangement involved thioxanthylium ions **3**. We have now found that 9-alkylidenethioxanthene-*N*-(*p*-toluenesulfonyl)sulfilimines **5** also rearranged to 9-(*N*-*p*-toluenesulfonamido)-9-vinylthioxanthenes **8**. This result provides convincing evidence for the involvement of **3**.

Results and Discussion

The desired sulfilimines **5a–c** were prepared by the reaction of 9-alkylidenethioxanthenes **4a–c** with chloramine

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

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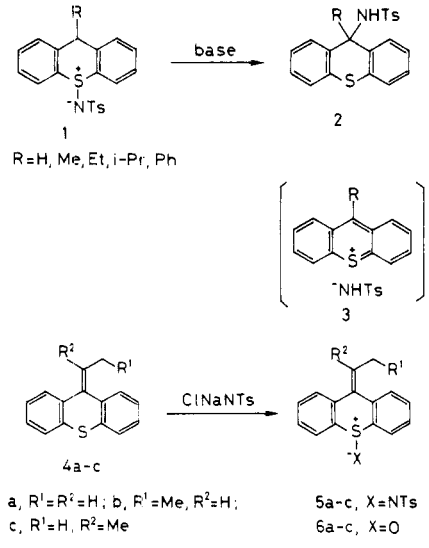
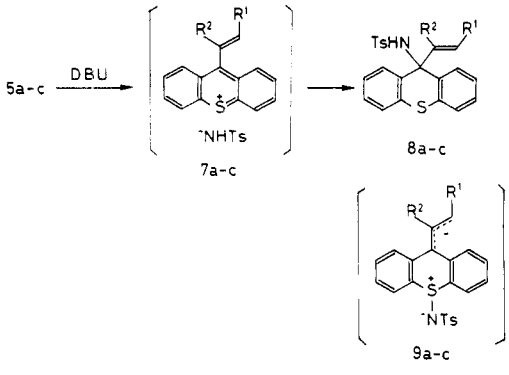


T trihydrate, a method which is analogous to the procedure previously employed for the preparation of 1 (R = Me, Et, *i*-Pr).[2] Thus, reaction of 9-ethylidenethioxanthene (**4a**) with 2 equiv of chloramine T in methylene chloride and methanol containing a catalytic amount of acetic acid at room temperature gave **5a** and the sulfoxide **6a** in 58 and 31% yields, respectively. A similar treatment of **4b,c** afforded the corresponding sulfilimines **5b,c** and sulfoxides **6b,c**, respectively. The structures of **5a–c** and **6a–c** were readily assigned on the basis of the spectroscopic data (see Experimental Section).

Treatment of **5a** with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in benzene for 20 h at room temperature gave 9-(*N*-*p*-toluenesulfonamido)-9-vinylthioxanthene (**8a**) in 90%



yield. The structure of **8a** was apparent from the following spectral data. The IR spectrum showed absorption bands at 3240 cm^{-1} (NH) and at 1320 and 1160 cm^{-1} (SO_2). The NMR spectrum revealed a broad singlet at δ 4.69 (NH) and a multiplet due to three vinylic protons between δ 5.6 and 6.6. The remaining signals were a singlet of the toluene ring methyl at δ 2.33 and a multiplet (12 H) in the aromatic region.

Similarly, **5b** gave **8b** in 88% yield. The trans stereochemistry of **8b** was assigned on the basis of the NMR coupling constant between the olefinic protons (J = 16 Hz). The sulfilimine **5c** also rearranged to **8c** but in refluxing benzene.[5]

The formation of **8a–c** can be rationalized in terms of thioxanthylium ions **7a–c**, which may arise via carbanion intermediates **9a–c**.[6] Examination of a scale model indicates that the vinyl group of the thioxanthylium ions **7a–c** can not conjugate with the thiopyrylium ring because it adopts the orthogonal geometry with respect to the planar or nearly planar tricyclic ring to minimize the nonbonding interaction with the peri hydrogen atoms (H-1 and H-8). Consequently preferential attack of *p*-toluenesulfonamide anion at the 9-position would be expected.

Experimental Section

Melting points are uncorrected. NMR spectra were determined with a Hitachi R-22 (90 MHz) spectrometer 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.

9-Ethylidenethioxanthene (4a). The procedure of Šindelář et al.[8] was employed. To a solution of thioxanthone (2.5 g, 12 mmol) in dry ether (20 mL) was slowly added under an argon atmosphere a solution of ethylmagnesium iodide [prepared from ethyl iodide (3.9 g, 25 mmol) and magnesium (0.6 g, 25 mmol)] in dry ether (10 mL) at room temperature. The reaction mixture was refluxed for 3 h. After cooling, the solution was washed with a saturated ammonium chloride solution, dried ($MgSO_4$), and concentrated. The residual oil was redissolved in methanol (30 mL), and concentrated sulfuric acid (1.5 mL) was added dropwise under cooling. The reaction mixture was refluxed for 45 min and diluted with water (25 mL), neutralized with a 10% sodium hydroxide solution, and extracted with chloroform. The extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel with *n*-hexane to give **4a** (2.0 g, 76%) as a colorless oil: NMR ($CDCl_3$) δ 6.8–7.5 (m, 8, aromatic protons), 5.82 (q, 1, J = 7.5 Hz, vinylic proton), 2.85 (d, 3, J = 7.5 Hz, CH_3); mass spectrum, m/e 224 (M^+).

9-*n*-Propylidenethioxanthene (4b). To a solution of thioxanthone (1.85 g, 9 mmol) in dry ether (20 mL) was added dropwise under an argon atmosphere a solution of triphenyl-*n*-propylphosphorane [prepared from *n*-propyltriphenylphosphonium bromide (3.8 g, 10 mmol) and *n*-butyllithium in *n*-hexane solution (5.2 mL, 9 mmol)] in dry ether (20 mL) at room temperature. The reaction mixture was stirred at the same temperature overnight and poured into water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether solution was washed with water, dried ($MgSO_4$), and concentrated to give a yellow oil which was chromatographed on silica gel with *n*-hexane to afford **4b** (840 mg, 40%) as a colorless oil: NMR ($CDCl_3$) δ 6.9–7.5 (m, 8, aromatic protons), 5.79 (t, 1, J = 8 Hz, vinylic proton), 2.40 (quintet, 2, J = 8 Hz, CH_2CH_3), 1.07 (t, 3, J = 8 Hz, CH_2CH_3); mass spectrum, m/e 238 (M^+).

9-Isopropylidenethioxanthene (4c). To a solution of thioxanthone (2.1 g, 10 mmol) in dry ether (40 mL) was added dropwise under an argon atmosphere a solution of triphenylisopropylphosphorane [prepared from isopropyltriphenylphosphonium iodide (5 g, 11.5 mmol) and *n*-butyllithium in *n*-hexane solution (7.7 mL, 11.0 mmol)] in dry ether (20 mL) at room temperature. The reaction mixture was refluxed for 3 days. Workup as described above for the preparation of **4b** gave **4c** (560 mg, 24%) as colorless crystals: mp 92–93 °C (from ethanol); NMR ($CDCl_3$) δ 7.0–7.5 (m, 8, aromatic protons), 1.96 (s, 6, CH_3).

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92. Found: C, 80.71; H, 5.93.

Reaction of 4a with Chloramine T. To a stirred solution of **4a** (1 g, 45 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 (2.5 g, 8.9 mmol) at room temperature. After 20 min, methylene chloride (30 mL) was added to the reaction mixture, and the solution was washed with a saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and

(5) No reaction took place at room temperature because of the low solubility of **5c**.

(6) The possibility of a concerted 1,6-elimination mechanism[7] cannot be ruled out.

(7) Anh, N. G. *Chem. Commun.* **1968**, 1089. Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2116.

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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

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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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