Synthesis of Dewar Pyrroles 4. 5-Phenyl-1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene [*N*-Phenyl(Dewar Pyrrole)] (4a). To an ice-cold solution of **3a** (49.6 mg, 0.111 mmol) in *n*-pentane (0.3 mL) was added triphenylphosphine (29.1 mg, 0.111 mmol). At this time, the ^{19}F NMR spectrum of the reaction mixture showed signals different from those of **3a**. In the IR spectrum, the absorption at 1700 cm^{-1} ascribable to a cyclobutenic double bond appeared. But the reaction proceeded further, and **4a** changed to another product, **5**, at room temperature. The solvent was removed, and the residue was worked up by preparative TLC. **5** was obtained in a yield of 16.4 mg (35.6%) as a colorless oil: IR (*n*-pentane) 3430 (NH), 1715 (cyclobutenic double bond), 1618, 1210, (CF) cm^{-1}; ^1H NMR (CCl_4) δ 4.72 (NH, 1 H, br), 7.2–7.5, 6.75–7.04 (aromatic H, 4 H, m); ^{19}F NMR ($CDCl_3$) –0.8 (3 F, m), 0 (3 F, m), 5.2 (3 F, m), 10.8 (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* 415.0243.

5-Cyclohexyl-1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene [*N*-Cyclohexyl(Dewar Pyrrole)] (4b). After irradiation of **2b** (785 mg, 1.73 mmol) in *n*-pentane (30 mL) for 6 h with a low-pressure mercury lamp, the reaction mixture was treated with triphenylphosphine (454.0 mg, 1.73 mmol). The precipitated sulfide was filtered off, the filtrate was concentrated, and the residue was worked up by preparative TLC to give **4b** (544.7 mg, 79.3% yield) as a colorless oil: bp 65 °C (7 mmHg); IR (CCl_4) 2940, 2860, 1700 (cyclobutenic double bond), 1160 (CF) cm^{-1}; ^1H NMR (CCl_4) δ 2.63 (CH–N, 1 H, m), 1.15–1.95 (CH_2, 10 H, m); ^{19}F NMR (CCl_4) 1.52 (6 F, s), 2.72 (6 F, s) ppm; ^{13}C NMR ($CDCl_3$) δ 140.4 (sp^2, q, J_{CCF} = 45 Hz), 121.2 (sp^3, q, J_{CF} = 274 Hz), 118.1 (sp^3, q, J_{CF} = 272 Hz), 55.1 (sp^3, d, J_{CH} = 134 Hz), 50.0 (sp^3, q, J_{CCF} = 45 Hz), 32.0, 25.9, and 23.8 (sp^3, t, J_{CH} = 127 Hz); mass spectrum, *m/e* 421 (M^+, w); high-resolution mass spectrum, calcd for $C_{14}H_{11}NF_{12}$ *m/e* 421.0700, found *m/e* 421.0681.

5-*tert*-Butyl-1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene [*N*-*tert*-Butyl(Dewar Pyrrole)] (4c). To a solution of **3c** (325 mg, 0.761 mmol) in *n*-pentane (3 mL) was added triphenylphosphine (excess). The solution was stirred at room temperature for 30 min. By use of a vacuum line, low-boiling materials were separated from triphenylphosphine and the sulfide. The separated solution was worked up by preparative GLC (SE-30, 3 m, 70 °C). **4c** was isolated as a colorless oil: 235.2 mg (78.2% yield); IR (CCl_4) 2970, 1710 (cyclobutenic double bond), 1255–1275, 1190–1210, 1170 (CF) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 ($C(CH_3)_3$, s); ^{19}F NMR ($CDCl_3$) 0.2 (6 F, s), 2.4 (6 F, s); mass spectrum, *m/e* 339 ($M^+ - C_4H_8$), 56 (C_4H_8). *N*-*tert*-Butyl(Dewar pyrrole) (**4c**) was comparatively stable at room temperature, but it decomposed slowly to give tetrakis(trifluoromethyl)pyrrole over several weeks at room temperature. This fact is consistent with the evidence that the mass spectrum showed not a parent peak but an $M^+ - C_4H_8$ peak [$(CH_3)_2C{=}CH_2$].

1,2,3,4-Tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene (N-Unsubstituted Dewar Pyrrole) (4d). A solution of **2d** (2.0 g, 5.01 mmol) in Et_2O (30 mL) was placed in the quartz vessel equipped with a cold finger and irradiated with a low-pressure mercury lamp under vacuum for ca. 20 h. The reaction mixture was concentrated on a vacuum line. To the residue was added *n*-pentane, and undissolved starting material (**2d**) was recovered by filtration (175.5 mg after purification). The filtrate was treated with triphenylphosphine (excess). Then, the product and solvent were separated from the phosphine sulfide on a vacuum line. The solution was worked up by preparative GLC (SE-30, 6 m, 38 °C) to give **4d** (634.9 mg, 40.9% yield) as a light yellow oil: IR (CCl_4) 3300 (NH), 1700 (cyclobutenic double bond), 1290, 1250, 1160–1230 (CF) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.16 (NH, m); ^{19}F NMR ($CDCl_3$) 1.6 (br s, 6 F), 2.4 (br s, 6 F) ppm; mass spectrum, *m/e* 339 (M^+); high-resolution mass spectrum, calcd for C_8HNF_{12} *m/e* 338.9917, found *m/e* 338.9910; ^{13}C NMR ($CDCl_3$) δ 148.7 (sp^2, q, J_{CCF} = 47.6 Hz), 120.8 (sp^3, q, J_{CF} = 272.2 Hz), 117.5 (sp^3, q, J_{CF} = 272.2 Hz), 44.5 (sp^3, q, J_{CCF} = 48.8 Hz).

Transformation of 8b to 4b. A solution of **8b** (200.8 mg, 0.447 mmol) in *n*-pentane (5 mL), obtained by desulfurization of **2b**, was irradiated with a high-pressure mercury lamp for 12 h. The reaction mixture was concentrated on a vacuum line, and the residue was worked up by preparative TLC. The yield of **4b** was 122.2 mg (64.9%). The **4b** obtained was identical with the product obtained by denitrogenation and desulfurization.

Diels–Alder Reaction of 4b,d with Furan. 4-Cyclohexyl-2,3,5,6-tetrakis(trifluoromethyl)-4-aza-10-oxatetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]dec-8-ene (6b). *N*-Cyclohexyl(Dewar pyrrole) (**4b**; 205 mg, 0.487 mmol) was dissolved in $CHCl_3$ (3 mL), and furan (excess) was added. After the mixture was stirred at room temperature for 30 min, the solvent and furan were evaporated, and the residue was recrystallized from CH_3OH to give **6b** (212.9 mg, 89.4% yield) as colorless crystals. The mother liquor was worked up to give **6b** (14 mg) by evaporation and sublimation: mp 123–125 °C; IR (CCl_4) 2940, 2860, 1210, 1170 (CF) cm^{-1}; ^1H NMR (CCl_4) δ 6.6 (=CH, 2 H, br s), 5.31 (CH–O, 2 H, s), 3.0 (N–CH, 1 H, m), 1.0–2.1 (CH_2, 10 H, m); ^{19}F NMR (CCl_4) –4.0 (6 F, s), –0.4 (6 F, s) ppm; mass spectrum, *m/e* 421 (M^+ – furan), 68 (furan). Anal. Calcd for $C_{18}H_{15}NOF_{12}$: C, 44.18; H, 3.09; N, 2.86; F, 46.60. Found: C, 43.79; H, 3.22; N, 2.90; F, 46.51.

2,3,5,6-Tetrakis(trifluoromethyl)-4-aza-10-oxatetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]dec-8-ene (6d). Compound **3d** (84.5 mg, 0.249 mmol) obtained by denitrogenation of **2d** was dissolved in *n*-pentane (3 mL). To this solution was added triphenylphosphine (78.1 mg, 0.298 mmol), and the sulfide was filtered off. Then, furan (37.1 mg, 0.546 mmol) was added to this filtrate and the mixture stirred for 30 min at room temperature. Solvent was evaporated off and the residue was sublimed to give **6d** (57.4 mg, 61.9% yield) as colorless crystals: mp 61–64 °C; IR (CCl_4) 3370 (NH), 1140–1220 (CF) cm^{-1}; ^1H NMR (CCl_4) δ 6.62 (=CH, 2 H, s), 5.35 (CH–O, 2 H, s), 3.72 (NH, 1 H, m); ^{19}F NMR (CCl_4) –0.8 (6 F, s), 2.8 (6 F, s) ppm; mass spectrum, *m/e* 387 (M^+ – HF).

Registry No. 2a, 64724-54-5; **2b**, 64724-55-6; **2c**, 73688-02-5; **2d**, 68318-50-3; **3a**, 64724-56-7; **3b**, 64724-57-8; **3c**, 73688-03-6; **3d**, 73688-04-7; **4b**, 64724-58-9; **4c**, 73688-05-8; **4d**, 68318-51-4; **5**, 64747-38-2; **6b**, 64724-59-0; **6d**, 68318-52-5; **8b**, 73688-06-9.

Organic Fluorine Compounds. 34.[1] Some Reactions of Valence-Bond Isomers of Tetrakis(trifluoromethyl)pyrroles

Yoshiro Kobayashi,* Akira Ando, Kosuke Kawada, and Itsumaro Kumadaki

Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

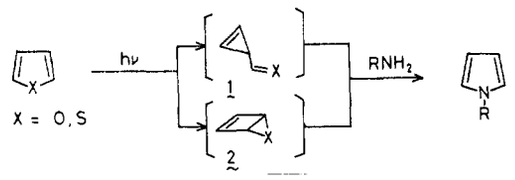
Received November 26, 1979

By use of the valence-bond isomers of trifluoromethylated pyrrole compounds, the mechanism of photochemical transformation of five-membered aromatic compounds was studied. The formerly postulated intermediates, Dewar pyrroles or cyclopropenyl imines, did not give pyrroles in thermal reactions, while only the Dewar pyrroles rearranged to pyrroles on photolysis. Although the reaction of trifluoromethylated Dewar thiophene with aniline gave the corresponding pyrrole, neither the Dewar pyrrole nor the cyclopropenyl imine is the intermediate, as postulated previously.

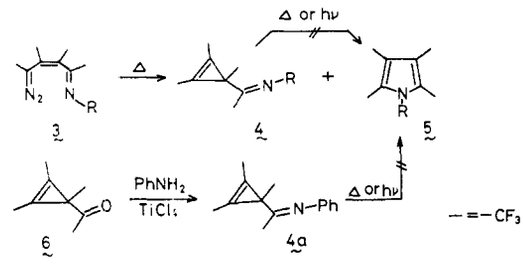
In the previous papers, we described some valence-bond isomers of pyrroles. These compounds appeared useful for studies on the mechanism of photochemical transformations of five-membered heterocyclic compounds.

0022-3263/80/1945-2968$01.00/0

Scheme I



Scheme II

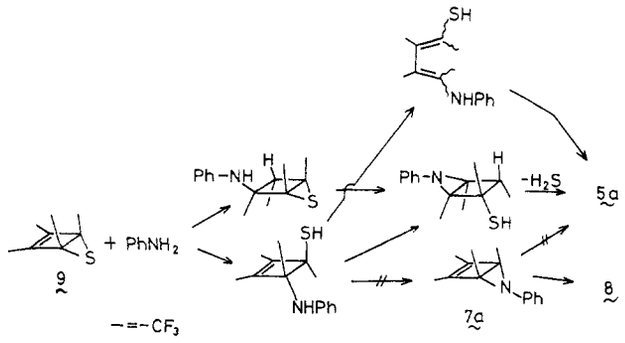


Therefore, some thermal and photochemical reactions of these compounds have been examined.

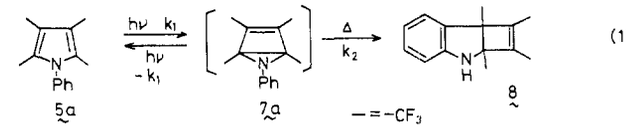
On photolysis of five-membered heteroaromatic compounds, isomerization of substituents and transposition of heteroatoms have been observed.[2] Valence-bond isomers were proposed as intermediates for these transformations, but none of them had been isolated until the preparation of tetrakis(trifluoromethyl)(Dewar thiophene).[3] This compound attracted our attention, since Couture et al.[4] had proposed similar valence-bond isomers as intermediates in the phototransformation of furan or thiophene to pyrroles in the presence of primary amines, as shown in Scheme I. Lemal et al.[5] have reported the synthesis of tris(trifluoromethyl)cyclopropenyl trifluoromethyl ketone. Thus, we have now two pairs of these postulated intermediates for trifluoromethylated compounds: **1** (X = O or X = NR) and **2** (X = S or X = NR).

We have examined the reactivity of these compounds to see if these compounds could be the intermediates of photochemical transformations. As mentioned in a preceding paper, diazo imines **3** are converted to cyclopropenyl imine **4** and/or pyrrole compounds **5**. *N*-Cyclohexylcyclopropenyl imine **4b** (R = C_6H_{11}) was not converted to the pyrrole compound **5b** on thermolysis. To examine the effect of the substituent, we examined the reaction of *N*-phenylcyclopropenyl imine **4a** (R = Ph), which was synthesized by the reaction of the cyclopropenyl ketone[6] (**6**) with aniline in the presence of titanium tetrachloride (Scheme II). In this case, the *N*-phenyl compound was recovered on thermolysis or photolysis. Therefore, cyclopropenyl N-substituted imines are not intermediates for the thermolysis of **3**. This experiment supports the following mechanism: compound **4** and/or **5** must have been produced directly from **3** by a concerted loss of a nitrogen atom and ring formation or by denitrogenation of **3** to a carbene followed by its attack on intramolecular double bonds. The cyclopropenyl ketone **6** is also stable at room

Scheme III



temperature, and for conversion to furan it is necessary to treat it with bromine.[5] These results do not support the intermediacy of **4** for the photoconversion of the pyrrole compounds, although tetrakis(trifuloromethyl) compounds might be considered a special case of the pyrrole derivatives. Then, we examined the possibility of the intermediacy of the tetrakis(trifluoromethyl)(Dewar pyrroles) (**7**). Hiraoka[7] and Day[8] independently proposed a Dewar pyrrole as an intermediate by the phototransformation of 2-cyanopyrrole to 3-cyanopyrrole. Day et al.[8] isolated the adduct of 2,5-bonded Dewar pyrrole with furan on photolysis of 2-cyanopyrrole with furan and proposed the "walk" mechanism for the nitrogen atom of Dewar pyrrole, but they did not observe the Dewar pyrrole itself. N-Unsubstituted or *N*-alkyltetrakis(trifuloromethyl)(Dewar pyrroles) (**7**) are thermally stable at the temperature where phototranspositions are observed, while the *N*-phenyl isomer **7a** isomerized spontaneously to a cyclobutindole compound, **8**. These results exclude the possibility of photochemical formation of the Dewar intermediate followed by thermal ring opening to the pyrrole compound. Photolysis of the Dewar pyrroles gave the corresponding pyrroles. Therefore, there is the possibility of photochemical isomerization of the pyrroles to the Dewar form and photochemical reversion to the pyrrole form. Actually, irradiation of **5a** with a high-pressure mercury lamp gave the cyclobutindole compound **8** very slowly. This result suggested that **5a** isomerized slowly to the Dewar isomer **7a**, which reverted photochemically to **5a** or rearranged thermally to **8**, as shown in eq 1. In this case, rate k_1 must



(1)

be slower than k_{-1} and/or k_2, since **7a** was not observed by ^{19}F NMR or GLC. Other pyrroles (**5b–d**) might possibly isomerize to the Dewar form **2**, but the reverse (**2** → **5**) seemed to occur more rapidly; thus, no net isomerization was observed.

To probe the possible intervention of Dewar thiophene according to Couture's mechanism for the photoreaction of thiophene (see Scheme I), we examined the reaction of tetrakis(trifluoromethyl)(Dewar thiophene) (**9**) with aniline. Thus, treatment of **9** with aniline in carbon tetrachloride gave *N*-phenyl-2,3,4,5-tetrakis(trifluoromethyl)-pyrrole (**5a**). This result is, however, not in accordance with the mechanism proposed by Couture et al. They proposed that either the Dewar form or the cyclopropenyl

(1) Part 33: Kobayashi, Y.; Ando, A.; Kawada, K.; Kumadaki, I. *J. Org. Chem.*, preceding paper in this issue.
(2) Lablache-Combier, A. "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; Wiley: New York, 1976; p 123.
(3) Wiebe, H. A.; Braslavsky, S.; Heicklen, J. *Can. J. Chem.* **1972**, *50*, 2721. Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Tetrahedron Lett.* **1974**, 2841.
(4) Couture, A.; Delevallee, A.; Lablache-Combier, A. *Tetrahedron* **1975**, *31*, 785.
(5) Lemal, D. M.; Boriack, C. J.; Laganis, E. D. *Tetrahedron Lett.* **1978**, 1015.
(6) Compound **6** was synthesized by Lemal et al., but formation of its imine is reported to be unsuccessful.
(7) Hiraoka, H. *J. Chem. Soc., Chem. Commun.* **1970**, 1306; **1971**, 1610.
(8) (a) Barltrop, J.; Day, A. C.; Moxon, P. D.; Ward, R. W. *J. Chem. Soc., Chem. Commun.* **1975**, 786. (b) Barltrop, J. A.; Day, A. C.; Ward, R. W. *Ibid.* **1978**, 131.

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

Yasumitsu Tamura,* Yasushi Takebe, Chisato Mukai, and Masazumi Ikeda

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

Received February 21, 1980

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

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

0022-3263/80/1945-2970$01.00/0