Synthesis and Rearrangement of Thioxanthene *N*-*p*-Toluenesulfonylsulfilimine[1]

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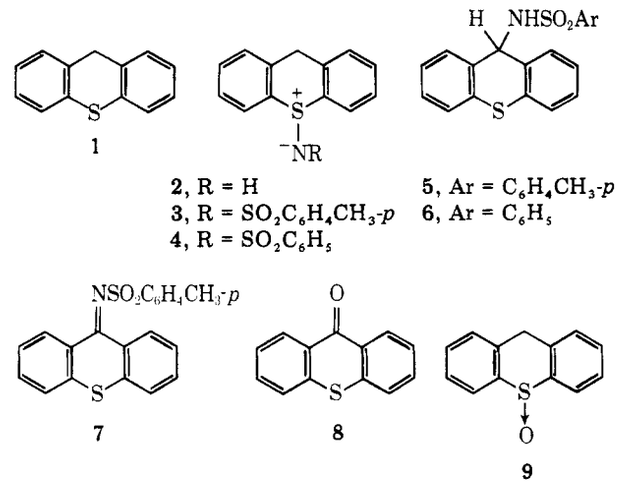
The reaction of thioxanthene with chloramine-T in methanol–methylene chloride in the presence of small amounts of acetic acid gave thioxanthene *N*-*p*-toluenesulfonylsulfilimine (**3**) and 9-(*N*-*p*-toluenesulfonamido)-thioxanthene (**5**). The sulfilimine **3** underwent acid- or base-catalyzed rearrangement to **5**. Mechanisms for the formation of **3** and **5** and for the rearrangement of **3** to **5** are discussed.

Despite current interest in the chemistry of thioxanthene 10-oxides[2] and 10-alkyl or aryl salts,[3] little information is available about the nitrogen analogue, thioxanthenesulfilimines. Recently we have noticed the unusual behavior of a 10-aminothioxanthenium salt which, upon treatment with base, produces a dimeric compound presumably via the nonisolable free sulfilimine **2**.[4,5] This result prompted us to examine the behavior of the corresponding *N*-*p*-toluenesulfonylsulfilimine **3**. In this paper we describe details of the preparation of **3** and its rearrangement to 9-(*N*-*p*-toluenesulfonamido)thioxanthene (**5**).[7]



Results and Discussion

Syntheses. The reaction of sulfides with chloramine-T provides a general synthetic route to *N*-*p*-toluenesulfonylsulfilimines.[8] However, as previously noted,[7] treatment of thioxanthene (**1**) with chloramine-T gives many compounds, including thioxanthene *N*-*p*-toluenesulfonylsulfilimine (**3**)[9] and 9-(*N*-*p*-toluenesulfonamido)thioxanthene (**5**), depending upon the reaction conditions.

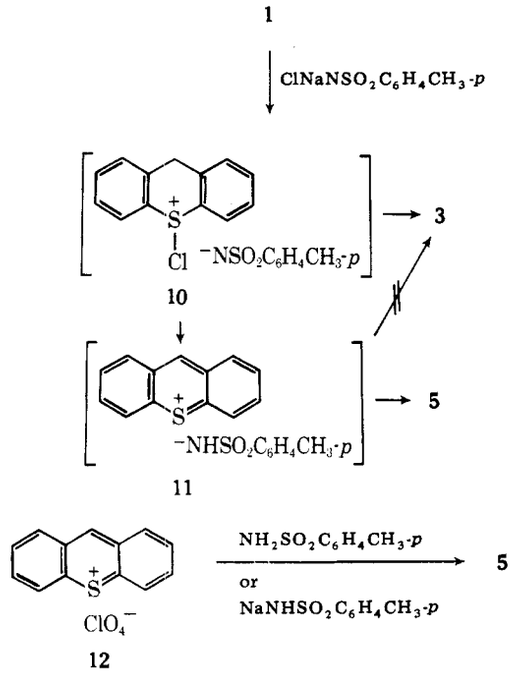
For the preparation of the sulfilimine **3**, the following procedure gave the most satisfactory and reproducible result. A solution of equimolar quantities of **1** and chloramine-T trihydrate in methanol–methylene chloride (2:1) in the presence of small amounts of acetic acid was stirred for 60 min at room temperature. After evaporation of the solvent under reduced pressure the crude material was chromatographed on silica gel and eluted with benzene–ethyl acetate to give **3** and **5** in 38 and 26% yields, respectively. That the reaction is catalyzed by acetic acid became evident by the fact that when **1** was treated with chloramine-T in the absence of acetic acid, the reaction proceeded very slowly and, in addition to unreacted **1**, as many as five products were formed: **3**, **5**, 9-(*N*-*p*-toluenesulfonimido)thioxanthene (**7**), thioxanthone (**8**), and thioxanthene 10-oxide (**9**).

The structures of these products were easily confirmed by their spectral evidence and chemical interconversions. The sulfilimine **3** showed the molecular ion peak at *m/e* 367 and two strong fragment ion peaks at *m/e* 211 ($M^+ - p$-$CH_3C_6H_4SO_2$-H) and 197 (thioxanthylium ion) in its mass spectrum. Its IR spectrum showed strong absorption at 1300, 1150, and 1095 cm^{-1}, typical of an SO_2 group, and at 970 cm^{-1}, a characteristic band for an S^+–N^- bond.[10-13] In the NMR spectrum two benzylic protons appeared as an AB quartet at δ_A 4.32 and δ_B 3.88 with J_{AB} = 17 Hz. Compound **3** smoothly rearranged to **5** by refluxing in benzene containing small amounts of concentrated HCl or by treating with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in benzene at room temperature. The IR spectrum of **5** showed an NH absorption band at 3367 cm^{-1} and the NMR spectrum revealed an AB quartet at δ_A 5.59 (a benzylic proton) and δ_B 5.27 (NH) with J_{AB} = 8 Hz. Treatment of **5** with an equimolar quantity of chloramine-T in methanol–acetic acid (20:1) at room temperature gave **7** in 72% yield. Confirmation of structure **7** was given by acid hydrolysis to thioxanthone (**8**) and *p*-toluenesulfonamide.

Under the similar conditions used for the preparation of **3**, the reaction of thioxanthene (**1**) with chloramine-B dihydrate gave thioxanthene *N*-benzenesulfonylsulfilimine (**4**) and 9-(*N*-benzenesulfonamido)thioxanthene (**6**) in 55 and 40% yields, whose structures were confirmed by comparison of their spectral data with those of **3** and **5**, respectively.

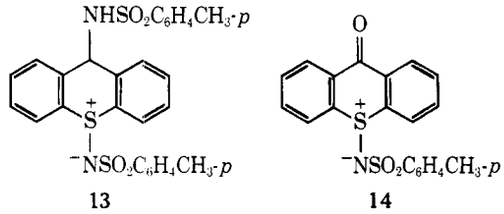
Because the sulfilimine **3** was shown to undergo acid- or base-promoted rearrangement to **5**, it was initially believed that **5** was derived from **3** under the reaction conditions. However, since **3** proved to be totally stable to the reaction conditions used,[14] it was concluded that both **3** and **5** must arise directly from **1**. A mechanistic rationalization of the formation of **3** and **5** involves an assumption that **1** is first converted to chlorosulfonium salt **10** (Scheme I). Such a process is in accord with the generally accepted mechanism[15] for the formation of *N*-*p*-toluenesulfonylsulfilimines from sulfides and chloramine-T. A direct attack of *p*-toluenesulfonamide anion on the sulfur atom of **10** may lead to **3**, and a competitive ejection of hydrogen chloride from **10** followed by an attack of *p*-toluenesulfonamide anion at the **9** position of the resulting thioxanthylium ion **11** may account for the formation of **5**. An intriguing alternative route to **3** would involve the same thioxanthylium ion **11**, which could be attacked by *p*-toluenesulfonamide anion on the sulfur atom. This type

Scheme I



of reaction has in fact been observed in the reaction of thioxanthylium perchlorate (12) with phenyllithium.[3c] However, this possibility was eliminated by the fact that no deuterium was incorporated into 3 when the reaction of 1 with chloramine-T was carried out in methanol-*d*–methylene chloride. Furthermore, 12 treated with either *p*-toluenesulfonamide or sodium *p*-toluenesulfonamide in acetonitrile gave exclusively 5.

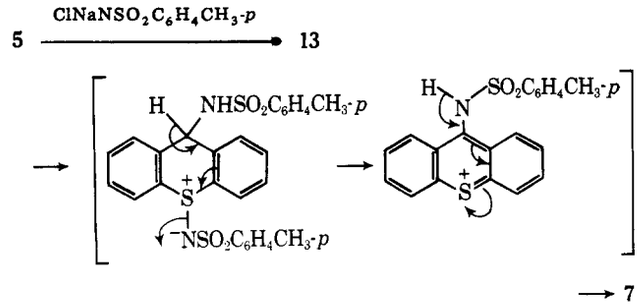
To obtain mechanistic information on the formation of secondary product 7 the reaction of 5 with chloramine-T was further investigated. Treatment of 5 with an equimolar quantity of chloramine-T trihydrate in methanol–methylene chloride (2:1) containing small amounts of acetic acid resulted in the formation of two new sulfilimines 13 and 14, in addition



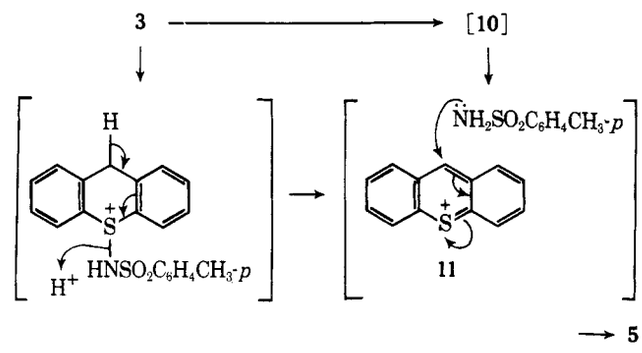
to 7 and unreacted 5. Evidence for the structures of 13 and 14 was derived from elemental analyses and spectra of these substances (see Experimental Section). The isolation of 13, together with the fact that 13 was converted into 7 simply by refluxing in ethanol for 5 h, suggests a mechanism for the formation of 7, which involves initial formation of the sulfilimine 13 followed by a series of elimination reactions as shown in Scheme II. The possibility of a direct oxidation of 5 by chloramine-T may be a less likely alternative, since treatment of 5 with chloramine-T in methanol in the absence of acetic acid recovered starting material even after stirring for 2 days at room temperature.

Acid-Promoted Rearrangement. We next investigated in some detail the acid-promoted rearrangement of 3. As described before, sulfilimine 3 undergoes rearrangement to 5 by refluxing in benzene containing small amounts of concentrated HCl. When a benzene solution of equimolar quantities of 4 and *p*-toluenesulfonamide (or 3 and benzenesulfonamide) was refluxed in the presence of small amounts of concentrated HCl, a mixture of 5 and 6 was obtained in a ratio of 2:1 (by

Scheme II



Scheme III

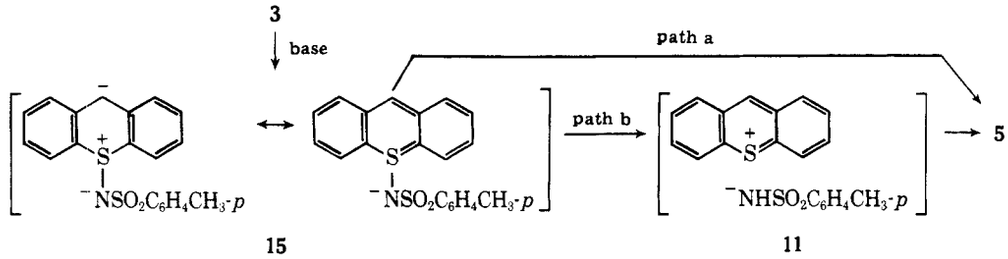


NMR spectroscopy). This observation indicates that the rearrangement is intermolecular. A reasonable mechanism for this rearrangement involves protonation at the imino nitrogen of 3 followed by sulfur–nitrogen bond cleavage with synchronous elimination of proton at the 9 position to lead to thioxanthylium ion 11, which is then attacked by *p*-toluenesulfonamide to give 5 (Scheme III). There is an analogy for this type of reaction found in the rearrangement of thioxanthene 10-oxide to 9-hydroxythioxanthene in concentrated sulfuric acid.[2] An alternative pathway to 11 could involve displacement by chloride ion on the sulfur atom to give 10, followed by elimination of hydrogen chloride. Strong support for the intervention of 11 was derived from the fact that treatment of thioxanthylium perchlorate (12) with a mixture of equimolar amounts of *p*-toluenesulfonamide and benzenesulfonamide in acetonitrile gave the same ratio (2:1) of a mixture of 5 and 6. The difference in the ratio may be attributed to the difference in nucleophilicity of two sulfonamides, which is most likely a reflection of the electron-donating effect of the methyl group. In comparison, the reaction of 12 with equimolar amounts of sodium *p*-toluenesulfonamide and sodium benzenesulfonamide in acetonitrile or dimethylformamide gave a 1:1 mixture of 5 and 6, in which the intrinsic strong nucleophilicity of the anions appears to over-shadow the small effect of the methyl group.

Base-Promoted Rearrangement. At room temperature in the presence of small quantities of base such as DBU or triethylamine, sulfilimine 3 underwent almost quantitative conversion to 5.

In principle, two mechanisms for this rearrangement could be considered as shown in Scheme IV: (a) a concerted intramolecular 1,4-sigmatropic rearrangement via a thianthracene anion (15); or (b) an intermolecular, dissociation–recombination process involving thioxanthylium ion 11. Path a is permitted by orbital symmetry considerations and parallels the mechanism proposed for the base-catalyzed rearrangement of 10-arylthioxanthenium salts to 9-arylthioxanthenes.[3a,c] Path b also involves the initial formation of 15, but this anion could then undergo sulfur–nitrogen bond cleavage to give thioxanthylium ion 11. This step is then followed by attack of *p*-toluenesulfonamide anion at the 9 position of 11

Scheme IV



to give **5**. A similar process to [**3** → **11**] has been proposed in the base-catalyzed Pummerer-type reaction of some sulfilimines.[16] The fact that a red color developed at the beginning of the reaction when dimethylformamide was used as solvent supports the involvement of **15** or **11** as intermediate.

In order to obtain further mechanistic information on this rearrangement, crossover experiments were carried out. Thus, when a solution of equimolar amounts of benzenesulfonylsulfilimine **4** and sodium *p*-toluenesulfonamide[17] in dimethylformamide[18] was stirred at room temperature for 2.5 h, a ca. 1:3 mixture of **5** and **6** was obtained. With *p*-toluenesulfonylsulfilimine **3** and sodium benzenesulfonamide, a ca. 3:1 mixture of **5** and **6** was obtained. Incorporation of the sulfonamide added was relatively low in both cases and the product ratios [**5**/**6**] observed were not consistent with that (**5**/**6** = ca. 1:1) obtained from the reaction of thioxanthylium perchlorate (**12**) with sodium benzenesulfonamide and sodium *p*-toluenesulfonamide in dimethylformamide. These observations would suggest that the migrating sulfonamide anion of **11** is not completely disrupted from the thioxanthylium system, or that the process [**11** → **5**] in path b is so fast that two sulfonamide anions cannot be mixed up completely prior to going to the final product. An alternative possibility that part of **5** is produced via an intramolecular concerted process (path a) is less likely, although it was not possible to rule it out completely.

Experimental Section

Melting points are uncorrected. NMR spectra were determined with a Varian HR-60 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with a Hitachi EPI-G3 spectrophotometer and UV spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6MG instrument with a direct inlet system operating at 70 eV.

Reaction of 1 with Chloramine-T. Thioxanthene (**1**) (990 mg) and chloramine-T·$3H_2O$ (1.4 g) were added all at once to a stirred solution of methanol (25 mL) and CH_2Cl_2 (12.5 mL) containing acetic acid (0.05 mL) at room temperature. The solution immediately turned to yellow and soon after a white powder precipitated. After 60 min, $CHCl_3$ (50 mL) was added to the reaction mixture and the solution was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residual solid was chromatographed on silica gel. Elution with benzene–AcOEt (1:5) gave 9-(*N*-*p*-toluenesulfonamido)thioxanthene (**5**) (460 mg, 26%) as white crystals: mp 172–173 °C (from benzene–*n*-hexane); IR ($CHCl_3$) 3367, 1330, 1160, 1098 cm^{-1}; UV_{max} (CH_3OH) 223 sh (log ε 4.50), 263 nm (4.19); NMR ($CDCl_3$) δ 7.0–7.7 (m, 12, aromatic protons), 5.59, 5.27 (ABq, 1 each, J = 8 Hz, benzylic proton and NH, respectively), 2.33 (s, 3, CH_3); mass spectrum *m/e* (rel intensity) 367 (3.4, M^+), 211 (66), 197 (100).

Anal. Calcd for $C_{20}H_{17}NO_2S_2$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.49; H, 4.79; N, 3.69.

Further elution with the same solvent gave thioxanthene *N*-*p*-toluenesulfonylsulfilimine (**3**) (675 mg, 38%) as white crystals: mp 138–139 °C (from benzene–methanol); IR ($CHCl_3$) 1300, 1150, 1095, 970 (S^+–N^-) cm^{-1}; UV_{max} (CH_3OH) 227 (log ε 4.50), 264 nm (3.58); NMR ($CDCl_3$) δ 7.25–8.2 (m, 12, aromatic protons), 4.32, 3.88 (ABq, 1 each, J = 17 Hz, benzylic protons), 2.37 (s, 3, CH_3); mass spectrum *m/e* (rel intensity) 367 (2.7, M^+), 211 (56), 197 (100).

Anal. Calcd for $C_{20}H_{17}NO_2S_2$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.44; H, 4.91; N, 3.75.

Reaction of 1 with Chloramine-B. By using the similar procedure as described above, thioxanthene *N*-benzenesulfonylsulfilimine (**4**) (194 mg, 55%) and 9-(*N*-benzenesulfonamido)thioxanthene (**6**) (143 mg, 40%) were obtained from **1** (198 mg) and chloramine-B·$2H_2O$ (250 mg).

Compound **4** had: mp 183–185 °C (from benzene–methanol); IR ($CHCl_3$) 1300, 1150, 1085, 965 (S^+–N^-) cm^{-1}; UV_{max} (CH_3OH) 223 sh (log ε 4.36), 265 (3.53), 272 nm (3.51); NMR ($CDCl_3$) δ 7.3–8.1 (m, 13, aromatic protons), 4.32, 3.92 (ABq, 1 each, J = 17 Hz, benzylic protons); mass spectrum *m/e* (rel intensity) 353 (5.6, M^+), 211 (65), 197 (100).

Anal. Calcd for $C_{19}H_{15}NO_2S_2$: C, 64.58; H, 4.28; N, 3.96. Found: C, 64.50; H, 4.25; N, 4.13.

Compound **6** had: mp 158–161 °C (from benzene–*n*-hxane); ir ($CHCl_3$) 3360, 1330, 1158, 1093 cm^{-1}; UV_{max} (CH_3OH) 213 sh (log ε 4.54), 263 nm (4.19); NMR ($CDCl_3$) δ 7.05–7.75 (m, 13, aromatic protons), 5.65, 5.25 (1 each, ABq, J = 7.5 Hz, benzylic proton and NH, respectively); mass spectrum *m/e* (rel intensity) 353 (6.2, M^+), 211 (73), 197 (100).

Anal. Calcd for $C_{19}H_{15}NO_2S_2$: C, 64.58; H, 4.28; N, 3.96. Found: C, 64.69; H, 4.28; N, 4.10.

Reaction of 1 with Chloramine-T without Acetic Acid. To a solution of **1** (2.0 g) in CH_2Cl_2 (10 mL) was added a solution of chloramine-T·$3H_2O$ (3.13 g) in methanol (80 mL). The mixture was refluxed for 3 min, then stirred at room temperature for 2 h, and concentrated. The residue was extracted with $CHCl_3$ and the extract was washed with 10% NaOH solution and water, dried ($MgSO_4$), and concentrated. The yellow residual solid was submitted to column chromatography on silica gel. Successive elution with benzene, benzene–AcOEt, and AcOEt gave unreacted **1** (1.35 g, 67%), thioxanthone (**8**) (30 mg, 1.4%), 9-(*N*-*p*-toluenesulfonimido)thioxanthene (**7**) (24 mg, 0.7%), **5** (391 mg, 11%), thioxanthene 10-oxide (**9**) (272 mg, 11%), and **3** (191 mg, 5.2%) in this order.

Compounds **8** and **9** were identified by direct comparisons with authentic samples.

Compound **7** had: mp 212 °C (from ether); IR ($CHCl_3$) 1540, 1310, 1160, 1090 cm^{-1}; UV_{max} (CH_3OH) 224 (log ε 4.35), 269 nm (4.47); NMR ($CDCl_3$) δ 8.5–8.8 (m, 2, aromatic protons), 7.2–8.05 (m, 10, aromatic protons), 2.40 (s, 3, CH_3); mass spectrum *m/e* (rel intensity) 365 (82, M^+), 301 (72), 300 (80), 211 (30), 210 (100), 209 (68), 184 (19), 183 (31), 155 (15), 139 (33).

Anal. Calcd for $C_{20}H_{15}NO_2S_2$: C, 65.73; H, 4.14; N, 3.83. Found: C, 65.95; H, 3.99; N, 3.77.

Reaction of 3 with Chloramine-T. A solution of **3** (184 mg) and chloramine-T·$3H_2O$ (464 mg) in methanol (10 mL) was refluxed for 4.5 h. After the solvent was removed, the residue was dissolved in $CHCl_3$ and the solution was washed with 10% NaOH solution and water, dried ($MgSO_4$), and concentrated. The residue was submitted to preparative TLC on silica gel and benzene–AcOEt (2:1) as solvent to give **7** (111 mg, 61%) as a major product.

Reaction of 5 with Chloramine-T. A. To a solution of **5** (1.0 g) and chloramine-T·$3H_2O$ (0.78 g) in methanol (20 mL) was added dropwise acetic acid (1 mL) with stirring. After 20 h, the precipitated crystals were collected and recrystallized from methanol–benzene to give **7** (720 mg, 72%).

B. To a solution of **5** (1.34 g) in CH_2Cl_2–methanol (1:4) (50 mL) was added a solution of chloramine-T·$3H_2O$ (1.13 g) in methanol (25 mL) and 1 drop of acetic acid at room temperature. After stirring for 30 min, the reaction mixture was concentrated and extracted with $CHCl_3$. The extract was washed with 5% NaOH solution and water, dried ($MgSO_4$), and concentrated. The residue was submitted to dry column chromatography using silica gel and benzene–AcOEt as solvent to give **7** (419 mg, 32%), **5** (225 mg, 17%), 9-(*N*-*p*-toluenesulfonamido)thioxanthone *p*-toluenesulfonylsulfilimine (**13**) (343 mg, 18%), and thioxanthene *p*-toluenesulfonylsulfilimine (**14**) (256 mg, 18%).

Compound **13** had: mp 174–176 °C (after washing with ether); IR (KBr) 3400, 1290, 1160, 1140, 1090, 965 (S^+–N^-) cm^{-1}; the NMR spectrum could not be measured because of low solubility in most

organic solvents for NMR; its mass spectrum showed the same fragmentation pattern as that of **7**, due to prior decomposition of **13**.

Anal. Calcd for $C_{27}H_{24}N_2O_4S_3$: C, 60.42; H, 4.51; N, 5.22. Found: C, 60.41; H, 4.59; N, 5.29.

Compound **14** had: mp 203–204 °C (from CH_2Cl_2–*n*-hexane); IR (KBr) 1680, 1335, 1140, 1090, 940 (S^+–N^-) cm^{-1}; NMR ($CDCl_3$) δ 8.25–8.50 (m, 2, aromatic protons), 7.20–7.95 (m, 10, aromatic protons), 2.43 (s, 3, CH_3); mass spectrum *m/e* (rel intensity) 381 (1, M^+), 226 (100, $M^+ - p$-$CH_3C_6H_4SO_2$-H), 212 (67, thioxanthene ion radical).

Anal. Calcd for $C_{20}H_{15}NO_3S_2$: C, 62.97; H, 3.96; N, 3.67. Found: C, 62.78; H, 3.88; N, 3.93.

Conversion of 13 to 7. A mixture of **13** (40 mg) in ethanol (5 mL) was refluxed for 5 h and concentrated. The residue was chromatographed on silica gel with benzene as solvent to give **7** (10 mg, 37%), mp 212 °C (from ether).

Hydrolysis of 7. A solution of **7** (365 mg) in methanol (15 mL) and concentrated HCl (0.5 mL) was refluxed for 2.5 h. The mixture was concentrated and $CHCl_3$ was added to the residual solid. The insoluble solid was collected and recrystallized from H_2O to give *p*-toluenesulfonamide (131 mg, 81%). Concentration of the $CHCl_3$ layer followed by recrystallization of the residual solid from benzene–methanol gave **8** (157 mg, 74%).

Rearrangement of 3 to 5. A. With Acid Catalysis. A solution of **3** (357 mg) in benzene (20 mL) containing concentrated HCl (0.2 mL) was refluxed for 5 h (the reaction was followed by TLC). The solution was washed with 5% NaOH solution and water, dried ($MgSO_4$), and concentrated. The residue was recrystallized from benzene–*n*-hexane to give **5** (279 mg, 76%).

Use of acetic acid–water (1:1) in place of concentrated HCl gave a similar result.

B. With Base Catalysis. To a stirred suspension of **3** (80 mg) in benzene (5 mL) was added DBU (20 mg) at room temperature. After 4 h (the reaction was followed by TLC), benzene (20 mL) was added to the mixture and the benzene solution was washed with 5% HCl and water, dried (Na_2SO_4), and concentrated. The residue was purified by preparative TLC on silica gel with $CHCl_3$ as solvent to give **5** (64 mg, 84%).

Crossover Experiments. A. With Acid Catalysis. A solution of **4** (80 mg) and *p*-toluenesulfonamide (39 mg) in benzene (5 mL) containing concentrated HCl (0.04 mL) was refluxed for 7 h. The reaction mixture was cooled and concentrated. The residue was purified by preparative TLC on silica gel with $CHCl_3$ as solvent to give a mixture of **5** and **6** (37 mg) in a ratio of 2:1 (by NMR spectroscopy). Similar treatment of **3** and benzenesulfonamide gave a similar result.

B. With Base Catalysis. (i) To a solution of sodium benzenesulfonamide (49 mg) in dimethylformamide (15 mL) was added all at once **3** (100 mg). At the beginning of the reaction the solution turned to red, but soon after was decolorized. The reaction mixture was stirred at room temperature for 2.5 h. Workup gave a mixture of **5** and **6** (50 mg) in a ratio of 3:1 (by NMR spectroscopy). With **4** (100 mg) and sodium *p*-toluenesulfonamide (49 mg), a 1:3 mixture of **5** and **6** (50 mg) was obtained.

(ii) A mixture of **4** (80 mg) and *p*-toluenesulfonamide (40 mg) was stirred in benzene (5 mL) in the presence of DBU (40 mg) at room temperature. Workup gave a crude material (65 mg) whose NMR spectrum indicated that it consisted of only **6**.

The use of other solvents such as dimethylformamide, *tert*-butyl alcohol, acetone, or dioxane gave the same results, but, when the same mixture was treated in methanol, a ca. 1:1 mixture of **5** and **6** was obtained in total yield of 33%.

Reaction of 12 with Sodium *p*-Toluenesulfonamide. Thioxanthylium perchlorate (**12**)[19] (150 mg) and sodium *p*-toluenesulfonamide (97 mg) were added to acetonitrile (30 mL) with stirring at room temperature. The red solution was gradually decolorized. After 10 min, the mixture was poured into water and extracted with $CHCl_3$. The extract was dried (Na_2SO_4) and concentrated. The residue was submitted to preparative TLC on silica gel with $CHCl_3$ as solvent to give **5** (108 mg, 61%) and **1** (12 mg).

Reaction of 12 with Sodium *p*-Toluenesulfonamide and Sodium Benzenesulfonamide. Using the procedure as described above, a 1:1 mixture of **5** and **6** (76 mg) was obtained from the reaction of **12** (150 mg) with equimolar amounts of sodium *p*-toluenesulfonamide (97 mg) and sodium benzenesulfonamide (90 mg). The use of dimethylfomamide as solvent gave the same result.

Reaction of 12 with *p*-Toluenesulfonamide. Thioxanthylium perchlorate (**12**) (150 mg) and *p*-toluenesulfonamide (86 mg) were added to acetonitrile (30 mL). The red solution was not decolorized even after stirring for 2 days. Workup gave **5** (30 mg, 17%).

Reaction of 12 with *p*-Toluenesulfonamide and Benzenesulfonamide. Using the procedure as described above, a 2:1 mixture of **5** and **6** (28 mg) was obtained from the reaction of **12** (150 mg) with equimolar amounts of p-toluenesulfonamide (86 mg) and benzenesulfonamide (79 mg).

Registry No.—**1**, 261-31-4; **3**, 58508-92-2; **4**, 58508-89-5; **5**, 60914-90-1; **6**, 63076-58-4; **7**, 60914-91-2; **12**, 2567-20-6; **13**, 63076-59-5; **14**, 58508-91-1; chloramine-T, 127-65-1; chloramine-B, 127,52-6; *p*-toluenesulfonamide, 70-55-3; sodium *p*-toluenesulfonamide, 18522-92-4; sodium benzenesulfonamide, 18522-93-5; benzenesulfonamide, 98-10-2.

References and Notes

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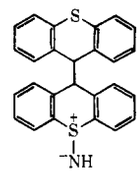
(5) The structure of the dimer reported in ref 4 should be revised to **16**, because the deaminated product obtained from the dimer by nitrous acid treatment or thermolysis was identified as dithioxanthyl by direct comparison with an authentic sample prepared by irradiation of an ethanolic solution of **1** in the presence of oxygen.[6] The stereochemistry of **16** is unknown.



16

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(8) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1052 (1922).
(9) Although Shah[10] has recently claimed the syntheses of **3**, **4**, and **14**, their melting points, and UV and IR spectral data are incompatible with ours.
(10) J. J. Shah, *Can. J. Chem.*, **53**, 2381 (1976).
(11) Y. Tanaka and Y. Tanaka, *Chem. Pharm. Bull.*, **13**, 399, 858 (1965).
(12) A. Kucsman, I. Kapovits, and F. Ruff, *Tetrahedron*, **22**, 1575 (1966).
(13) K. Tsujihara, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Jpn.*, **43**, 2153 (1970).
(14) It should be emphasized here that sulfilimine **3** undergoes the rearrangement to **5** when refluxed in benzene in the presence of small amounts of acetic acid and water (1:1) (but no rearrangement took place without water). In addition we have found that **3** is converted to **7** by refluxing in methanol with an excess of chloramine-T trihydrate for 4.5 h. Thus, the previous observation[7] that treatment of thioxanthene (**1**) with chloramine-T trihydrate in methanol–acetic acid (20:1) at 60–70 °C produces only trace amounts of **3** and instead **5** and **7** as the major products may be rationalized by assuming that once formed **3** rearranged to **5** under the reaction conditions (as described later, **7** is a secondary product from **5**).
(15) F. Ruff, K.Komoto, N. Furukawa, and S. Oae, *Tetrahedron*, **32**, 2763 (1976), and references cited therein.
(16) For a recent review, see J. G. Tillett, *Chem. Rev.*, **76**, 747 (1976).
(17) It should be noted that, when *p*-toluenesulfonamide and DBU as base were used instead of sodium *p*-toluenesulfonamide in the crossover experiments, no incorporation of the sulfonamide was observed in various solvents such as benzene, dimethylformamide, *tert*-butyl alcohol, acetone, or dioxane. However, an equimolar mixture of **4** and *p*-toluenesulfonamide in methanol was treated in the presence of DBU to give a ca. 1:1 mixture of **5** and **6**. Although the total yield of the rearranged products was low (33%), it is possible that the rearrangement in methanol involves a species **11** in which the migrating sulfonamide anion is completely dissociated from the cation.
(18) Owing to low solubility of sodium benzenesulfonamide and sodium *p*-toluenesulfonamide in nonpolar solvents dimethylformamide was used.
(19) W. Bonthrone and D. H. Reid, *Chem. Ind. (London)*, 1192 (1960).