Anal. Calcd for $C_{15}H_8OS$: C, 76.24; H, 3.41; S, 13.56. Found: C, 75.82; H, 3.29; S, 13.44.

Crude **13** was recrystallized from 95% ethanol to afford orange plates: mp 100.5–101 °C (lit.[13] mp 99–100 °C, orange plates from benzene); ir 5.83 (C=O) and 6.26 μ (C=C); NMR ($CDCl_3$) δ 7.61–7.20 (m); mass spectrum *m/e* 242 (M + 2), 240 (M^+, base), 205 (–Cl), 177 (–Cl, –CO), 176, and 88.

Reaction of Thionyl Chloride with β-Phenylcinnamic Acid. A mixture of 4.48 g (0.02 mol) of β-phenylcinnamic acid,[19] 0.2 ml of pyridine, and 16.8 g (0.14 mol) of thionyl chloride was heated at reflux (bath temperature 95–100 °C) for 48 h. The infrared spectra recorded after 24 and 48 h were shown to be identical. After excess thionyl chloride was removed by distillation the residue was dissolved in 50 ml of hexanes, filtered to remove pyridine hydrochloride, and concentrated to yield 4.38 g of yellow oil, a mixture of acid chlorides. The mixture (100 mg) in 2 ml of acetone was heated with 2 ml of 2 N sodium hydroxide solution on a steam bath till acetone was evaporated and a clear aqueous solution was formed. Acidification with dilute hydrochloric acid afforded, after filtration and drying, 80 mg of a mixture of acids. Recrystallization of the mixture from benzene gave 25 mg of **8b**, mp 198–200 °C (lit.[8] mp 199–200 °C), the infrared spectrum being identical with that of **8b** previously obtained. Further crystallization of the mother liquor from ligroin afforded 50 mg of crude 2-chloro-3-phenylpropenoic acid, mp 127–136 °C (lit[13] mp 136 °C).

To a stirred solution of half (2.20 g) of the above mixture of acid chlorides in 150 ml of dry methylene chloride was added portionwise at 2–3 °C approximately 2.2 equiv (2.26 g) of aluminum chloride. The temperature of the solution (dark green) was raised and maintained at 25 °C for 30 min. The solution was decomposed with 50 ml of 6 N hydrochloric acid, the layers were separated, and the aqueous layer was extracted with methylene chloride (50 ml). The combined methylene chloride solution was successively washed with water, saturated sodium bicarbonate solution, and saturated salt solution, dried ($MgSO_4$), and evaporated to yield 1.90 g of a mixture of solids. The mixture was separated on an alumina (activity grade III, 70 g) column. Elution with 50 ml of petroleum ether–ether (10:1) gave after recrystallization from ligroin, 0.80 g (33.2%) of ketone **13**, mp 99–101 °C (lit.[13] mp 99–100 °C). Further elution with benzene (500 ml) afforded, after recrystallization from ligroin, 0.82 g (35%) of **14** as red needles, mp 194–196 °C (lit.[14] mp 195–196 °C); the infrared spectra of **13** and **14** were identical with those of authentic samples.

Benzo[*b*]thiophene 14 from Sulfenyl Chloride 11d. To 1.83 g (5 mmol) of **11d** (83% purity) in 30 ml of dry benzene was added 1.5 g (1.1 mmol) of aluminum chloride portionwise at 10 °C. The mixture was stirred at 10–15 °C for 1 h and decomposed with 6 N hydrochloric acid (50 ml), and the layers were separated. The aqueous layer was extracted with benzene (50 ml × 2). The combined benzene layers were successively washed with water and saturated sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to yield 1.73 g of dark red solid. The solid was placed on a column containing 50 g of alumina (activity grade II) and eluted with petroleum ether–benzene (5:1) into seven fractions (50 ml each) and with a 1:1 mixture of the same solvent pair into ten more fractions (75–100 ml each). Recrystallization of fractions 5–9 from methanol afforded a total of 0.5 g (42%) of **14** as red needles, mp 195–196 °C. Mixture melting point with an authentic sample showed no depression, and the infrared spectrum was identical with that of an authentic sample.

Registry No.—**3b**, 103-26-4; **3d**, 830-09-1; **3e**, 619-89-6; **4a**, 21815-91-8; **4b**, 34576-87-9; **4c**, 59812-34-9; **4d**, 59812-35-0; **4e**, 59812-36-1; **6**, 59812-37-2; **7a**, 501-52-0; **7b**, 606-83-7; **7c**, 4593-90-2; **8a**, 6314-28-9; **8b**, 29491-86-9; **8c**, 41280-76-6; **8d**, 3133-81-1; **9a**, 1083-30-3; **9b**, 5195-24-4; **10a**, 59812-38-3; **10b**, 59812-39-4; **10c**, 59812-40-7; **11a**, 21815-89-4; **11c**, 39252-25-0; **11d**, 39252-24-9; **13**, 13093-22-6; **14**, 23339-77-7; thionyl chloride, 7719-09-7; methyl *p*-nitrobenzoate, 619-50-1; benzalpinacolone, 538-44-3; 2-chlorocarbonylbenzo[*b*]thiophene, 39827-11-7; 3-phenylbutanoic acid, 4593-90-2; β-phenylcinnamic acid, 606-84-8; 2-chloro-3-phenylpropenoic acid, 1727-39-5.

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Trapping of Thiaziridinimines with Imines and Nitriles

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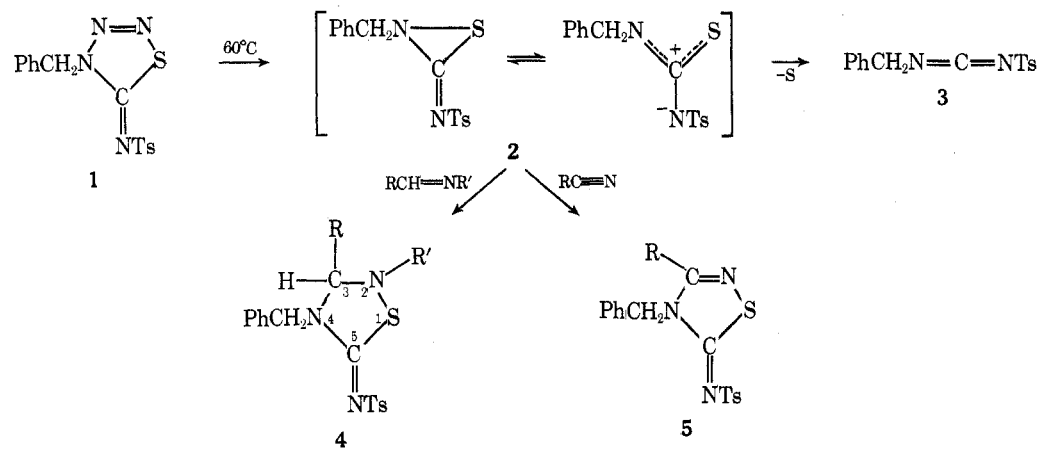
Thermolysis of 4-benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**1**) at 60–70 °C in the presence of imines and nitriles furnished respectively 5-tosylimino-1,2,4-thiadiazolidines (**4**) and 5-tosylimino-1,2,4-thiadiazolines (**5**) in good yields. Structure elucidation was based on spectral analyses and, in the case of **5**, on an independent synthesis and a crystal structure analysis. The ^{13}C NMR spectra of the new heterocycles are discussed by comparison with several model compounds.

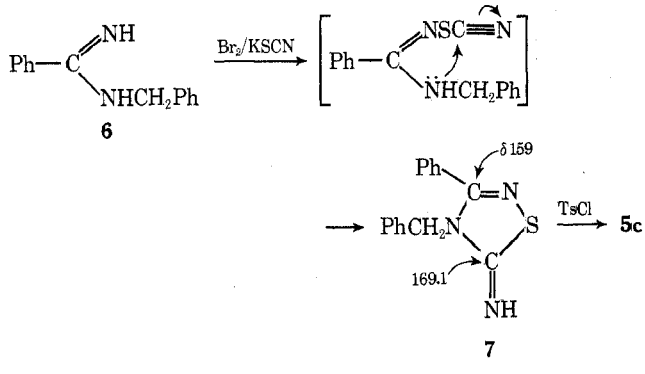
Thiaziridinimines or their ring-opened 1,3-dipolar species (e.g., **2**) have never been isolated, but their existence during the thermal conversion of 4-alkyl-5-sulfonyl-1,2,3,4-thiatriazolines into sulfonylcarbodiimides (e.g., **1** → **3**), has recently been demonstrated.[1,2] Thus, intermediate **2** was efficiently trapped with suitable olefins, acetylenes, keto-stabi-



lized phosphorus ylides, and heterocumulenes. Further work on the reactivity of thiaziridinimines has now shown that intermediate **2** can also be intercepted with imines and nitriles to give adducts **4** and **5**, respectively, having a 1,2,4-thiadiazoli(di)ne ring structure.

Cycloadducts. When imines were heated in CCl_4 with an equimolar amount of 4-benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**1**) at 60–70 °C for 2 h, compounds **4a–d** were obtained in fairly good yields. Nitriles, however, proved to be less efficient for trapping intermediate **2**, but good results were obtained by using them as solvent in our experiments. The results are summarized in Table I.

The reaction products are characterized by ir (C=NTs absorptions at 1545–1550 cm^{-1} for **4a–d** and at 1500–1530 cm^{-1} for **5a–d**), ^1H NMR, mass spectra, microanalyses, and the following independent synthesis. *N*-Benzylbenzamidine (**6**), prepared by the $AlCl_3$ catalyzed reaction of benzonitrile with benzylamine,[3] was treated with bromine and potassium thiocyanate.[4] The resulting 3-phenyl-4-benzyl-5-imino-1,2,4-thiadiazoline (**7**) was then tosylated in the presence of

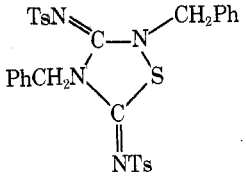


pyridine to give **5c**, identical in all respects with the reaction product of **1** and benzonitrile. Treatment of **5c** with KOH in ethanol at reflux temperature furnished *N*-benzyl-*N'*-tosylurea and benzoic acid in high yields.

Table I. 5-Tosylimino-1,2,4-thiadiazoli(di)nes

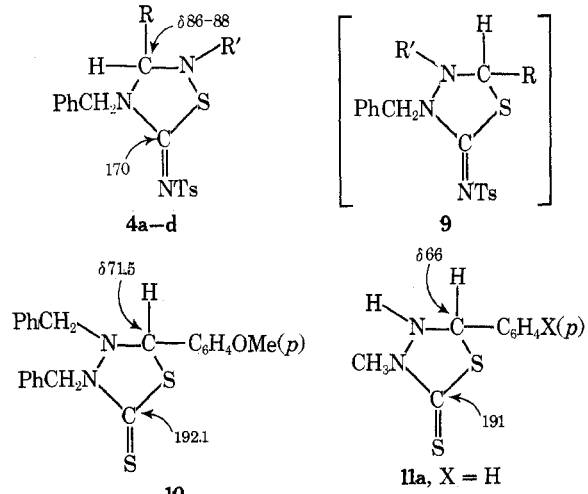
Compd	R	R'	Yield, %	Mp, °C
4a	C_6H_5	CH_3	77	155
4b	C_6H_5	*p*-ClC_6H_4	80	129–131
4c	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	47	189–192
4d	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	68	151–154
5a	CH_3		25	135–136.5
5b	$C_6H_5CH_2$		62	137–139
5c	C_6H_5		68	163–165
5d	*p*-$MeOC_6H_4$		77	143–144

Our method provides a new entry into the 1,2,4-thiadiazole ring system.[5] The only side product isolated in many reactions with nitriles was 2,4-dibenzyl-3,5-ditosylimino-1,2,4-thiadiazolidine (**8**), mp 221–223 °C. This compound, which resulted



from cycloaddition of **2** to **3** during the thermolysis reaction, has also been obtained in small amounts in previous trapping experiments.[1]

^{13}C NMR Analysis of Thiadiazoli(di)nes. The compounds **4a–d** showed the expected C=NTs ring carbon absorption at δ 170 ppm in the ^{13}C NMR spectra.[1] The other ring carbon atom resonated at δ 87 ppm pointing to a C–N(N) grouping in the adduct. Indeed, if addition had occurred in the reverse sense to give **9**, the C–N(S) ring carbon would be expected to absorb at higher field (ca. δ 70 ppm). This is shown for the model compounds **10, 11a,** and **11b** from the literature.[6,7] For compounds **5a–d** the situation is less straightforward. In order to distinguish between the C_3 and C_5 ring carbon absorptions, undecoupled NMR spectra were analyzed. The C_3 absorptions (at δ 156–157 ppm) were then broadened owing to multiple coupling, whereas the C_5 absorptions (at δ 177 ppm) were split into a triplet, only coupled with the benzyl protons. In addition, selective decoupling of the methyl hydrogens in **5a** enabled us to locate the C_3 carbon absorption



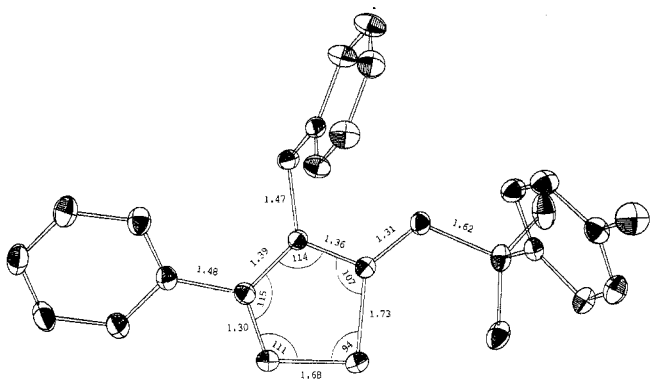
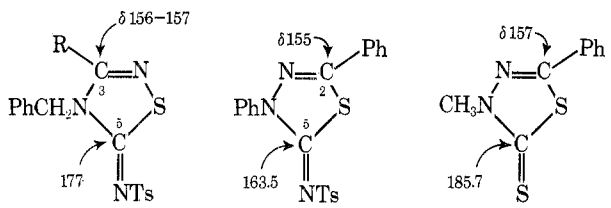


Figure 1.

at δ 155.6 ppm. For an interpretation of these results, we have made use of model compounds **12** and **13**, having a reversed structure about the endocyclic C=N moiety.[7,8] From the absorption values for C_3 in structures **5a–d** and C_2 in structures **12** and **13**, we are forced to the conclusion that differentiation between the two isomeric rings cannot be made on the basis of the chemical shift of the nitrile carbon atom in the adducts, as it was done for the imine adducts. In addition, the absorption values for the C_5 ring atoms in **5a–d** occurred at unusually low field (δ 177 ppm) compared with similar systems such as **1** (δ 166 ppm), **12** (δ 163.5 ppm), and others.[1] The difference between **5a–d** and **12**, however, parallels the larger



5a–d **12** ($CDCl_3$ as solvent) **13** ($CDCl_3$ as solvent)

difference observed very recently[9] for the C_5 absorptions in the aromatic systems isothiazole (δ 148.6 ppm) and thiazole (δ 118.8 ppm).

X-Ray Analysis of 5c. In view of the unusual ^{13}C NMR results and the knowledge that related ring systems are prone to undergo rearrangements,[10] we have determined the crystal structure of compound **5c**, confirming that it is in fact 3-phenyl-4-benzyl-5-tosylimino-1,2,4-thiadiazoline. The bond lengths (Table II and Figure 1) are as would be expected for a thiadiazoline structure. All rings are planar within 0.01 Å and the atoms directly linked to the thiadiazoline ring also lie within 0.01 Å of the ring plane.

Experimental Section

Ir spectra were recorded with a Perkin-Elmer Model 521 spectrometer, mass spectra with an AEI MS-12 instrument, and ^1H NMR spectra with a JOEL MH-100 or Varian XL-100 spectrometer. For ^{13}C NMR spectra, the XL-100 apparatus was equipped with a device for pulsed Fourier transform operation. All chemical shifts are relative to Me_4Si.

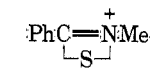
1-Benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**1**), mp 101–103 °C dec, was prepared as reported[1] by the reaction of benzyl azide with 1 equiv of tosyl isothiocyanate in CCl_4 at room temperature.

2-(*p*-Methoxyphenyl)-3,4-dibenzyl-1,3,4-thiadiazolidine-5-thione (**10**), mp 136–137 °C, was obtained by heating *N,N'*-dibenzylhydrazine with anisaldehyde and carbon disulfide according to the method of Huisgen et al.[6] Samples of model compounds **11a, 11b,** and **13** were kindly provided by Dr. Petersen of the Bayer industry, Leverkusen, Germany.[7]

2,4-Diphenyl-5-tosylimino-1,3,4-thiadiazoline (**12**), mp 189–191 °C, was prepared by treatment of *N*-(α-chlorobenzylidene)-*N'*-phenylhydrazine with thiourea as reported,[8] followed by tosylation of the resulting 2,4-diphenyl-5-imino-1,3,4-thiadiazoline (**12,** H instead of Ts) in the presence of triethylamine.

Synthesis of 5-Tosylimino-1,2,4-thiadiazolidines 4a–d. Equimolar amounts (0.01 mol) of **1** and imine were heated in CCl_4 (25–50 ml) at 60–70 °C for 2 h and the reaction residue was then worked up by crystallization from methanol.

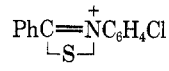
Compound **4a:** mp 155 °C; ^1H NMR ($CDCl_3$) δ 2.50 (s, 3 H, *p*-CH_3), 2.55 (s, 3 H, CH_3N), 3.85 (d, 1 H, benzyl proton, J = 15 Hz), 5.15 (s, 1 H, ring CH), 5.45 (d, 1 H, J = 15 Hz), 6.9–7.5 (m, 14 H), and 7.9 (d, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 437 (29, $M^{\cdot+}$), 360 (4, $M^{\cdot+}$ – Ph), 346 (1, $M^{\cdot+}$ – Tol), 224 (2, $M^{\cdot+}$ – TsNCS), 151 (74, $M^{\cdot+}$ – TsNCNBz), 150 (100, i), 119 (12), 118 (26), 91 (93).



i

Anal. Calcd for $C_{23}H_{23}N_3O_2S_2$ (437): C, 63.13; H, 5.26; N, 9.61; O, 7.32; S, 14.65. Found: C, 63.15; H, 5.25; N, 9.50; O, 7.35; S, 14.50.

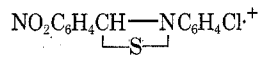
Compound **4b:** mp 129–131 °C; ^1H NMR ($CDCl_3$) δ 3.53 (s, 3 H, *p*-CH_3), 3.87 (d, 1 H, J = 15 Hz), 5.37 (d, 1 H, J = 15 Hz), 5.75 (s, 1 H, ring CH), 6.7–7.47 (m, 16 H), and 7.9 (d, 2 H); mass spectrum *m/e* (rel intensity) 533 (5, $M^{\cdot+}$), 320 (10, $M^{\cdot+}$ – TsNCS), 319 (6, $M^{\cdot+}$ – TsNCS – H), 247 (18, $M^{\cdot+}$ – TsNCNBz), 246 (22, ii), 216 (18), 215 (16), 214 (22), 194 (4), 180 (5), 165 (4), 155 (20), 91 (100).



ii

Anal. Calcd for $C_{28}H_{24}ClN_3O_2S_2$ (533): C, 62.98; H, 4.50; N, 7.87. Found: C, 63.16; H, 4.79; N, 7.69.

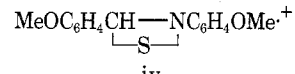
Compound **4c:** mp 189–192 °C; ^1H NMR δ 2.51 (s, 3 H, *p*-CH_3), 5.3 (s, 1 H, ring CH), 5.41 (d, 1 H, J = 15 Hz), 5.98 (d, 1 H, J = 15 Hz), 6.74–7.67 (m, 13 H), 7.92 (d, 2 H), and 8.3 (d, 2 H); mass spectrum *m/e* (rel intensity) 578 (5, $M^{\cdot+}$), 365 (3, $M^{\cdot+}$ – TsNCS), 292 (7, iii), 286 (4), 275 (6), 260 (14), 245 (3), 239 (3), 230 (4), 229 (4), 213 (6), 91 (100).



iii

Anal. Calcd for $C_{28}H_{23}ClN_4O_4S_2$ (578): C, 58.08; H, 3.98; N, 9.68. Found: C, 58.16; H, 4.13; N, 9.50.

Compound **4d:** mp 151–154 °C; ^1H NMR ($CDCl_3$) δ 2.51 (s, 3 H, *p*-CH_3), 3.78 (s, 3 H, *p*-OCH_3), 3.87 (s, 3 H, *p*-OCH_3), 3.90 (d, 1 H, J = 15 Hz), 5.39 (d, 1 H, J = 15 Hz), 5.64 (s, 1 H, ring CH), 6.58–7.44 (m, 15 H), and 7.92 (d, 2 H); mass spectrum *m/e* (rel intensity) 559 (2, $M^{\cdot+}$), 346 (1, $M^{\cdot+}$ – TsNCS), 286 (6), 273 (3, iv), 241 (89), 226 (78), 171 (2), 156 (4), 155 (40), 91 (100).



iv

Anal. Calcd for $C_{30}H_{29}N_3O_4S_2$ (559): C, 64.40; H, 7.51. Found: C, 64.74; H, 7.38.

Synthesis of 5-Tosylimino-1,2,4-thiadiazolines 5a–d. Compound **1** (0.01 mol) was thermolyzed at 60 °C in the presence of a 20-fold excess of nitrile (tenfold in the case of *p*-$MeOC_6H_4CN$) for 2 h and then heated at 80 °C for another 1 h. The excess of nitrile was distilled off in vacuo and the oily residue was crystallized from dry ether (40 ml) to give solids which in all cases except for **5d** were contaminated with 8 (15–30% by NMR). Purification was performed by fractional crystallization from methanol or in the case of **5a** by chromatography on a silica gel column using EtOAc–$CHCl_3$ (1:20 ratio) as the eluent.

Compound **5a:** mp 135–136.5 °C; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3 H, CH_3), 2.39 (s, 3 H, *p*-CH_3), 5.12 (s, 2 H, benzyl CH_2), 6.97–7.32 (m, 7 H), and 7.74 (d, 2 H); mass spectrum *m/e* (rel intensity) 361 (4), 360 (7), 359 (39, $M^{\cdot+}$), 206 (4), 205 (10), 204 (85, $M^{\cdot+}$ – Tos), 181 (3), 163 (21), 91 (100).

Anal. Calcd for $C_{17}H_{17}N_3O_2S_2$ (359): C, 56.83; H, 4.73; N, 11.70. Found: C, 56.76; H, 4.92; N, 11.72.

Compound **5b:** mp 137–139 °C; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3 H, *p*-CH_3), 3.90 (s, 2 H, benzyl CH_2), 5.00 (s, 2 H, benzyl CH_2), 6.80–7.36 (m, 12 H), and 7.70 (d, 2 H); mass spectrum *m/e* (rel intensity) 437 (4), 436 (8), 435 (36, $M^{\cdot+}$), 346 (2), 345 (4), 344 (25, $M^{\cdot+}$ – Bz), 282 (3), 281 (9), 280 (47, $M^{\cdot+}$ – Ts), 190 (1), 189 (2, $M^{\cdot+}$ – Ts – Bz), 181 (1), 91 (100).

Anal. Calcd for M·+ (determined by high-resolution exact-mass measurements): 435.1074. Found: 435.10323.

Compound **5c:** mp 163–165 °C; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3 H, p-CH_3), 5.13 (s, 2 H, benzyl CH_2), 6.68–7.60 (m, 12 H), and 7.73 (d, 2 H); mass spectrum *m/e* (rel intensity) 423 (4), 422 (8), 421 (36, M·+), 356 (2, M·+ − SO_2 − H), 268 (3), 267 (10), 266 (62, M·+ − Ts), 234 (1, M·+ − Ts − S), 181 (2), 165 (2), 91 (100).

Anal. Calcd for $C_{22}H_{19}N_3O_2S_2$ (421): C, 62.71; H, 4.51; N, 9.98. Found: C, 62.66; H, 4.70; N, 10.05.

Compound **5d:** mp 143–144 °C; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3 H, p-CH_3), 3.79 (s, 3 H, p-OCH_3), 5.13 (s, 2 H, benzyl CH_2), 6.73–7.36 (m, 11 H), and 7.69 (d, 2 H); mass spectrum *m/e* (rel intensity) 453 (4), 452 (8), 451 (38, M·+), 386 (2, M·+ − SO_2 − H), 298 (3), 297 (8), 296 (48, M·+ − Ts), 264 (1, M·+ − Ts − S), 190 (2), 91 (100).

Anal. Calcd for $C_{23}H_{21}N_3O_3S_2$ (451): C, 61.20; H, 4.66; N, 9.31. Found: C, 61.20; H, 4.95; N, 9.19.

For the independent synthesis of **5c**, the procedure of Goerdeler et al.[4] was utilized to prepare **7**. This compound (1.3 g) was dissolved in dry benzene (20 ml) containing 0.4 g of pyridine. An equimolar amount of tosyl chloride (0.95 g) was added dropwise with stirring and the reaction mixture was left overnight at room temperature. The precipitate (PyHCl) was filtered off and the filtrate was evaporated in vacuo to give a solid (**5c**, 76%) which was crystallized from methanol.

Basic Hydrolysis of 5c. Compound **5c** (4.2 g) was dissolved in a 2.4 M solution of KOH in ethanol (200 ml). The solution was refluxed for 2 h, then poured into ice–water (100 ml) and acidified with 2 N aqueous hydrochloric acid. The precipitate (*N*-benzyl-*N'*-tosylurea)[1] was isolated and dried in vacuo at 70 °C, yield 92%, mp 178–180 °C. The mother liquor was extracted twice with ether and the extracts were dried and then evaporated to give benzoic acid in 82% yield.

Crystal Structure Determination of 5c. Crystal data: $C_{22}H_{19}N_3O_2S_2$ (421.54); monoclinic, a = 10.049 (5), b = 19.985 (3), c = 10.526 (5) Å, β = 107.97 (3), d_m = 1.39 (1) g cm^{-3}, d_c (Z = 4) = 1.392 g cm^{-3}, μ (Cu Kα) = 25.17 cm^{-1}. Systematic absences $0k0$ for k odd and $h0l$ for l odd establish the space group as $P2_1/c$. Intensity data from a crystal 0.33 × 0.30 × 0.14 mm were collected for a quarter of reciprocal space out to 2θ = 144° with graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å) using a Nonius CAD-4 diffractometer in the θ–2θ mode; 3941 independent reflections were measured of which 883 had $I < 3\sigma(I)$ and were considered as unobserved. The data were corrected for absorption by the method of Busing and Levy[11] and for the usual geometric and polarization factors. The structure was solved by direct methods. Hydrogen atoms were located by the use of difference Fourier techniques. The structure was refined with individual isotropic temperature factors for the hydrogen atoms, individual anisotropic temperature factors for all other atoms, and correction for anomalous dispersion of the sulfur atoms to a final R value of 3.9% for the observed reflections. All computations were carried out using the local version of the x-ray 72 program system.[12]

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Registry No.—**1**, 42770-61-6; **4a**, 59938-44-2; **4b**, 59938-45-3; **4c**, 59938-46-4; **4d**, 59938-47-5; **5a**, 59938-48-6; **5b**, 59938-49-7; **5c**, 59938-50-0; **5d**, 59938-51-1; **7**, 59938-52-2; RCH=NR' (R = C_6H_5; R' = CH_3), 622-29-7; RCH=NR' (R = C_6H_5; R' = p-ClC_6H_4), 15383-71-8; RCH=NR' (R = p-$NO_2C_6H_4$; R' = p-ClC_6H_4), 25105-56-0; RCH=NR' (R = R' = p-$MeOC_6H_4$), 3261-60-7; RC≡N (R = CH_3), 75-05-7; RC≡N (R = $C_6H_5CH_2$), 140-29-4; RC≡N (R = C_6H_5), 100-47-0; RC≡N (R = p-$MeOC_6H_4$), 874-90-8.

Supplementary Material Available. Tables of bond lengths and angles and final atomic parameters of **5c** (5 pages). Ordering information is given on any current masthead page.

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Structure and Reactions of an Unusual Thionyl Chloride Oxidation Product. 9-Chloroacridinium 2-Chloro-1-(chlorosulfinyl)-2-oxoethylide

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9-Oxo-10-acridanacetic acid (1) reacts with thionyl chloride to give the title compound (2) in 95% yield. The structure **2** is established by x-ray crystallography. Exposures of **2** to amines, alcohols, and water indicate that, in addition to the anticipated reactions at the acyl chloride and the 9-chloroacridinium sites, the chlorosulfinyl group of **2** is readily cleaved. Controlled methanolysis, however, afforded the unstable thioamide *S*-oxide **7**. Pyrolysis of **2** leads to 9-chloroacridine.

9-Oxo-10-acridanacetic acid (**1**)[1] is a compound of some interest as an antiviral agent.[2] In the course of derivatization of **1**, we attempted to prepare the corresponding acid chloride by treatment with thionyl chloride. The dissolution of **1** ($C_{15}H_{11}NO_3$) with thionyl chloride in refluxing 1,2-dimethoxyethane was followed by crystallization of a copious amount (95%) of crimson red prisms, mp 206–208 °C, having the elemental composition of $C_{15}H_8Cl_3NO_2S$. We wish to record the structure (**2**) and reactions of this unusual intermediate.

The structure **2** has been determined by x-ray crystallography, details of which are described below. A stereodrawing