Anal. Calcd for $C_{25}H_{18}N_3F\cdot H_2O$: C, 75.55; H, 5.07; N, 10.57. Found: C, 75.89; H, 4.83; N, 10.64.

From 1 and Diphenylketene-*N*-*p*-iodophenylimine. The adduct was obtained in 50% yield: mp 249–251 °C; IR 3010 (w), 1625 (s), 1560 (m), 1540 (s), 1490 (m), 1435 (m), 1300 (m), 1140 (s), 1000 (w), 950 (w), 840 (m), 760 (m), 750 (s), 735 (w), 710 (w), 700 (m) cm^{-1}; NMR δ 6.8–8.5 (m).

Anal. Calcd for $C_{25}H_{18}N_3I\cdot\frac{1}{2}H_2O$: C, 60.49; H, 3.79; N, 8.47. Found: C, 60.49; H, 3.86; N, 8.47.

Reaction of 2-Bromopyridine-*N*-imine with 3. From these reagents using similar quantities and conditions for the other reactions, only diphenyl *N*-*p*-tolylacetamide (the amide corresponding to **3**) was isolated.

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Registry No.—**1**, 25275-41-6; **3**, 5110-45-2; **4**, 69027-81-2; **7**, 69027-82-3; **8** (Y = OMe), 40012-82-6; **8** (Y = H), 14181-84-1; **8** (Y = F), 41563-37-5; **8** (Y = I), 69027-83-4; *N*-aminopyridinium iodide, 6295-87-0; diphenylketene-*N*-(2,6-dimethylphenyl)imine, 42549-11-1; pyridine-d_5-*N*-imine, 69027-84-5; 2-picoline-*N*-imine, 51135-75-2; 2,3-dihydro-3,3-diphenyl-2-(2,6-dimethylphenylimino) -1*H*-pyrrolo[3,2-*b*]pyridine, 69027-85-6; 2,3-dihydro-3,3-diphenyl-2-(*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]-d_3-pyridine, 69027-86-7; 2,3-dihydro-3,3-diphenyl-5-methyl-2- (*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-87-8; 2,3-dihydro-3,3-diphenyl-2-(*p*-anisylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-88-9; 2,3-dihydro-3,3-diphenyl-2-(phenylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-89-0; 2,3-dihydro-3,3-diphenyl-2-(*p*-fluorophenylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-90-3; 2,3-dihydro-3,3-diphenyl-2-(*p*-iodophenylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-91-4; 2-bromopyridine-*N*-imine, 69027-92-5.

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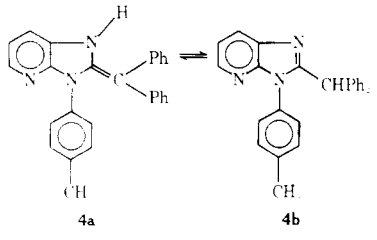
(4) One reviewer suggested that structures **4a** and **4b** were consistent with the data and should have been observed. We did not observe these compounds.



4a 4b

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Oxythioacetyl Chloride

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King and Durst[1] first clearly established the existence of the oxythioacyl chlorides, having isolated and established the structure of both geometric isomers of oxythiobenzoyl chloride (**1**). Other aryl derivatives as well as some complex, sterically hindered aliphatic analogues are also known but simple aliphatic derivatives have not yet been reported in spite of their possible synthetic utility.[2] In connection with current work

1 2

on the synthesis of alkyl-substituted thiirene oxides[3,4] we had occasion to examine the synthesis of the acetyl analogue **2**. Although **2** could be generated in ether solution at −30 °C by dehydrochlorination of sulfinyl chloride **4** according to the method devised by Strating, Thijs, and Zwanenburg[5] for compound **1** (see Scheme I), isolation of the pure substance proved to be impossible.[6]

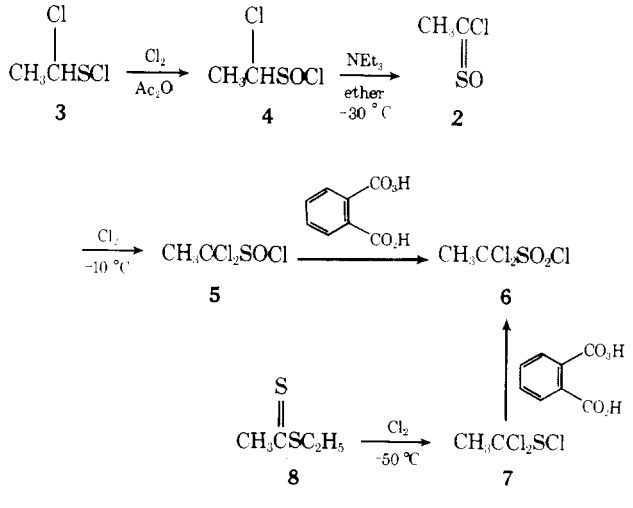
The structure of **2** was established by its reaction with chlorine to give α,α'-dichloroethanesulfinyl chloride (**5**) which itself was identified by oxidation to the corresponding sulfonyl chloride **6**. The latter was unambiguously synthesized by oxidation of α,α'-dichloroethanesulfenyl chloride (**7**), the chlorinolysis product of ethyl dithioacetate (**8**). Sulfinyl chloride (**4**) was identified by comparison with spectral data kindly provided by King[7] who obtained it by treatment of the corresponding sulfinic acid with thionyl chloride. Oxythioacetyl chloride (**2**) did not react with diazomethane at low temperatures and above room temperature underwent spontaneous decomposition. With 1 phenyldiazomethane gave not the expected episulfoxide but instead 2,5-diphenyl-1,3,4-thiadiazole.[4,8]

Experimental Section[9]

1-Chloroethanesulfenyl Chloride (3). 1-Chloroethanesulfenyl chloride can be obtained in yields of 3–30% by chlorination of a solution of trithioacetaldehyde in CH_2Cl_2 at −10 °C.[10] A superior preparation was adapted from a more recent general method of Douglass and co-workers.[11] A solution of 30 g (0.25 mol) of ethyl disulfide in 400 mL of pentane was placed in a 1-L three-neck flask equipped with a mechanical stirrer, gas in- and outlet tubes, and a low-temperature thermometer. After cooling to −60 °C in a dry ice–acetone bath a gentle stream of Cl_2 was flashed over the surface of the vigorously stirred solution by evaporation of 53 g (0.76 mol) of precondensed chlorine. After the addition of Cl_2 was completed, the thick slurry of white crystals was slowly warmed to room temperature. Vigorous stirring was essential due to the evolution of HCl at the decomposition temperature of the sulfur trichloride (ca. 13 °C). Following decomposition the solvent was removed with a water aspirator from a water bath and the residual yellow-orange oil distilled to give 50.9 g (78%) of the sulfenyl chloride as a yellow-orange liquid: bp 49 °C (40 mm) (lit.[10b] bp 47–50 °C (40 mm)); NMR ($CDCl_3$) δ 1.88 (d, 3, CH_3), 5.40 (q, 1, CH).

1-Chloroethanesulfinyl Chloride (4). 1-Chloroethanesulfinyl chloride was prepared by adaptation of a method of Douglass and co-workers.[12] Freshly prepared 1-chloroethanesulfenyl chloride (50.9 g, 0.39 mol) was mixed with 40.0 g (0.39 mol) of acetic anhydride in a 250-mL three-neck flask equipped with a gas dispersion tube, a $CaCl_2$ drying tube, a low-temperature thermometer, and a magnetic

Scheme I



stirring bar. The flask was cooled to −40 °C and Cl_2 gas was slowly bubbled into the stirred solution by evaporation of 27.6 g (0.39 mol) of precondensed chlorine at such a rate that the temperature did not exceed −30 °C. After addition was completed the reaction mixture was stirred at −30 °C for an hour. The acetyl chloride was removed by rotary evaporation from a water bath at 60 °C with the aid of a water aspirator, and the residual oil was distilled to yield 45.4 g (78%) of the sulfinyl chloride: bp 68 °C (22 mm) (lit.[13] bp 36–38 °C (3.7 mm)); IR ($CHCl_3$) 1150 cm^{-1} (S=O); NMR ($CDCl_3$) δ 1.91 (d, 3, CH_3), 5.14, 5.20 (q, 1, CH). The infrared and NMR spectra were identical to those obtained from a sample of the material prepared from 1-chloroethanesulfonyl chloride by the method of King.[7]

Treatment of 1-Chloroethanesulfinyl Chloride (4) with Triethylamine. Trapping of the Intermediate Thioacetyl Chloride *S*-Oxide (2) with Chlorine. Into a 250-mL three-neck flask equipped with an addition funnel, gas in- and outlet tubes, and a magnetic stirrer was placed 100 mL of hexane and 8.10 g (0.080 mol) of triethylamine. To this stirred solution at −30 °C was added dropwise a solution of 11.80 g (0.080 mol) of 1-chloroethanesulfinyl chloride in 50 mL of hexane. After addition was completed, the precipitate of triethylammonium chloride was filtered and washed with two 50-mL portions of cold (−30 °C) hexane, and the combined filtrate and washings were quickly returned to the cooling bath. All attempts to use this solution of thioacetyl chloride *S*-oxide in reactions with diazoalkanes were unsuccessful. To prove its intermediacy in the solution it was treated with Cl_2 in the cold. While maintaining the temperature at −30 °C, Cl_2 was flashed over the stirred solution by evaporation of 7.1 g (0.10 mol) of precondensed chlorine. Evaporation of the solvent in vacuo with a water aspirator from a 50 °C water bath and distillation of the residual brown oil yielded 7.3 g (50%) of a colorless liquid, bp 59 °C (14 mm), identified by its spectral data as 1,1-dichloroethanesulfinyl chloride (**5**) [IR ($CHCl_3$) 1175 cm^{-1} (S=O); NMR ($CDCl_3$) δ 2.42, (s, CH_3)]. For identification 2.28 g (0.013 mol) of the 1,1-dichloroethanesulfinyl chloride was added to 60 mL of ethereal perphtalic acid[14] (0.047 M; 0.028 mol) at 0 °C. The phthalic acid formed was filtered and rinsed with ice-cold chloroform. The combined rinsings and filtrate were evaporated from a water bath at 50 °C with a water aspirator, yielding an oily solid, which was recrystallized from pentane to give 1.5 g (65%) of 1,1-dichloroethanesulfonyl chloride (**6**), mp 37–38.5 °C. The sulfonyl chloride was identified by comparison of IR and NMR spectral data and a mixture melting point with an authentic sample prepared by the oxidation of 1,1-dichloroethanesulfenyl chloride (**7**).

1,1-Dichloroethanesulfenyl Chloride (7). A solution of 19.5 g (0.167 mol) of ethyl dithioacetate[15] dissolved in 100 mL of pentane was cooled to −40 °C. Anhydrous Cl_2, evaporated from 35.5 g (0.50 mol) of precondensed chlorine, was flashed over the surface of the stirred solution. The solid ethanesulfur trichloride was filtered through a plug of glass wool set in a chilled (−30 °C) funnel. The pentane was evaporated from the filtrate by means of a water aspirator and the residual yellow liquid was distilled to give 27.4 g (70%) of the sulfenyl chloride: bp 45 °C (28mm) (lit.[16] bp 46 °C (28 mm)); NMR ($CDCl_3$) δ 2.54 (s, CH_3).

1,1-Dichloroethanesulfonyl Chloride (6). An ethereal solution of perphthalic acid[14] (488 mL, 0.47 M, 0.230 mol) was added to a solution of 20.79 g (0.115 mol) of 1,1-dichloroethanesulfenyl chloride in 100 mL of anhydrous ether at 0 °C. The mixture was stored overnight in a refrigerator at −5 °C. The phthalic acid formed was removed by filtration and the solid was washed with three 50-mL portions of anhydrous ether. The ether was removed from the combined filtrate and washings by rotary evaporation with a water aspirator to yield a yellow oily solid. Recrystallization from pentane yielded 9.0 g (38%) of the sulfonyl chloride: mp 36–38 °C; IR ($CHCl_3$) 1390 cm^{-1}, 1175 (SO_2); NMR ($CDCl_3$) δ 2.57 (s, CH_3). An analytical sample was prepared by two further recrystallizations from pentane followed by vacuum sublimation, mp 37.0–38.5 °C.

Anal. Calcd for $C_2H_3Cl_3O_2S$: C, 12.17; H, 1.54; S, 16.25. Found: C, 12.27; H, 1.54; S, 16.47.

Treatment of Oxythiobenzoyl Chloride with Phenyldiazomethane. *cis*-Oxythiobenzoyl chloride (2.1 g) was prepared according to the procedure of King and Durst[1] from 9.6 g (0.05 mol) of phenylmethanesulfonyl chloride and 8 mL (0.057 mol) of triethylamine in 750 mL of cyclohexane (freshly distilled from CaH_2). A solution of phenyldiazomethane (ca 0.0121 mol) in ether was prepared according to the method of Yates and Shapiro[17] from 5.8 g of sodium hydroxide, 11 mL of water, 72 mL of methanol, and a solution of 4 g of azibenzil in 90 mL of ether. To a solution of 2.1 g (0.0121 mol) of oxythiobenzoyl chloride in 20 mL of anhydrous ether was added dropwise an ethereal solution of phenyldiazomethane (ca. 0.0121 mol) at room temperature. Gas evolution was noted and after complete addition the mixture was refluxed for 30 min, 2 mL (0.014 mol) of triethylamine was added, and the mixture was refluxed for 2 h. The precipitated triethylamine hydrochloride was filtered and washed with 15 mL of cold (5–10 °C) ether. The filtrate was washed with three 20-mL portions of 3 N hydrochloric acid and two 15-mL portions of water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to afford a solid admixed with an orange oil. Addition of 5 mL of a 1:1 mixture of ether–ligroin (bp 67–71 °C) to the mixture followed by filtration afforded 0.9 g of white plates, mp 141–143 °C. Recrystallization from ligroin (bp 67–71 °C) yielded 0.8 g (33.6%) of 2,5-diphenyl-1,3,4-thiadiazole, mp 142.5–144 °C (lit.[8] mp 141–142 °C), which was identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

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Registry No.—2, 68965-48-0; **3,** 19852-37-0; **4,** 28691-57-8; **5,** 68965-49-1; **6,** 68965-50-4; **7,** 19852-35-8; **8,** 870-73-5; trithioacetaldehyde, 2765-04-0; ethyl disulfide, 110-81-6; *cis*-oxythiobenzoyl chloride, 7214-46-2; phenylmethanesulfonyl chloride, 1939-99-7; phenyldiazomethane, 766-91-6; 2,5-diphenyl-1,3,4-thiadiazole, 1456-21-9.

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N-(α-Chloroalkyl)phthalimides

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The reaction of formaldehyde with amides and imides to give *N*-(hydroxymethyl)amides and -imides **1,** followed by conversion of **1** into the *N*-halomethyl derivatives **2,** consti-