VII and 1 mol of urea were mixed together and heated to 160–170° in 15 min. At 140° the mixture started evolving NH_3, and became turbid. After 30 min at 170° the mixture was a white solid. After cooling down, about 120 mg of starting material VII was extracted with toluene. The residue consisted of pure hydantoin XIII (identified by comparison of its ir spectrum with the ir spectrum of hydantoin obtained by a Strecker synthesis with 2,2,6,6-tetramethyl-4-oxopiperidine).

The oxazolidone XVI was made in an analogous procedure with amino alcohol XV.

Amino Alcohol XV.—Amino acid ester VII (214 mg) and 115 mg of $LiAlH_4$ were stirred in 5 ml of ether for 15 min. Water (0.8 ml) was added and then 30 ml of ether. Filtration and evaporation of the solvents yielded 200 mg of XV, mp 121.5° (petroleum ether–benzene), ir (Nujol) 3620, 3340, 3160, 1580 cm^{-1}.

Anal. Calcd: C, 64.5; H, 11.8; N, 15.05. Found: C, 64.85; H, 11.98; N, 15.04.

Esr Spectra.—The spectra described here have been taken at X band in a Varian E-3 spectrometer. Some preliminary studies were done with different solvents. The solutions were degassed and sealed off in a vacuum line. Radical concentrations were sufficiently low to eliminate intermolecular exchange broadening. The spectra were taken at 20°.

A selection of spectra of biradicals III, IX, XIX, and XX is shown in Figure 2. Figure 3 shows the spectra of biradical XI in five solvents of different polarities. Biradicals I and X showed three sharp lines and two broad lines inbetween. This type of spectrum has been discussed by Ferruti and coworkers.[5]

Registry No.—I, 34386-54-4; III, 34386-55-5; VII, 34386-56-6; IX, 34402-55-6; X, 34386-57-7; XI, 34402-56-7; XV, 32923-90-3; XIX, 21184-43-0; XX, 34386-59-9.

Sulfur Dioxide Extrusion from 2,5-Diaryl-4-hydroxy-3-ketotetrahydrothiophene 1,1-Dioxides. A Novel Synthesis of 1,4-Diarylbutane-2,3-diones[1]

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Received January 4, 1972

Five 2,5-diaryl-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-dioxides (**4a–e**) were prepared and reduced with zinc dust in acetic acid–ethanol–THF at 5–10° to 2,5-diaryl-4-hydroxy-3-ketotetrahydrothiophene 1,1-dioxides (**5a–e**). These products, in acetic acid–sodium acetate solution at 100–110°, underwent fragmentation to 1,4-diarylbutane-2,3-diones (**6a–e**) with loss of sulfur dioxide. Nmr analysis showed that the latter products consisted of mixtures of diketo and monoenol forms, with the monoenol predominating. It is proposed that the fragmentation reaction proceeds *via* a concerted elimination of sulfur dioxide from a 3-sulfolene intermediate.

α diketones have found a wide range of use in organic synthesis. However, one class of α diketones, the 1,4-diarylbutane-2,3-diones, appears infrequently in the chemical literature. The synthesis of only two compounds of this type has been reported: 1,4-diphenylbutane-2,3-dione and the 1,4-bis(4′-methoxyphenyl) analog. The former was prepared[2] by reaction of benzylmagnesium chloride with phenylacetaldehyde cyanohydrin, followed by hydrolysis and oxidation of the resulting acyloin with cupric acetate. The acyloin condensation has been reported to fail with ethyl phenylacetate.[3] According to a more recent report,[4] however, the reaction of ethyl 4′-methoxyphenylacetate proceeds in good yield to the corresponding acyloin, which upon oxidation gives 1,4-bis(4′-methoxyphenyl)-butane-2,3-dione.

For the general synthesis of substituted 1,4-diarylbutane-2,3-diones, the cyanohydrin method suffers from the lengthy preparation of intermediates. The acyloin method appears limited in its scope and is certainly unsuitable for the synthesis of analogs with halogen substituents since it involves the use of metallic sodium. We report here a new method for the synthesis of 1,4-diarylbutane-2,3-diones, which is fairly general in its scope and uses readily available starting materials. This method involves the intermediate synthesis of 2,5-diaryl-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-dioxides (*e.g.*, **4**), a class of compounds first prepared by Overberger and coworkers.[5]

Following the general route of Overberger[5a,c] (see Scheme I), treatment of 3,4-dimethylbenzyl chloride **1a** with sodium sulfide in aqueous ethanol yielded the sulfide **2a** (95%), which was oxidized with 30% hydrogen peroxide in acetic acid to sulfone **3a** (92%). Condensation of **3a** with excess diethyl oxalate in the presence of sodium ethoxide gave the cyclic diketo sulfone **4a** (80%), which exists in the tautomeric forms indicated.

We were interested in determining if compounds such as **4a** could be converted into 1,4-diarylbutane-2,3-diones by the action of reducing agents which are known to cause reductive cleavage of β-keto sulfones to ketones.[6] When **4a** was treated with zinc dust in acetic acid–ethanol–THF mixtures at 5–10° for 30 min, the major product isolated was the hydroxyketo sulfone **5a** (73%) rather than the butanedione **6a**. Thin layer chromatography (silica gel, benzene) of samples of the reaction mixture indicated the formation of only a minor amount of **6a** as a fast-moving spot. At higher temperatures further reduction of these products becomes a significant side reaction. The structure of

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[1] This investigation was supported in part by Research Contract DADA-17-71-C-1001 from the U. S. Army Medical Research and Development Command, Office of the Surgeon General. This is Publication No. 1031 from the Army Research Program on Malaria.

[2] (a) P. Ruggli and B. Hegedüs, *Helv. Chim. Acta*, **25**, 1285 (1942); (b) P. Ruggli and P. Zeller, *ibid.*, **28**, 741 (1945).

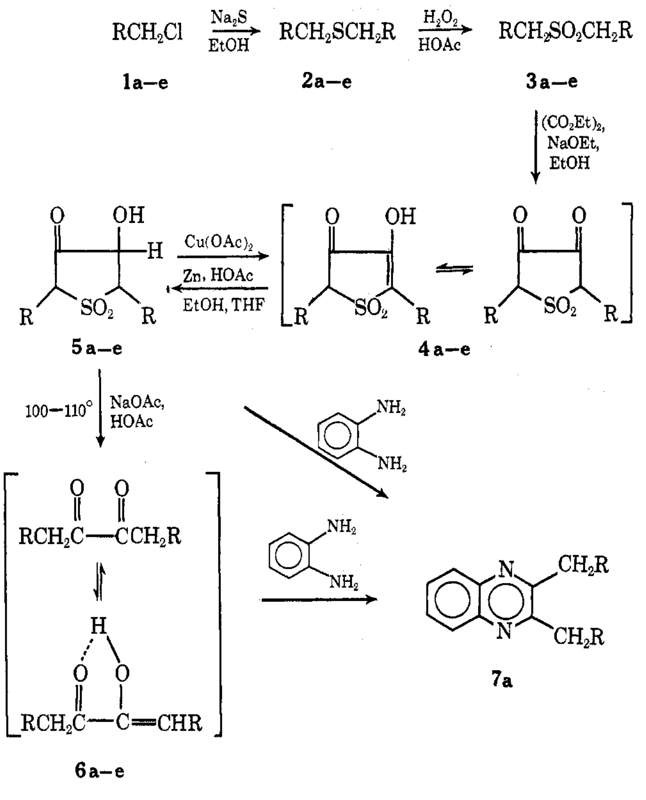
[3] N. R. Campbell, J. N. Dunsmuir, and M. E. H. Fitzgerald, *J. Chem. Soc.*, 2743 (1950).

[4] I. Hagedorn, U. Eholzer, and A. Lüttringhaus, *Chem. Ber.*, **93**, 1584 (1960).

[5] (a) C. G. Overberger, S. P. Ligthelm, and E. A. Swire, *J. Amer. Chem. Soc.*, **72**, 2856 (1950); (b) C. G. Overberger and J. M. Hoyt, *ibid.*, **73**, 3305, 3957 (1951); (c) C. G. Overberger, R. A. Gadea, J. A. Smith, and I. C. Kogon, *ibid.*, **75**, 2075 (1953).

[6] (a) E. J. Corey and M. Chaykovsky, *ibid.*, **86**, 1640 (1964); **87**, 1345 (1965). (b) H. O. House and J. K. Larson, *J. Org. Chem.*, **33**, 61 (1968).

SCHEME I



a, $R = 3,4\text{-}(CH_3)_2C_6H_3-$
b, $R = 4\text{-}ClC_6H_4-$
c, $R = 3,4\text{-}Cl_2C_6H_3-$
d, $R = 3\text{-}CF_3C_6H_4-$
e, R = 2-naphthyl

5a was verified by nmr spectrometry[7] and by reoxidation to **4a** with cupric acetate in aqueous methanol–acetic acid solution (93%).

When **5a** was heated under nitrogen in acetic acid at 100–110°, a slow decomposition occurred, with loss of sulfur dioxide and formation of butanedione **6a**, along with other products. In the presence of excess sodium acetate, however, sulfur dioxide extrusion occurred cleanly and rapidly at this temperature, with almost quantitative conversion into **6a**. The oily solid product thus isolated was found, by nmr spectrometry, to be a mixture of diketo (28%) and monoenol (72%) tautomeric forms. Product composition was determined by comparing the integral ratio of the diketo and monoenol methylene singlets (see Experimental Section). The existence of any significant amount of a doubly enolized tautomer was discounted since only one signal appeared in the vinyl region of the spectrum, which was attributed to the monoenol methine (half the integral area of the monoenol methylene). Verification of this was accomplished by determining the spectrum of the pure monoenol tautomer, isolated by fractional crystallization from hexane. Further proof that the fragmentation reaction proceeded cleanly to **6a** was shown by conversion of the crude mixture of tautomers into the quinoxaline **7a** (95%) upon treatment with *o*-phenylenediamine in refluxing ethanol; **7a** was also obtained (88%) when **5a** was refluxed with the diamine in ethanol–acetic acid.[8,9]

Following the same reaction scheme, four other cyclic diketo sulfones (**4b–e**) were prepared and transformed in good yield into the corresponding butanediones (**6b–e**). In each instance the products were isolated as a mixture of diketo and monoenol tautomers with the latter predominating. All the intermediate hydroxy keto sulfones were isolated and characterized except for **5e** (R = 2-naphthyl), which proved to be somewhat unstable during work-up and was therefore converted directly into **6e**. Steric factors may play an important role in the fragmentation of the 2-naphthyl compound. In fact, overall yields of butanediones in all of these examples may be improved by eliminating the isolation of the hydroxyketo sulfones. There was always some fragmentation during work-up of the reduction mixture, due presumably to the presence of acetic acid and zinc acetate.

The mechanism of sulfur dioxide extrusion from compounds such as **5** has not been fully investigated. However, in light of what is known about the thermal fragmentation of 2,5-dihydrothiophene 1,1-dioxides (3-sulfolenes) to dienes and sulfur dioxide,[10] it seems attractive, in this instance, to propose that a 3-sulfolene-type intermediate may be involved. According to this view, in acetic acid at 100–110° in the presence of excess sodium acetate, compounds **5a–e** undergo rapid equilibration to tautomeric enol and enediol forms. At this temperature[11] the latter tautomer, which can be considered a 3-sulfolene, undergoes fragmentation with concerted elimination of sulfur dioxide and formation of **6a–e**. Consistent with this mechanism is the finding that the reaction occurs only slowly in acetic acid alone, or in ethanol–sodium acetate solution. It appears that both an acid and a base are necessary for the reaction to occur rapidly, presumably because they promote enolization to the sulfolene.

Inasmuch as cyclic diketo sulfones such as **4a–e** can be prepared easily in large quantities and in excellent yields, we believe this method to be a practical preparation of 1,4-diarylbutane-2,3-diones. Also, since these cyclic sulfones can be alkylated at a methine position,[5b] the method is applicable in principle to the

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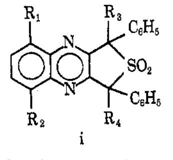
[7] The vicinal methine protons in compounds **5a–d** appear as a pair of doublets in deuterioacetone and deuteriopyridine with $J = 6.8$–7.0 Hz. By analogy to values found for 2,3-dihydrothiophene ($J_{trans} = 7.5$ Hz; $J_{cis} = 10.0$ Hz) we tentatively assign a trans configuration for the vicinal methines in **5a–d**. See R. J. Abraham in "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press, New York, N. Y., 1967, p 142.

[8] In the reaction of **5a** with *o*-phenylenediamine, a dark green color develops, which changes to orange as the reaction progresses. It is possible that this signals the transient appearance of an enamine which undergoes fragmentation, with loss of sulfur dioxide, prior to cyclization to the quinoxaline.

[9] Moriconi and coworkers have used compounds of type **4** for the preparation of thienoquinoxaline dioxides (i) and have studied the pyrolytic,

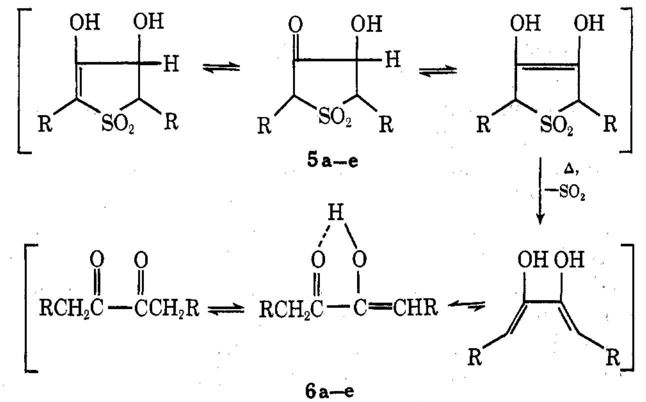


i

photolytic, oxidative, and reductive extrusion of sulfur dioxide from these compounds. See E. J. Moriconi, R. E. Misner, and T. E. Brady, *J. Org. Chem.*, **34**, 1651 (1969); **36**, 479 (1971).

[10] For recent work on the stereoelectronic course of these fragmentations, see (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966), and references cited therein.

[11] It has been shown[10a] that *cis*-2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide undergoes fragmentation with vigorous gas evolution at 100°, while the trans isomer requires a temperature of 150° or higher.[10] Under the equilibrating conditions of our system, the facile elimination of sulfur dioxide at 100° is understandable.



preparation of 1,4-diarylbutane-2,3-diones substituted at one of the methylene positions.

Experimental Section[12]

Bis(3,4-dimethylbenzyl) Sulfide (2a).—To a stirred solution of 3,4-dimethylbenzyl chloride[13] (186 g, 1.2 mol) in ethanol (360 ml), at 50°, was added slowly a solution of sodium sulfide (60% technical flakes, 78 g, 0.6 mol) in water (100 ml), at such a rate as to maintain reflux (~30 min). The mixture was stirred under reflux for 18 hr, cooled, and poured into a mixture of crushed ice and water (1.2 l.). Filtration gave a white solid (154 g, 95%), mp 45–50°. Recrystallization of a sample twice from ethanol gave colorless plates, mp 67–68°.

Anal. Calcd for $C_{18}H_{22}S$: C, 79.94; H, 8.20; S, 11.86. Found: C, 79.88; H, 8.35; S, 12.03.

Bis(3,4-dimethylbenzyl) Sulfone (3a).—To a stirred solution of **2a** (150 g, 0.556 mol) in glacial acetic acid (800 ml) was added slowly 30% hydrogen peroxide (340 g, 3.0 mol) at such a rate as to maintain the temperature at 70–80° (~45 min). After being stirred at 70° for an additional 3 hr, the mixture was cooled, and water (500 ml) was added. The white solid was filtered, washed thoroughly with water, and dried (155 g, 92.3%, mp 147–150°). Recrystallization of a sample twice from ethanol gave white crystals, mp 160–162°.

Anal. Calcd for $C_{18}H_{22}O_2S$: C, 71.48; H, 7.33; S, 10.60. Found: C, 71.40; H, 7.46; S, 10.42.

Bis(3,4-dichlorobenzyl) Sulfone (3c).—Following the above procedure, **2c**[14] gave the sulfone as a white solid (89%), mp 187–188° (from ethanol).

Anal. Calcd for $C_{14}H_{10}Cl_4O_2S$: C, 43.77; H, 2.62; Cl, 36.92; S, 8.33. Found: C, 43.70; H, 2.63; Cl, 37.01; S, 8.49.

Bis(3-trifluoromethylbenzyl) Sulfide (2d) and Sulfone (3d).—To a stirred solution of *m*-trifluoromethylbenzyl chloride[15] (100 g, 0.514 mol) in alcohol (500 ml) was added slowly sodium sulfide (60% technical flakes, 33.4 g, 0.257 mol) in water (50 ml). The mixture was heated under reflux for 5 hr, cooled, and poured into 1 l. of water. Extraction of the oily mixture with dichloromethane and evaporation of the combined extracts under vacuum afforded **2d** (90 g, quantitative yield) as a yellow oil. The oil was dissolved in glacial acetic acid (700 ml), and the solution was heated to 70–80° and stirred while 30% hydrogen peroxide (148 g, 1.3 mol) was added slowly. After 5 hr at 70–80°, the mixture was cooled and poured into crushed ice and water (1.2 l.). The white solid was filtered, washed thoroughly with water, and dried (86.5 g, 88%, mp 141–145°). Recrystallization from benzene gave colorless needles, mp 148–149°.

Anal. Calcd for $C_{16}H_{12}F_6O_2S$: C, 50.26; H, 3.16; F, 29.81; S, 8.38. Found: C, 50.16; H, 3.04; F, 30.19; S, 8.46.

2,5-Bis(3′,4′-dimethylphenyl)-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-Dioxide (4a).—A solution of sodium ethoxide was prepared from sodium (10.9 g, 0.475 g-atom) and absolute ethanol (600 ml). To this was added **3a** (65.5 g, 0.216 mol) and diethyl oxalate (63.1 g, 0.432 mol). The mixture was refluxed for 8 hr, cooled, and poured into water (1 l.). Some insoluble material was filtered off and the filtrate was acidified with concentrated hydrochloric acid to pH 2. The aqueous phase was decanted, and the remaining sticky solid was triturated with 50% aqueous ethanol. Filtration gave a light tan solid (53.5 g, mp 240–245°). An additional 8 g of material was obtained by extracting the aqueous phase with chloroform (total yield 80%). Recrystallization of a sample twice from ethanol gave colorless needles: mp 251–252°; ir ($CHCl_3$) 5.90 (s), 7.41 (s), 7.62 (s), 8.60 (m), 8.98 (m), 9.15 μ (m).

Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66; S, 9.00. Found: C, 67.52; H, 5.74; S, 8.89.

2,5-Bis(3′,4′-dichlorophenyl)-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-Dioxide (4c).—A solution of sodium ethoxide was prepared from sodium (3.75 g, 0.163 g-atom) and absolute alcohol (230 ml). To this was added sulfone **3c** (28.5 g, 0.0741 mol) and diethyl oxalate (43.3 g, 0.296 mol). The reaction mixture was refluxed for 7 hr, cooled, and poured into water (2 l.). The insoluble material was filtered off and the filtrate was acidified with concentrated hydrochloric acid to pH 2. The solid was filtered and dried (30 g, 92.3%), mp 262–265°. Recrystallization twice from ethyl acetate–hexane gave white crystals: mp 266–268°; ir (KCl) 5.81 (s), 6.81 (m), 7.33 (s), 7.80 (s), 8.62 (s), 8.89 (s), 9.22 μ (s).

Anal. Calcd for $C_{16}H_8Cl_4O_4S$: C, 43.86; H, 1.84; Cl, 32.37; S, 7.31. Found: C, 43.72; H, 1.71; Cl, 32.55; S, 7.19.

2,5-Bis(3′-trifluoromethylphenyl)-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-Dioxide (4d).—To a solution of sodium ethoxide prepared from sodium (1.26 g, 0.0548 g-atom) and absolute ethanol (70 ml) was added **3d** (10 g, 0.0261 mol) and diethyl oxalate (15.2 g, 0.104 mol). After being refluxed for 4 hr, the solution was cooled, poured into water (300 ml), and acidified with concentrated hydrochloric acid to pH 2. Filtration gave a white solid (11.1 g, 97.5%), mp 202–204°. Recrystallization from benzene gave white crystals: mp 203–205°; ir (KCl) 5.83 (s), 7.32 (s), 7.52 (s), 7.80 (s), 8.52 (s), 8.90 (s), 9.08 (s), 9.30 μ (s).

Anal. Calcd for $C_{18}H_{10}F_6O_4S$: C, 49.54; H, 2.31; F, 26.12; S, 7.34. Found: C, 49.57; H, 2.00; F, 26.21; S, 7.39.

2,5-Bis(3′,4′-dimethylphenyl)-4-hydroxy-3-ketotetrahydrothiophene 1,1-Dioxide (5a).—A stirred solution of **4a** (21.4 g, 0.06 mol) in glacial acetic acid (75 ml), ethanol (75 ml), and tetrahydrofuran (75 ml) was cooled to 5° in an ice bath, and zinc dust (19.5 g, 0.3 g-atom) was added.[16] After 10 min the temperature rose to 9°, and after 30 min the greenish yellow color of the mixture became gray and the temperature subsided. The mixture was filtered immediately under suction, and the filtered solids were washed with ethanol (50 ml). The combined filtrates were concentrated under vacuum to about one-third volume, and water (400 ml) was added slowly with stirring. The precipitated cream-colored solid was filtered, washed with water, and dried (20 g), mp 178–183° dec. Recrystallization from ethyl acetate–hexane gave colorless prisms (15.7 g, 73%), mp 204–206° dec. One more recrystallization furnished the analytical sample: mp 206–207° dec; ir (KCl) 6.02 (m), 7.82 (s), 8.92 (s), and 9.18 μ (s). The nmr spectrum (deuterioacetone) showed the two vicinal methine hydrogens as a pair of doublets centered at δ 4.47 and 5.22 (J = 6.8 Hz); in deuteriopyridine they appear at δ 5.15 and 5.70 (J = 6.8 Hz).

Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.01; H, 6.19; S, 8.95. Found: C, 66.95; H, 6.10, S, 9.02.

Oxidation of 5a to 4a.—A mixture of **5a** (0.5 g, 1.4 mmol) and copper acetate monohydrate (0.560 g, 2.8 mmol) in 50% aqueous acetic acid (25 ml) and methanol (10 ml) was refluxed for 2 hr. The cooled mixture was diluted with water (100 ml) and extracted with chloroform. The extracts were washed with water, dried over sodium sulfate, and evaporated to leave **4a** as a pale yellow solid (0.463 g, 93%), mp 244–246°, identified by its ir spectrum.

2,5-Bis(4′-chlorophenyl)-4-hydroxy-3-ketotetrahydrothiophene 1,1 Dioxide (5b).—A stirred solution of **4b**[5a] (9.6 g, 0.026 mol) in glacial acetic acid (80 ml), ethanol (80 ml), and tetrahydrofuran (80 ml) was cooled to 7° in an ice bath, and zinc dust (8.44 g, 0.13 g-atom) was added. After about 12 min the color of the

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[12] Ir spectra were taken with a Perkin-Elmer Model 137B double-beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60 instrument, with tetramethylsilane as the internal standard. Melting points were measured in Pyrex capillary tubes in a Mel-Temp apparatus (Laboratory Devices, Inc., Cambridge, Mass.) and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Werby Laboratories, Boston, Mass.

[13] Aldrich Chemical Co., Inc., Milwaukee, Wis.

[14] M.G. Voronkov, A. N. Pereferkovich, and S. V. Mikhailova, *Zh. Prikl. Khim* (Leningrad), **42**, 1155 (1969); *Chem. Abstr.*, **71**, 80852h (1969).

[15] Pierce Chemical Co., Rockford, Ill.

[16] Tetrahydrofuran is added to increase the solubility of the cyclic sulfones. The zinc dust used was purchased from Fisher Scientific Co.

mixture changed from greenish yellow to gray. The mixture was filtered immediately under suction and the solids were washed with ethanol (50 ml). The combined filtrates were evaporated under vacuum to a yellow oil, to which was added ethanol (10 ml). After further addition of water (150 ml), filtration gave a pale yellow solid (6.7 g). Trituration of this solid with 1:1 ethyl acetate–hexane (50 ml) and filtration gave almost colorless crystals (5.15 g, 53%), mp 238–244° dec. Recrystallization from ethyl acetate–hexane gave colorless prisms: mp 242–245° dec; ir (KCl) 6.02 (m), 6.72 (m), 7.82 (s), 8.85 (s) and 9.19 μ (s); nmr (deuteriopyridine) δ 5.18 (d) and 5.64 (d) (J = 6.8 Hz, vicinal methine protons).

Anal. Calcd for $C_{16}H_{12}Cl_2O_4S$: C, 51.76; H, 3.26; Cl, 19.10; S, 8.64. Found: C, 51.95; H, 3.14; Cl, 18.97; S, 8.42.

2,5-Bis(3′,4′-dichlorophenyl)-4-hydroxy-3-ketotetrahydrothiophene 1,1-Dioxide (5c).—A stirred solution of **4c** (8.76 g, 0.020 mol) in glacial acetic acid (50 ml), ethanol (50 ml), and tetrahydrofuran (50 ml) was cooled to 5° in an ice bath, and zinc dust (6.5 g, 0.1 g-atom) was added. The temperature was maintained at 5–10° for 1 hr and 5 min, after which the color changed from greenish yellow to gray. The mixture was filtered immediately and the solids were washed with ethanol (50 ml). The combined filtrates were evaporated to one-third volume, water (150 ml) was added, and the mixture was extracted with ethyl acetate. The extracts were washed with water, dried over sodium sulfate, and evaporated to leave a yellow oil. The oil was dissolved in benzene (30 ml) and scratched to induce crystallization. Cooling and filtration gave a white solid (3.55 g), mp 205–207° dec. Addition of hexane (20 ml) to the filtrate and cooling gave additional solid (1.4 g), mp 197–202° dec (total yield 56.2%). Recrystallization from ethyl acetate–hexane gave colorless prisms: mp 206–207° dec; ir (KCl) 6.07 (m), 6.82 (s), 7.37 (s), 7.83 (s), 8.88 (s), 9.16 μ (s); nmr (deuteriopyridine) δ 5.18 (d) and 5.62 (d) (J = 7.0 Hz, vicinal methine protons).

Anal. Calcd for $C_{16}H_{10}Cl_4O_4S$: C, 43.66; H, 2.29; Cl, 32.22; S, 7.29. Found: C, 43.32; H, 2.13; Cl, 32.50; S, 7.29.

2,5-Bis(3′-trifluoromethylphenyl)-4-hydroxy-3-ketotetrahydrothiophene 1,1-Dioxide (5d).—A stirred solution of **4d** (8.7 g, 0.02 mol) in glacial acetic acid (50 ml), ethanol (50 ml), and tetrahydrofuran (50 ml) was cooled to 3° in an ice bath, and zinc dust (6.5 g, 0.1 g-atom) was added. The temperature rose to ~10° after 16 min, and the color changed from greenish yellow to gray. The mixture was filtered immediately and the solids were washed with ethanol (50 ml). The combined filtrates were evaporated under vacuum to one-third volume, water (150 ml) was added, and the mixture was extracted with ethyl acetate. The extracts were washed with water, dried over sodium sulfate, and evaporated to a yellow oil. Trituration with a warm mixture of benzene (20 ml) and hexane (10 ml), cooling, and filtering gave a white solid (6.85 g, 78%), mp 195–199° dec. Recrystallization from ethyl acetate–hexane afforded colorless prisms: mp 197–200° dec; ir (KCl) 6.08 (m), 7.40 (s), 7.55 (s), 7.85 (s), 8.55 (s), 8.90 (s), 9.30 μ (s); nmr (deuterioacetone) δ 4.85 (d) and 5.48 (d) (J = 7.0 Hz); nmr (deuteriopyridine) δ 5.37 (d) and 5.76 (d) (J = 7.0 Hz, vicinal methine protons).

Anal. Calcd for $C_{18}H_{12}F_6O_4S$: C, 49.32; H, 2.76; F, 26.00; S, 7.32. Found: C, 49.31; H, 2.49; F, 26.26; S, 7.57.

Preparation of 1,4-Diarylbutane-2,3-diones.—The general procedure for the fragmentation reaction was to dissolve 1 to 2 g of **5a–d** and 5 molar equiv of sodium acetate in 20–30 ml of glacial acetic acid. With nitrogen bubbling through, the mixture was heated to 100–110° for 30 min. Completion of the reaction was monitored by tlc (silica gel, benzene). The solution was cooled, water (70 ml) was added, and the mixture was extracted with benzene. The extracts were washed three times with water, dried over sodium sulfate, and evaporated to a yellow solid (or an oil which crystallized when scratched) consisting of a mixture of diketo and monoenol (hydrogen bonded) forms. Nmr spectra were taken to determine product composition and the solids were recrystallized for analysis. The results are summarized below.

6a was obtained in 98% yield: oily solid; nmr (CCl_4, 0.5 M) δ 3.74 (s, diketo CH_2), 3.88 (s, monoenol CH_2), 6.36 (s, =CH–), 7.13 (s, hydrogen bonded –OH); 72% monoenol form. Recrystallization twice from hexane gave very pale yellow prisms: mp 85–86° (monoenol); ir ($CHCl_3$) 2.90 (m), 6.02 (s), 6.17 (s), 7.27 μ (s).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.28; H, 7.80.

6b was obtained in 97.6% yield: mp 115–131°; nmr ($CDCl_3$, 0.5 M) δ 3.93 (s, diketo CH_2), 4.07 (s, monoenol CH_2), 6.47 (s, =CH–); 86% monoenol form. Recrystallization twice from isopropyl ether gave very pale yellow prisms: mp 130–132° (monoenol); ir ($CHCl_3$) 2.92 (m), 6.03 (s), 6.17 (s), 6.77 (s), 7.26 (s), 9.20 (s), 9.90 μ (s).

Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.74; Cl, 23.08. Found: C, 62.47; H, 3.85; Cl, 22.86.

6c was obtained in 97.5% yield: oily solid; nmr ($CDCl_3$, 0.25 M) δ 3.96 (s, diketo CH_2), 4.07 (s, monoenol CH_2), 6.40 (s, =CH–); 83% monoenol form. Recrystallization twice from benzene–hexane gave pale yellow prisms: mp 155–157° (monoenol); ir ($CHCl_3$) 2.91 (m), 6.0 (s), 6.12 (s), 6.83 (s), 7.25 (s), 7.64 (s), 8.87 (s), 9.72 μ (s).

Anal. Calcd for $C_{16}H_{10}Cl_4O_2$: C, 51.10; H, 2.68; Cl, 37.71. Found: C, 51.16; H, 2.51; Cl, 37.90.

6d was obtained in 97.6% yield: mp 67–72°; nmr ($CDCl_3$, 0.5 M) δ 4.07 (s, diketo CH_2), 4.20 (s, monoenol CH_2), 6.57 (s, =CH–); 77% monoenol form. Recrystallization twice from hexane gave very pale yellow needles: mp 76–80° (mixture of diketo and monoenol); ir ($CHCl_3$) 2.90 (m), 5.82 (m), 6.0 (m), 6.12 (m), 6.92 (m), 7.21 (m), 7.55 (s), 8.59 (s), 8.85 (s), 9.30 μ (s).

Anal. Calcd for $C_{18}H_{12}F_6O_2$: C, 57.76; H, 3.23; F, 30.46. Found: C, 57.64; H, 3.16; F, 30.60.

1,4-Bis(2′-naphthyl)butane-2,3-dione (6e).—A stirred solution of **4e**[17] (4.0 g, 0.01 mol) in glacial acetic acid (100 ml), ethanol (50 ml), and tetrahydrofuran (200 ml) was cooled to 8° in an ice bath, and zinc dust (3.25 g, 0.05 g-atom) was added. The temperature was maintained at 8–10° for 1 hr and 5 min, at which time the greenish yellow color changed to gray. The mixture was filtered immediately and the solids were washed with 40 ml of ethanol. The combined filtrates were evaporated under vacuum to ~125 ml, and sodium acetate (4.1 g, 0.05 mol) was added. The mixture was heated at 100–110° for 30 min, with nitrogen bubbling through, and then cooled. Addition of water (150 ml), with stirring, and filtration of the granular precipitate yielded a light tan solid (3.1 g, 91.6%): mp 172–178°; nmr ($CDCl_3$, 0.125 M) δ 4.11 (s, diketo CH_2), 4.32 (s, monoenol CH_2), 6.78 (s, =CH–); 78% monoenol form. Recrystallization from ethyl acetate gave yellow prisms: mp 174–179° (mixture of diketo and monoenol); ir (KCl) 5.85 (s), 6.02 (m), 6.12 (m), 6.68 (m), 7.21 (m), 7.38 (m), 7.62 μ (m).

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.83; H, 5.54.

2,3-Bis(3′,4′-dimethylbenzyl)quinoxaline (7a) from (5a).—A mixture of **5a** (0.717 g, 0.002 mol) and *o*-phenylenediamine (0.216 g, 0.002 mol) in ethanol (10 ml) and glacial acetic acid (2 ml) was heated to reflux. The color of the solution became dark green and changed to orange after 5 min. After being refluxed for 3 hr, the solution was cooled, water (30 ml) was added, and the mixture was neutralized with dilute aqueous sodium hydroxide. Filtration gave the quinoxaline as a tan solid (0.646 g, 88%), mp 95–99°. Recrystallization twice from ethanol gave colorless needles, mp 108–110°. The solid gave a purple quinoxaline test with concentrated sulfuric acid.[18]

Anal. Calcd for $C_{26}H_{26}N_2$: C, 85.20; H, 7.15; N, 7.65. Found: C, 85.07; H, 7.45; N, 7.43.

7a from 6a.—When the crude fragmentation product **6a** was refluxed with 1 molar equiv of *o*-phenylenediamine in ethanol, the quinoxaline was obtained in 95% yield.

Registry No.—**2a**, 34277-82-2; **3a**, 34277-83-3; **3c**, 34277-84-4; **3d**, 34277-85-5; **4a**, 34277-86-6; **4c**, 34277-87-7; **4d**, 34277-88-8; **5a**, 34277-89-9; **5b**, 34277-90-2; **5c**, 34277-91-3; **5d**, 34277-92-4; **6a** diketone, 34277-93-5; **6a** monoenol, 34297-65-9; **6b** diketone, 34277-94-6; **6b** monoenol, 34277-95-7; **6c** diketone, 34297-66-0; **6c** monoenol, 34277-96-8; **6d** diketone, 34277-97-9; **6d** monoenol, 34277-98-0; **6e** diketone, 34277-99-1; **6e** monoenol, 34278-00-7; **7a**, 34278-01-8.

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(17) Compound **4e** was prepared by the method of Overberger,[5a] except that the intermediate β-naphthylmethyl sulfone was obtained from the corresponding sulfide by oxidation with 30% hydrogen peroxide in acetic acid (84%), rather than by oxidation with chromic anhydride.

(18) W. J. Hickinbottom, "Reactions of Organic Compounds," 3rd ed, Longmans, Green and Co., London, 1957, p 439.