and the presence of **10A** (δ 53.6). Distillation of the residue under reduced pressure yielded 21.8 g of **10A** (88 mmol, 88% yield): bp 128–131 °C (0.5 mm); ^{11}B NMR δ 53.6 (s, THF); MS, *m/e* M^+ 248; n^{20}_D 1.4923; $[\alpha]^{22}_D$ 5.52° (*c* 3.3, THF).

General Procedure for the Syntheses of Chiral Dialkylmonoalkoxyborohydrides. The procedure for the synthesis of K 9-*O*-Ipc-9-BBNH (**6B**) is representative. An oven-dried, 100-mL, round-bottom flask equipped with a Teflon stopclock on a sidearm was attached a condenser connected to a mercury bubbler. The flask was cooled to room temperature under a stream of nitrogen. To the flask was transferred potassium hydride as an oil suspension by using a double-ended needle. The potassium hydride was allowed to settle and most of the oil decanted with a double-ended needle. Then the potassium hydride was washed with pentane (3 × 50 mL). To this oil-free potassium hydride (2.4 g, 60 mmol), suspended in THF (40 mL), was added the THF solution (40 mL) of **6A** (10.96 g, 40 mmol) via a doulbe-ended needle with vigorous stirring. The reaction was monitored both by hydrolysis of centrifuged aliquots and ^{11}B NMR. The reaction became slightly exothermic after a 10–30-min induction period. It was complete within 2 h, producing the addition compound **6B**. After the reaction was complete, the condenser was replaced with a tapered ground-glass adaptor equipped with a stopclock, and the excess potassium hydride was allowed to settle for 48 h. An aliquot of the clear solution was hydrolyzed in a THF–glycerine–2 N HCl mixture (1:1:1) and the hydrogen evolved was measured, indicating the concentration of **6B** as 0.48 M (96% yield): ^{11}B NMR, δ −1.51 (d, THF, J_{B-H} = 75.6 Hz at ca. 0.1 M); IR, ν_{B-H} = 2003 cm^{-1}. The solution stored under a positive pressure of nitrogen revealed no change in hydride concentration and in ^{11}B NMR spectra over a period of several months. The concentration of boron was estimated as 1,5-cyclooctanediol following oxidation of an aliquot with alkaline hydrogen peroxide, indicating [B] = 0.50 M. The content of potassium was measured as KOH following hydrolysis of an aliquot. Titration with standard acid indicated [K^+] = 0.49 M. Therefore, a stoichiometry of K:B:H as 1:1:1 was established.

General Procedure for Asymmetric Reduction of Prochiral Ketones. The following procedure for the asymmetric reduction of acetophenone with **6B** is representative. The THF solution of acetophenone (5 mL, 5 mmol) precooled to −78 °C was added to the solution of **6B** in THF (0.48 M, 11.5 mL, 5.5 mmol) at −78 °C via a double-ended needle. After a 24-h reaction, unreacted hydride was quenched by injecting anhydrous HCl in Et_2O precooled to −78 °C. Then the mixture was raised to 25 °C and the solvent evaporated. The reduction product was extracted with pentane after hydrolysis of the residue with dilute HCl, followed by conversion of the borinic acid moiety into the "ate" complex[4] using aqueous NaOH. The pentane layer was washed with brine, dried ($MgSO_4$), and filtered and the solvent evaporated. Bulb-to-bulb distillation of the residue yielded a mixture of product 1-phenylethanol and (−)-isopinocampheol. The distilled mixture was directly utilized for derivatization with MTPA-Cl. The corresponding MTPA esters of the product alcohols were prepared according to the procedure in the literature.[17] Capillary GC analysis (Supelcowax, 15M) of MTPA esters revealed a composition of 73.5% *S* and 26.5% *R* (i.e., 47% ee). GC analysis of the product mixture obtained by alkaline H_2O_2 oxidation in a separate small-scale experiment indicated 95% yield of product 1-phenylethanol. For a reduction of 3-methyl-2-butanone, a slightly modified procedure was used. After carrying out the reduction in 10-mmol scale for 6 h at −78 °C, unreacted hydride was destroyed by injecting ca. 1 equiv of precooled MeOH and stirring for 1 h at −78 °C. After raising the temperature to 25 °C, it was important to evaporate all the solvent and volatiles before hydrolyzing the product ate complex with dilute HCl. The residue was extracted with pentane following the same procedure as before. The product alcohol was separated from the solvent pentane by distillation using a Widmer column. Capillary GC analysis of MTPA esters of the product alcohols indicated a composition of 19.5% *R* and 80.5% *S* (i.e., 61% ee). GC analysis of a separate experiment indicated 98% yield of 3-methyl-2-butanol after alkaline H_2O_2 oxidation.

Acknowledgment. We are grateful to the United States Army Research Office for the financial assistance (ARO DAAG 29-85-K 0062). B.T.C. also express his thanks to the Korean Science and Engineering Foundation for the postdoctorate fellowship provided during this research.

Registry No. **5B**, 101696-41-7; (−)-**6**, 1196-00-5; (−)-**6A**, 103068-09-3; **6B**, 103190-48-3; (+)-**7**, 15356-60-2; (+)-**7A**, 103068-10-6; **7B**, 103148-25-0; (−)-**8**, 4017-88-3; (−)-**8A**, 103148-24-9; **8B**, 103190-49-4; (+)-**9**, 39947-48-3; (+)-**9A**, 103068-11-7; **9B**, 103148-26-1; (+)-**10A**, 103068-12-8; **10B**, 103148-27-2; 9-BBN, 280-64-8; $BH_2Cl{\cdot}Et_2O$, 36594-41-9; LimBCl, 81805-73-4; (−)-limonene, 5989-54-8; cyclohexanol, 108-93-0; acetophenone, 98-86-2; 3-methyl-2-butanone, 563-80-4; (*R*)-1-phenylethanol, 1517-69-7; (*S*)-1-phenylethanol, 1445-91-6; (*R*)-3-methyl-2-butanol, 1572-93-6; (*S*)-3-methyl-2-butanol, 1517-66-4.

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Chemistry of 1,1-Dioxothiopyrans. 1. Syntheses and Reactions of 2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide and 4*H*-Thioflaven-4-one, 1,1-Dioxide

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Improved syntheses and certain reactions of 2,6-diphenyl-4*H*-thiopyan-4-one 1,1-dioxide and 4*H*-thioflaven-4-one 1,1-dioxide are reported. Many of these derivatives, which display *reversible*, one-electron reduction waves in their cyclic voltammograms between $E^\circ_{1/2}$ = −0.10 and −0.40 V (vs. SCE), are of interest as a potential new class of organic acceptors. Single-crystal X-ray analysis of 4-(dicyanomethylene)-2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (DCTD) showing its molecular dimensions and packing order is described.

2,6-Diphenyl-4*H*-thiopyran-4-one (**1**)[1] has been the key building block for the syntheses of a variety of donors,[2] sensitizers,[3] and dyes[4] of interest in research on organic conductors and photoconductors. The properties of many

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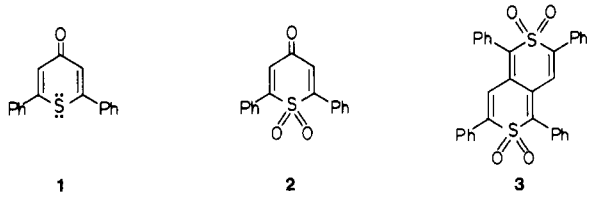
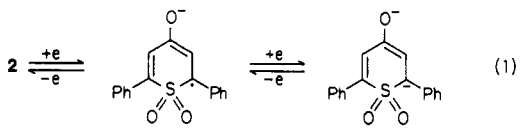


1 2 3

of these derivatives of 1 are attributed in large part to the availability of one of the lone pairs of electrons on sulfur for p-π conjugation. This propensity for delocalization involving one of the pairs of periplanar electrons on sulfur in the thiopyranyl system is reflected also in the stability associated with the aromatic 6π thiopyrylium structure[5] and is the foundation of most of its rich chemistry.[6]

Our recent success in the synthesis of the first thiopyrano[4,3-*c*]thiopyran disulfone **3**[7] as a new acceptor, having a reversible reduction half-wave potential at $E°_{1/2}$ = –0.6 V in DMF on Pt (vs. SCE), led us to explore further the synthesis and chemistry of the related sulfone derivative **2**. We are particularly interested in 2,6-diphenyl-4*H*-thiopyran-4-one 1,1-dioxide (**2**) because it can be envisaged not only as a unique thiopyranone without the lone pair of electrons on sulfur but also as a group 6 analogue of quinone.

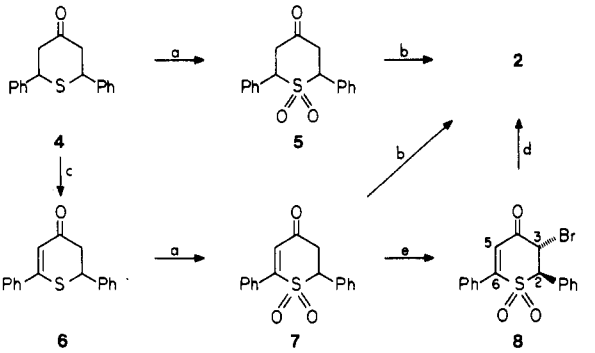
From the outset, it was exciting to find that **2** displays two one-electron, *reversible* reduction waves at $E°_{1/2}$ = –0.61 and –1.11 V in CH_2Cl_2 vs. SCE, much like *p*-benzoquinone, which also has two at $E°_{1/2}$ = –0.48 (reversible) and –1.12 V (irreversible) in CH_3CN. The electrochemically reduced species of **2** can be attributed to the formation of the resonance-stabilized radical anion and dianion shown in eq 1. Although the sulfone **2** was known



(1)

in the literature for 60 years,[9] its chemistry was little explored. Convinced that the $E°_{1/2}$ of **2** could be modified by substitution, especially with electron-withdrawing groups, we have studied the synthesis and properties of this type of compound as a potential new class of organic acceptors and report herewith an improved synthesis of **2** and some of its fascinating chemistry. The closely related 4*H*-thioflaven-4-one 1,1-dioxide (**10**) is also included. Many of these derivatives display *reversible* one-electron reduction waves in their cyclic voltammograms, a property considered indispensable for the design of an organic acceptor. In addition, we present the X-ray single-crystal analysis of the malononitrile derivative of **2**, which recently was shown to exhibit photoinduced electron-transport properties through polymeric thin films in electrophotography.[8]

Scheme I[a]



[a] (a) 40% peracetic acid (PAA), room temperature; (b) catalytic I_2/Me_2SO/catalytic concentrated H_2SO_4; (c) NCS/pyr; (d) Et_3N; (e) $Br_2/h\nu$.

Synthesis of 2

The sulfone **2** was originally synthesized by Arndt and co-workers[9] in 1925 by heating **1** with hydrogen peroxide in acetic acid. Their yield was unreported. Repeating their work, we have found this preparation to be far from satisfactory, with yields of 18–29% of a product contaminated with starting material. We therefore sought as our initial goal an improvement in the synthesis of **2**. Our approach is outlined in Scheme I.

Since the lone pair of electrons on sulfur in **1** is highly delocalized by p-π conjugation, we reasoned that removing the double bonds in **1** should give a compound that is readily oxidized. Indeed, when **4** and **6**[10] were exposed to 2 equiv of *m*-chloroperbenzoic acid in methylene chloride, the corresponding sulfones **5** and **7** were obtained in high yields. We found later that, for large-scale preparation, 40% peracetic acid (PAA) in CH_2Cl_2 or acetic acid at room temperature was preferred. Photolytic bromination of **7** with bromine in CH_2Cl_2 and a sunlamp gave the 3-*trans*-bromo derivative **8** ($J_{2,3}$ = 13.5 Hz) from which **2** was prepared by dehydrobromination with Et_3N. This approach worked well on a small scale but was less satisfactory for large scale preparations, particularly the photolytic bromination step, which appeared to be radical in nature.

Direct dehydrogenation of **7** with specially prepared "active MnO_2"[11] in $CHCl_3$ gave **2** in excellent yield, but handling large amounts of MnO_2 and reduced manganese were also formidable for large preparations. Our best procedure for the dehydrogenation was to heat **7** in Me_2SO on a steam bath in the presence of a catalytic amount of I_2 and concentrated sulfuric acid,[12] from which **2** was isolated in 85% yield. Under the same conditions, the tetrahydro compound **5** gave **2** directly in 57–81% yield; this is the procedure of choice for large-scale preparations of **2**.

Synthesis of Thioflaven-4-one 1,1-Dioxide (10)

The sulfone **10** was also originally prepared by Arndt and co-workers[9] using the sequence of bromination, oxidation, and dehydrobromination (pyridine) on the dihydro

(1) Chen, C. H. *Heterocycles* **1977**, *7*, 231. Chen, C. H.; Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1977**, *42*, 2777.
(2) Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1980**, *45*, 2448, 2453, 2458. Reynolds, G. A.; Chen, C. H. *Ibid* **1981**, *46*, 184; *J. Heterocycl. Chem.* **1981**, *18*, 627, 1235. Chen, C. H.; Doney, J. J.; Reynolds, G. A. *J. Org. Chem.* **1982**, *47*, 680. Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519. Nakasiyi, K.; Nakatsuka, M.; Murata, I. *J. Chem. Soc., Chem. Commun.* **1981**, 1143.
(3) Fox, C. J.; Light, W. A. U.S. Patent 3 706 554, 1972.
(4) Reynolds, G. A.; Drexhage, K. H. *J. Org. Chem.* **1977**, *42*, 885.
(5) Luttringhaus, A.; Engelhard, N. *Angew. Chem.* **1961**, *73*, 218.
(6) For a brief review of the chemistry of thiopyrans, see: Kharchenko, V. G.; Chalaya, S. N.; Konovalova, T. M. *Khim. Geterotsikl. Soedin.* **1976**, 1003.
(7) Chen, C. H.; Reynolds, G. A.; Smith, D. L.; Fox, J. L. *J. Org. Chem.* **1984**, *49*, 5136.
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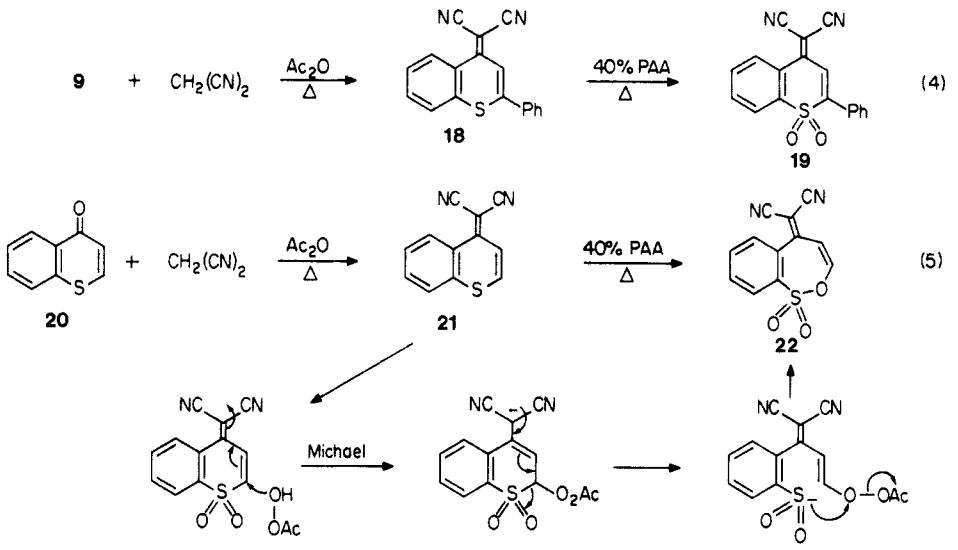
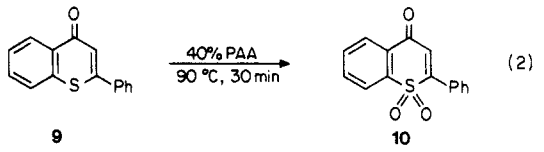
(9) Arndt, F.; Nachtweg, P.; Pusch, J. *Chem. Ber.* **1925**, *58*, 1612, 1633.
(10) Chen, C. H.; Reynolds, G. A.; Van Allan, J. A. *J. Org. Chem.* **1977**, *42*, 2777.
(11) Chen, C. H.; Reynolds, G. A.; Cossar, B. C. *J. Org. Chem.* **1981**, *46*, 2752. See also: U.S. Patent 2 459 714, 1949.
(12) Fatma, W.; Iqbal, J.; Ismail, H.; Ishratullah, Kh.; Sheida, W. A.; Rahman, W. *Chem. Ind. (London)* **1979**, *315*.



derivative of **9**. We found, however, that **9**, prepared readily from thiophenol, ethyl benzoylacetate, and polyphosphoric acid,[13] can be oxidized directly by heating with commercial 40% PAA on a steam bath to give the desired sulfone **10** in 80% yield (eq 2). In contrast to **1**, the lone pair on sulfur of **10**, because of the fused benzene ring, is more accessible to oxidation than that of **1**.



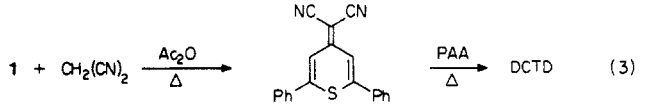
Reactions of 2, the Dihydro Derivative 7, and 10

A. Knoevenagel Condensation. The best method for converting the ketone group of **2** to other electron-withdrawing substituents is condensation of **2** with compounds such as $CH_2(CN)CO_2R$, $CH_2(CN)_2$, 1,3-dicarbonyl, and 1,3-disulfonylmethylene derivatives under the conditions of the Knoevenagel condensation.[14]

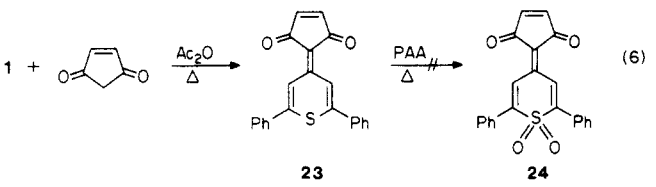
Among the numerous active-methylene compounds that have been tried, however, only malononitrile, Meldrum's acid, and 1,3-indandione gave the respective condensation products **11**, **12**, and **13** (Scheme II).

Compounds that failed under a variety of reaction conditions are mostly sulfones such as (phenylsulfonyl)-acetonitrile, benzyl phenyl sulfone, and bis(phenylsulfonyl)methane. Ethyl cyanoacetate could not be condensed with **2** under the normal experimental conditions, but in the presence of 2 equiv of $TiCl_4$ and 4 equiv of pyridine in THF[15] the desired product (**14**) was obtained in 88% yield.

B. Synthesis of DCTD and Its Thiochroman Analogue. The compound isolated from the condensation of malononitrile and **2** was 4-(dicyanomethylene)-2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (**11**, DCTD). This compound is of particular interest because it can be envisaged as a sulfone analogue of tetracyanoquinodimethane (TCNQ), a well-known organic acceptor.[16] In particular, DCTD (of various 1,1-dioxothiopyrans) was shown to have interesting and effective photoinduced electron-transport properties through thin polymer films in electrophotography.[8] We therefore spent much effort to improve the synthesis of DCTD. Among the many base and solvent combinations that we tried on the Knoevenagel reaction, such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or piperidine and benzene, acetonitrile, methanol, ethanol, or *n*-BuOH, a catalytic amount of piperidine and ethanol yielded the best result (69% on an 8-g run).



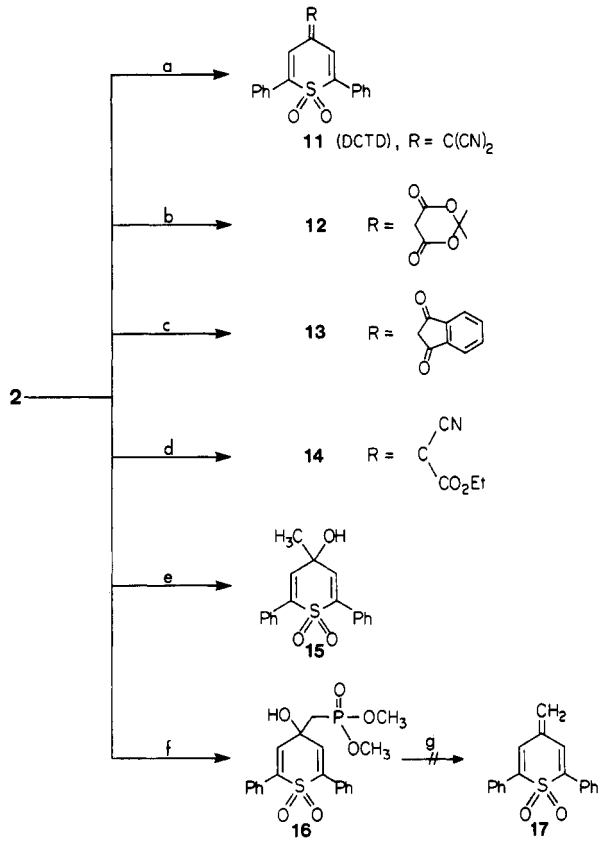
The acetic anhydride condensation of the thiopyrone **1** with malononitrile gave 4-(dicyanomethylene)thiopyran quantitatively (eq 3), but the peracetic acid oxidation was difficult and the yield of DCTD was poor. Nevertheless, this was the only successful approach for the synthesis of the thioflavene analogue **19**, which could not be prepared by any other procedures (eq 4). When this reaction was tried on the parent thiochroman-4-one[10] (**20**), without the C-2 substituent, an interesting product was isolated in 29% yield from the PAA oxidation of **21**. From its spectroscopic data and elemental analysis, we assigned the structure of this colorless solid to be **22**, which we believe to result from an initial Michael addition of PAA at C-2 followed by ring expansion involving the incipient sulfinate anion, as depicted in eq 5. This reaction formally resembles a Baeyer–Villager oxidation at the sulfone which, to our knowledge, is unprecedented. A similar condensation was also tried on **1** with 1,3-cyclopent-4-enedione, from which only a small amount of **23** was formed on heating with acetic anhydride. The subsequent oxidation with PAA, unfortunately, did not produce the sulfone derivative **24** (eq 6).



C. Hydride Reduction of 2 and 7. The direct reduction of **2** with 2.2 equiv of diisobutylaluminum hydride (DIBAL) in THF at −78 °C gave several products along with a large amount of starting material. None of the products had a ^1H NMR spectrum corresponding to that expected for the desired 4*H*-sulfone **26**. The DIBAL (1.1

(13) Bossert, F. *Liebigs Ann. Chem.* **1965**, *680*, 40.
(14) Knoevenagel, F. *Justus Liebigs Ann. Chem.* **1896**, *288*, 321.
(15) Lehnert, W. *Tetrahedron* **1973**, *29*, 635.
(16) Jefford, C. W.; Wallace, T. W.; Com, N.-T. H.; Rimbault, C. G. *J. Org. Chem.* **1979**, *44*, 689.

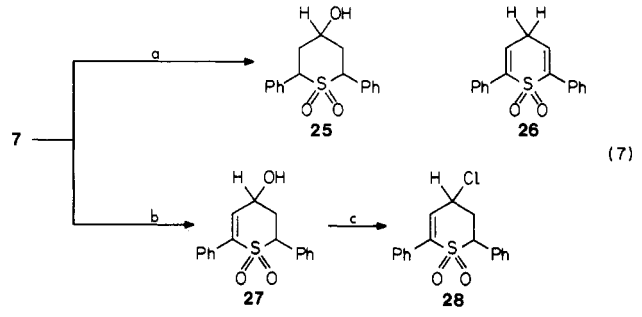
Scheme II[a]



[a] (a) $CH_2(CN)_2$/piperidine/EtOH/Δ; (b) Meldrum's acid/piperidine/EtOH/Δ; (c) 1,3-indandione/piperidine/CH_3OH/Δ; (d) $CH_2(CN)CO_2Et/2TiCl_4$/4-pyridine/THF; (e) CH_3MgI/THF/−78 °C; (f) $CH_3P(O)(OCH_3)_2$/*n*-BuLi/THF/−78 °C; (g) *n*-BuLi/THF/Δ.

equiv) reduction of **7** under the same conditions gave a 1:1 mixture of the alcohol **27** and starting material, which were difficult to separate. These results suggest that the Lewis acidic DIBAL probably coordinates with the sulfone function in preference to the carbonyl.

Sodium borohydride in isopropyl alcohol as well as lithium borohydride in THF at room temperature reduced both the double bond and the carbonyl functions of **7** to give the tetrahydro sulfone alcohol **25** (eq 7). The best



(7)

(a) $NaBH_4$/*i*-PrOH/r.t. or $LiBH_4$/THF/r.t.; (b) $NaBH_4/CoCl_3 \cdot 6H_2O$/MeOH/r.t.; (c) $SOCl_2$/pyr./−15 °C

reagent we found to selectively reduce **7** to the desired allylic alcohol **27** was the $NaBH_4$–$CoCl_3$ complex[16] in methanol. Because **27** is quite soluble in water, isolation from aqueous media after decomposition of the excess $NaBH_4$ and purification posed some problems. Nevertheless, the crude **27** could be isolated in quantitative yield by salting out with NaCl and using the crude product, after drying. Thionyl chloride reacted with **27** in pyridine to give the 4-chloro compound **28**, which is an unusually

Table I. Electrochemical Properties of Derivatives of Sulfones 2 and 10

compd	$E^\circ_{1/2}$, V[a] I	II
12	−0.10	−0.56
11	−0.13	−0.75
13	−0.17	−0.62
19	−0.28	−0.77
14	−0.33	−0.79
30	−0.34	−0.62
2	−0.61	−1.11
10	−0.74	−1.51

[a] Sample concentration 2×10^{-4} M; solvent CH_3CN; supporting electrolyte 0.1 M tetrabutylammonium tetrafluoroborate; indicating electrode Pt; reference electrode SCE. Half-wave potential for reversible system.

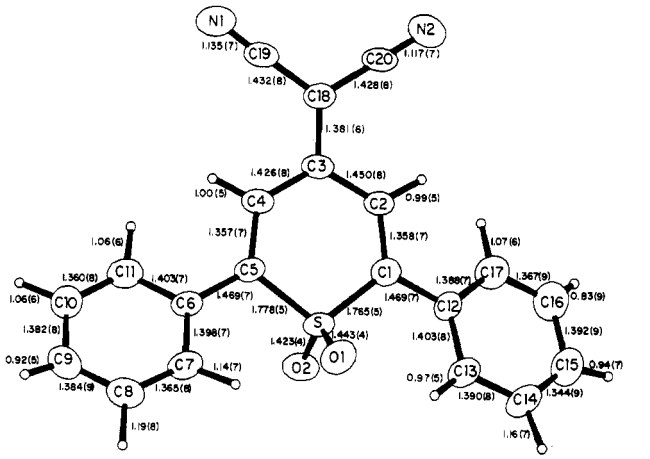


Figure 1. Plot of the DCTD molecule with 50% probability thermal ellipsoids. Hydrogen atoms were drawn with arbitrary radii and labels were omitted for clarity.

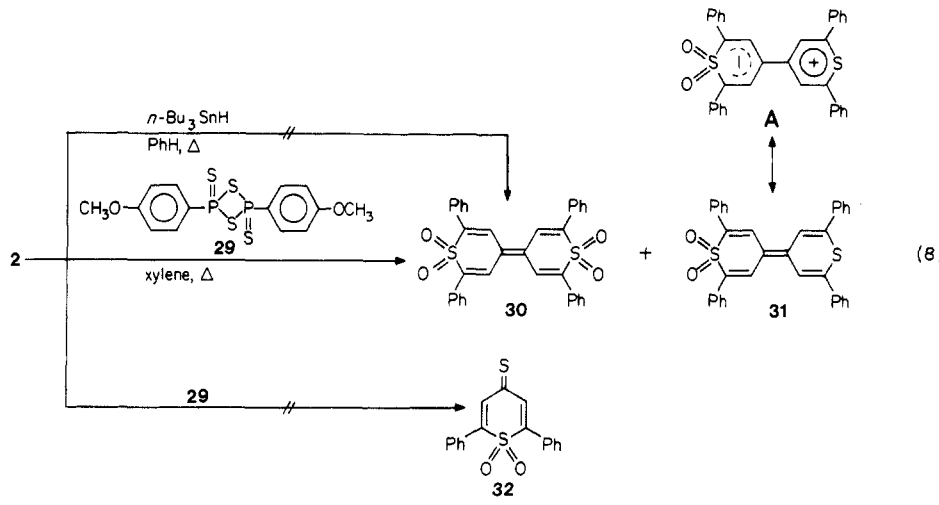
stable solid that can be recrystallized from methanol.

D. Wittig and Organometallic Reactions of 2. Methylmagnesium iodide in THF at −78 °C reacted well with **2** to give the corresponding tertiary alcohol **15** in 73% yield (Scheme II), but **2** failed to react with sodium cyclopentadienide, and the results of the (trimethylsilyl)-lithium/hexamethylphosphoramide (HMPA)[17] addition were also inconclusive, presumably because of the complication caused by electron-transfer reactions.

The Wittig reagent prepared from methyltriphenylphosphonium bromide and sodium *tert*-amylate in toluene did not condense with **2** to give the 4-methylene sulfone **17**. A Wittig–Horner reagent generated from dimethyl methylphosphonate and *n*-BuLi in THF at −78 °C did add to the carbonyl of **2**, but the reaction stopped at the intermediate alkoxide stage to give, on protonation, the corresponding 4-hydroxy compound **16**, which retains the dimethylphosphonyl group. Surprisingly, the usual olefination (expected to give **17**) involving the elimination of the dimethylphosphate anion from the lithiated alkoxide (prepared independently from **16** and *n*-BuLi) was not observed even under forcing conditions (THF reflux, 24 h).

E. Thionation and Reductive Dimerization of 2. Several attempts were made to reductively dimerize **2** directly with tri-*n*-butyltin hydride to the novel bis-sulfone dimer **30**, without success. Since the Lawesson's reagent **29** is known to convert ketones to thiones,[18] we then fo-

(17) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.
(18) Pederson, B.; Scheibye, S., Wilson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223. Scheibye, S.; Shabana, S.; Lawesson, S.-O. *Tetrahedron* **1982**, *38*, 993.



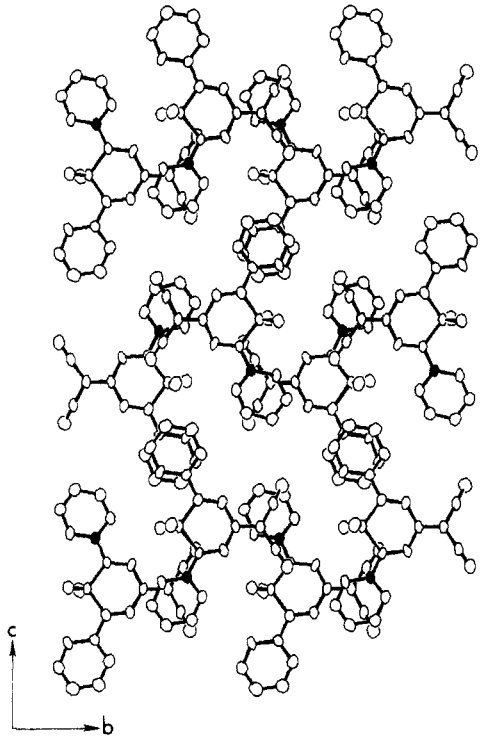


Figure 2. (100) Projection of the DCTD molecular packing. Atom C6 was darkened for identification.

cused our attention on the synthesis of the thione **32**, which would be expected to reductively dimerize on heating with copper.[19]

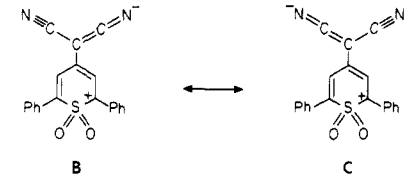
Heating a mixture of 0.6 equiv of **29** and **2** in toluene gave two major products, the bis-sulfone dimer **30** and the monosulfone dimer **31**. The desired **30**, however, was selectively prepared by adding **29** *portionwise* to **2** in xylene (eq 8). This result suggests that Lawesson's reagent **29**, being a reducing agent,[20] can reductively couple the intermediate thione **32** formed in situ to give the dimer **30**. If the **29** was present in excess, the yellow bis-sulfone **30** apparently could be further reduced to the mono-sulfone dimer **31**. This was supported by heating **2** with a large excess of **29** in xylene, from which the mono-sulfone **31** was formed predominantly. The red color of **31** (λ_{max} 495 nm) suggests considerable contribution of the delocalized structure A, involving the lone pair on sulfur. To our knowledge, this interesting reductive coupling reaction involving Lawesson's reagent is unprecedented. Another explanation for the formation of the dimer **30** is that it is a thermal dimerization product of the thione **32**. It is known that the thione of **1** thermally dimerizes.[9]

Cyclic Volammetric Properties of Derivatives of 2, 10, and Related Compounds

Most of the thiopyran and thiochroman sulfone derivatives have two reversible one-electron reduction waves, which are tabulated in Table I in order of their first half-wave potentials. Most of these thiopyran sulfones have the first reversible reductive $E_{1/2}$ ranging from −0.1 to −0.6 V, which are quite sensitive to electron-withdrawing substituents at C-4.

X-ray Single-Crystal Analysis of DCTD

Figure 1 shows the molecule with atomic labeling and bond distances. Bond angles and positional and thermal parameters are given in supplementary tables. Bonds C1–C2, C4–C5, and C3–C18 are all longer than a normal double bond (1.34 Å),[21] whereas bonds C2–C3, C3–C4, C18–C19, and C18–C20 are all shorter than normal single bonds (1.48 Å for Csp^2–Csp^2 and 1.46 Å for Csp^2–Csp).[21] These results indicate a significant contribution of canonical forms B and C to the structure represented formally by **11**.



B C

The thiopyran ring is only approximately planar with deviations between −0.025 and +0.038 Å from the least-squares plane. The dicyanomethylene group (including C3) and the C6- and C12-phenyl rings are planar and described dihedral angles of 3.4°, 31.1°, and −33.1°, respectively, with the thiopyran ring.

Figure 2 shows the molecular packing. The molecules pack plane-to-plane with overlap between the C6-phenyls and the dicyanomethylene groups and also between neighboring C12-phenyls. These groups are not coplanar, so there is no interplanar spacing in the usual sense. Because of symmetry, all the overlaps shown in the figure

(19) Schonberg, A.; Schutz, O.; Nickel, S. *Chem. Ber.* **1928**, *61*, 1375.
(20) Lawesson, S.-O., private communication.
(21) Sutton, L. E. *Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement*; The Chemical Society: London, 1965.

are equivalent. The repeat unit along the *a* axis, not visible in the figure, is directly underneath and generates a second, similar set of overlaps, but with a different spacing. The closest contacts in the overlap involving the dicyanomethylene group (including C3) are about 3.4–4.2 Å (provided in the supplementary material). There are no contacts less than the sum of van der Waals radii in the structure. It is interesting that the overlap occurs between the + and − portions of the charge-separated form (structures B and C). This implies possible asymmetry in the thiopyran ring. However, within the precision of our results, the partial positive charge appears to be equally distributed between C1 and C5.

Experimental Section

^{1}H NMR spectra were recorded on Varian EM-390 and Bruker WH 270-MHz spectrometers, with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on a Bruker spectrometer at 67.89 MHz, with Me_4Si as internal standard; the multiplicity was determined by the off-resonance proton decoupling. Mass spectra were obtained on an AEI MS-30 mass spectrometer. Field-desorption mass spectra were recorded on a Varian MAT-731 spectrometer. Microanalyses were done by the Analytical Sciences Division, Kodak Research Laboratories. Melting points (uncorrected) were obtained on a Thomas-Hoover capillary melting-point apparatus. UV spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were recorded on Perkin-Elmer 137 and Beckman IR 4250 spectrophotometers. A Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer were used in the standard three-electrode configuration to obtain reduction potentials by cyclic voltammetry.

2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide (2). To a stirred solution of 26.8 g (0.1 mol) of 2,6-diphenyl-2,3,5,6-tetrahydro-4*H*-thiopyran-4-one (**4**)[9] in 125 mL of methylene chloride was slowly added 30 mL of 40% peracetic acid with external cooling to keep the temperature below 30 °C. The solution was stirred overnight, during which time it became a solid cake. The 2,6-diphenyltetrahydro-4*H*-thiopyran-4-one 1,1-dioxide (**5**) was collected and washed thoroughly with methanol: yield 30.0 g; mp 236–237 °C (lit.[9] mp 235 °C). This solid was dissolved in 100 mL of dimethyl sulfoxide (Me_2SO), and 1 g of iodine and 0.5 mL of sulfuric acid were added. The mixture was heated on a steam bath for 24 h, cooled to room temperature, and poured into 100 mL of water. The mixture was stirred for 2 h, and the solid was collected and washed with water and then methanol. The product was recrystallized from toluene, giving 24.0 g (81% yield) of **2**, mp 145–146 °C (lit.[9] mp 144–145 °C).

We also prepared **2** by oxidation of 2,6-diphenyl-4*H*-thiopyran-4-one (**1**) or 2,6-diphenyl-2,3-dihydro-4*H*-thiopyran-4-one (**6**) with peracetic acid, followed by dehydrogenation with iodine and sulfuric acid in Me_2SO. Arndt prepared **2** by the oxidation of the thiopyranone **1** with hydrogen peroxide,[9] but no yield was reported. Peracetic acid oxidation under a variety of conditions gave **2** in 18–29% yield. The procedure with the dihydrothiopyrone **6** gave **2** in 85% overall yield, but we consider the synthesis from **4** to be the method of choice.

2,6-Diphenyl-2,3-dihydro-4*H*-thiopyran-4-one 1,1-Dioxide (7). A solution of 4.4 g (16.5 mmol) of dihydrothiopyran **6** in 50 mL of glacial acetic acid was stirred with 13 g of 40% peracetic acid in acetic acid at room temperature overnight. The reaction mixture was poured into water (400 mL) containing a small amount of methanol. The precipitated solid was filtered, washed thoroughly with H_2O, and air-dried, giving 4.4 g (89%) of crude **7**, which was used for subsequent reactions. An analytical sample was obtained by recrystallization from methanol: mp 137–138 °C; field-desorption mass spectrum, m/e 298 M^+; ^{1}H NMR ($CDCl_3$) δ 3.15 (qd, 1), 3.8 (dd, 1), 6.45 (dd, 1), 7.1–7.8 (m, 10).

Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.4; H, 4.7; S, 10.7. Found: C, 68.3; H, 4.8; S, 10.5.

***trans*-3-Bromo-2,6-diphenyl-2,3-dihydro-4*H*-thiopyran-4-one 1,1-Dioxide (8) and Its Dehydrobromination.** A solution of 2 g (6.7 mmol) of crude **7** and 1.1 g (1 equiv) of bromine in 100 mL of methylene chloride was irradiated with a sunlamp for 2 h; the reddish brown color of Br_2 slowly disappeared. A small sample of this reaction mixture was concentrated, and the residue was crystallized from $CHCl_3$: mp 206–207 °C; field-desorption mass spectrum, m/e 375 ($^{79}Br_1$) ($M^+ - 1$); IR (KBr) 1700 (C=O), 1135, 1320 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.9 (d, $J_{2,3}$ = 13.5 Hz, 1, H_3), 5.65 (d, $J_{3,2}$ = 13.5 Hz, 1, H_2), 6.7 (s, 1, H_5), 7.1–7.8 (m, 10, Ar H); ^{13}C NMR (CD_3CN + 1% Me_2SO-d_6) δ 53.78 (d, C-3), 71.89 (d, C-2), 132.36 (d, C-5), 155.15 (s, C-6), 187.04 (s, C=O).

Anal. Calcd for $C_{17}H_{13}BrO_3S$: C, 54.1; H, 3.5; S, 8.5. Found: C, 54.1; H, 3.5; S, 8.5.

The bulk of this reaction mixture was treated with 2 g (2.8 equiv) of triethylamine to effect dehydrobromination at room temperature, giving 0.8 g (recrystallized from ethanol) of 2,6-diphenyl-4*H*-thiopyran-4-one 1,1-dioxide (**2**) after the usual aqueous workup.

4*H*-Thioflaven-4-one 1,1-Dioxide (10). A mixture of 1.0 g (4.2 mmol) of 4*H*-thioflaven-4-one (**9**) and 5 mL of peracetic acid was heated on a steam bath for 30 min and allowed to stand overnight. The solid was collected and recrystallized from alcohol, giving 0.86 g of **10** (76%): mp 135–136 °C.

Anal. Calcd for $C_{15}H_{10}O_3S$: C, 66.7; H, 3.7; S, 11.9. Found: C, 66.6; H, 3.8; S, 12.1.

Arndt prepared **10** in three steps by oxidizing the dihydrothioflavone, brominating the resulting sulfone, and dehydrohalogenating the bromo derivative.[9]

4-(Dicyanomethylene)-2,6-diphenyl-4*H*-thiopyran 1,1-Dioxide (11, DCTD). A mixture of 8 g (0.0464 mol) of **2**, 3.1 g (0.047 mol) of malononitrile, 50 mL of ethyl alcohol, and 20 drops of piperidine was refluxed for 1 h. The reaction mixture was cooled to room temperature, and the solid was collected and recrystallized from 100 mL of toluene: yield 6.4 g of DCTD (69%); mp 216–217 °C; field-desorption mass spectrum, m/e 344 (M^+); IR (KBr) 2225 (CN), 1135, 1310 (SO_2), 1630, 1570 (C=C) cm^{-1}.

Anal. Calcd for $C_{20}H_{12}N_2O_2S$: C, 69.8; H, 3.5; N, 8.1; S, 9.6. Found: C, 69.5; H, 3.5; N, 8.4; S, 9.6.

2,6-Diphenyl-4-(2,2-dimethyl-4,6-dioxo-*m*-dioxan-5-ylidene)-4*H*-thiopyran 1,1-Dioxide (12). A mixture of 1.32 g (5 mmol) of **2**, 0.80 g (5.5 mmol) of Meldrum's acid, 10 mL of ethyl alcohol, and 5 drops of piperidine was refluxed for 1 h and allowed to stand overnight, and the yellow solid was collected. The solid was recrystallized from alcohol, giving 1.10 g of **12** (52% yield): mp 214–215 °C; field-desorption mass spectrum, m/e 422 (M^+ for $C_{23}H_{18}O_6S$).

Anal. Calcd for $C_{23}H_{18}O_6S$: C, 65.4; H, 4.3; S, 7.6. Found: C, 65.4; H, 4.3; S, 7.5.

2,6-Diphenyl-4-(1,3-dioxoindan-2-ylidene)-4*H*-thiopyran 1,1-Dioxide (13). A mixture of 1.0 g (3.38 mmol) of **2**, 0.50 g (3.4 mmol) of 1,3-indandione, 4 drops of piperidine, and 50 mL of methanol was heated on a steam bath for 30 min and cooled to room temperature, and the solid was collected: yield 0.95 g (66%) from acetonitrile; mp 235–236 °C.

Anal. Calcd for $C_{26}H_{16}O_4S$: C, 73.6; H, 3.8; S, 7.6. Found: C, 73.4; H, 3.8; S, 7.8.

2,6-Diphenyl-4-(cyano(ethoxycarbonyl)methylene)-4*H*-thiopyran 1,1-Dioxide (14). To an ice-cooled solution of dry THF (120 mL) under argon was added dropwise a solution of 6.6 mL (0.06 M) of $TiCl_4$ in 15 mL of CCl_4. The resulting bright yellow suspension was added quickly to a solution of 8.9 g (0.03 M) of **2** and 3.4 g (0.03 M) of ethyl cyanoacetate in 70 mL of THF. The mixture was stirred for 20 min in an ice bath, and 9.5 g (0.12 M) of dry pyridine was then added. The mixture was stirred at room temperature overnight, and 30 mL of H_2O and a small amount of ether were added. The organic phase was separated, washed with dilute $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated to give 11.4 of a highly fluorescent yellow solid, which was recrystallized from toluene containing a little hexane to give a 9.14-g first crop. A second crop of 1.2 g of similar purity was also obtained from the mother liquid by adding more hexanes. Total yield was 88%: mp 156–157 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (t, 3), 4.45 (q, 2), 7.48 (d, 1, vinylic), 7.55 (m, 6, Ar H), 7.88 (m, 4, 4, Ar H), 8.6 (d, 1 vinylic).

Anal. Calcd for $C_{22}H_{17}NO_4S$: C, 67.5; H, 4.4; N, 3.6. Found: C, 67.6; H, 4.4; N, 3.6.

2,6-Diphenyl-4-hydroxy-4-methyl-4*H*-thiopyran 1,1-Dioxide (15). To a solution of 1 g (3.38 mmol) of **2** in 50 mL of THF was added by syringe 1.4 mL (1.2 equiv) of a 2.9 M solution

of methylmagnesium iodide in THF at −78 °C under argon. The reaction mixture was slowly equilibrated to room temperature overnight, poured into dilute HCl and brine, and extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated to a brown oil, which slowly solidified at room temperature. Recrystallization from benzene/hexanes (1:1) gave 0.77 g (73%) of **15**: mp 140–141 °C; field-desorption mass spectrum, m/e 312 M^+, 294 ($M^+ - H_2O$); ^1H NMR ($CDCl_3$) δ 1.5 (s, 3, Me), 3.95 (br s, 1, OH), 6.33 (s, 2, $H_3 + H_5$), 7.0–7.7 (m, 10, Ar H).

Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.2; H, 5.2; S, 10.3. Found: C, 69.3; H, 5.3; S, 10.3.

4-((Dimethoxyphosphinyl)methyl)-2,6-diphenyl-4-hydroxy-4*H*-thiopyran 1,1-Dioxide (16). To a solution of 500 mg (4.03 mmol) of dimethyl methylphosphonate in 50 mL of dry THF at −78 °C was added by syringe 2.55 mL (1.2 equiv) of *n*-BuLi (1.6 M in hexanes) followed by 1 g (3.38 mmol) of **2**. The reaction mixture was equilibrated to room temperature overnight, poured into aqueous NH_4Cl, and extracted with ether. The organic phase separated, dried ($MgSO_4$), and evaported to a brown gum, which was recrystallized from benzene and hexanes to give 500 mg (35%) of **16**: mp 149–150 °C; field-desorption mass spectrum, m/e 426 M^+; ^1H NMR ($CDCl_3$) 2.45 (d, J_{PCH} = 16.5 Hz, 2, CH_2P), 3.74 (d, J_{POCH} = 10.5 Hz, 6, $2CH_3$), 6.6 (s, 2, $H_3 + H_5$), 7.3–7.8 (m, 10, Ar H).

Anal. Calcd for $C_{20}H_{21}O_6PS$: C, 57.1; H, 5.0; P, 7.4; S, 7.6. Found: C, 57.2; H, 5.2; P, 7.3; S, 7.5.

4-(Dicyanomethylene)-4*H*-thioflavene 1,1-Dioxide (19). A mixture of 1.35 g (5 mmol) of **9**, 0.50 g (7.5 mmol) of malononitrile, and 10 mL of acetic anhydride was refluxed for 1 h and chilled, and the 4-(dicyanomethylene)-4*H*-thioflaven-4-one (**18**) was collected; yield 0.75 g (52.5%). A mixture of 0.50 g (1.75 mmol) of **18** and 4 mL of 40% peracetic acid was heated for 15 min on a steam bath. The yellow color became very pale, and most of the solid dissolved. The mixture was chilled, and the solid was collected and recrystallized twice from toluene, giving 0.35 g (63% yield) of **19**: mp 177–178 °C; field-desorption mass spectrum, m/e 318 (M^+ for $C_{18}H_{10}N_2O_2S$).

Anal. Calcd for $C_{18}H_{10}N_2O_2S$: C, 67.9; H, 3.2; N, 8.8. Found: C, 67.7; H, 3.1; N, 8.7.

Reaction of 4-(Dicyanomethylene)-4*H*-benzo-1-thiopyran (21) with Peracetic Acid. A mixture of 1.61 g (10 mmol) of 4*H*-benzo-1-thiopyran-4-one (**20**), 0.70 g (10.6 mmol) of malononitrile, and 15 mL of acetic anhydride was refluxed for 1 h and chilled, and 0.70 g of 4-(dicyanomethylene)-4*H*-benzo-1-thiopyran (**21**) was collected: mp 164–166 °C; field-desorption mass spectrum, m/e 210 (M^+ for $C_{12}H_6N_2S$).

A mixture of 0.70 g (3.3 mmol) of **21** and 3 mL of 40% peracetic acid was heated on a steam bath for 15 min. The solid dissolved, giving a pale yellow solution. After standing for several hours, the white solid was collected and recrystallized from CH_3CN: yield 0.25 g (29%); mp 235 °C dec. The field-desorption mass spectrum shows m/e 258, which corresponds to the starting material plus three oxygen atoms. The structure **22** was assigned to the product on the basis of the following spectroscopic data: 270-MHz ^1H NMR ($CDCl_3$) δ 6.94 (d, $J_{3,4}$ = 12 Hz, 1, H_3), 7.98 (d, $J_{4,3}$ = 12 Hz, 1, H_4), 7.88–8.20 (m, 4, Ar H); ^{13}C NMR 177.74 (s, C_1), 148.85 (d, C_4), 148.46 (s, C_5), 133.34 (d), 132.56 (d), 127.86 (d), 127.73 (s, C_{10}), 123.15 (d, C_3), 113.44 (s, CN); C_2 is missing, probably owing to long relaxation T_1.

Anal. Calcd for $C_{12}H_6N_2O_3S$: C, 55.8; H, 2.3; N, 10.9. Found: C, 56.0; H, 2.4; N, 10.8.

4-(1,3-Dioxocyclopent-4-en-2-ylidene)-2,6-diphenyl-4*H*-thiopyran (23). A mixture of 1.3 g (13.5 mmol) of cyclopent-4-ene-1,3-dione and 1.5 g (5.7 mmol) of **1** in 25 mL of acetic anhydride was heated in an oil bath at 125–140 °C for 3 h. On cooling, the precipitated solid was filtered and washed with a small amount of cold HOAc, giving 0.45 g of crude **24**. Purification by Soxhlet extraction with ether gave 100 mg (5%) of pure **23**, which crystallized on standing as long dark needles: mp 234–235 °C dec; field-desorption mass spectrum, m/e 342 M^+; IR (KBr) 1650 cm^{-1} (C=O).

Anal. Calcd for $C_{22}H_{14}O_2S$: C, 77.2; H, 4.1; S, 9.4. Found: C, 76.8; H, 3.9; S, 9.5.

2,6-Diphenyl-4-hydroxy-4*H*-thiopyran 1,1-Dioxide (25) from 7. A solution of 100 mg (0.34 mmol) of **7** in 25 mL of dry THF at room temperature was allowed to react with 10 mg of lithium borohydride. After 4 h of stirring, the reaction mixture was poured into water and extracted with methylene chloride. The organic phase was separated, dried ($MgSO_4$), and concentrated, giving an oil that slowly solidified on standing. Recrystallization from a small amount of chloroform gave 20 mg (20%) of **25**: mp 181–182 °C; field-desorption mass spectrum, m/e 302 M^+; IR (KBr) 1130, 1300 (SO_2), 3450 (OH broad) cm^{-1}, no $\nu_{C=O}$.

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.5; H, 6.0; S, 10.6. Found: C, 67.1; H, 6.0; S, 10.4.

The same product was obtained also by sodium borohydride reduction in isopropyl alcohol at room temperature.

5,6-Dihydro-2,6-diphenyl-4-hydroxy-4*H*-thiopyran 1,1-Dioxide (27). A mixture of 2.4 g (8 mmol) of **7** and 2.8 g of $CoCl_2 \cdot 6H_2O$ was dissolved in 250 mL of MeOH by warming. The solution was cooled to room temperature, 320 mg of $NaBH_4$ was added, and the mixture was stirred for 30 min. The reaction mixture was poured into 300 mL of brine in a beaker; the finely divided precipitate was allowed to coagulate and settle to the bottom of the beaker for 2 days while excess MeOH was allowed to evaporate in a hood. This crude solid was filtered, washed with water, and air-dried, giving 2.5 g (100%) of the crude dihydro alcohol **27**: field-desorption mass spectrum, m/e 300 (M^+ for $C_{17}H_{16}O_3S$), 282 ($M^+ - H_2O$); ^1H NMR ($CDCl_3$) δ 2.3 (d, 1, OH), 2.4–3.3 (m, 2, methylene), 4.35 (dd, $J_{a,a}$ = 13.5 and $J_{a,e}$ = 3 Hz, 1, benzylic H_6), 4.65 (m, 1, methine), 6.35 (pseudo t, 1, olefinic H_3), 7.25–7.65 (m, 10, Ar H). This compound was used subsequently without further purification.

4-Chloro-2,6-diphenyl-5,6-dihydro-4*H*-thiopyran 1,1-Dioxide (28). Crude **27** (500 mg, 1.67 mmol) was dissolved in 10 mL of dry pyridine at −15 °C under argon, and 0.2 mL of freshly distilled thionyl chloride was added by syringe. The reaction mixture was allowed to equilibrate to room temperature overnight and poured into 200 mL of water. The precipitate was filtered, washed with water, boiled with 200 mL of ethanol, and filtered, and the filtrate was concentrated. The residue was recrystallized from MeOH, giving 250 mg (39%) of **28**: mp 157–158 °C; field-desorption mass spectrum, m/e 318 (^{35}Cl) M^+; ^1H NMR ($CDCl_3$) δ 2.65 (m, 1, H_{5a}), 3.42 (m, 1, H_{5e}), 4.84 (dd, partially buried, 1, H_6 benzylic), 4.95 (m, 1, H_4), 6.33 (dd, 1, H_3 vinylic) 7.15–7.65 (m, 10, Ar H).

Anal. Calcd for $C_{17}H_{15}ClO_2S$: C, 64.0; H, 4.7; Cl, 11.1; S, 10.1. Found: C, 63.6; H, 4.8; Cl, 11.2; S, 10.3.

Mixture of 2,2′,6,6′-Tetraphenyl-$\Delta^{4,4'}$-bithiopyran 1,1,1′,1′-Tetraoxide (30) and 1,1-Dioxide (31). A mixture of 1.3 g (5 mmol) of **2**, 1.2 g (3 mmol) of the Lawesson reagent **29**,[18] and 10 mL of dry toluene was stirred and heated at 110 °C for 2 h, when TLC (CH_2Cl_2) showed that no more starting material was present and a pale yellow product and a more polar red product were formed. The reaction mixture was evaporated to dryness, the residue was heated to boiling with 75 mL of ethyl alcohol and cooled, and the solid was collected (1.18 g). A 50-mg sample was chromatographed on a Chromatron Model 7924, eluting with CH_2Cl_2, giving 20 mg of the dioxide (**31**) (red zone) and 18 mg of the tetraoxide (**30**) (yellow zone). For **30**: field-desorption mass spectrum, m/e 560 (M^+ for $C_{34}H_{24}O_4S_2$); mp 344–345 °C.

Anal. Calcd for $C_{34}H_{24}O_4S_2$: C, 72.8; H, 4.3; S, 11.4. Found: C, 72.7; H, 4.4; S, 11.7.

For **31**: field-desorption mass spectrum, m/e 528 (M^+ for $C_{34}H_{24}O_2S_2$); mp 315–316 °C.

Anal. Calcd for $C_{34}H_{24}O_2S_2$: C, 77.2; H, 4.6; S, 12.1. Found: C, 76.8; H, 4.5; S, 12.0.

Selective Synthesis of the Disulfone 30. A solution of 1.3 g (5 mmol) of **2** in 25 mL of refluxing xylene was stirred, and 1 g of **29** was added in small portions over 2 h. The reaction mixture was chilled, and 1.0 g of solid was collected; TLC showed only a small amount of the red **31**. The product was Soxhlet extracted with CH_2Cl_2, and the extract was evaporated to 50 mL and allowed to stand overnight. Solid **30** (0.51 g) was collected: mp 344–345 °C.

Selective Synthesis of the Monosulfone 31. A mixture of 1.0 g of **2**, 3.0 g (excess) of **29**, and 25 mL of xylene was refluxed for 3 h. The mixture was chilled, and the solid was collected; TLC showed mostly the red **31** and only a little **30**. The crude material was chromatographed, and **31** was recrystallized from CH_3CN, yielding 0.35 g; mp 315–316 °C.

Table II. Crystal Data of DCTD, $C_{20}H_{12}N_2O_2S$

space group	$P2_12_12_1$
extinctions	$h00$, h odd; $0k0$, k odd; $00l$, l odd
cell constants,	
a, Å	7.589 (2)
b	9.794 (4)
c	21.900 (4)
α, deg	90
β	90
γ	90
V, Å^3	1628 (1)
no. molecules/unit cell (Z)	4
D calc, g cm^{-3}	1.405
F(000)	712
absorption coeff. (μ, MoKα) cm^{-1}	2.04
temperature, °C	23 (1)
scan technique	ω-2θ
scan rate, deg 2θ min^{-1}	1.8 to 20
2θ limit, deg	50
no. of unique reflections measured	1659
no. of reflections used in refinement ($I > 1\sigma$)	1242
no. of variable parameters	274
crystal dimensions, mm	0.17 × 0.24 × 0.28

X-ray Single-Crystal Analysis. Data Collection. DCTD can be recrystallized from a variety of organic solvents, such as ethanol, isopropyl alcohol, toluene, and ethyl acetate. Only crystals obtained by slow recrystallization from ethyl acetate at room temperature were suitable for X-ray analysis.

A chunky sample was cut from a larger tabular yellow crystal, glued onto a thin glass rod, and used for data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The setting angles for 25 accurately centered reflections were used to refine the unit cell parameters given in Table II.

Each reflection was scanned from 2θ(Mo Kα_1) − 0.6° to 2θ(Mo Kα_2) + 0.6°. The scan width was extended 25% at each end to measure background. Three standard reflections were remeasured every hour, and the data set was corrected for a small but consistent decrease in I over the data collection period. The average correction factor was 1.015 (on I).

The net intensities were calculated according to $I = AS\kappa(C - RB)$, and the standard deviations were $\sigma^2(I) = (AS\kappa)^2(C + R^2B)$ and $\sigma(F_o) = [(I + \sigma(I))/\mathrm{Lp}]^{1/2} - F_o$, where A is the attenuator factor, S is the scan rate, κ is the scale, C is the total integrated peak count, R is the ratio of peak time to background time, B is the total background count, $(\mathrm{Lp})^{-1}$ is the Lorentz-polarization correction, and $F_o = (I/\mathrm{Lp})^{1/2}$ is the observed structure factor. No absorption correction was necessary.

Structure Solution and Refinement. The structure was solved by direct methods using MULTAN 11/82.[22] An E-map calculated with the best phase set (216 E's > 1.45) yielded 17 of the 25 non-hydrogen atoms. Subsequent difference electron density maps gave all remaining atoms including hydrogens.

Refinement was by full-matrix least squares. The function minimized was

$$\Sigma w(|F_o| - \kappa|F_c|)^2$$

where $w^{-1} = \sigma^2(F_o) + (0.04F_o)^2$. Scattering factors and anomalous dispersion corrections for all atoms were from ref 23. The agreement indices are

$$R = \Sigma||F_o| - \kappa|F_c||/\Sigma|F_o|$$

and

$$R_w = (\Sigma w(|F_o| - \kappa|F_c|)^2/\Sigma wF_o^2)^{1/2}$$

Refinement converged to give final values $R = 0.053$, $R_w = 0.063$, and $\kappa = 1.413$ (4). During the final stages of refinement, the absolute configuration was determined by refining the opposite enantiomorph and applying Hamilton's[24] significance test to the results ($R_w = 0.0646$ for original vs. 0.0648 for the opposite). The original model is accepted at the 0.025 significance level.

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Supplementary Material Available: Bond angles (Table III), positional parameters and their estimated standard deviations (Table IV), anisotropic thermal parameters (Table V), and closest intermolecular contacts to dicyanomethylene group (Table VI) for DCTD (4 pages). Ordering information is given on any current masthead page.

(22) Programs used in this study were part of the Structure Determination Package (SDP-PLUS) Version 1.0, Enraf-Nonius Corp., Delft, Holland.

(23) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, Chapter 2.

(24) Hamilton, W. C. *Acta Crysrtallogr.* **1965**, *18*, 502.