clear polymer was poured out. The polymer turned into a hard solid on standing at room temperature. Its ^{31}P NMR analysis showed complete conversion of the monomer (disappearance of its absorption at 153.65 ppm) and that the polymer made at 160, 180, and 200 °C had 3.3% 9.4% and 23.5%, respectively, of oxaphospholan 3 (δ 58.5). The oxaphospholane was distilled from the polymer at 120 °C (0.1 mmHg) (lit.[27] bp 142 °C (0.2 mmHg)). It supercooled at room temperature and then suddenly solidified, liberating a large amount of heat; mp 69 °C. Anal. Calcd for $C_{17}H_{20}O_3P$: C, 59.3; H, 6.0; P, 17.0. Found: C, 59.4; H, 6.2; P, 16.9

Preparation and in Situ Decomposition of Poly(2,2-dimethyltrimethylene phenylphosphinate) (2a). A mixture of 84.0 g (0.4 mol) of 4,4-dimethyl-2-phenyl-1,3,2-dioxaphosphorinane (1a) and 5.3 g (0.0152 mol) of 3-iodo-2,2-dimethylpropyl methylphenylphosphinate (2a·I, $n = 1$)[5] was shaken in a heavy-walled glass tube. The mixture was thoroughly flushed by using an alternating N_2/vacuum cycle, sealed under vacuum, and heated at 195–200 °C for 24 h. It first got viscous, indicating the formation of the polymer, and then became quite fluid due to decomposition to oxaphospholane **3a**. The tube was broken and the oxaphospholan distilled at 152–153 °C (0.5 mmHg) as a colorless liquid, 75 g (89%). It supercooled at room temperature and then quickly solidified, giving a large amount of heat; mp 67 °C.

The viscous residue (12 g) left behind was dissolved in 25 mL of refluxing acetone and filtered. On cooling, a white solid separated which was collected by filtration and washed with 10 mL of acetone, 2.2 g (3%). Its analytical sample, prepared by recrystallization from acetone, had mp 198 °C. Anal. Calcd. for $C_{17}H_{20}O_3P_2$ (**4a**): C, 61.1; H, 6.0; P, 18.6. Found: C, 61.1; H, 6.0; P, 18.2. Its IR spectrum (KBr) showed P=O stretch at 1238 (s) and P—O—P asymmetric stretch at 912 cm^{-1} (s);[28] NMR ^{31}P δ 39.1. Refluxing in 20 mL of aqueous acetone for 2 h completely hydrolyzed it to 2,2-dimethyl-1,3-propanediyl bis(phenylphosphinic acid (**5a**) which separated as white solid and was collected by filtration, mp 175 °C. Anal. Calcd for $C_{17}H_{22}O_4P_2$: P, 17.6. Found: P, 17.4. Its ^{1}H NMR Me_2SO-d_6) δ 1.07 (2 CH_3), 2.13 (2 CH_2, d, $J_{PH} = 13.7$ Hz), 9.54 (2 OH, br); ^{31}P NMR δ 36.77.

X-ray Structure Determination of 3a. A colorless rectangular plate with dimensions 0.35 × 0.20 × 0.70 mm obtained by crystallization from cyclohexane/petroleum ether (bp 38–54 °C) was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer equipped with a Mo K_α source, graphite monochromator, and an FTS low-temperature refrigeration unit operating at −70 °C. The CAD4 routines indicated a monoclinic unit cell space group $C2/c$ with dimensions $a = 26.688$ (5) Å, $b = 7.612$ (1) Å, $c = 11.305$ (3) Å, $\beta = 98.88$ (2)°. With $Z = 8$ the calculated density of $P_1O_2C_{11}H_{15}$ is 1.231 g/cm^{-1}. A total of 1096 independent reflections with $I \geq 2\sigma(I)$ were obtained from $2° \leq \theta \leq 25°$ using the ω-scan mode with $\omega = 0.7 + 0.35(\tan\theta)$. The structure was solved with direct methods (MULTAN)[29] and refined by using full matrix anisotropic least squares with 127 variables to a conventional $R = 8.8\%$ and $R_w = 8.6\%$. Hydrogens were both located from difference electron density maps and calculated and included as fixed atom contributors in idealized positions with isotropic temperature factors. All atoms refined satisfactorily with the exception of ring atom C(3) which showed an elongated thermal ellipsoid. The largest peak on a final difference map was 0.3 e/Å near atom C(3).

Thermolysis of 3-Iodo-2,2-dimethylpropyl Methylphenylphosphinate (2a·I, $n = 1$). A 3.0-g sample was taken in a heavy-walled glass tube, purged thoroughly by using alternating an N_2/vacuum cycle, and sealed under vacuum. It was heated at 200 °C in a Wood's metal bath for 8 h. The material turned brown and was isolated by breaking the tube. Bulb-to-bulb distillation at 104 °C (0.2 mmHg) gave 2 drops of a colorless liquid. ^{1}H NMR showed two sharp singlets at 1.24 and 3.27 ppm in 2:3 ratio, consistent with the structure of 1,3-diiodo-2,2-dimethylpropane; and its mass of 324 was confirmed by GC/mass spectrum.

Registry No. 1, 7526-32-1; **1a**, 7526-31-0; 2 (n = 1), 68900-54-9; **2a** (n = 1), 68900-52-7; **3**, 16324-19-9; **3a**, 68900-53-8; **4a**, 93454-13-8; **5a**, 93454-14-9; n-PrBr, 106-94-5; 1,3-diiodo-2,2-dimethylpropane, 66688-49-1.

Supplementary Material Available: Table of fractional atomic coordinates and anisotropic thermal parameters for compound **3a** (1 page). Ordering information is given on any current masthead page.

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(27) Grayson, M.; Farley, C. E. *J. Chem. Soc., Chem. Commun.* **1967**, 830.

(28) Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 2nd ed.; Wiley: New York, 1958; p 311.

(29) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerg, J. P. "MULTAN 78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; York, England, and Louvain-la-Neuve, Belgium, 1978.

Thiopyranothiopyran Chemistry. 1. Synthesis of 1,3,5,7-Tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-Tetraoxide

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Received March 12, 1984

During a synthetic study aimed at the hitherto unknown thiopyrano[4,3-*c*]thiopyran system, the disulfone derivative 1,3,5,7-tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-tetraoxide (4) was synthesized. The approach starting from 2,6-diphenyl-3-formylthiopyran-4-one (11) via the key intermediate 3-[2(*Z*)-(benzylthio)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (12), whose absolute configuration was confirmed by X-ray analysis, is described in detail. Cyclization of the corresponding sulfoxide 3-[2(*Z*)-(benzylsulfinyl)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (15) with LDA/THF at −78 °C gives 2,6,7,9-tetraphenyl-1,8-dithiaspiro[4,5]-deca-2,6,9-trien-4-one (18), which is rationalized by a basic Pummerer rearrangement. The corresponding sulfone (*Z*)-**16**, under similar conditions, annulates to give a new, rearranged dihydrothiopyrano[3,4-*b*]thiopyran (**20**), whose formation is explained by a double Michael addition of the lithiated anion of (*Z*)-16. A cyclic voltammogram of 4, which shows characteristics of an organic acceptor, is included.

The novel 12π thiopyrano[4,3-*c*]thiopyran system **1**, which is isoelectronic with heptalene,[1] has been proposed as a new class of donors on the basis of the concept of "intermolecular migration of aromaticity" in the mixed-

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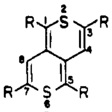
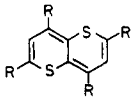
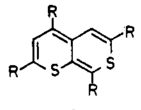
valent charge-transport process.[2] This fully conjugated sulfur heterocycle and the closely related [3,2-*b*]-**2** and [3,4-*b*]-**3** systems belong to the family of the *classical*



1



2

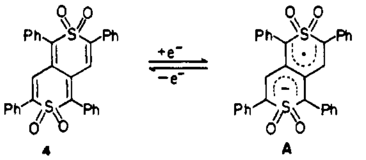


3

thiopyranothiopyrans that do not involve a tetravalent sulfur in their conjugation.[3] Recent calculations have suggested that these heterocycles are all slightly antiaromatic.[4] Since neither the parent compounds nor any of their derivatives have been reported, it was predicted that the stability of these compounds (if isolatable) would depend largely on their abilities to assume a nonplanar conformation much like that of the 1,4-dithiin system.[5]

There has been only one report on the attempted synthesis of **2**,[6,7] but, surprisingly, no efforts have been reported on the synthesis of the thiopyrano[4,3-*c*]thiopyran system **1**. As a prelude to further studies of these theoretically interesting and potentially useful systems, we have explored the synthesis of **1** and herewith report our approach, which led to the first synthesis of a tetraphenyl-substituted disulfone derivative of thiopyrano[4,3-*c*]thiopyran **4** and a dihydro monosulfone derivative of [3,4-*b*]-**3**.

Compound **4**, being an electron-deficient system, is of interest in its own right as a potential organic acceptor. In the presence of a suitable donor, the disulfone **4** is



4 **A**

expected to form a resonance-stabilized radical anion, depicted as A.[8] Furthermore, based on our earlier observations concerning the conductivities of various charge-transfer salts of $\Delta^{4,4'}$-4*H*-bithiopyrans, the deliberate choice of tetraphenyl substituents is also advantageous in enhancing the stability of the resulting benzylic radical.[9,10]

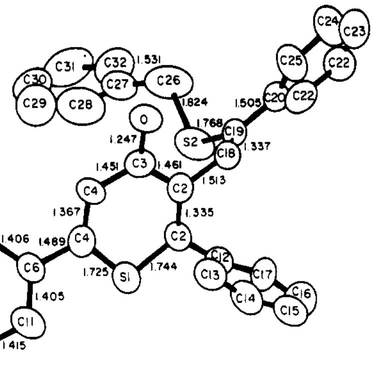
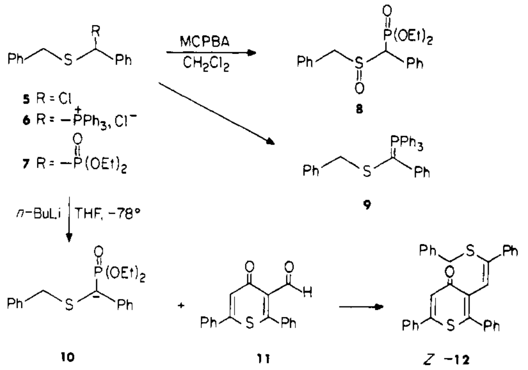


Figure 1. Plot of **12** showing selected bond lengths (Å) and numbering scheme. Estimated standard deviations vary from 0.004 to 0.017 Å.

Scheme I



Results and Discussion

Synthesis of 3-[2(*Z*)-(Benzylthio)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (12). Taking advantage of the symmetry embodied in the [4,3-*c*] system, we sought to build **1** (R = Ph) starting with 2,6-diphenyl-3-formyl-4*H*-thiopyran-4-one (**11**)[11] and the appropriate nucleophile, the substituted dibenzyl sulfide, as outlined in Scheme I. We had anticipated that the bulky phenyl substituent on this nucleophile would be more sterically demanding than the aralkylthio group and a Wittig reaction of **6** and the aldehyde **11** would lead to the desired *Z* isomer **12**,[12] which is essential for the subsequent ring closure. In reality, however, the bright orange ylide **9** derived from the triphenylphosphonium chloride **6**[13] by deprotonation was too inert to be useful for condensation. To increase the reactivity, we prepared the diethoxyphosphinyl derivative **7** by an Arbuzov reaction of triethyl phosphite and the highly reactive α-chlorodibenzyl sulfide (**5**)[13] at room temperature. Compound **7** was deprotonated smoothly at −78 °C with *n*-BuLi in THF to give the yellowish Wittig–Horner reagent **10**, which readily condensed with **11** to give stereospecifically a single isomer, characterized as **12**, in 74% yield. The stereoconfiguration of **12**, which cannot be determined with certainty by NMR, was later confirmed by single-crystal X-ray crystallography to be the desired *Z* isomer. The higher stereospecificity observed for this reaction, which was not totally unexpected,[14]

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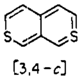
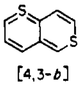
[1] Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 4658.

[2] Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.

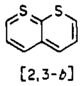
[3] Conjugated systems involving the following three modes of ring fusion can be classified as the family of the *nonclassical* thiopyranothiopyrans. For pertinent references, see: Schlessinger, R. H.; Ponticello, I. S. *J. Am. Chem. Soc.* **1967**, *89*, 3641. Tamura, Y.; Matsushima, H.; Ikeda, M.; Sumoto, K. *Synthesis* **1974**, 277. Senkler, G. H., Jr.; Stackhouse, J.; Maryanoff, B. E.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 5648, 5650, 5651. Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139.



[3,4-*c*]



[4,3-*b*]



[2,3-*b*]

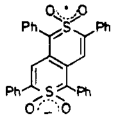
[4] Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907.

[5] Parham, W. E.; Wynberg, H.; Hasek, W. R.; Howell, P. A.; Curtis, R. N.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1954**, *76*, 4957.

[6] Young, T. E.; Heitz, L. J. *J. Org. Chem.* **1973**, *38*, 1562.

[7] A benzo[*d*]-fused tetrahydro derivative of thiopyrano[3,2-*b*]thiopyran was reported recently in a total synthesis of 1,6-dithiabenz[3,4]-estra-3,5(10),8,14-tetraen-17-one: Krishna, M. V.; Ramadas, S. R. *Heterocycles* **1981**, *16*, 405.

[8] On the basis of the observation by Cava and McGrady (*J. Org. Chem.* **1975**, *40*, 72), the contribution of the canonical form involving the d-orbital participation of the sulfonyl sulfur in A is presumably insignificant.



[9] Sandman, D. J.; Epstein, A. J.; Holmes, T. J.; Fisher, A. P., III. *Chem. Commun.* **1977**, 177.

[10] Perlstein, J. H.; Van Allan, J. A.; Isett, L. C.; Reynolds, G. A. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 61.

[11] Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1979**, *44*, 3144.

[12] Maercker, A. "Organic Reactions"; Wiley: New York, 1967; Vol. 14, pp 270–490.

[13] Mitchell, R. H. *Tetrahedron Lett.* **1973**, 4395.

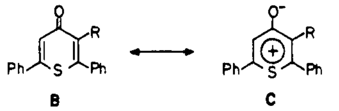
is consistent with the normal course of the Wittig–Horner reaction reported in the literature.

Mild oxidation of 7 with 1 equiv of *m*-chloroperbenzoic acid (MCPBA) gave the corresponding sulfoxide 8 only in low yield. Hence, its reaction with 11 for the synthesis of the corresponding sulfoxide 15 was not pursued.

Single-Crystal X-ray Diffraction Analysis of 12. Colorless single crystals of 12 were obtained by slow recrystallization from methanol. Figure 1 shows a plot of the molecule 12 with selected bond lengths and numbering scheme, which provides the unequivocal assignment of the *Z* stereochemistry about the C18=C19 double bond. The hydrogen atoms and bond angles are omitted for clarity.

Benzylic atom C26 and some of the atoms of the attached C27–C32 phenyl group had very large thermal parameters and root-mean-square amplitudes as high as 0.67 Å. The motion is primarily associated with C26 and C28 through C31 and appears to pivot around the C27–C32 bond. Disordered positions could not be resolved on electron density maps. Inspection of intermolecular contacts showed that these atoms occupy a relatively large cavity in the structure and therefore have more room for motion. In no way does the motion of the fragment compromise the conclusion that the benzyl sulfur atom (S2) and the thiopyran ring are cis relative to the C18=C19 double bond.

Bond lengths and angles have normal values. In particular, the C18=C19 bond is a good localized double bond. The bond lengths for the thiopyran ring are consistent with contributions of structures B and C in the ratio of ca. 2/1.[16]

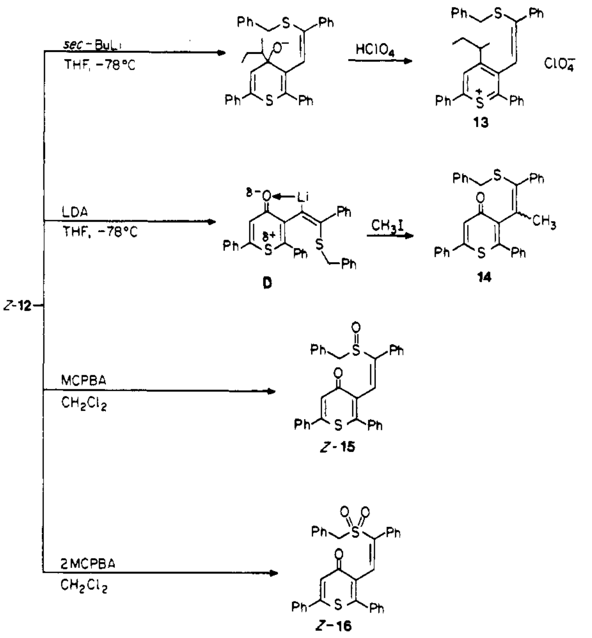


The significant contribution of the canonical form C[17] is also reflected in the IR spectrum of 12, which shows carbonyl stretching at 1600 cm^{-1}.

The six atoms of the thiopyran ring are coplanar with 0.034 Å maximum and 0.022 Å root-mean-square deviations of the atoms from a unit-weighted least-squares plane; however, the deviations are systematic, and the plane is creased along the S1–C3 direction to form two planes that enclose a dihedral angle of 4.0°.

Derivatives and Attempted Cyclization of 12. With the key intermediate (*Z*)-12 in hand, the best approach to the synthesis of tetraphenylthiopyrano[4,3-c]thiopyran 1 (R = Ph) would be the direct ring closure of the sulfur-stabilized benzylic carbanion[18] derived from (*Z*)-12. Representative reactions of (*Z*)-12 are outlined in Scheme II. Several observations can be made from these results: (1) The benzylic proton adjacent to sulfur in 12 was not acidic enough to compete with the direct nucleophilic addition of a base, such as *sec*-BuLi, to the thiopyrone function,[19] and upon subsequent acidification with perchloric acid, only the thiopyrylium salt 13 was isolated. (2) A nonnucleophilic base like lithium diisopropylamide (LDA) did not add to the carbonyl. Instead, it deprotonated the vinylic proton to give, presumably, a lithiated species in which the cationic lithium is stabilized by coordinating with the adjacent, negative carbonyl oxygen of the thiopyrone, as shown in D. A similar type of oxo-stabilized vinyllithium species has been reported.[20] The assignement of structure D is based on a MeI quenching experiment, which yielded a methylated compound whose spectroscopic data were consistent with structure 14. The desired carbanion of (*Z*)-12 was not obtained when the base was a mixture of potassium diisopropylamide (KDA) and lithium *tert*-butoxide.[21] (3) On the basis of the X-ray crystallographic analysis and further experiments, it is clear that the carbonyl group in 12 is relatively nonreactive and also appears to be sterically hindered. Thus, neither methylation with "Magic methyl" nor thionation with Lawesson's reagent,[22] in attempts to *activate* the carbonyl function, yielded the expected methoxythiopyrylium fluorosulfonate or the corresponding thione derivative. These interesting but rather dismal results at the beginning of this project led us to modify our original approach and to explore other alternatives involving the higher oxidation states of (*Z*)-12.

Scheme II



One alternative was to increase the acidity of the benzylic proton by oxidizing the adjacent sulfide to a sulfoxide or sulfone. Compound (*Z*)-12 was selectively oxidized with 1 and 2 equiv of *m*-chloroperbenzoic acid (MCPBA) in methylene chloride to give 15 and 16, respectively, in high yields. The MCPBA oxidation is mild[23] enough that we think the isomerization of the double bond in (*Z*)-12 is unlikely.[24] The increase in acidity of the benzylic protons in 15 and 16 is supported by their ^{1}H NMR spectra, in which the chemical shift of the benzylthio protons of (*Z*)-12 (δ 3.23, s) is shifted downfield to δ 3.51, 4.06, AB (q) and δ 4.3 (br s), respectively. The IR carbonyl stretching fre-

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[14] Baker, S.; Sims, R. J. *Synthesis* **1981**, 117.

[15] Tewari, R. S.; Kumari, N.; Kendurkar, P. *J. Chem. Eng. Data* **1976**, *21*, 125.

[16] The stabilization of C is associated with the formation of the aromatic thiopyrylium form. For a ^{1}H NMR study, see: Tolmache, A. I.; Kornilov, M. Yu.; Shulezhko, L. M.; Turov, A. V. *Teor. Eskp. Khim.* **1975**, *11*, 556.

[17] Hirsch, J. A.; Kosley, R. W., Jr.; Morin, R. P.; Schwartzkopf, G.; Brown, R. D. *J. Heterocycl. Chem.* **1975**, *12*, 785.

[18] α-Sulfur-substituted organometallics are well-known species. For a recent review, see: Krief, A. *Tetrahedron* **1980**, *36*, 2531.

[19] 2,6-Diphenyl-4*H*-thiopyran-4-one, although inert to most nucleophiles, reacts with MeLi and Grignard reagents. Reynolds, G. A.; Van Allan, J. A. *J. Heterocycl. Chem.* **1976**, *13*, 1089.

[20] Marino, J. P.; Kostusyk, J. L. *Tetrahedron Lett.* **1979**, 2489.

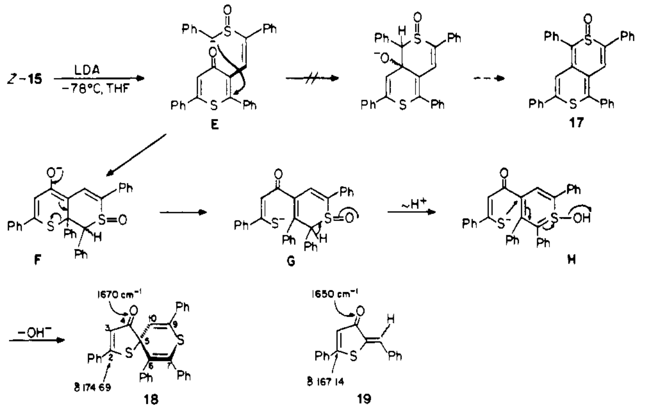
[21] Raucher, S.; Koolpe, G. A. *J. Org. Chem.* **1978**, *43*, 3794. Renger, B.; Hugel, H.; Wykypiel, W.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2630.

[22] Lawesson, S.-O. *Tetrahedron* **1981**, *37*, 1819.

[23] Chen, C. H. *Tetrahedron Lett.* **1976**, *25*. Chen, C. H.; Donatelli, B. A. *J. Org. Chem.* **1976**, *41*, 3053.

[24] A detailed NMR study of these compounds by variable-temperature technique supports the proposed *Z* configurations of **15**, **16**, and **20**: Kelts, L. W.; Uebel, J. J.; Chen, C. H., in preparation.

Scheme III

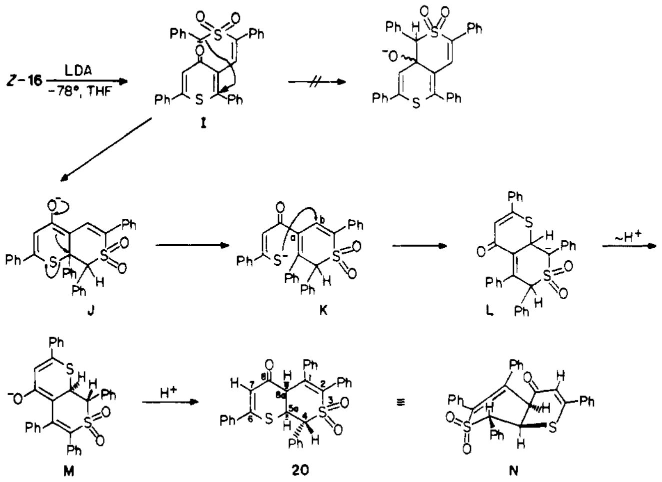


quencies of all three compounds remain at about 1590 cm^{-1}. The delocalized electrons on sulfur in the thiopyrone system are not readily oxidizable under the normal conditions.

Cyclization of Sulfoxide (*Z*)-15. Treating (*Z*)-15 with LDA at −78 °C in THF under argon instantly produced a dark green solution, which changed into a dark red solution on equilibration to room temperature. After aqueous workup and purification by chromatography, we recovered ca. 50% of starting material and 13% of a new compound whose mass, IR, and ^{1}H and ^{13}C NMR spectra are in complete agreement with the assigned spiro structure 18. Aside from the routine assignments, certain spectroscopic features are worth noting. The IR spectrum shows a carbonyl stretching frequency at 1670 cm^{-1}, suggesting a normal α,β-unsaturated ketone, and the $\nu_{S=O}$ at 1030 cm^{-1} disappeared. The ^{13}C NMR spectrum shows a unique downfield singlet at δ 174.69 (in addition to the C-4 carbonyl at δ 202.61), which is assigned to the C-2 adjacent to sulfur. These data compare favorably with those of a model compound, 2-benzylidene-3-keto-5-phenyl-2,3-dihydrothiophene (19),[25] which has $\nu_{C=O}$ at 1650 cm^{-1} and the corresponding ^{13}C NMR peak at δ 167.14.

The formation of this unusual product can be explained by the sequence proposed in Scheme III. The carbanion E apparently was not reactive enough under the reaction conditions to attack the deactivated thiopyranyl ketone to give the desired ring-closure product 17. Instead, a Michael addition takes place at the C-2 position of the thiopyrone ring, giving the enolate F, which, subsequently, leads to the cleavage of the C–S bond to generate a more stable 1,3-ketothiocarbonyl enolate G. A prototropic shift was followed by a unique anionic ipso cyclization of the intermediate H eliminating the hydroxide ion to give 18 in a manner much like the base-catalyzed sulfoxide dehydration (Pummerer-type rearrangement) reported by Cava and co-workers in the synthesis of tetraphenylthieno[3,4-*c*]thiophene[26] and *p*-quinobis(1,3-benzodithiole) *S*-oxide.[27]

Scheme IV



Cyclization of Sulfone (*Z*)-16. 1,2,4,6-Tetraphenyl-5a,8a-dihydrothiopyrano[3,4-*b*]thiopyran-8-(4*H*)-one 3,3-Dioxide (20). Intramolecular annulation of (*Z*)-16 under conditions similar to those used with the sulfoxide (*Z*)-15 (LDA in THF followed by mild acid workup) gave, in addition to mostly recovered starting material, a new colorless, crystalline product. This interesting compound, isolated in ca. 10% yield, was characterized as the *novel* dihydrothiopyrano[3,4-*b*]thiopyran sulfone derivative 20—*the first member of the hitherto unknown [3,4-b]-3 family.* Its IR spectrum has strong carbonyl stretching at 1652 cm^{-1}, reminiscent of a typical dihydrothiopyrone derivative.[28] The ^{1}H NMR spectrum of 20 shows one vinylic proton at δ 6.48 (s) and three distinctively coupled alkyl protons at δ 4.61 (d), 4.90 (dd), and 5.03 (d), which are consistent with the assigned H_{8a}, H_{5a}, and H_4 protons, respectively. The large coupling constant (J = 12.8 Hz) observed between H_4 and H_{5a} suggests that they are trans diaxial with a dihedral angle of ca. 180°. In contrast, the observed coupling constant between H_{5a} and H_4 is quite small (J = 3.6 Hz), suggesting that they are cis oriented in an equatorial–axial disposition (dihedral angle approximates 60°), which confirms the least strained cis-bicyclic ring junction. Additional support is obtained from its ^{13}C NMR spectrum, which shows only three sp^3 carbons, each coupled with only one hydrogen. A conformation consistent with the spectral properties of 20 is depicted in N. In this conformation both of the cis-fused dihydrothiopyranyl rings exist in a preferred half-chair conformation,[29] and above all, the bulky phenyl group at C-4 and the 5-sulfur are also in the least congested equatorial positions.

A mechanism that explains the formation of this new thiopyrano[3,4-*b*]thiopyran ring system is proposed in Scheme IV. As in the previously attempted cyclization of the sulfoxide (*Z*)-15, the anion I could not add to the deactivated thiopyrone. Instead, a Michael addition takes place to give J, which leads to the cleavage of the C–S bond. The resulting thioenolate K, which cannot add to position a via the basic Pummerer elimination[26] to give the spiro intermediate as in Scheme III, Michael-adds, in turn, at the least hindered vinylic sulfone position to give the α-sulfone-stabilized carbanion L. The similar type of cyclization of methyl styryl sulfone with ketone enolates has been reported recently.[30] The final prototropic shift producing the stable conjugated enolate M is presumably irreversible, because the α-sulfonyl proton, which is also conjugated with the ketone in L, is the most acidic.

Cyclization of Disulfone Derivative 21. For (*Z*)-16 to annulate at C-4 of the thiopyrone, it became increasingly evident that the electrophilicity of the C-4 carbonyl function must be enhanced. Because we had found earlier

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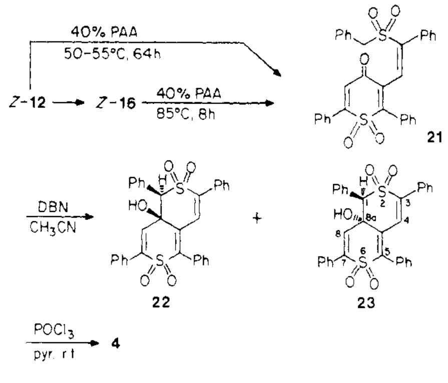
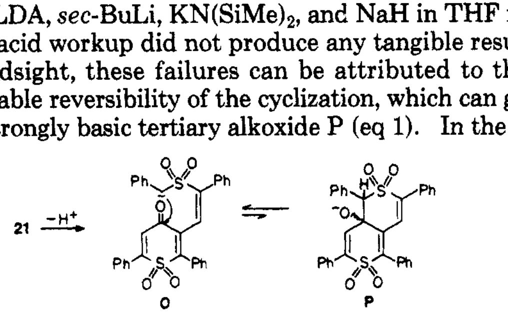
Scheme V



that the thiopyrone functionality in (*Z*)-**12** could not be activated by forming either the methoxythiopyrylium salt or the thione derivative, we resorted to increasing the oxidation state of (*Z*)-**16** even further to the disulfone derivative **21**.

We envisioned that by disruption of the delocalization associated with the lone pair on sulfur in the thiopyran-4-one system through the formation of a sulfone, the C-4 carbonyl might resume its normal electrophilicity as a true α,β-unsaturated ketone in a nucleophilic addition reaction. Thus, further oxidation of the monosulfone **16** with excess 40% peracetic acid (PAA) at 85 °C gave the disulfone **21** in 89% yield (Scheme V). Alternatively, **21** was prepared in 91% yield directly from the disulfide (*Z*)-**12** by exhaustive oxidation with 40% PAA at 50–55 °C for 64 h. The ease and the high yield of this oxidation are quite remarkable, particularly because the oxidation of 2,6-diphenyl-4*H*-thiopyran-4-one itself in PAA at 100 °C gave only ca. 20% of the corresponding sulfone along with unreacted starting materials.[31] We have no direct proof of the *Z* configuration of **21** except that the chemical shift (δ 4.15) and, particularly, the anisotropic environment of the benzylic protons, which appear as a broad singlet, are very similar to those of (*Z*)-**16**. In addition, the barrier to fluctuation observed in the variable-temperature ^{1}H NMR spectra of both **16** and **21**[24] is consistent with the expected *Z* configurations in which the diastereotopic benzylic protons are nonequivalently situated in the congested vicinity of the carbonyl group. The most encouraging sign that the carbonyl group may have increased reactivity comes from the IR spectrum of **21**, in which the carbonyl stretching frequency is now at 1655 cm^{-1}—a shift of 65 cm^{-1} from the corresponding thiopyrone derivative **16**.

The reaction of **21** under strongly basic conditions such as LDA, *sec*-BuLi, KN(SiMe)$_2$, and NaH in THF followed by acid workup did not produce any tangible results. On hindsight, these failures can be attributed to the unfavorable reversibility of the cyclization, which can generate a strongly basic tertiary alkoxide P (eq 1). In the absence



(1)

of any proton source in situ, P, which was not captured, presumably could revert to the less basic benzylic sulfonyl anion O, which could then regenerate the starting material on acidification or fragment to give other undesired products under forcing conditions.

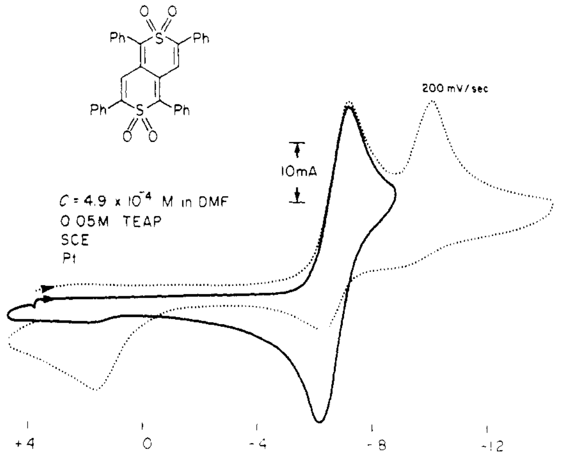


Figure 2. Cyclic voltammograms of **4** in DMF (4.9 × 10^{-4} M).

The ideal base needed to effect the intramolecular cyclization of **21**, therefore, should be strong enough to abstract a benzylic sulfone proton to generate a finite concentration of O and also acidic enough in the protonated form to quench the annulated alkoxide P. Among the many bases tried, only sodium isoamylate and DBN were promising. In particular, 1 equiv of 1,5-diazabicyclo[4,3]non-5-ene (DBN) in an aprotic solvent of high dielectric constant, such as acetonitrile, gave the best results. The reaction was very fast at room temperature and produced essentially quantitatively a pair of diastereoisomeric alcohols **22** and **23** in ca. 1:1 ratio as estimated by ^{1}H NMR. The less soluble isomer was isolated in pure form and was assigned the structure of the trans alcohol **23**. This assignment was based on its ^{1}H NMR spectrum in which H_1 (δ 4.76) is deshielded by the adjacent oxygen atom,[32,33] whereas H_1 of **22** is at δ 4.72. A small coupling ($J_{\text{H-OH}}$ = 1.9 Hz) was also observed for **23** in Me$_2$SO-d_6. For preparative purposes, these isomers were not separated but were used directly without purification.

Dehydration by a variety of reagents and conditions, which included the combination of mesylation, trifluoroacetylation, trimethylsilation, triflation, and various bases, was not entirely fruitful. The best procedure we found for dehydrating **22**/**23** was to use thionyl chloride in pyridine (−15 °C to room temperature), from which the desired disulfone **4** was isolated in 48% yield (based on **20**) as a yellowish, very insoluble solid. Phosphoryl chloride in pyridine at high temperature (100 °C) worked also, but the yield was inferior.

Although many reagents can reduce sulfoxides to sulfides,[34] reagents that can effectively reduce sulfones are rare. To our knowledge, only LAH[35] and diisobutylaluminum hydride (Dibal)[36] have been used successfully. In one special case, oxysulfoxonium salts of certain aryl alkyl sulfones were reduced to sulfoxides by using sodium borohydride/alumina.[37] Attempts to reduce the disulfone **4** with excess diisobutylaluminum hydride in diglyme at 60 °C (heterogeneous) resulted in total recovery of starting material, presumably because of insolubility. Under forcing conditions (110 °C, 72 h), **4** slowly reacted to

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[31] Arndt did not report the yield in his original paper: Arndt, F.; Nachtweg, P.; Rusch, J. *Chem. Ber.* **1925**, *58*, 1633. In our work, the yields were 18–29%.

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[35] Bordwell, F. G.; McKellin, W. H. *J. Am. Chem. Soc.* **1951**, *73*, 2251.

[36] Gardner, J. N.; Kaiser, S.; Krubiner, A.; Lucas, H. *Can. J. Chem.* **1973**, *51*, 1419.

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produce a complex mixture of products, none of which has a mass corresponding to either the monosulfone sulfide or the desired disulfide 1 (R = Ph) (assay via field-desorption mass spectrometry).

Physical Properties of 4. The extreme insolubility of this material, unfortunately, has greatly hampered our efforts in studying its anticipated acceptor properties in solution. Although it dissolves slowly in a large amount of hot diglyme or nitromethane, it is only sparingly soluble in Me$_2$SO or DMF at ambient temperature. A cyclic voltammogram of 4, which shows its propensity to accept electrons, was nevertheless obtained at room temperature in DMF, after first heating 4 at 100 °C and sonicating to dissolve (Figure 2). A quasi-reversible 1e$^-$ reduction wave, which peaked at $E_I{}^{\circ\prime} = -0.62$ V, was observed with a Pt electrode and 0.05 M DMF solution of tetraethylammonium perchlorate (TEAP) as the electrolyte. The reversibility of the first wave is consistent with the formation of the stable radical anion proposed in A. The second wave, which peaked at about –1.0 V, is irreversible and is consistent with the formation of an unstable, highly energetic dianion species that, presumably, led to fragmentation. A one-electron transfer at the first wave was confirmed by coulometric determination.

Experimental Section

Melting points, obtained on a Mel-Temp or a Thomas-Hoover melting-point apparatus, are uncorrected. ^{1}H and ^{13}C NMR spectra of CDCl$_3$ solutions were recorded on JEOL FX-270 and Bruker WH-270 spectrometers, with Me$_4$Si as the internal standard. Mass spectra were obtained on an AEI MS-30 mass spectrometer. Field-desorption mass spectra were recorded on a Varian MAT-731 spectrometer. IR spectra were obtained on a Beckman IR 4250 spectrophotometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories. The cyclic voltammogram was recorded on a PARC-173 potentiometer.

Diethyl α-(Benzylthio)benzylphosphonate (7). Crude α-chlorodibenzyl sulfide (5)[13] prepared from 72.5 g (0.338 mol) of dibenzyl sulfide and 45.4 g (0.34 mol) of sulfuryl chloride in carbon tetrachloride was freed from CCl$_4$ on a rotary evaporator at 40 °C for 3 h. The resulting colorless oil was slowly added dropwise to 57 g (0.34 mol) of triethyl phosphite. The exothermic reaction was controlled by a cooling bath so that ethyl chloride steadily evolved throughout the addition. After the addition, the reaction mixture was heated on a steam bath for 1 h and vacuum distilled to give 81.5 g (70% based on dibenzyl sulfide) of 7: bp 160–168 °C (13–18 μm); ^{1}H NMR (CDCl$_3$) δ 1.1 (t, 3, J = 6 Hz, POCH$_2$CH_3), 1.23 (t, 3, J = 6 Hz, POCH$_2$CH_3), 3.62 (q, 2, J = 9 Hz, SCH_2Ph), 3.7 [d, 1, J = 15 Hz, SCH(Ph)P)], 3.7–4.3 (m, 4, POCH_2CH$_3$), 7.2 and 7.6 (2 br s, 10, Ar H).

Anal. Calcd for C$_{18}$H$_{23}$O$_3$PS: C, 61.7; H, 6.6; P, 8.8; S, 9.2. Found: C, 61.3; H, 6.9; P, 8.9; S, 9.7.

Diethyl α-(Benzylsulfinyl)benzylphosphonate (8). A solution of 2 g of *m*-chloroperbenzoic acid in 75 mL of methylene chloride was added dropwise to an ice-cooled solution of 3.2 g (9.14 mmol) of the sulfide 7. After 1 h, the reaction mixture was washed with aqueous NaHCO$_3$ and with water, dried (MgSO$_4$), and evaporated to give 3.7 g of crude 8, which was crystallized from 300 mL of hexanes, giving a small amount of analytically pure sample: mp 70–71 °C; ^{1}H NMR (CDCl$_3$) δ 1.13 (t, 3, J = 7 Hz, POCH$_2$CH_3), 1.33 (t, 3, J = 7 Hz, POCH$_2$CH_3), 3.4–4.5 (m, 7), 7.1–7.5 (m, 7, Ar H); IR (KBr) 1250 (P=O), 1025 (S=O) cm^{-1}.

Anal. Calcd for C$_{18}$H$_{23}$O$_4$PS: C, 59.0; H, 6.3; P, 8.5. Found: C, 58.6; H, 6.6; P, 8.6.

3-[2(*Z*)-(Benzylthio)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (12). To a solution of 11.4 g (0.0325 mol) of diethyl α-(benzylthio)benzylphosphonate (7) in 150 mL of dry THF was added by syringe 15.6 mL (1.1 equiv) of *n*-BuLi (2.3 M in hexanes) at –78 °C under argon. After 20 min, 9.4 g of 2,6-diphenyl-3-formyl-4*H*-thiopyran-4-one (11)[11] in 150 mL of THF was added dropwise over 30 min. The dark brown reaction mixture was equilibrated to ambient temperature in 3 h and poured into 700 mL of aqueous NH$_4$Cl, from which a brown solid slowly precipitated on stirring in an open breaker. Filtration, washing with water, and recrystallization from 260 mL of methanol gave 11.7 g (74%) of pure (*Z*)-12: mp 107–108 °C; ^{1}H NMR (CDCl$_3$) δ 3.23 (s, 2, PhCH_2S), 6.25 (s, 1, H$_5$), 6.9–7.8 (m, 10, Ar H and 1 vinylic); mass spectrum (EI), *m/e* (relative intensity) 397 M$^+$ – PhCH$_2$), 365 (M$^+$ – PhCH$_2$S, 100); IR (KBr) 1600 (C=O) cm^{-1}.

Anal. Calcd for C$_{32}$H$_{24}$OS$_2$: C, 78.7; H, 5.0; S, 13.1. Found: C, 78.4; H, 5.4; S, 12.7.

3-[2(*Z*)-(Benzylthio)-2-phenylethenyl]-4-*sec*-butyl-2,6-diphenylthiopyrylium Perchlorate (13). To a solution of 12 (300 mg, 0.61 mmol) in 15 mL of dry THF was added by syringe 0.54 mL (1.2 equiv) of *sec*-BuLi (1.4 M in cyclohexane) at –78 °C under argon. After 1 h at –78 °C, the dark green reaction mixture was allowed to equilibrate to ambient temperature (turning dark red at ca. 0 °C) and poured into 300 mL of dilute (10%) perchloric acid, from which an orange solid immediately precipitated. This solid was filtered, washed with water, air-dried, and boiled with 200 mL of hexanes, from which 100 mg of the crude thiopyrylium perchlorate 13 was obtained. The crude 13 was recrystallized from 50 mL of benzene, giving 67 mg of pure 13: mp 196–197 °C; mass spectrum (FD), *m/e* 529 (M$^+$ – ClO$_4$); IR (KBr) 1090 cm^{-1} (br ClO$_4^-$), no C=O.

Anal. Calcd for C$_{36}$H$_{33}$S$_2$ClO$_4$: C, 68.7; H, 5.3; Cl, 5.7; S, 10.2. Found: C, 68.8; H, 5.2; Cl, 5.5; S, 10.3.

3-[3-(Benzylthio)-3-phenyl-2-propen-2-yl]-2,6-diphenyl-4*H*-thiopyran-4-one (14). Reaction of 12 with LDA. To a solution of 150 mg (0.31 mmol) of 12 in 15 mL of dry THF at –78 °C under argon was added by syringe 1.2 equiv of LDA, which was freshly prepared from 65 μL (0.45 mmol) of diisopropylamine and 0.15 mL of *n*-BuLi (2.4 M in hexanes) in 1 mL of THF. The dark blue solution that formed immediately was stirred at –78 °C for 15 min before it was quenched with methyl iodide. The resulting reddish brown solution was warmed to ambient temperature and evaporated to give a dark red residue whose TLC revealed a complex mixture of products. By preparative TLC on silica gel twice, a light yellowish band (R_f 0.64, EtOAc/hexanes, 1:2 v/v) was separated and eluted with methylene chloride to give a small amount of 14: mass spectrum (FD), *m/e* (relative intensity) 503 (M$^+$ + 1) for C$_{33}$H$_{26}$OS$_2$, 379 (M$^+$ – PhCH$_2$S, 100); ^{1}H NMR (CDCl$_3$) δ 2.13 (s, 3, CH$_3$), 3.3 (s, 2, PhCH$_2$S-), 6.4 (s, 1, H$_5$ vinylic), 6.8–7.8 (m, 20, ArH).

3-[2(*Z*)-(Benzylsulfinyl)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (15). To a solution of 1.5 g (3.07 mmol) of (*Z*)-12 in 30 mL of methylene chloride cooled with ice was added dropwise a solution of 590 mg (1 equiv) of MCPBA (Kodak Laboratory Chemicals) in 40 mL of methylene chloride over 15 min. The reaction mixture was stirred in the ice bath for 30 min more and then washed with aqueous sodium bicarbonate and with water. The methylene chloride phase was dried (MgSO$_4$) and evaporated to give a white solid, which was recrystallized from 250 mL of benzene and hexanes (1:3 v/v) to give 1.36 g (88%) of the sulfoxide (*Z*)-15: mp 198–199 °C dec; IR (KBr) 1590 (C=O), 1030 (S=O) cm^{-1}; mass spectrum (FD), *m/e* (relative intensity) 504 (M$^+$ weak), 413 (M$^+$ – PhCH$_2$), 365 (M$^+$ – PhCH$_2$SO, 100); ^{1}H NMR (CD$_2$Cl$_2$) δ 3.51, 4.06 (AB q, 2, J = 13 Hz, PhCH$_A$H$_B$SO-), 6.33 (s, 1, H$_5$ vinylic), 7.0–7.8 (m, 21, Ar H and olefinic).

Anal. Calcd for C$_{32}$H$_{24}$O$_2$S$_2$: C, 76.2; H, 4.8; S, 12.7. Found: C, 76.1; H, 4.9; S, 12.3.

3-[2(*Z*)-(Benzylsulfonyl)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (16). To a solution of 3 g (6.15 mmol) of the sulfide (*Z*)-12 in 60 mL of methylene chloride was added a solution of 2.4 g (2.2 equiv) of MCPBA in 100 mL of methylene chloride at room temperature. The reaction mixture was stirred overnight and washed with aqueous sodium bicarbonate followed by water. The methylene chloride was dried (MgSO$_4$) and evaporated to give a solid that was recrystallized from 300 mL of ethanol, giving 3 g (94%) of pure sulfone (*Z*)-16: mp 209–210 °C; ^{1}H NMR (CD$_2$Cl$_2$) δ 4.3 (br s, 2, PhCH$_2$SO$_2$), 6.55 (s, 1, H$_5$ vinylic), 7.2–7.8 (m, 21, Ar H and vinylic); IR (KBr) 1590 (C=O), 1118, 1138, 1312 (SO$_2$) cm^{-1}.

Anal. Calcd for C$_{32}$H$_{24}$O$_3$S$_2$: C, 73.8; H, 4.6; S, 12.3. Found: C, 73.5, H, 4.3; S, 11.9.

3-[2(*Z*)-(Benzylsulfonyl)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide (21) from (*Z*)-16. A mixture of 500 mg (0.96 mmol) of the monosulfone (*Z*)-**16** and 40 mL of peracetic acid (40%, FMC) was heated in an oil bath at 85 °C for 8 h. After cooling, the reaction mixture was poured into 350 mL of brine, and the precipitated bright yellow solid was filtered, washed with water, and air-dried to give 470 mg (89%) of essentially pure disulfone **21** that was suitable for subsequent reactions. An analytical sample of 110 mg was obtained by recrystallizing 130 mg of this material from 50 mL of ethanol: mp 218–219 °C; mass spectrum, (FD), *m/e* 488 ($M^+ - SO_2$), 397 ($M^+ - PhCH_2SO_2$); IR (KBr) 1655 (C=O), 1310, 1038 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.15 (m, 2, $PhCH_2SO_2$) 6.28 (s, 1, H_5 vinylic), 6.86 (s, 1, olefininc), 7–7.9 (m, 20, Ar H).

Anal. Calcd for $C_{32}H_{24}O_5S_2$: C, 69.5, H, 4.4; S, 11.6. Found: C, 69.1; H, 4.4; S, 11.8.

From the Sulfide (*Z*)-12. To a solution of 1 g (2.05 mmol) of the sulfide (*Z*)-**12** in 10 mL of methylene chloride was added dropwise 80 mL of peracetic acid (40%) at ambient temperature. The resulting solution was heated in an oil bath at 50–55 °C for 64 h. The mixture was poured into 300 mL of brine, from which the precipitated yellow solid was filtered, washed thoroughly with water, and air-dried to give 1.03 g (91%) of the desired disulfone **21**.

2,6,7,9-Tetraphenyl-1,8-dithiaspiro[4,5]deca-2,6,9-trien-4-one (18). To a solution of 435 mg (0.86 mmol) of the sulfoxide (*Z*)-**15** in 40 mL of dry THF cooled to −78 °C under argon was added 1.2 equiv of freshly prepared LDA in THF. The dark green solution that was produced instantaneously was allowed to equilibrate to room temperature overnight. The resulting dark red solution was poured into 300 mL of aqueous NH_4Cl solution from which the precipitated brown solid was filtered, washed with water, and air-dried to give 450 mg of crude product. A TLC assay of this material (silica gel, ethyl acetate/hexanes, 1:2 v/v) showed ca. 50% starting material **15** at R_f 0.44 and a major spot at R_f 0.82. The latter was separated by preparative TLC (silica gel) with CH_2Cl_2/hexanes (2:1 v/v), giving 55 mg of pure **18**: mp 154–155 °C (methanol); mass spectrum (FD), *m/e* 486 (M^+); IR (CCl_4) 1670 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.12 (s, 1, olefinic), 6.9–7.6 (m, 21, Ar H and olefinic); ^{13}C NMR ($CDCl_3$) δ 69.88 (s, C-5), 114.62 (d, C-10), 125.14, 125.68, 126.73, 127.62, 127.70, 127.78, 127.97, 128.32, 128.84, 128.97, 129.81, 130.40, 132.19, 132.51, 133.89 (s), 136.78 (s), 139.97 (s), 141.65 (s), 141.97 (s), 174.69 (s, C-2), 202.61 (s, C-4 carbonyl).

Anal. Calcd for $C_{32}H_{22}OS_2$: C, 79.0; H, 4.6; S, 13.2. Found: C, 78.7; H, 4.7; S, 12.8.

1,2,4,6-Tetraphenyl-5a,8a-dihydrothiopyrano[3,4-*b*]thiopyran-8(4*H*)-one 3,3-Dioxide (20). A solution of 750 mg (1.44 mmol) of the sulfone (*Z*)-**16** in 100 mL of dry THF was cooled (−78 °C bath), and 1.2 equiv of LDA (freshly prepared from 245 µL of diisopropylamine and 1 mL of a 1.6 M hexane solution of *n*-BuLi in 2 mL of THF) was added by syringe under argon. The resulting dark brown solution was allowed to equilibrate to ambient temperature overnight. The reaction mixture was poured into 400 mL of saturated aqueous ammonium chloride, from which, on slow evaporation, a reddish brown solid was formed. The solid was collected by filtration, washed with water, and recrystallized from 50 mL of ethanol, giving 75 mg (10%) of **20**. The mother liquor, which was shown by TLC and FD mass spectrum to be mostly starting material, was evaporated, and the residue was recrystallized from 20 mL of MeOH to give 50 mg of **16**.

An analytical sample of **20** was obtained as a colorless solid by washing with acetonitrile followed by recrystallization from a small amount of THF: mp 280 °C dec; IR (KBr) 1652 (C=O), 1132, 1305, 1320 (SO_2) cm^{-1}; mass spectrum (FD), *m/e* 520 (M^+), 456 ($M^+ - SO_2$); ^{1}H NMR ($CDCl_3$ containing ca. 5% Me_2SO-d_6) δ 4.61 (d, 1, H_{8a}, $J_{8a,5a}$ = 3.6 Hz), 4.90 (dd, 1, H_{5a}, $J_{8a,5a}$ = 3.6 Hz, $J_{5a,4}$ = 12.8 Hz), 5.03 (d, 1, H_4, $J_{4,5a}$ = 12.8 Hz), 6.48 (s, 1, H_7), 7–7.6 (m, 20, Ar H); ^{13}C NMR (same solvent) δ 43.13 (d, C-5a), 54.77 (d, C-8a), 65.39 (d, C-4), 190.77 (C-8 carbonyl).

Anal. Calcd for $C_{32}H_{24}O_3S_2$: C, 73.8; H, 4.6. Found: C, 73.6; H, 4.6.

Diastereomeric Mixture of 1*H*-1,8a-Dihydro-8a-hydroxy-1,3,5,7-tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-Tetraoxide (22 and 23). To a solution of 1.03 g (1.86 mmol) of the disulfone **21** in 50 mL of acetonitrile was added 232 mg (1 equiv) of DBN at room temperature. After 1 h, the dark reaction mixture was poured into a beaker containing 100 mL of 2 N sulfuric acid and 200 mL of brine. The precipitated brown gum was extracted with methylene chloride, washed with water, dried ($MgSO_4$), and evaporated to give 1 g of crude diastereoisomeric **22** and **23** in a ratio of ca. 1:1 with R_f 0.23 and 0.34 (in EtOAc/hexane, 1:2 v/v, silica gel), respectively: mass spectrum (FD), *m/e* 552 (M^+ for $C_{32}H_{24}O_5S_2$), 5.34 ($M^+ - H_2O$); IR (KBr) 1125, 1305 (SO_2) cm^{-1}, no $\nu_{C=O}$. This material was satisfactory for use in subsequent reactions.

***trans*-1*H*-1,8a-Dihydro-8a-hydroxy-1,3,5,7-tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-Tetraoxide (23).** The crude diastereomeric mixture (165 mg) was recrystallized consecutively from chloroform and acetonitrile to give 20 mg of a colorless single isomer assigned as pure trans **23** (R_f 0.34, silica gel in EtOAc/hexane, 1:2 v/v): mp 319–321 °C dec; IR (KBr) 1030, 1300 (SO_2), 3420 (OH) cm^{-1}, no $\nu_{C=O}$; mass spectrum (FD), *m/e* (relative intensity) 552 (M^+, 100), 534 ($M^+ - H_2O$, 30); ^{1}H NMR ($CDCl_3$) δ 4.76 (s, 1, $PhCHSO_2$), 6.1 (s, 1, H_8 olefinic), 6.52 (s, 1, H_8 olefinic), 4.37 (s, 1, OH deuterium exchangeable), 7.3–7.7 (m, 20, Ar H). A small coupling (*J* = 1.9 Hz) between the OH and the adjacent benzylic H was also detected in Me_2SO-d_6.

Anal. Calcd for $C_{32}H_{24}O_5S_2$: C, 69.5; H, 4.4. Found: C, 69.5; H, 4.4.

Crude Cis Isomer 22. The residue obtained by evaporating the mother liquor from the above recrystallization of the trans isomer **23** was chromatographed by preparative TLC twice on silica gel (2 mm thick) in EtOAc/hexane, 1:1 v/v, giving a small amount of the more polar cis isomer **22** (contaminated with ca. 22% of the trans isomer **23**, as estimated by ^{1}H NMR): mass spectrum (FD), *m/e* 552 (M^+ for $C_{32}H_{24}O_5S_2$), 534 ($M^+ - H_2O$); IR ($CDCl_3$) 1310, 1120 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.72 (s, 1, $PhCHSO_2$), 4.95 (br s, 1, deuterium exchangeable OH), 6.24 (s, 1, H_8 olefinic), 6.7 (s, 1, H_4 olefinic), 7.2–7.7 (m, 20, Ar H).

1,3,5,7-Tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-Tetraoxide (4). To a solution of 400 mg (0.72 mmol) of the crude diastereoisomers **22** and **23** in 20 mL of dry pyridine was added under argon 0.15 mL of freshly distilled thionyl chloride at −15 °C (ethylene glycol/dry ice bath). The reaction mixture was allowed to equilibrate to room temperature over 2 h and stirred at ambient temperature for 2 days. The brown reaction mixture was poured into 200 mL of brine, from which the precipitated solid was filtered and washed thoroughly with water followed by acetonitrile until the filtrate was colorless. The residual solid (195 mg) was dissolved in 200 mL of hot nitromethane and concentrated to 75 mL, which gave, after cooling, 185 mg (48% based on the starting *seco*-disulfone **21**) of pure **4** as light yellowish solid: mp 401–402 °C dec; mass spectrum (FD), *m/e* 534 (M^+); IR (KBr) 1300, 1125 (SO_2) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 6.64 (s, 2, $H_8 + H_4$ olefinic), 7.4–7.7 (m, 20, Ar H).

Anal. Calcd for $C_{32}H_{22}O_4S_2$: C, 71.9; H, 4.1; S, 12.0. Found: C, 71.5; H, 4.2; S, 11.6.

X-ray Analysis. The crystal system of **12** is triclinic, space group $P\bar{1}$ (from successful structure refinement) with 2 molecules in the unit cell. A suitable crystal of **12**, 0.08 × 0.19 × 0.38 mm, was chosen for data collection. All data were taken at 23 ± 1 °C on an Enraf-Nonius CAD-4 diffractometer. The parameters of intensity data collection are given in Table I.

Cell constants were obtained by computer centering of 25 reflections, followed by least-squares refinement of the setting angles. As a check on crystal and electronic stability, three reflections were remeasured periodically. A slight drift in the standard intensities was observed. The intensities were corrected for this drift with correction factors between 0.98 and 1.10.

The structure was solved in space group $P\bar{1}$ by direct methods with the program MULTAN,[38] using 250 reflections with $E > 1.81$. An *E* map, calculated for the phase set with the best combined figure of merit (2.65), yielded 28 atoms. The remaining 7 atoms were located in a difference electron density map. Hydrogen atoms were not located.

Refinement was by full-matrix least squares. The function minimized was $\Sigma w(|F_o| - K|F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2$. Scattering factors, including the anomalous scattering corrections

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[38] Computer programs used for this study were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revision 3B, 1980.

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Table I. X-ray Analysis of 12, $C_{32}H_{24}OS_2$

parameter	
cell dimensions	
a, Å	10.381 (3)
b, Å	15.004 (3)
c, Å	9.433 (3)
α, deg	109.67 (2)
β, deg	112.82 (2)
γ, deg	79.56 (2)
V, Å^3	1273.1 (13)
Z (molecules per unit cell)	2
D_c, g cm^{-3}	1.275
μ (Mo Kα), cm^{-1}	2.30
λ, Å	0.7107
unique reflections	3305
scan range, deg	2θ(Mo Kα_1) −0.6° to 2θ(Mo Kα_2) + 0.6°
scan rate, 2θ/min	1.8–20°
range of data	$0° < 2\theta(\text{Mo K}\alpha) < 45°$

for all atoms, were obtained from International Tables for X-ray Crystallography, Vol. IV, 1974. Refinement proceeded smoothly and converted to $R = \sum ||F_o| - K|F_c||/\sum |F_o| = 0.077$ and $R_w = (\sum w\,(|F_o| - K|F_c|)^2/\sum wF_o^2)^{1/2} = 0.085$ for the 35 non-hydrogen atoms with anisotropic temperature factors. A total of 316 parameters were varied and 2045 reflections were used. The estimated standard deviation of an observation of unit weight was 2.47. A final different electron density map showed a maximum density of 0.44 e/Å^3. In a final electron density map, the peak electron densities of the atoms were relatively low—only 19.0 and 15.4 e/Å^3 for S1 and S2 down to a low of 2.6 e/Å^3 for C26.

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Registry No. **4**, 93383-45-0; **5**, 51317-73-8; **7**, 70660-17-2; **8**, 93383-33-6; **11**, 70940-96-4; (*Z*)-**12**, 93383-34-7; **13**, 93383-36-9; **14**, 93383-37-0; (*Z*)-**15**, 93383-38-1; (*Z*)-**16**, 93383-39-2; **18**, 93383-41-6; **20**, 93383-42-7; **21**, 93383-40-5; **22**, 93383-43-8; **23**, 93383-44-9; $(PhCH_2)_2S$, 538-74-9; $P(OEt)_3$, 122-52-1.

Supplementary Material Available: Atomic parameters (Table II), generalized anisotropic thermal parameters (Table III), bond lengths (Table IV), and bond angles (Table V) for compound **12** (4 pages). Ordering information is given on any current masthead page.

Thiopyranothiopyran Chemistry. 2. Synthesis of 2,4-Diphenyl-4*H*-benzo[*e*]thiopyrano[3,4-*b*]thiopyran-10-one[†]

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2,4-Diphenyl-4*H*-benzo[*e*]thiopyrano[3,4-*b*]thiopyran-10-one was synthesized by lithiation of 3-[2(*Z*)-(benzylsulfinyl)-2-phenylethenyl]-4*H*-thiochroman-4-one, whose absolute configuration was established by X-ray crystallography. The yellow, insoluble solid obtained from this reaction was assigned the structure 2,6-diphenyl-2*H*-4-(2-mercaptobenzoyl)thiopyran 1-oxide (11), which, on brief heating with AcOH, yielded the title compound in 87% yield. Treatment of 11 with 1% aqueous cupric acetate in methylene chloride gave a new rearranged product, which was identified as 9,11-diphenylbenzo[*b*]-1,8-dithiaspiro-[4,5]deca-6,9-dien-4-one. Mechanisms that would account for the formation of both of these compounds are proposed.

In the first part of this series,[1] we described the synthesis of the novel dihydrothiopyrano[3,4-*b*]thiopyranyl sulfone derivative **2**, which we believe to be derived from an addition–elimination reaction of the lithiated anion A at C-2 of (*Z*)-**1** followed by an intramolecular Michael addition of C, as depicted in Scheme I. The yield of **2**, however, was only 10%, and most of the starting material **1** was recovered. We attributed the low yield of this reaction to the phenyl substituent at C-2, which was somewhat hindered to nucleophilic attack. Thus, we reasoned that a compound without the C-2 substituent should readily undergo the initial Michael addition to give an enolate intermediate similar to B. Since this Michael adduct already embodies the desired thiopyrano[3,4-*b*]thiopyranyl framework, it might be trapped under favorable conditions without further rearrangement. This paper describes the synthesis and the stereochemistry of the thiochroman derivative **6** and its cyclization to give the desired thiopyrano[3,4-*b*]thiopyran **12**.

Results and Discussion

Synthesis of 3-[2(*Z*)-(Benzylthio)-2-phenylethenyl]-4*H*-thiochroman-4-one (5) and Derivatives.

Single-Crystal X-ray Diffraction Analysis of the Sulfone 8.

3-Formyl-4*H*-thiochroman-4-one (**3**),[2] readily prepared from thiochroman-4-one, was condensed with the Wittig–Horner reagent of diethyl α-(benzylthio)benzylphosphonate (**4**)[1] in THF at −78 °C to give **5** in 81% yield as a single isomer. The high stereospecificity of this reaction, though not totally unexpected,[1] is quite remarkable. Since only the *Z* isomer can ring close to the desired [3,4-*b*] system, it is crucial, at this stage of the synthesis, that the stereochemistry of **5** be confirmed. Various NMR techniques involving NOE and shift reagents were attempted, but, unfortunately, they failed to yield enough information to allow us to assign the stereoconfiguration of **5**.

Oxidation of **5** with 1 and 2 equiv of *m*-chloroperbenzoic acid (MCPBA) in methylene chloride gave the sulfoxide **6** and the sulfone **8**, respectively, in high yields. Since single crystals suitable for X-ray diffraction analysis were difficult to prepare from either the sulfide **5** or the sulfoxide **6**, crystallographic analysis was performed on a single crystal of the sulfone **8**, which was obtained by slow recrystallization from acetonitrile at room temperature. A stereodrawing of **8** with atomic labeling and bond lengths,

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[†] Dedicated to Dr. George A. Reynolds on the occasion of his retirement from the Kodak Research Laboratories.

(1) Chen, C. H.; Reynolds, G. A.; Smith, D. L.; Fox, J. L. *J. Org. Chem.*, preceding paper in this issue.

(2) Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1979**, *44*, 3144.

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