Syntheses of 4*H*-Thiopyran-4-one 1,1-Dioxides as Precursors to Sulfone-Containing Analogues of Tetracyanoquinodimethane

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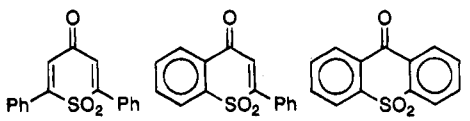
Received October 24, 1994®

Synthetic routes to the unsubstituted 4*H*-thiopyran-4-one 1,1-dioxide (**5a**), 2,6-dialkyl-substituted, 2-aryl- or 2-heteroaryl-6-alkyl-substituted, 2,6-diaryl- or diheteroaryl-substituted, and 2-heteroaryl-6-aryl-substituted 4*H*-thiopyran-4-one 1,1-dioxides **5b–s** are described. Sodium hydrosulfide hydrate in buffered aqueous alcohol can be used as a substitute for hydrogen sulfide gas for the introduction of sulfur to methyl acrylate, to 1,5-disubstituted-1,4-pentadien-3-ones **13**, or to 1,5-disubstituted-1,4-pentadiyn-3-ones **17**. The double dehydrogenation of 2,3,5,6-tetrahydrothiopyran-4-one 1,1-dioxides **13** with iodine–DMSO–sulfuric acid gives thiopyran-4-one 1,1-dioxides **5** in good yield and small amounts of 1,4-pentadien-3-ones **13**. 2,3,5,6-Tetrahydrothiopyran-4-one 1,1-dioxide (**9**) and 5,6-dihydrothiopyran-4-one 1,1-dioxide (**12**), which lack aryl or heteroaryl substituents, give poor yields of 4*H*-thiopyran-4-one 1,1-dioxide (**5a**) with iodine–DMSO–sulfuric acid.

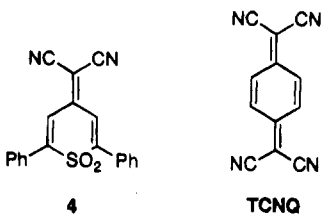
Introduction

The sulfone oxidation state in thiopyranone 1,1-dioxide derivatives stabilizes anion radicals relative to thiopyranones with sulfur(II) oxidation state.[1–6] 4*H*-Thiopyranone 1,1-dioxide **1**,[1–3] benzo[*b*]thiopyranone 1,1-dioxide **2**,[1,2,4] and thioxanthone 1,1-dioxide (**3**)[5,6] have been described as sulfur-containing analogues of quinone, naphthoquinone, and anthraquinone, respectively. Compounds **1–3** exhibit reversible electrochemistry for reduction to the anion radical with $E°$ in the range of −0.43 to −0.74 V (vs SCE). The anion radical of **3** has sufficient



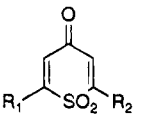
1 **2** **3**

lifetime that EPR studies[7] and spectroscopic studies[6] have both been made. The condensation of malononitrile with sulfone **1** generates 4-(dicyanomethylene)-2,6-diphenyl-4*H*-thiopyran 1,1-dioxide (**4**), which has been described as a sulfone-containing analogue of tetracyanoquinodimethane (TCNQ).[1] This molecule and related compounds have been utilized as electron-transport materials in electrophotographic applications.[2]



4 **TCNQ**

In order to fine tune the acceptor and electron-transport properties, synthetic routes to these compounds are needed, which permit the introduction of a variety of different substituents. Herein, we describe two general synthetic routes to symmetrical and unsymmetrical, alkyl-, aryl-, and heteroaryl-2,6-disubstituted thiopyranone 1,1-dioxides **5**, which are the penultimate precursors to analogues of **4**, as well as an improved procedure for preparation of the unsubstituted 4*H*-thiopyran-4-one 1,1-dioxide (**5a**). One innovation in the synthetic routes is the use of commercially available sodium hydrosulfide hydrate as a substitute for hydrogen sulfide gas. The generality of the iodine–sulfuric acid–dimethyl sulfoxide (DMSO) mixture[1,8] to "dehydrogenate" 2,3,5,6-tetrahydrothiopyran-4-one 1,1-dioxides to 4*H*-thiopyran-4-one 1,1-dioxides **5** is described.



5a, $R_1 = R_2 = H$
5b, $R_1 = R_2 =$ Ph
5c, $R_1 = R_2 =$ 2-thienyl
5d, $R_1 = R_2 =$ 2-furyl
5e, $R_1 =$ Ph, $R_2 =$ 2-thienyl
5f, $R_1 =$ Ph, $R_2 =$ 2-furyl
5g, $R_1 = R_2 =$ 3-thienyl
5h, $R_1 =$ Ph, $R_2 =$ 3-thienyl
5i, $R_1 = R_2 = m$-$O_2NC_6H_4$
5j, $R_1 = R_2 = p$-anisyl
5k, $R_1 =$ Ph, $R_2 = \beta$-styryl
5l, $R_1 =$ Ph, $R_2 =$ *tert*-Bu
5m, $R_1 =$ Ph, $R_2 = n$-Bu
5n, $R_1 =$ Ph, $R_2 =$ Me
5o, $R_1 =$ Ph, $R_2 =$ H
5p, $R_1 =$ 2-thienyl, $R_2 =$ *tert*-Bu
5q, $R_1 = p$-FC_6H_4, $R_2 =$ *tert*-Bu
5r, $R_1 = R_2 =$ Me
5s, $R_1 = R_2 =$ *tert*-Bu

Synthesis of 4*H*-Thiopyran-4-one 1,1-Dioxide (5a). One synthesis of the parent sulfone **5a** is outlined in Scheme 1. The procedure of Gershbein and Hurd[9] for the addition of hydrogen sulfide to methyl acrylate was modified to use sodium hydrosulfide hydrate. This commercially available material typically analyzes as a dihydrate (1.8–2.3 waters of hydration for several different lots) and can be used as a substitute for hydrogen

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® Abstract published in *Advance ACS Abstracts*, March 1, 1995.

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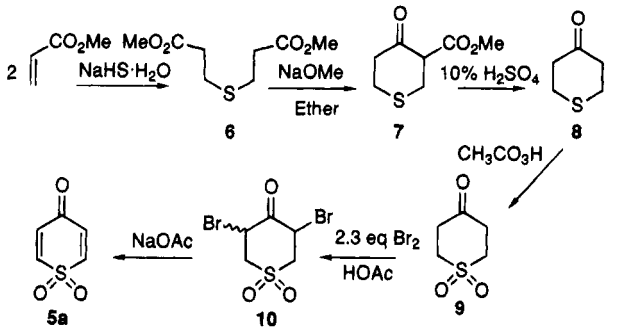
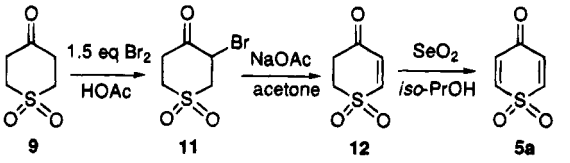
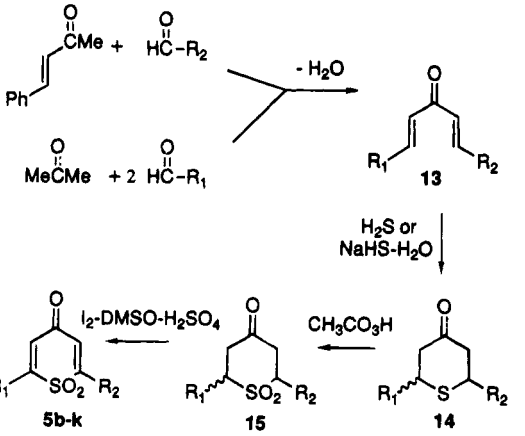
Scheme 1



Scheme 2



Scheme 3



sulfide gas in many reactions. A methanolic solution of methyl acrylate was added to an aqueous solution of sodium hydrosulfide hydrate buffered with sodium bicarbonate. The diorganosulfide **6** was isolated in 96% yield following distillation. From this point, the procedure of Fehnel and Carmack[10] was followed with slight modifications (as detailed in the Experimental Section) to give **5a** in 25% isolated yield overall.

The problematic step in the synthesis of **5a** as outlined in Scheme 1 is the addition of bromine to **9** to give the dibromides **10**. Multiple products are formed upon addition of 2.3 equiv of bromine to sulfone **9** in acetic acid at 60–90 °C. One crystalline product, which was identified as a single isomer of **10**, was isolated in 61–66% yields.

By ^{1}H NMR spectroscopy, the crystalline product appears to be the *cis*-isomer. The protons attached to the carbon bearing bromine appear as a doublet-of-doublets pattern at δ 5.43 with coupling constants of 5 and 13 Hz, which are consistent with a vicinal *trans*-diaxial coupling of 13 Hz and a vicinal *cis*-axial–equatorial coupling of 5 Hz. The methylene protons appear as a doublet-of-doublets pattern (J = 13 and 15 Hz) and as a doublet-of-doublets-of-doublets pattern (J = 4, 5, and 15 Hz) at δ 4.27 and 4.14, respectively. The 15-Hz coupling is consistent with geminal coupling of the methylene protons while the 5-Hz and 13-Hz couplings are to the vicinal methine protons. The 4-Hz coupling constants is consistent with W-form coupling between the two equatorial methylene protons. The ^{1}H–^{1}H COSY spectrum of *cis*-**10** was consistent with this assignment with the W-form coupling missing from the off-diagonal components.

The crude reaction mixture contained several other products as detected by ^{1}H NMR spectroscopy. The *trans*-isomer of **10** was the minor component of a 13-to-1 mixture of isomers **10**. Following selective crystallization of *cis*-**10** from the reaction mixture, a one-to-one mixture of *cis*- and *trans*-**10**, was isolated in 5% yield via chromatography. The methine protons of *trans*-**10** appear as a doublet-of-doublets pattern at δ 5.75 with coupling constants of 4.5 and 12 Hz. One methylene proton appears as a 2-proton doublet-of-doublets pattern at δ 4.54 with coupling constants of 12 and 15 Hz and the other appears as a 2-proton multiplet pattern centered at δ 4.50. We were unable to assign coupling constants in the latter pattern unambiguously. The yields of the combined mixture of *cis*- and *trans*-**10** were 65–70% under a variety of conditions with varying concentrations of reactants (2.0–3.0 equiv of bromine) and temperatures (60 °C to refluxing acetic acid) of reaction.

One tribromide product was isolated from the bromination reaction mixture in 10% yield. Although this material gave a correct elemental analysis, mass spectral analysis indicated trace amounts of higher molecular weight polybromides, which were not removed by repeated recrystallizations. Monobromide **11** was isolated in 5% yield via chromatography on silica gel. The remaining products in the reaction mixture were not readily characterized.

A more efficient route to **5a** is outlined in Scheme 2. Monobromination of **9** with 1.5 equival of bromine gave monobromide **11** in 87% yield with unreacted **9** recovered in 8% yield. Dehydrobromination with sodium acetate in acetone gave 5,6-dihydro-4*H*-thiopyran-4-one 1,1-dioxide (**12**) in 87.5% yield. Selenium dioxide oxidation of **12** in refluxing 2-propanol gave 4*H*-thiopyran-4-one 1,1-dioxide (**5a**) in 80% isolated yield. Although this route incorporates one more step than the route described in Scheme 1, the overall yield is significantly higher.

Synthesis of 2,6-Diaryl- or Heteroaryl-Substituted 4*H*-Thiopyran-4-one 1,1-Dioxides. The synthetic route to symmetrical and unsymmetrical sulfones **5** with 2,6-aryl/heteroaryl substituents and alkyl substituents is outlined in Scheme 3. The double Michael addition of sodium hydrosulfide hydrate to 1,4-pentadienones **13** gave tetrahydrothiopyrans **14**. Oxidation of the thiopyran sulfur of **14** produced sulfones **15**.[2,11] The iodine–DMSO–sulfuric acid system is the reagent of choice for large-scale reactions for one-pot conversion of saturated sulfones **15** to thiopyran-4-one 1,1-dioxides **5**.

The symmetrical 1,5-disubstituted-1,4-pentadien-3-ones **13** were prepared by condensation of the appropriate commercially-available benzaldehyde derivative or heterocyclic carboxaldehyde derivative with acetone. The unsymmetrical 1,5-disubstituted-1,4-pentadien-3-ones **13** were prepared by condensation of the appropriate commercially available heterocyclic carboxaldehyde derivative with commercially available 4-phenyl-3-buten-2-one.

The corresponding tetrahydrothiopyran-4-ones **14** were prepared by the addition of sodium hydrosulfide hydrate to the 1,4-pentadien-3-ones **13**. The additions of hydrogen sulfide to **13b** and **13c** were compared to the addition

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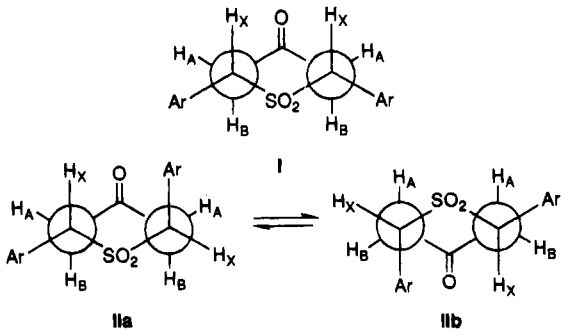
of sodium hydrosulfide hydrate. For **14b** and **14c**, yields of both isomers with hydrogen sulfide gas (94 and 85%, respectively) and sodium hydrosulfide hydrate (94 and 85%, respectively) were nearly identical. The ratio of isomers was nearly identical in each case (roughly 85:15 in favor of the *trans*-isomer).

Oxidation of the sulfides **14** to the sulfones **15** was accomplished with 30–35% peracetic acid in acetic acid. The isomer ratio was unaffected by the oxidation. In the case of the symmetrical sulfones **15b** and **15c**, the two isomers were separable by a combination of fractional crystallization and column chromatography. For the sulfones **15d–k**, the mixtures of isomers were converted directly to the corresponding 4*H*-thiopyran-4-one 1,1-dioxides **5**.

The structures of the isomers **15** were assigned from the coupling constants among the methine and methylene protons, which differ between the two isomers. As shown in structure **I**, the *cis*-isomers should be predominantly in the chair form with equatorial aryl substituents. In



this conformation, the *trans*-diaxial coupling (H_B–H_X) would be large, the *cis*-axial–equatorial coupling (H_A–H_X) would be much smaller, W-form coupling between the two equatorial methylene protons (H_B–$H_{B'}$) would be optimal, and the geminal coupling would be large. In the *trans*-isomers, two isoenergetic (or nearly isoenergetic in the case of the unsymmetrically substituted sulfones) conformations are available as shown in structures **IIa** and **IIb**. While the geminal coupling would remain large, the *trans*-diaxial coupling in one conformer would be averaged with a *trans*-diequatorial coupling in the other. Consequently, values of the vicinal coupling constants in the *trans*-isomers should be between the values of the *cis*-axial–equatorial coupling and the *trans*-diaxial coupling of the *cis*-isomers.

The ^{1}H NMR spectra of the *cis*- and *trans*-isomers of **15b** illustrate the points above. The ^{1}H NMR spectra in d_6-DMSO for *cis*- and *trans*-**15b** are shown in Figure 1. For *trans*-**15b**, the methine protons are observed as a doublet-of-doublets pattern at δ 5.05 with coupling constants of 4 and 11 Hz for the *cis*- and *trans*-vicinal couplings, respectively. The geminal coupling of 16 Hz is observed in a doublet-of-doublets pattern at δ 3.65 (geminal coupling, *trans*-vicinal coupling of 11 Hz, and W-form coupling of $\leq$1 Hz) and in a doublet-of-doublets pattern at δ 3.03 (geminal coupling, *cis*-vicinal coupling of 4 Hz, and W-form coupling of $\leq$1 Hz). Conformational interconversion has also averaged the chemical shifts of the two methylene protons such that they differ by 0.62 ppm as opposed to the 0.95 ppm difference observed in the *cis*-isomer (*vide infra*). Coupling assignments were confirmed via the ^{1}H–^{1}H COSY spectrum of *trans*-**15b**, which is shown in Figure 2.

For *cis*-**15b**, the methine protons are observed as a doublet-of-doublets pattern at δ 5.21 with coupling

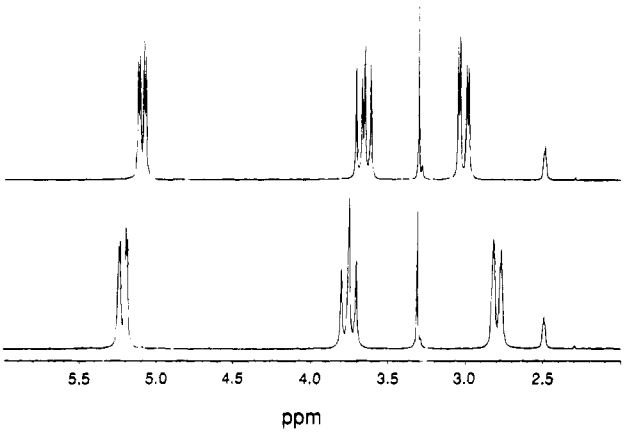


Figure 1. 300-MHz ^{1}H NMR spectra in d_6-DMSO of the methine and methylene protons of *trans*-**15b** (upper trace) and *cis*-**15b** (lower trace).

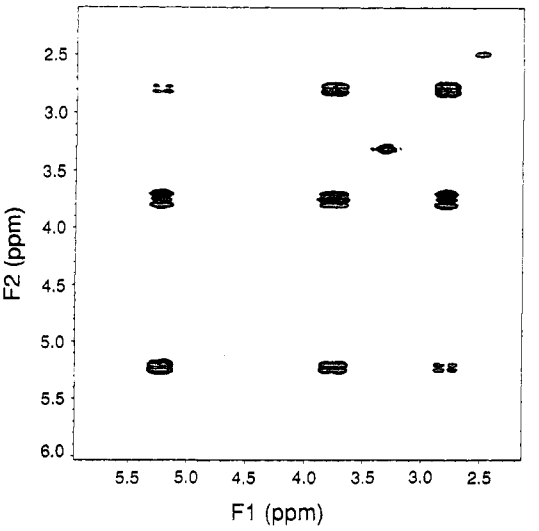
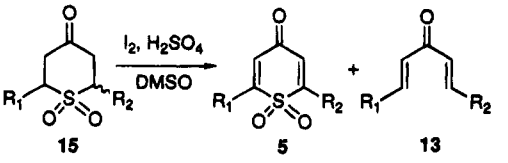


Figure 2. 300-MHz ^{1}H–^{1}H COSY spectrum in d_6-DMSO of the methine and methylene protons of *trans*-**15b**.

Scheme 4



constants of 3 and 13.5 Hz for the *cis*-axial-equatorial coupling and the *trans*-diaxial coupling, respectively. The geminal coupling of 13.5 Hz is observed in a "triplet" pattern at δ 3.75 (geminal coupling and the *trans*-diaxial coupling of 13.5 Hz) and a broadened doublet pattern at δ 2.78 (geminal coupling; *cis*-vicinal coupling of 3 Hz and W-form coupling of $\leq$3 Hz broaden each line of the doublet to a poorly resolved triplet). Similar coupling patterns were observed for the isomeric *cis*- and *trans*-isomers of **15c** and **15d**.

Introduction of Double Bonds in Tetrahydrothiopyran-4-one 1,1-Dioxides 13. The introduction of unsaturation in the 2,3,5,6-tetrahydrothiopyran-4-one 1,1-dioxides **15** was accomplished with iodine and sulfuric acid in DMSO (Scheme 4),[1,8] which appears to be a general reaction for systems of this type (Table 1). Small amounts of 1,4-pentadien-3-ones **13** were also detected in these reactions (Table 1). The thiopyran-4-one 1,1-dioxides **5** are stable to the conditions of reaction sug-

Table 1. Products from Oxidation of Tetrahydro-4*H*-thiopyran-4-one 1,1-Dioxides 9, Dihydro-4*H*-thiopyran-4-one 1,1-Dioxides 12, and Tetrahydro-4*H*-thiopyran-4-one 1,1-Dioxides 15 with Iodine and Sulfuric Acid in DMSO[a]

starting sulfone	R_1	R_2	product compd	% yield	compd	% yield
9	H	H	**5a**	10	–	–
12	H	H	**5a**	31	–	–
15b	Ph	Ph	**5b**	92	**13b**	3
cis-**15b**	Ph	Ph	**5b**	90	**13b**	5
trans-**15b**	Ph	Ph	**5b**	90	**13b**	5
15c	2-thienyl	2-thienyl	**5c**	92	**13c**	5
cis-**15c**	2-thienyl	2-thienyl	**5c**	90	**13c**	3
trans-**15c**	2-thienyl	2-thienyl	**5c**	90	**13c**	5
15d	2-furyl	2-furyl	**5d**	14	–	–
15e	Ph	2-thienyl	**5e**	89	**13e**	7
15f	Ph	2-furyl	**5f**	40	–	–
15g	3-thienyl	3-thienyl	**5g**	85	**13g**	trace
15h	Ph	3-thienyl	**5h**	89	**13h**	trace
15i	3-$O_2NC_6H_4$	3-$O_2NC_6H_4$	**5i**	85	**13i**	trace
15j	*p*-anisyl	*p*-anisyl	**5j**	90	**13j**	5
15k	Ph	*β*-styryl	**5k**	90	**13k**	5

[a] The *cis*- and *trans*-mixture of isomers was employed in each case except where noted.

gesting that pentadienones **13** arise from **15**. Formation of **13** requires the loss of the elements of SO_2 and H_2 from the tetrahydro derivatives **15**.

The furyl-substituted derivatives **15d** and **15f** gave much lower yields of thiopyran-4-one 1,1-dioxides **5** than other derivatives **15**. Furthermore, dienones **13d** and **13f** were not observed with these derivatives. Dienones **13d** and **13f** and the tetrahydro compounds **15d** and **15f** are sensitive to the acidic conditions of the reaction. Upon standing in hot DMSO–sulfuric acid without iodine, all four compounds are lost (as monitored by thin-layer chromatography).

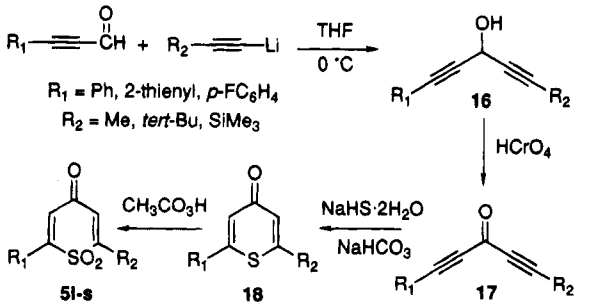
Sulfone **9** reacts with iodine and sulfuric acid in DMSO to give a 10% yield of **5a**. 5,6-Dihydrothiopyran-4-one 1,1-dioxide (**12**) reacts with iodine and sulfuric acid in DMSO to give **5a** in 31% yield. The introduction of double bonds to dihydro- and tetrahydrothiopyran-4-ones appears to be facilitated by the presence of aryl and/or heteroaryl groups that can be brought into conjugation with the ketone upon oxidation.

Comparable yields of oxidation products **5b** and **5c** were obtained from either the *cis*- or *trans*-isomers of **15b** and **15c**, respectively. The stereochemistry of the substrate had little effect on either the yield or rate of oxidation.

Synthetic Routes to 2-Aryl (or 2-Heteroaryl)-6-alkyl-4*H*-thiopyran-4-one 1,1-Dioxides and 2,6-Dialkylthiopyran-4-one 1,1-Dioxides. Synthetic routes to unsymmetrical 1,4-pentadiyn-3-ones have been described as well as subsequent conversion of these materials to telluropyran-4-ones.[12] If similar chemistry with introduction of sulfur were to allow preparation of 4*H*-thiopyran-4-ones from these intermediates, then subsequent oxidation of sulfur would give synthetic entry to 4*H*-2-aryl-6-alkylthiopyran-4-one 1,1-dioxides.

The sulfones **5l–s** were prepared via the synthetic route outlined in Scheme 5. The addition of a lithium acetylide to a propargyl aldehyde derivative gave the corresponding diynol **16**. The preparation of the 2-thienylpropargyl aldehyde required for the synthesis of **5p** has been described.[12] The diynols were oxidized without

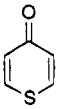
Scheme 5



further purification to the 1,4-pentadiyn-3-ones **17** with chromic acid.[12] The addition of sodium hydrosulfide hydrate to the diynones under basic conditions gave the corresponding 4*H*-thiopyran-4-ones **18**. Peracetic acid oxidation converted the thiopyranone to the corresponding sulfones **5**.

In this series of reactions, the double Michael addition of sodium hydrosulfide hydrate across the diynone is the low-yielding step of the reaction sequence. Yields were similarly poor with disodium sulfide. Gaseous hydrogen sulfide, however, gave much poorer yields.

While the symmetrical sulfones **5r** and **5s** were prepared from 2,6-dimethyl-4*H*-thiopyran-4-one (**18r**) and 2,6-di-*tert*-butyl-4*H*-thiopyran-4-one (**18s**),[13] respectively, by peracetic acid oxidation of the thiopyranone sulfur atom, the oxidation of 4*H*-thiopyran-4-one (**19**)[14] with peracetic acid gave **5a** in only trace quantities under a varity of reaction conditions. Oxidation of **19** with *Oxone* ($2KHSO_5$-$KHSO_4$-K_2SO_4)[15] in aqueous methanol gave **5a** in 23% isolated yield.



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Summary and Conclusions

The use of sodium hydrosulfide hydrate as a substitute for hydrogen sulfide gas in the syntheses of thiopyran 1,1-dioxides **5** was demonstrated. Although hydrogen sulfide gas has been utilized to introduce sulfur in the preparation of these compounds,[1,9] its handling is problematic with respect to both toxicity and odor. The use of sodium hydrosulfide hydrate in buffered aqueous alcohol gives comparable yields and is much easier to handle experimentally.

The net double dehydrogenation of saturated sulfones **15** with aryl or heteroaryl substituents to 4*H*-thiopyran-4-one 1,1-dioxides **5** with iodine–DMSO–sulfuric acid is a general procedure as compiled in Table 1. With sulfones **9** and **12**, which lack conjugating aryl or heteroaryl groups, the yields of 4*H*-thiopyran-4-one 1,1-dioxide (**5a**) are much lower. The furyl groups in derivatives **15d** and **15f** appear to be sensitive to the acidic, oxidative conditions employed in the reaction and, consequently, yields are lower in these systems.

Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer. Infrared spectra were re-

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corded on a Beckman IR 4250 instrument. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N Analyzer. THF and CH_2Cl_2 were purchases as anhydrous from Aldrich Chemical Co. and were used as received. Oxone, 4-phenyl-3-buten-2-one, 4-methoxybenzaldehyde, 2-formylthiophene, and 2-formylfuran were used as received from Aldrich Chemical Co. Acetonitrile (MCB spectrograde) was dried over 4A molecular sieves (Eastman Laboratory Chemicals, baked at 400 °C). DMSO, dibenzalacetone, and iodine were used as received from Eastman Laboratory Chemicals.

Addition of Sodium Hydrosulfide to Methyl Acrylate. Methyl acrylate (17.2 g, 0.200 mol) was dissolved in 200 mL of MeOH. To this solution was added sodium hydrosulfide hydrate (13.8 g, 0.15 mol) in 100 mL of water and 100 mL of saturated $NaHCO_3$ (mildly exothermic addition). After addition was complete, the reaction mixture was stirred 1 h at ambient temperature. The reaction mixture was diluted with 400 mL of water, and the products were extracted with ether (3 × 150 mL). The combined ether extracts were washed with brine, dried over Na_2SO_4, and concentrated. The residual oil was purified via distillation to give 19.8 g (96%) of the 1,5-dicarbomethoxy-3-thiapentane (**6**), bp 110–112 °C (0.5 torr) [lit.[9] bp 148.5–149 °C (8 torr)].

Preparation of Tetrahydrothiopyran-4-one. A. Cyclization of 1,5-Dicarbomethoxy-3-thiapentane (6). Compound **6** was dissolved in 250 mL of ether. Sodium methoxide (11.5 g, 0.212 mol) was added. The resulting slurry was stirred at reflux for 6 h. The product was acidified by the addition of 20 mL of acetic acid followed by 100 mL of water. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated to give 13.1 g (78%) of 3-carbomethoxy-2,3,5,6-tetrahydrothiopyran-4-one (**7**) as a colorless oil that was used without further purification.

B. Decarboxylation. Tetrahydrothiopyran-4-one **7** (13.1 g, 0.753 mol) was heated at reflux for 3 h in 250 mL of 10% H_2SO_4. The reaction mixture was cooled to rt, and the products were extracted with ether (3 × 150 mL). The combined ether extracts were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The residue was recrystallized from EtOAc–hexanes (1/2 V/V) to give 6.88 g (79%) of **8** as a white crystalline solid, mp 58–60 °C (lit.[14] mp 58–62 °C).

Oxidation of Tetrahydrothiopyran-4-one (8) to 2,3,5,6-Tetrahydro-4*H*-thiopyran-4-one 1,1-Dioxide (9). To a stirred solution of **8** (5.30 g, 0.0431 mol) in 50 mL of EtOAc was added dropwise 35% peracetic acid (26 g, 0.11 mol) at a slow enough rate to avoid reflux. The product crystallized from the reaction mixture following addition. The reaction mixture was chilled and the product was collected by filtration. The crystals were washed with cold EtOAc and dried to give 5.69 g (89%) of **9** as a white crystalline solid, mp 140–142 °C (lit.[14] mp 141–142 °C).

Bromination of Sulfone 9 To Give Dibromides 10. Bromine (6.40 g, 0.0400 mol) in 30 mL of acetic acid was added dropwise to a refluxing solution of sulfone **9** (2.96 g, 0.0200 mol) in 100 mL of acetic acid. Upon cooling to rt, a white solid precipitated, which was collected by filtration, washed with ether, and dried to give 2.71 g (44%) of one dibromide **10**, mp 213–216 °C (lit.[14] 220–222 °C): ^{1}H NMR (DMSO-d_6) δ 5.426 (d × d, 2 H, J = 5, 13 Hz), 4.27 (d × d, 2 H, J = 13, 15 Hz), 4.14 (d × d × d, 2 H, J = 4, 5, 13 Hz); IR (KBr) 2982, 2930, 1755, 1332, 1285, 1266, 1123, 890 cm^{-1}.

The filtrate was concentrated to half volume to give a tan solid (3.03 g, 49%). This material was recrystallized from 50 mL of acetic acid to give 1.33 g (22%) of the dibromide described above, mp 213–216 °C. Combined yield was 4.04 g (66%).

The mother liquors were concentrated, and the residue was purified via chromatography on silica gel eluted with 20% ethyl acetate–CH_2Cl_2. The first product (R_f = 0.65) was identified as a tribromide (1.15 g, 10%), mp 178–181 °C: ^{1}H NMR (DMSO-d_6) δ 4.81 (d × d, 1 H, J = 3.5, 12.7 Hz), 4.47 (d × d, 1 H, J = 3.8, 14.9 Hz), 4.24 (d, 1 H, J = 14.9 Hz), 3.98 (d × t, J = 3.8, 13.7 Hz) 3.71 ("t" (d × d), 1 H, J = 12.7, 13.7 Hz); FDMS, m/z 388 ($C_5H_5{}^{81}Br_3O_3S$). Anal. Calcd for $C_5H_5Br_3O_3S$: C, 17.83; H, 1.50; S, 9.52. Found: C, 18.11; H, 1.72; S, 9.13.

A second product (R_f = 0.5) was identified as a mixture of both dibromide isomers of **10** (0.31 g, 5%) on the basis of ^{1}H NMR spectroscopy. The second dibromide: ^{1}H NMR (DMSO-d_6) 5.75 (d × d, 2 H, J = 4.5, 12 Hz), 4.54 (d × d, 2 H, J = 12, 15 Hz), 4.50 (m, 2 H).

Preparation of 4*H*-Thiopyran-4-one 1,1-Dioxide (5a). The dibromides **10** (1.90 g, 6.21 mmol) and NaOAc (4.10 g, 0.050 mol) in 100 mL of acetone were stirred for 72 h at rt. The reaction mixture was diluted with 400 mL of water, and the products were extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were washed with brine (2 × 100 mL), dried over Na_2SO_4, and concentrated. The residue was recrystallized from $CHCl_3$–ether to give 0.63 g (70%) of the sulfone **5a**, mp 134–136 °C (lit.[10] 173–174 °C).

Preparation of 3-Bromo-2,3,5,6-tetrahydrothiopyran-4-one 1,1-Dioxide (11). To a solution of **9** (2.10 g, 0.0142 mol) in 100 mL of acetic acid at 60 °C was added bromine (3.40 g, 0.0213 mol) in 20 mL of acetic acid. Following addition, the reaction was cooled to 5 °C and a small amount (0.65 g) of unreacted starting material precipitated. The filtrate was concentrated to give a pink solid that was slurried with ether and collected by filtration to give 1.85 g (87% based on recovered starting material) of a white solid, mp 173–179 °C: ^{1}H NMR (d_6-DMSO) δ 5.38 (d × d, 1 H, J = 5.5, 12.5 Hz), 4.14 (d × d, 1 H, J = 12.5, 13.2 Hz) 3.99 (d × t, 1 H, J = 5, 13.2 Hz), 3.75 (d × t, 1 H, J = 4.5, 13.3 Hz), 3.45 (m, 1 H), 3.02 (d × t, 1 H, J = 5, 14 Hz), 2.84 (d × t, 1 H, J = 4.5, 15 Hz); IR (KBr) 2980 (w), 2925 (w), 1722 (s), 1280 (s), 1131 cm^{-1}. Anal. Calcd for $C_5H_7BrO_3S$: C, 26.44; H, 3.11. Found: C, 26.12; H, 2.95.

Preparation of 5,6-Dihydrothiopyran-4-one 1,1-Dioxide (12). A mixture of **11** (2.39 g, 0.0104 mol) and NaOAc·3H_2O (4.92 g, 0.060 mol) in 60 mL of acetone were stirred at rt for 72 h. The reaction mixture was filtered through Celite, and the filter cake was washed with acetone. The combined filtrates were concentrated and the residue was recrystallized from acetic acid–ether to give 1.33 g (87.5%) of a white crystalline solid, mp 150–152 °C: ^{1}H NMR ($CDCl_3$) δ 7.18 (d, 1 H, J = 11.2 Hz), 6.38 (d, 1 H, J = 11.2 Hz), 3.60 (d × t, 2 H, J = 1, 6 Hz), 3.205 (t, 2 H, J = 6 Hz); ^{13}C NMR (d_6-DMSO) δ 192.1, 143.1, 133.5, 49.0, 35.6. IR (KBr) 3035, 2995, 2946, 1694 (s), 1601, 1409, 1307, 1278, 1200, 1136, 1121, 1108, 959, 854, 782 cm^{-1}. Anal. Calcd for $C_5H_6O_3S$: C, 41.09; H, 4.14. Found: C, 40.73; H, 4.10.

Preparation of 5a with Selenium Dioxide. Selenium dioxide (2.20 g, 0.020 mol) and **12** (0.584 g, 4.00 mmol) in 25 mL of 2-propanol were heated at reflux for 15 h. The reaction mixture was filtered through Celite into 200 mL of CH_2Cl_2. The filtrate was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The residue was recrystallized from $CHCl_3$–ether to give 0.461 g (80%) of **5a**, mp 134–136 °C.

General Procedure for the Preparation of Dienones 13. Preparation of (*E,E*)-1,5-Di(2-thienyl)-1,4-pentadien-3-one (13c). A mixture of 29.8 g (0.266 mol) of 2-thiophenecarboxaldehyde, 80 mL of EtOH, 40 mL of water, 7.7 g (0.160 mol) of acetone, and 2 mL of 10% NaOH was stirred for 15 h at rt. The yellow crystalline solid was collected by filtration and dried to give 28.4 g (85%) of **13c** as a yellow solid, mp 115–117.5 °C: ^{1}H NMR ($CDCl_3$) δ 7.72 (d, 2 H, J = 15 Hz), 7.39 (d, 2 H, J = 5.0 Hz), 7.32 (d, 2 H, J = 3.6), 7.06 (d × d, 2 H, J = 3.6, 5.0 Hz), 6.79 (d, 2 H, J = 15 Hz); IR (KBr) 3090, 1670, 1575, 1310, 1275, 1245, 1105, 980, 865, 795 cm^{-1}; FDMS, m/z 246 ($C_{13}H_{10}OS_2$). Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09. Found: C, 63.28; H, 4.12.

(*E,E*)-1,5-Di(2-furyl)-1,4-pentadien-3-one (13d). A mixture of 65.3 g (0.68 mol) of 2-furaldehyde, 150 mL of EtOH, 75 mL of water, 19.7 g (0.41 mol) of acetone, and 2 mL of 10% NaOH was treated as described to give 70 g (96%) of **13d** as a yellow solid, mp 50–53 °C: ^{1}H NMR ($CDCl_3$) δ 7.51 (d, 2 H, J = 1.8 Hz), 7.48 (d, 2 H, J = 15.6 Hz), 6.91 (d, 2 H, J = 15.6 Hz), 6.685 (d, 2 H, J = 3.6 Hz), 6.495 (d × d, 2 H, J = 1.8, 3.6 Hz); IR (KBr) 1625, 1020, 750 cm^{-1}; FDMS, m/z 214 ($C_{13}H_{10}O_3$. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 73.21; H, 4.71.

(*E,E*)-1-Phenyl-5-(2-thienyl)-1,4-pentadien-3-one (13e). A mixture of 65.2 g (0.447 mol) of (*E*)-4-phenyl-3-buten-2-one,

50 g (0.446 mol) of 2-thiophenecarboxaldehyde, 4 mL of 10% NaOH, 50 mL of water, and 75 mL of EtOH was treated as described to give 90.0 g (84%) of (*E,E*)-1-phenyl-5-(2-thienyl)-1,4-pentadien-3-one (**13e**) as a yellow solid, mp 92–96 °C: ^{1}H NMR ($CDCl_3$) δ 7.85 (d, 1 H, J = 16 Hz), 7.71 (d, 1 H, J = 16 Hz), 7.61 (m, 1 H), 7.40 (m, 5 H), 7.29 (m, 1 H), 7.12 (m, 1 H), 7.03 (d, 1 H, J = 16 Hz), 6.87 (d, 1 H, J = 16 Hz); IR (KBr) 1650, 1615, 1595, 1345, 705 cm^{-1}; FDMS, *m/z* 240 ($C_{15}H_{12}OS$). Anal. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 74.66; 4.73.

(*E,E*)-1-Phenyl-5-(2-furyl)-1,4-pentadien-3-one (13f). A mixture of 40.0 g (0.274 mol) of (*E*)-4-phenyl-3-buten-2-one, 26.3 g (0.274 mol) of 2-furaldehyde, 2 mL of 10% NaOH, 100 mL of water, and 120 mL of EtOH was treated as described to give (*E,E*)-1-phenyl-5-(2-furyl)-1,4-pentadien-3-one (**13f**) as an oil which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.71 (d, 1 H, J = 16 Hz), 7.59 (m, 2 H), 7.51 (d, 1 H, J = 18 Hz), 7.49 (d, 1 H, J = 16 Hz), 7.40 (m, 3 H), 6.99 (d, 1 H, J = 16 Hz), 6.90 (d, 1 H, J = 16 Hz), 6.69 (d, 1 H, J = 3.6 Hz), 6.49 (d × d, 1 H, J = 1.8, 3.6 Hz); IR (KBr) 1650, 1615, 1595, 1345, 705 cm^{-1}; IR (NaCl, film) 2980, 1600, 1480, 1450, 1340, 1280, 1200, 1175, 1090, 1015, 975, 880, 745, 700 cm^{-1}; FDMS, *m/z* 224 ($C_{15}H_{12}O_2$).

An analytical sample was prepared by chromatography on silica gel eluted with CH_2Cl_2 to give a glass following evaporation of solvent. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40. Found: C, 80.45; H, 5.43.

(*E,E*)-1,5-Di(3-thienyl)-1,4-pentadien-3-one (13g). 2-Thiophencarboxaldehyde (29.8 g, 0.266 mol), 80 mL of EtOH, 40 mL of water, 7.7 g (0.16 mol) of acetone, and 2 mL of 10% NaOH was treated as described to give 28.4 g (85%) of **13c** as a yellow solid, mp 115–117.5 °C: ^{1}H NMR ($CDCl_3$) δ 7.69 (d, 2 H, J = 16 Hz), 7.56 (br s, 2 H), 7.35 (br s, 4 H), 6.85 (d, 2 H, J = 16 Hz); IR (KBr) 3090, 1670, 1610, 1575, 1310, 1275, 1245, 1105, 980, 865, 795 cm^{-1}; FDMS, *m/z* 246 ($C_{13}H_{10}OS_2$). Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09. Found: C, 63.17; H, 4.00.

(*E,E*)-1-Phenyl-5-(3-thienyl)-1,4-pentadien-3-one (13h). A mixture of 65.2 g (0.447 mol) of (*E*)-4-phenyl-3-buten-2-one, 50 g (0.446 mol) of 3-thiophenecarboxaldehyde, 4 mL of 10% NaOH, 50 mL of water, and 75 mL of EtOH was treated as described to give 90.0 g (84%) of (*E,E*)-1-phenyl-5-(2-thienyl)-1,4-pentadien-3-one (**13h**) as a yellow solid, mp 111–115 °C: ^{1}H NMR ($CDCl_3$) δ 7.71 (d, 1 H, J = 16 Hz), 7.69 (d, 1 H, J = 16 Hz), 7.56 (m, 3 H), 7.36 (m, 5 H), 7.03 (d, 1 H, J = 16 Hz), 6.86 (d, 1 H, J = 16 Hz); IR (KBr) 1600, 1350, 1200, 980 cm^{-1}; FDMS, *m/z* 240 ($C_{15}H_{12}OS$). Anal. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 74.89; 4.04.

(*E,E*)-1,5-Di(3-nitrophenyl)-1,4-pentadien-3-one (13i). A mixture of 95.3 g (0.557 mol) of *m*-nitrobenzaldehyde, 500 mL of EtOH, 250 mL of water, 18.3 g (0.316 mol) of acetone, and 2 mL of 10% NaOH was treated as described to give 69.8 g (85%) of **13i** as a yellow solid, mp 108–116 °C: FDMS, *m/z* 324 ($C_{17}H_{12}N_2O_5$). Anal. Calcd for $C_{17}H_{12}N_2O_5$: C, 62.96; H, 3.73; N, 8.64. Found: C, 63.23; H, 3.58; N, 8.66.

1,5-Di-*p*-anisyl-1,4-pentadien-3-one (13j). A mixture of 68.0 g (0.50 mol) of *p*-anisaldehyde, 150 mL of EtOH, 75 mL of water, 14.5 g (0.25 mol) of acetone, and 2 mL of 10% NaOH was treated as described to give 69.8 g (95%) of **13j** as a yellow solid, mp 124–126 °C: ^{1}H NMR (CD_2Cl_2) δ 7.70 (d, 2 H, J = 16 Hz), 7.60 (AA′BB′, 4 H), 6.96 (d, 2 H, J = 16 Hz), 6.95 (AA′BB′, 4 H), 3.86 (s, 6 H); IR (KBr) 1655, 1631, 1600, 1513, 1250, 1178 cm^{-1}; FDMS, *m/z* 294 ($C_{19}H_{18}O_3$). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.23; H, 6.18.

1,7-Diphenyl-1,4,6-heptatrien-3-one (13k). A mixture of 40.0 g (0.274 mol) of (*E*)-4-phenyl-3-buten-2-one, 36.2 g (0.274 mol) of *trans*-cinnamaldehyde, 2 mL of 10% NaOH, 100 mL of water, and 120 mL of EtOH was treated as described to give 69.3 g (97%) of 1,7-diphenyl-1,4,6-heptatrien-3-one (**13k**) as a yellow crystalline solid, mp 104.5–108.5: ^{1}H NMR (CD_2Cl_2) δ 7.705 (d, 1 H, J = 16 Hz), 7.65–7.32 (m's, 10 H), 7.07 (d, 1 H, J = 15 Hz), 7.00 (m, 1 H), 6.64 (d, 1 H, J = 15 Hz); IR (KBr) 1625, 1585, 1358, 1095 cm^{-1}; FDMS, *m/z* 260 ($C_{19}H_{16}O$). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.61; H, 6.22.

Preparation of 2,3,5,6-Tetrahydro-2,6-di(2-thienyl)-thiopyran-4-one (14c) with Hydrogen Sulfide Gas. A solution of 20.0 g (0.0812 mol) of (*E,E*)-1,5-di(2-thienyl)-1,4-pentadien-3-one (**13c**), 2 g of NaOAc, and 75 mL of DMF in 225 mL of ethanol was heated via steam bath. Hydrogen sulfide gas was slowly bubbled into the reaction mixture until the pentadienone was consumed. The reaction mixture was cooled to rt and diluted with 500 mL of water. The aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The oily residue (20.1 g, 88%) was a mixture of isomers: ^{1}H NMR ($CDCl_3$) δ 7.26 (d × d, 2 H, J = 1.3, 5 Hz), 6.92 (m, 4 H), 4.58 (m, 2 H), 3.06 (m, 4 H) [roughly 85:15 mixture of isomers]; IR (NaCl, film) 3110, 2940, 1711, 1675, 1435, 1410, 1390, 1255, 1230, 703 cm^{-1}; FDMS, *m/z* 280 ($C_{13}H_{12}OS_3$).

Large chunky crystal grew in the oil upon standing, which were collected by filtration, washed with cold 5% EtOAc in hexane, and dried to give 14.3 g of one isomer of **14c**, mp 114.5–118 °C: ^{1}H NMR ($CDCl_3$) δ 7.26 (d × d, 2 H, J = 1.3, 5 Hz), 7.04 (d × d × d, 2 H, J = 0.9, 1.3, 3.5 Hz), 6.96 (d, × d, 2 H, J = 3.5, 5 Hz), 4.65 (d × d, 2 H, J = 3.5, 11.5 Hz), 3.12 (d × d, 2 H, J = 3.5, 13.6 Hz), 3.00 (d × d, 2 H, J = 11.5, 13.6 Hz); IR (KBr) 3110, 2950, 1705, 1220, 699 cm^{-1}; FDMS, *m/z* 280 ($C_{13}H_{12}OS_3$). Anal. Calcd for $C_{13}H_{12}O_1S_3$: C, 55.70; H, 4.32; S, 34.32. Found: C, 55.63; H, 4.32; S, 33.76.

For 2,3,5,6-Tetrahydro-2,6-diphenylthiopyran-4-one (14b). A solution of 100 g (0.43 mol) of dibenzalacetone (**13b**), 10 g of NaOAc, and 225 mL of DMF in 500 mL of EtOH was treated as described to give 105.2 g (92%) of an 15:85 mixture of *cis*- and *trans*-**14b** as a yellow crystalline solid: ^{1}H NMR: δ 7.40 (m, 10 H), [4.30 (d × d, 2 H, J = 1.2, 3.8 Hz, major isomer), 4.27 (d × d, 2 H, minor isomer)], 3.03 (m, 4 H).

Recrystallization from 10% EtOAc–hexanes gave pure *trans*-2,3,5,6-tetrahydro-2,6-diphenylthiopyran-4-one (**14b**), mp 86–88 °C (lit. mp[3] 88 °C).

General Procedure for the Addition of Sodium Hydrosulfide Hydrate to Dienones 13. Preparation of 2,3,5,6-Tetrahydro-2,6-diphenylthiopyran-4-one (14b). A solution of 100 g (0.43 mol) of dibenzalacetone (**13b**) in 500 mL of 2-propanol was added to a solution of 113 g of dibasic potassium phosphate in 500 mL of water. After the reagents were mixed, 46 g (0.50 mol) of sodium hydrosulfide hydrate was added. The resulting mixture was stirred overnight at rt. The reaction mixture was poured into 1 L of water, and the products were extracted with CH_2Cl_2 (4 × 250 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was slurried in EtOH, filtered, and dried to give 107.8 g (94%) of a yellow crystalline solid that was an 85:15 mixture of isomers by ^{1}H NMR (*vide supra*).

2,3,5,6-Tetrahydro-2,6-di(2-thienyl)thiopyran-4-one (14c): yellow oil, 85% that was used in the next step without further purification.

2,3,5,6-Tetrahydro-2,6-di(2-furyl)thiopyran-4-one (14d): oil, 90%; ^{1}H NMR analysis of the residue was consistent with a 25:75 mixture of *cis*- and *trans*-isomers, respectively. The oily residue was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.36 (d, 2 H, J = 1.8 Hz), 6.28 (d × d, 2 H, J = 1.8, 3.6 Hz), [6.22 (45), 6.15 (55)] (d, 2 H, J = 3.6 Hz), 4.42 (m, 2 H), 3.01 (d, 4 H); IR (film, NaCl) 1712 cm^{-1}; FDMS, *m/z* 248 ($C_{13}H_{12}O_3S$).

2,3,5,6-Tetrahydro-2-phenyl-6-(2-thienyl)thiopyran-4-one (14e): oil, 86%, as a 70:30 mixture of diastereomers, which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 7.21 (m, 1 H), 7.01 (m, 1 H), 6.95 (m, 1 H), 4.64 (m, 1 H), 4.30 (m, 1 H), 3.25–2.83 (m, 4 H); IR (KBr) 1710, 1670, 1240, 700 cm^{-1}; FDMS, *m/z* 274 ($C_{15}H_{14}OS_2$). Anal. Calcd for $C_{15}H_{14}OS_2$: C, 58.80; H, 4.61. Found: C, 58.87; H, 4.72.

2,3,5,6-Tetrahydro-2-(2-furyl)-6-phenylthiopyran-4-one (14f): oil, 99%. The product, a 45:55 mixture of *cis*- and *trans*-isomers, respectively, was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.20–7.45 (m, 6 H), 6.32 (d × d, 1 H, J = 1.8, 3.6 Hz), [6.25 (45), 6.19 (55)] (d, 1 H, J = 3.6 Hz), 4.49 (m, 1 H), 4.25 (m, 1 H), 3.05 (m, 4 H); FDMS, *m/z* 258 ($C_{15}H_{14}O_2$).

2,3,5,6-Tetrahydro-2,6-di(3-thienyl)thiopyran-4-one (14g): yellow oil, 86%, that was used without further purification: IR (film, NaCl) 1710 cm^{-1}; FDMS, *m/z* 280 ($C_{13}H_{12}OS_3$).

2,3,5,6-Tetrahydro-2-(3-thienyl)-6-phenylthiopyran-4-one (14h): oil, 88%, which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.20–7.45 (m, 8 H), [4.45, 4.20, 4.12, 3.58 (m's, 2 H)], 3.0 (m's, 4 H); IR (film, NaCl) 1710 cm^{-1}; FDMS, *m/z* 274 ($C_{15}H_{14}OS_2$).

2,3,5,6-Tetrahydro-2,6-di(3-nitrophenyl)thiopyran-4-one (14i): oil, 80%, which was used without further purification: IR (film, NaCl) 1710 cm^{-1}; FDMS, *m/z* 356 ($C_{17}H_{12}N_2O_5S$).

2,3,5,6-Tetrahydro-2,6-di-*p*-anisylthiopyran-4-one (14j): yellow oil (98.0 g, 86%) that was used without further purification: IR (film, NaCl) 1715 cm^{-1}; FDMS, *m/z* 328 ($C_{19}H_{20}O_3S$).

2,3,5,6-Tetrahydro-2-(β-styryl)-6-phenylthiopyran-4-one (14k): oil, 80%, which was used without further purification: IR (film, NaCl) 1705 cm^{-1}; FDMS, *m/z* 294 ($C_{19}H_{18}OS$).

General Procedure for the Oxidation of Tetrahydrothiopyrans 14 to Sulfones 15. Preparation of 2,3,5,6-Tetrahydro-2,6-diphenylthiopyran-4-one 1,1-Dioxide (15b). 30% Peracetic acid (48.2 g, 0.203 mol) was added dropwise to a solution of 2,3,5,6-tetrahydro-2,6-diphenylthiopyran-4-one (**14b**, 19.0 g, 0.067 mol) in 150 mL of EtOAc. After addition was complete, the reaction mixture was stirred 1 h at rt and was then diluted with 500 mL of ether and 500 mL of water. The organic phase was separated and the aqueous phase was extracted with an additional 300 mL of ether. The combined organic extracts were washed several times with dilute NaOH followed by 10% $NaHSO_3$. The organic filtrate was dried over $MgSO_4$ and concentrated. ^{1}H NMR analysis of the residue showed it to be an 85:15 mixture of the two isomers of the sulfone. The residue from the organic filtrate was slurried in hot CH_3CN to give 2.1 g (10%) of the *cis*-isomer of the sulfone as a white crystalline solid, mp 237–240 °C (lit.[3] mp 235 °C): ^{1}H NMR (d_6-DMSO) see text for complete assignment; δ 7.2 (m, 10 H), 5.21 (d × d, 2 H), 3.65 (d × d, 2 H), 3.03 (d × d, 2 H).

The CH_3CN solution was concentrated and the residue was purified by chromatography on silica gel eluted with 10% EtOAc in toluene to give the *trans*-isomer in 70% yield, mp 177–179.5 °C (lit.[3] mp 196 °C): ^{1}H NMR (d_6-DMSO see text for complete assignment; δ 7.2 (m, 10 H), 5.21 (d × d, 2 H), 3.75 (t, 2 H), 2.78 (d × d, 2 H).

2,3,5,6-Tetrahydro-2,6-di(2-thienyl)thiopyran-4-one 1,1-Dioxide (15c). 30% Peracetic acid (48.2 g, 0.203 mol) and 2,3,5,6-tetrahydro-2,6-di(2-thienyl)thiopyran-4-one (**14c**, 19.0 g, 0.0678 mol) in 150 mL of EtOAc were treated as described. Following $NaHSO_3$ addition, a chalky precipitate formed that was collected by filtration. The organic filtrate was dried over $MgSO_4$ and concentrated. ^{1}H NMR analysis of the chalky precipitate showed it to be a 1:1 mixture of the two stereoisomers of the sulfone. The residue from the organic filtrate was approximately a 90:10 mixture of the sulfone isomers. The chalky precipitate was recrystallized twice from CH_3CN to give 2.19 g (10%) of one isomer (most likely the *cis*-isomer) of the sulfone as a white crystalline solid, mp 256–258 °C (decomposition with gas evolution): ^{1}H NMR ($CDCl_3$) δ 7.66 (d × d, 2 H, J = 1, 4 Hz), 7.23 (d, 2 H, J = 4 Hz), 7.13 (m, 2 H), 5.52 (d × d, 2 H, J = 3, 14 Hz), 3.58 (t, 2 H, J = 14 Hz), 2.90 (br d, 2 H, J = 14 Hz); IR (KBr) 3120, 1725, 1318, 1263, 1230, 1120 (s), 730 cm^{-1}; FDMS, *m/z* 312 ($C_{13}H_{12}O_3S_3$). Anal. Calcd for $C_{13}H_{12}O_3S_3$: C, 49.98; H, 3.87; S, 30.79. Found: C, 50.00; H, 3.49; S, 30.17.

The residue from the filtrate was recrystallized from 1/1 (V/V) EtOAc/ether to give 11.1 g (52%) of the second isomer (most likely the *trans*-isomer), mp 164–165 °C: ^{1}H NMR ($CDCl_3$) δ 7.66 (d × d, 2 H, J = 1, 5 Hz), 7.15 (m, 4 H), 5.35 (d × d, 2 H, J = 4.5, 10 Hz), 3.46 (d × d, 2 H, J = 10, 16 Hz), 3.18 (d × d, 2 H, J = 4.5, 16 Hz); IR (KBr) 3100, 1725, 1320, 1220, 1121, 730, 708 cm^{-1}; FDMS, *m/z* 312 ($C_{13}H_{12}O_3S_3$). Anal. Calcd for $C_{13}H_{12}O_3S_3$: C, 49.98; H, 3.87; S, 30.79. Found: C, 49.85; H, 3.41; S, 30.46.

When this procedure was repeated, the isomer mixture (6:1) was isolated in 76% yield and was used without separation.

2,3,5,6-Tetrahydro-2,6-di(2-furyl)-4*H*-thiopyran-4-one 1,1-dioxide (15d): oil, 80%. ^{1}H NMR analysis of the residue was consistent with two isomers in roughly a 75:25 ratio. For the mixture: IR (film, NaCl) 1710 cm^{-1}; FDMS, *m/z* 280 ($C_{13}H_{12}O_5S$). For the major isomer: ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2 H, J = 1.8 Hz), 6.52 (d, 2 H, J = 3.6 Hz), 6.43 (d × d, 2 H, J = 1.8, 3.6 Hz), 4.67 (s, 2 H), 3.33 (d, 2 H, J = 12 Hz). For the minor isomer: ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2 H, J = 1.8 Hz), 6.57 (d, 2 H, J = 3.6 Hz), 4.69 (d × d, 2 H, J = 3, 12 Hz), 3.62 (t, 2 H, J = 12 Hz), 3.05 (d × d, 2 H, J = 3, 12 Hz).

2,3,5,6-Tetrahydro-2-phenyl-6-(2-thienyl)thiopyran-4-one 1,1-dioxide (15e): oil, 92%. The isomer ratio was 70:30 by ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 6 H), 7.15 (m, 1 H), 7.05 (m, 1 H), [4.86 (d × d), 4.74 (t){1 H}], 4.52 (m, 1 H), 3.8–2.9 (m, 4 H); IR (KBr) 1710, 1670, 1240, 700 cm^{-1}; FDMS, *m/z* 306 ($C_{15}H_{14}O_3S_2$).

2,3,5,6-Tetrahydro-2-phenyl-6-(2-furyl)-4*H*-thiopyran-4-one 1,1-dioxide (15f): oil, 98%; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.52 (m, 1 H), 6.45 (m, 1 H), 4.80–2.83 (m, 6 H); FDMS, *m/z* 290 ($C_{15}H_{14}O_4$).

2,3,5,6-Tetrahydro-2,6-di(3-thienyl)thiopyran-4-one 1,1-dioxide (15g): oil, 88%; IR (film, NaCl) 1710 cm^{-1}; FDMS, *m/z* 312 ($C_{13}H_{12}O_3S_3$).

2,3,5,6-Tetrahydro-2-phenyl-6-(3-thienyl)thiopyran-4-one 1,1-dioxide (15h): 85%, oil; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 8 H), 4.3–4.7 (m's, 2 H), 2.3-3.8 (m's, 4 H); IR (film, NaCl) 1705 cm^{-1}; FDMS, *m/z* 306 ($C_{15}H_{14}O_3S_2$).

2,3,5,6-Tetrahydro-2,6-di(3-nitrophenyl)thiopyran-4-one 1,1-dioxide (15i): oil, 88%; IR (film, NaCl) 1710 cm^{-1}; FDMS, *m/z* 388 ($C_{17}H_{12}N_2O_7S$).

2,3,5,6-Tetrahydro-2,6-di-*p*-anisylthiopyran-4-one 1,1-dioxide (15i): oil, 85%; IR (film, NaCl) 1715 cm^{-1}; FDMS, *m/z* 328 ($C_{19}H_{20}O_3S$).

2,3,5,6-Tetrahydro-2-(β-styryl)-6-phenylthiopyran-4-one 1,1-dioxide (15h): 85% oil, IR (film, NaCl) 1705 cm^{-1}; FDMS, *m/z* 326 ($C_{19}H_{18}O_3S$).

General Procedure for the Dehydrogenation of Sulfones 15 to 4*H*-Thiopyran-4-one 1,1-Dioxides 5 with Iodine–DMSO–Sulfuric Acid. Preparation of 2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide (5b). A solution of 54.0 g (0.160 mol) of 2,3,5,6-tetrahydro-2,6-diphenylthiopyran-4-one 1,1-dioxide (**15b**, as a mixture of stereoisomers), 200 mL of DMSO, 5 g of iodine, and 3 mL of concentrated H_2SO_4 was heated at 100 °C with mechanical stirring for 2 h. The reaction mixture was cooled to rt and was diluted with 1 L of water. The products were extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was slurried with EtOH, and the resulting solid was collected by filtration and dried to give 49.0 g (92%) of **5b** as a dark solid, mp 140–144 °C (lit.[1] mp 145–146 °C). The mother liquors were concentrated, and the residue was purified by chromatography on silica gel eluted with CH_2Cl_2 to give 1.2 g (3%) of **13b**.

Preparation of 2,6-Di(2-thienyl)-4*H*-thiopyran-4-one 1,1-Dioxide (5c). A solution of 55.0 g (0.160 mol) of 2,3,5,6-tetrahydro-2,6-di(2-thienyl)thiopyran-4-one 1,1-dioxide (**15c**), 200 mL of DMSO, 5 g of iodine, and 3 mL of concentrated H_2SO_4 was treated as described. The crystalline residue was slurried with ethanol, and the resulting solid was collected by filtration and dried to give 50.0 g (92%) of a dark solid, mp 162.5–163.5 °C: ^{1}H NMR (d_6-DMSO) δ 8.07 (d × d, 2 H, J = 1, 5 Hz), 7.94 (d × d, 2 H, J = 4, 5 Hz), 7.33 (d × d, 2 H, J = 4, 5 Hz), 7.06 (s, 2 H); ^{13}C NMR (d_6-DMSO) δ 178.4, 145.9, 134.0, 132.8, 129.5, 129.0, 124.5; IR (KBr) 3100, 1620 (s), 1553 (s), 1411, 1365, 1280, 1235, 1057, 876, 712 cm^{-1}; FDMS, *m/z* 308 ($C_{13}H_8O_3S_3$). Anal. Calcd for $C_{13}H_8O_3S_3$: C, 50.63; H, 2.61; S, 31.19. Found: 50.38, H, 2.53; S, 30.42.

The mother liquors were concentrated to give trace amounts of (*E,E*)-1,5-di(2-thienyl)-1,4-pentadien-3-one (**13c**) by ^{1}H NMR.

Comparison of *cis*- and *trans*-15c in the Preparation of 2,6-Di(2-thienyl)-4*H*-thiopyran-4-one 1,1-Dioxide (5c). A solution of 0.55 g (0.0016 mol) of pure *cis*- or *trans*-2,3,5,6-tetrahydro-2,6-di(2-thienyl)thiopyran-4-one 1,1-dioxide (*cis*- or *trans*-**15c**), 10.0 mL of DMSO, 0.1 g of iodine, and 0.1 mL of concentrated H_2SO_4 were treated as described to give 0.49 g (90%) of **5c** in each case. Chromatography of the mother liquors on silica gel eluted with CH_2Cl_2 gave 0.012 g (3%) of **13c** from the *cis*-isomer and 0.020 g (5%) of **13c** from the *trans*-isomer.

2,6-Di(2-furyl)-4*H*-thiopyran-4-one 1,1-dioxide (5d): 14%, mp 117–119 °C: ^{1}H NMR ($CDCl_3$) δ 7.66 (d, 2 H, J = 1.8 Hz),

7.37 (d, 2 H, J = 3.6 Hz), 6.86 (s, 2 H), 6.65 (d × d, 2 H, J = 1.8, 3.6 Hz); ^{13}C NMR (d_6-DMSO) δ 178.0, 149.0, 141.6, 141.3, 121.4, 118.2, 114.2; IR (KBr) 3140, 1630, 1580, 1540, 1470, 1330, 1310, 1290, 1250, 1225, 1140, 1040, 775 cm^{-1}; FDMS, m/z 276 ($C_{13}H_8O_5S$). Anal. Calcd for $C_{13}H_8O_5S$: C, 56.52; H, 2.92; S, 11.61. Found: C, 56.78; H, 2.91; S, 11.17.

2-Phenyl-6-(2-thienyl)-4*H*-thiopyran-4-one 1,1-dioxide (5e): 89%, mp 110–114 °C following slurrying with EtOH: ^{1}H NMR ($CDCl_3$) δ 7.93 (d, 1 H, J = 4 Hz), 7.81 (d × d, 2 H, J = 2, 8 Hz), 7.62 (d, 1 H, J = 5 Hz), 7.51 (m, 3 H), 7.19 (d × d, 1 H, J = 4, 5 Hz), 6.73 (d, 1 H, J = 2 Hz), 6.67 (d, 1 H, J = 2 Hz); ^{13}C NMR (d_6-DMSO) δ 178.9, 150.7, 146.6, 134.1, 132.9, 132.0, 129.5, 129.45, 129.2, 129.1, 128.3, 128.5, 124.1; IR (KBr) 1645, 1590, 1415, 1360, 1310, 1240, 1135, 900, 770, 720, 695 cm^{-1}; FDMS, m/z 302 ($C_{15}H_{10}O_3S_2$). Anal. Calcd for $C_{15}H_{10}O_3S_2$: C, 59.58; H, 3.33. Found: 59.90; H, 3.68.

The mother liquors were concentrated to dryness and the residue was purified by chromatography on SiO_2 eluted with CH_2Cl_2 to give 2.4 g (7%) of (*E*,*E*)-1-phenyl-5-(2-thienyl)-1,4-pentadien-3-one (**13e**) as a yellow solid, mp 92–96 °C.

2-Phenyl-6-(2-furyl)-4*H*-thiopyran-4-one 1,1-dioxide (5f): 40%, mp 117–119 °C: ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 2 H), 7.67 (d, 1 H, J = 1.8 Hz), 7.42–7.58 (m, 3 H), 7.38 (d, 1 H, J = 3.6 Hz), 6.875 (d, 1 H, J = 2.4 Hz), 6.66 (d, 1 H, J = 2.4 Hz), 6.65 (d × d, 1 H, J = 1.8, 3.6 Hz); ^{13}C NMR (d_6 DMSO) δ 178.7, 150.5, 149.0, 142.1, 141.9, 132.0, 129.5, 129.1, 129.0, 128.4, 120.9, 118.65, 114.3; IR (KBr) 3140, 1650, 1595, 1315, 1285, 1140, 1035, 905, 770 cm^{-1}; FDMS, m/z 286 ($C_{15}H_{10}O_4S$). Anal. Calcd for $C_{15}H_{10}O_4S$: C, 62.93; H, 3.52. Found: 62.59; H, 3.60.

2,6-Di(3-thienyl)-4*H*-thiopyran-4-one 1,1-dioxide (5g): 85%, mp 149–151 °C: ^{1}H NMR ($CDCl_3$) δ 8.21 (d, 2 H, J = 1 Hz), 7.48 (m, 4 H), 6.73 (s, 2 H); ^{13}C NMR (d_6-DMSO) δ 189.2, 138.4, 136.7, 130.3, 128.1, 126.0, 125.6; IR (KBr) 1635, 1585, 1305, 1135, 795 cm^{-1}; FDMS, m/z 308 ($C_{13}H_8O_3S_3$). Anal. Calcd for $C_{13}H_8O_3S_3$: C, 50.63; H, 2.61. Found: C, 50.82; H, 2.60.

2-Phenyl-6-(3-thienyl)-4*H*-thiopyran-4-one 1,1-dioxide (5h): 83%, mp 113–120 °C: ^{1}H NMR ($CDCl_3$) δ 8.20 (br s, 1 H), 7.82 (d × d, 2 H, J = 2, 8 Hz), 7.51 (m, 5 H), 7.74 (d, 1 H, J = 2 Hz), 6.67 (d, 1 H, J = 2 Hz); IR (KBr) 3150, 1635, 1580, 1310, 1135, 900, 890, 795, 765 cm^{-1}; FDMS, m/z 302 ($C_{15}H_{10}O_3S_2$). Anal. Calcd for $C_{15}H_{10}O_3S_2$: C, 59.58; H, 3.33; S, 21.21. Found: 59.23; H, 3.39; S, 20.11.

For 2,6-Di(3-nitrophenyl)-4*H*-thiopyran-4-one 1,1-dioxide (5i): 85%, mp 170–174 °C: ^{1}H NMR (CD_2Cl_2) δ 8.65 (d, 2 H, J = 1.8 Hz), 8.45 (d × m, 2 H, J = 8.4 Hz), 8.19 (d × m, 2 H, J = 8.0 Hz), 7.78 (d × t, 2 H, J = 1.5, 8.2 Hz), 6.85 (d, 2 H, J = 1.8 Hz); ^{13}C NMR (CD_2Cl_2) δ 179.0, 151.6, 149.3, 135.5, 131.5, 130.5, 130.1, 127.2, 124.8; IR (KBr) 1660 cm^{-1}; FDMS, m/z 386 ($C_{17}H_{10}N_2O_7S$). Anal. Calcd for $C_{17}H_{10}N_2O_7S$: C, 52.85; H, 2.61; N, 7.25; S, 8.30. Found: C, 52.57; H, 2.77; N, 7.24; S, 8.00.

2,6-Di-*p*-anisyl-4*H*-thiopyran-4-one 1,1-dioxide (5j): 90%), mp 176–179 °C: ^{1}H NMR (CD_2Cl_2) δ 7.82 (AA'BB', 2 H), 7.03 (AA'BB', 2 H), 6.68 (s, 2 H), 3.89 (s, 6 H); ^{13}C NMR (CD_2Cl_2) δ 180.1, 163.4, 153.4, 131.25, 126.6, 121.6, 115.5, 56.4; IR (KBr) 1650 cm^{-1}; FDMS, m/z 356 ($C_{19}H_{16}O_5S$). Anal. Calcd for $C_{19}H_{16}O_5S$: C, 64.03; H, 4.53; N, 9.00. Found: C, 64.11; H, 4.66; N, 8.59.

The mother liquors were concentrated and purified by chromatography on silica gel eluted with CH_2Cl_2 to give 3.7 g (5%) of **13j**.

2-(β-Styryl)-6-phenyl-4*H*-thiopyran-4-one 1,1-dioxide (5k): 90%, mp 153.5–157.5 °C: ^{1}H NMR (CD_2Cl_2) δ 7.84 (AA'BB', 2 H), 7.69 (d × d, 1 H, J = 2, 15 Hz), 7.7–7.4 (m's, 8 H), 6.92 (d × d, 1 H, J = 2, 15 Hz), 6.69 (t, 1 H, J = 2 Hz), 6.64 (br t, 1 H, J = 2 Hz); ^{13}C NMR (CD_2Cl_2) δ 180.0, 153.8, 152.0, 142.4, 135.8, 132.5, 131.4, 130.0, 129.9, 129.7, 129.5, 128.9, 128.8, 125.6, 117.4; IR (KBr) 1645 cm^{-1}; FDMS, m/z (386 ($C_{19}H_{14}O_3S$). Anal. Calcd for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38; N, 9.95. Found: C, 70.51; H, 4.53; N, 9.75.

General Procedure for Preparation of 1-Aryl-5-alkyl-1,4-pentadiyn-3-ols. Preparation of 1-Phenyl-5-*tert*-butyl-1,4-pentadiyn-3-ol (16l). A 1.6 *M* solution of *n*-BuLi in hexanes (50 mL, 0.080 mol) was added dropwise to a solution of *tert*-butylacetylene (6.97 g, 0.0850 mol) in anhydrous THF (50 mL) cooled to 0 °C under an argon atmosphere. Phenylpropargyl aldehyde (10.4 g, 0.0800 mmol) in 50 mL of anhydrous THF was added dropwise at 0 °C. The resulting solution was warmed to rt where stirring was maintained for 1 h. The reaction mixture was poured into cold 10% HCl (300 mL). The products were extracted with ether (3 × 100 mL). The combined ether extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residual oil was used without further purification. Product yield was 14.1 g (83%) of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 2 H), 7.32 (m, 3 H), 5.35 (br s, 1 H), 2.43 (br s, 1 H), 1.25 (s, 9 H); IR (film, NaCl) 3400 (br), 2962, 2255, 2187, 1489, 1300, 1260, 1029, 1011, 753, 687 cm^{-1}; FDMS, m/z 212 ($C_{15}H_{16}O$).

1-Phenyl-1,4-nonadiyn-3-ol (16m): 98% yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 2 H), 7.30 (m, 3 H), 5.35 (t, 1 H, J = 1.9 Hz), 2.80 (br s, 1 H), 2.25 (d × t, 2 H, J = 1.9, 7 Hz), 1.6–1.35 (m, 4 H), 0.91 (t 3 H, J = 7 Hz); IR (film, NaCl) 3240, 2850, 2830, 2740, 2185, 2115, 1550 cm^{-1}; FDMS, m/z 212 ($C_{15}H_{16}O$).

1-Phenyl-1,4-hexadiyn-3-ol (16n): 90%, red oil; ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 2 H), 7.30 (m, 3 H), 5.32 [(m, 1 H), quartet with D_2O], 2.98 [(d, 1 H, J = 6.8 Hz), exchanges with D_2O], 1.89 (d, 3 H, J = 2.1 Hz); IR (film, NaCl) 3340 (br, strong), 2290, 2215, 1597, 1440, 1300, 1147, 1010, 945 cm^{-1}; FDMS, m/z 170 ($C_{12}H_{10}O$).

1-(Trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-ol (16o): 98%, yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 2 H), 7.33 (m, 3 H), 5.35 (s, 1 H), 2.61 (br s, 1 H), 0.21 (s, 9 H); IR (film, NaCl) 3300 (br), 2955, 2228, 2170, 1488, 1247, 1030, 909, 830, 753, 687 cm^{-1}, FDMS, m/z 228 ($C_{14}H_{16}OSi$).

1-(2-Thienyl)-5-*tert*-butyl-1,4-pentadiyn-3-ol (16p). The residue was oxidized directly with chromic acid to give 1-(2-thienyl)-1,4-pentadiyn-3-one (**17p**) in 71% overall yield.

1-(4-Fluorophenyl)-5-*tert*-butyl-1,4-pentadiyn-3-ol (16q): 98%, yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.44 (d × d, 2 H, J = 5.5, 8.6 Hz), 7.00 (t, 2 H, J = 8.6 Hz), 5.32 (d, 1 H, J = 7 Hz)), 2.55 (d, 1 H, J = 7 Hz), 1.25 (s, 9 H); IR (film, NaCl) 3340, 2235, 1601 cm^{-1}; FDMS, m/z 230 (weak, $C_{15}H_{15}FO$).

General Procedure for Preparation of 1-Aryl-5-alkyl-1,4-pentadiyn-3-ones. Preparation of 1-Phenyl-5-*tert*-butyl-1,4-pentadiyn-3-one (17l). A 10% solution of chromic acid was prepared by the addition of 29.8 g (0.100 mol) of sodium dichromate dihydrate to a stirred solution of 40 g of H_2SO_4 in 180 g of ice. The resulting solution was stirred 0.5 h prior to use. A 75-mL portion of this solution was added dropwise to a solution of 14.1 g (0.0664 mol) of 1-phenyl-5-*tert*-butyl-1,4-pentadiyn-3-ol in 75 mL of acetone cooled to 0 °C. After addition was complete, the reaction mixture was warmed to rt where stirring was maintained for 1 h. The reaction mixture was diluted with 150 mL of water. The reaction mixture was extracted with ether (3 × 100 mL). The combined ether extracts were washed with brine (3 × 100 mL), dried over $MgSO_4$, and concentrated. The residue was purified via chromatography on silca gel eluted with CH_2Cl_2 to give 11.6 g (83%) of the diynone as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.61 (m, 2 H), 7.47 (m, 1 H), 7.39 (m, 2 H), 1.33 (s, 9 H); IR (film, NaCl) 2970, 2180, 1620, 1285, 1140, 932, 821, 755 cm^{-1}; FDMS, m/z 210 ($C_{15}H_{14}O$). Anal. Calcd for $C_{15}H_{14}O$: C 85.68; H, 6.71. Found: C, 85.43; H, 6.65.

1-Phenyl-1,4-nonadiyn-3-one (17m): 98%, yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.61 (m, 2 H), 7.43 (m, 1 H), 7.39 (m, 2 H), 2.45 (t, 2 H, J = 7 Hz), 1.7–1.4 (m, 4 H), 0.95 (t, 3 H, J = 7 Hz); IR (film, NaCl) 2955, 2930, 2865, 2210, 2190, 1620, 1595, 1488, 1443, 1281, 1180, 1170 cm^{-1}; FDMS, m/z 210 ($C_{15}H_{14}O$). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.34; H, 6.35.

1-Phenyl-1,4-hexadiyn-3-one (17n): 89%, mp 66–69 °C; ^{1}H NMR ($CDCl_3$) δ 7.61 (m, 2 H), 7.46 (m, 1 H), 7.39 (m, 2 H), 2.10 (s, 3 H); IR (KBr) 2190, 1620 cm^{-1}; m/z 168 ($C_{12}H_8O$). Anal. Calcd for $C_{12}H_8O$: C, 85.69; H, 4.79. Found: C, 85.25; H, 4.51.

1-(Trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-one (17o): 98%, oil; ^{1}H NMR ($CDCl_3$) δ 7.63 (δ, 2 H, J = 7.3 Hz), 7.49 (t, 1 H, J = 7.2 Hz), 7.40 (t, 2 H, J = 7.5 Hz), 0.29 (s, 9 H); IR (film, NaCl) 2945, 2190, 2130, 1615, 1482, 1436, 1271, 1245, 1120, 870, 739 cm^{-1}; FDMS, m/z 226 ($C_{14}H_{14}OSi$).

1-(2-Thienyl)-5-*tert*-butyl-1,4-pentadiyn-3-one (17p): 71% overall, yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.53 (m, 2 H), 7.08 (m, 1 H), 1.33 (s, 9 H); IR (KBr) 3100, 2965, 2200, 2170, 1615,

1270, 1205, 1125, 911 cm^{-1}; *m/z* 216 ($C_{13}H_{12}OS$). Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.58; H, 5.51.

For 1-(4-Fluorophenyl)-5-*tert*-butyl-1,4-pentadiyn-3-one (17q): 95%, yellow oil; ^1H NMR ($CDCl_3$) δ 7.62 (d × d, 2 H, J = 5.3, 8.6 Hz), 7.095 (t, 2 H, J = 8.6 Hz), 1.33 (s, 9 H); IR (NaCl, film) 2965, 2230, 2180, 1620, 1595 cm^{-1}; FDMS, *m/z* 228 ($C_{15}H_{13}FO$).

General Procedure for the Preparation of 2-Aryl-6-alkyl-4*H*-thiopyran-4-ones. Preparation of 2-Phenyl-6-*tert*-butyl-4*H*-thiopyran-4-one (18l). The 1-phenyl-5-*tert*-butyl-1,4-pentadiyn-3-one (**21**, 11.4 g, 0.0543 mol) was dissolved in 100 mL of EtOH. Sodium hydrosulfide hydrate (7.4 g, 0.080 mol) was dissolved in 50 mL of saturated $NaHCO_3$. The resulting solution was diluted with 50 mL of water and was added to the EtOH solution of the diynone. The resulting mixture was stirred at rt for 14 h. The reaction mixture was poured into 500 mL of water, and the products were extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified via chromatography on silica gel eluted with 25% EtOAc in CH_2Cl_2 to give 6.83 g (43%) of a pale yellow crystalline solid, mp 75.5–79 °C: ^1H NMR ($CDCl_3$) δ 7.60 (m, 2 H), 7.49 (m, 3 H), 7.12 (s, 1 H), 7.01 (s, 1 H), 1.41 (s, 9 H); IR (KBr) 1608, 1581, 1350, 874, 761, 731, 592 cm^{-1}; FDMS, *m/z* 244 ($C_{15}H_{16}OS$). Anal. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60. Found: C, 74.02; H, 6.48.

2-Phenyl-6-*n*-butyl-4*H*-thiopyran-4-one (18m): 28%, yellow oil; ^1H NMR ($CDCl_3$) δ 7.54 (m, 2 H), 7.42 (m, 3 H), 7.09 (s, 1 H), 6.82 (br s, 1 H), 2.63 (t, 2 H, J = 7.6 Hz), 1.66 (m, 2 H), 1.37 (m, 2 H), 0.91 (t, 3 H, J = 7.3 Hz); IR (film, NaCl) 2950, 2920, 2860, 1620, 1445, 1345, 1240, 878, 764, 730, 690 cm^{-1}; FDMS, *m/z* 244 ($C_{15}H_{16}OS$). Anal. Calcd for $C_{15}H_{16}OS$: C, 73.73; H, 6.60. Found: C, 73.92; H, 6.38.

2-Phenyl-6-methyl-4*H*-thiopyran-4-one (18n): 44%, yellow oil; ^1H NMR ($CDCl_3$) δ 7.56 (m, 2 H), 7.47 (m, 3 H), 7.11 (s, 1 H), 6.83 (s, 1 H), 2.43 (s, 3 H); IR (KBr) 1610, 1580 cm^{-1}; FDMS, *m/z* 202 ($C_{12}H_{10}OS$). Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.13; H, 5.02.

1-Phenyl-4*H*-thiopyran-4-one (18o): 44%, mp 90–92.5 °C; ^1H NMR ($CDCl_3$) δ 7.80 (d, 1 H, J = 10.3 Hz), 7.58 (m, 2 H), 7.51 (m, 3 H), 7.22 (d, 1 H, J = 1.3 Hz), 7.07 (d × d, 1 H, J = 1.3, 10.3 Hz); IR (KBr) 1608 (s), 1160, 880, 796, 751, 728, 690 cm^{-1}; FDMS, *m/z* 188 ($C_{11}H_8OS$). Anal. Calcd for $C_{11}H_8OS$: C, 70.17; H, 4.28; S, 17.03. Found: C, 69.96; H, 4.13; S, 17.22.

2-(2-Thienyl)-6-*tert*-butyl-4*H*-thiopyran-4-one (18p): 23%, red oil; ^1H NMR ($CDCl_3$) δ 7.47 (m, 2 H); 7.13 (s, 1 H), 7.12 (m, 1 H), 6.94 (s, 1 H), 1.40 (s, 9 H); IR (KBr) 3065, 2960, 1600, 1545, 1355, 1328, 1046, 974 cm^{-1}; FDMS, *m/z* 250 ($C_{13}H_{14}OS_2$). Anal. Calcd for $C_{13}H_{14}OS_2$: C, 62.36; H, 5.64. Found: C, 62.07; H, 5.92.

2-(4-Fluorophenyl)-6-*tert*-butyl-4*H*-thiopyran-4-one (18q): 38%, mp 125–128 °C (from MeOH); ^1H NMR ($CDCl_3$) δ 7.59 (d × d, 2 H, J = 5.2, 8.6 Hz), 7.17 (t, 2 H, J = 8.6 Hz), 7.06 (d, 1 H, J = 1 Hz), 7.00 (d, 1 H, J = 1 Hz) 1.41 (s, 9 H); IR (KBr) 2960, 1605, 1502, 1230, 874, 833 cm^{-1}; *m/z* 262 ($C_{15}H_{15}FOS$). Anal. Calcd for $C_{15}H_{15}FOS$: C, 68.67; H, 5.76; S, 12.22. Found: C, 68.21; H, 5.89; S, 12.00.

General Procedure for the Preparation of 2-Aryl-6-alkyl-4*H*-thiopyran-4-one 1,1-Dioxides and 2,6-Dialkylthiopyran-4-one 1,1-Dioxides. Preparation of 2-Phenyl-6-*tert*-butyl-4*H*-thiopyran-4-one 1,1-Dioxide (5l). The thiopyranone **22** (6.80 g, 0.0279 mol) was dissolved in 50 mL of EtOAc. An excess of 35% peracetic acid (30.4 g, 0.14 mol) was added. The resulting solution was heated at reflux for 3 h. The reaction mixture was poured into 200 mL of water. The products were extracted with EtOAc, and the combined organic extracts were washed with 10% $NaHSO_3$ to remove any unreacted peracetic acid, with saturated $NaHCO_3$, and with brine, dried over Na_2SO_4, and concentrated. The sulfone was purified via chromatography on silica gel eluted with 10% EtOAc in CH_2Cl_2 to give 5.24 g (68%) of the sulfone **5l** as a yellow oil: ^1H NMR ($CDCl_3$) δ 7.76 (m, 2 H), 7.60–7.45 (m, 3 H), 6.56 (d, 1 H, J = 2.5 Hz), 6.54 (d, 1 H, J = 2.5 Hz), 1.52 (s, 9 H); IR (film, NaCl) 2970, 1720, 1655, 1599, 1305, 1133, 908, 761, 690 cm^{-1}; FDMS, *m/z* 276 ($C_{15}H_{16}O_3S$). Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84; S, 11.60. Found: C, 65.08; H, 5.71; S, 11.16.

2-Phenyl-6-*n*-butyl-4*H*-thiopyran-4-one 1,1-dioxide (5m): 70%, yellow oil; ^1H NMR ($CDCl_3$) δ 7.96 (m, 2 H), 7.6–7.4 (m, 3 H), 6.63 (d, 1 H, J = 2.7 Hz), 6.41 (d × t, 1 H, J = 1, 2.7 Hz), 1.72 (m, 2 H), 1.48 (m, 2 H), 0.98 (t, 3 H, J = 7.3 Hz); IR (film, NaCl) 2960, 1656, 1632, 1308, 1140, 763, 692 cm^{-1}; FDMS, *m/z* 276 ($C_{15}H_{16}O_3S$). Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84; S, 11.60. Found: C, 65.68; H, 5.78; S, 11.11.

2-Phenyl-6-methyl-4*H*-thiopyran-4-one 1,1-dioxide (5n): 81%, mp 109.5–111 °C; ^1H NMR ($CDCl_3$) δ 7.79 (m, 2 H), 7.60–7.45 (m, 3 H), 6.64 (d, 1 H, J = 2.6 Hz), 6.43 (m, 1 H), 2.42 (d, 3 H, J = 1.2 Hz); IR (KBr) 1658, 1631, 1297, 1143 cm^{-1}; FDMS, *m/z* 234 ($C_{12}H_{10}O_3S$). Anal. Calcd for $C_{12}H_{10}O_3S$: C, 61.52; H, 4.30; S, 13.69. Found: C, 61.57; H, 4.32; S, 14.01.

2-Phenyl-4*H*-thiopyran-4-one 1,1-dioxide (5o): 35%, mp 183–184.5 °C; ^1H NMR ($CDCl_3$) δ 7.81 (m, 2 H), 7.62–7.45 (m, 3 H), 7.30 (d, 1 H, J = 10.8 Hz) 6.66 (d, 1 H, J = 2.7 Hz), 6.64 (d × d, 1 H, J = 2.7, 10.8 Hz); IR (KBr) 3030, 1653, 1649, 1619, 1582, 1308, 1145, 1115, 871, 793 cm^{-1}; FDMS, *m/z* 220 ($C_{11}H_8O_3S$); Anal. Calcd for $C_{11}H_8O_3S$: C, 59.99; H, 3.66. Found: C, 60.23; H, 3.69.

2-(2-Thienyl)-6-*tert*-butyl-4*H*-thiopyran-4-one 1,1-dioxide (5p): 39%, yellow oil; ^1H NMR ($CDCl_3$) δ 7.89 (d, 1 H, J = 3.7 Hz), 7.60 (d, 1 H, J = 5.1 Hz), 7.175 (m, 1 H), 6.63 (d, 1 H, J = 2.6 Hz), 6.52 (d, 1 H, J = 2.6 Hz), 1.50 (s, 9 H); IR (film, NaCl) 2970, 1646, 1363, 1308, 1150, 1040, 990, 843, 697 cm^{-1}; FDMS, *m/z* 282 ($C_{13}H_{14}O_3S_2$). Anal. Calcd for $C_{13}H_{14}O_3S_2$: C, 55.29; H, 5.00; S, 22.71. Found: C, 55.14; H, 5.07; S, 21.96.

2-(4-Fluorophenyl)-6-*tert*-butyl-4*H*-thiopyran-4-one 1,1-dioxide (5q): 98%, mp 64–65 °C; ^1H NMR ($CDCl_3$) δ 7.78 (m, 2 H), 7.18 (t, 2 H, J = 8.6 Hz), 6.54 (d, 1 H, J = 2.6 Hz), 6.53 (d, 1 H, J = 2.6 Hz), 1.51 (s, 9 H); IR (KBr) 2970, 1649, 1590, 1505, 1303, and 1130 cm^{-1}; FDMS, *m/z* 294 ($C_{15}H_{15}FO_3S$). Anal. Calcd for $C_{15}H_{15}FO_3S$: C, 61.21; H, 5.14; S, 10.89. Found: C, 61.28; H, 5.29; S, 9.99.

2,6-Dimethyl-4*H*-thiopyran-4-one 1,1-dioxide (5r): 60%, mp 136.5-139 °C; ^1H NMR ($CDCl_3$) δ 6.35 (s, 2 H), 2.36 (s, 6 H); IR (KBr) 2960, 1656, 1632, 1308, 1140, 763, 692 cm^{-1}; FDMS, *m/z* 172 ($C_7H_8O_3S$). Anal. Calcd for $C_7H_8O_3S$: C, 48.82; H, 4.68. Found: C, 48.73; H, 4.64.

2,6-Di-*tert*-butyl-4*H*-4-one 1,1-Dioxide (5s): 65%, mp 96.5–98.5 °C; ^1H NMR ($CDCl_3$) δ 6.55 (s, 2 H), 1.52 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 180.0, 163.5, 127.3, 38.1, 30.2; IR (film, NaCl) 2970, 1720, 1655 cm^{-1}; FDMS, *m/z* 256 ($C_{13}H_{20}O_3S$). Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.90; H, 7.86. Found: C, 60.92; H, 7.85.

Oxidation of 4*H*-Thiopyran-4-one (19) with Oxone. Oxone (3.68 g, 6.00 mmol) was added to **19** (0.224 g, 2.00 mmol) in 20 mL of MeOH and 10 mL of water. The resulting slurry was heated at reflux for 6 h and was then diluted with 150 mL of water. The products were extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Chromatography on silica gel eluted with 20% EtOAc in CH_2Cl_2 gave 0.066 g (23%) of **5a** and 0.113 g (50%) of **19**.

JO941785S