Dichlorocarbene Adducts of Sulfolenes and Their Chlorine Reduction Products: Hydrogen Chloride vs. Sulfur Dioxide Elimination. Thiopyran Dioxides and Thiopyrones

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Substituted 6,6-dichloro-3-thiabicyclo[3.1.0]hexane 3,3-dioxides (1) were prepared from sulfolenes (4) in a catalytic biphasic system and reduced with lithium aluminum hydride to monochlorinated (2) and dechlorinated products (3). Several of the chlorinated bicyclic sulfones (1 and 2) were found to undergo a simultaneous thermal elimination of hydrogen chloride and sulfur dioxide. Selective elimination of hydrogen chloride, with formation of thiopyran dioxides (9, 10) through ring enlargement, was achieved under basic conditions (use of lithium diisopropyl amide). Somewhat less selective was the fragmentation of the dichlorinated sulfones 1 in aqueous acids. Two isomeric thiopyran dioxides (9, 12) were the major products in hydrochloric acid, while further transformation of these products, with formation of thiopyrone derivatives 14–16, was occurring in hydrobromic acid. A seven-membered dienylic sultine (21) was formed in the reaction of one of the monochlorinated sulfones (*exo*-Cl-2c) with *n*-butyllithium.

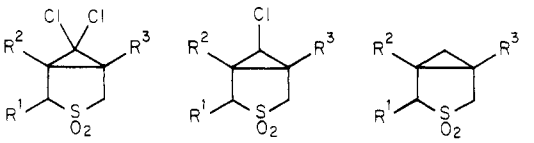
The 3-thiabicyclo[3.1.0]hexane 3,3-dioxide ring system has been thoroughly studied by Mock[1] with respect to the stereospecificity of the cheletropic elimination of sulfur dioxide. The preparation of the bicyclic sulfones involved, however, tedious addition of diazomethane to sulfolenes, followed by photolytic elimination of nitrogen. A dichlorocarbene adduct of butadiene sulfone was also prepared and studied by Mock, but the difficulties encountered in the preparation of such adducts were pointed out by the author.[1]

We have later found that bicyclic sulfones of type 1 could be prepared in good yields by addition of dichlorocarbene to substituted sulfolenes in a catalytic biphasic system and that these adducts could be further transformed to the mono- and didechlorinated products 2 and 3 by controlled hydrogenolysis. Compounds 1–3 were found to be useful in a number of synthetic transformations such as the preparation of cyclopentenones from 1,[2] of thiopyrans[3] or chlorinated dienes[1,4] from 1 and 2, and of pentadienylic sulfoxides[5] or 1,4-dienes[4] from 3. This paper deals with the preparation of compounds 1–3 and with thermal fragmentations and ring-enlargement reactions of the chlorinated derivatives 1 and 2.

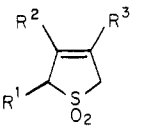
The promptness of systems 1 and 2 to undergo most of the chemical changes mentioned is due to two thermal reactions characteristic of such systems. The first is the cheletropic elimination of sulfur dioxide, as already mentioned, and the second is the electrocyclic opening of the three-membered ring, with elimination of an endo chlorine as hydrogen chloride. Both reactions are, indeed, known to be favorable, concerted processes,[1,6] requiring relatively low activation energies. The first process would lead here to open-chain, chlorinated dienes and the second to ring enlargement and formation of thiopyran derivatives.

We have found that in pure thermal fragmentations, both processes sometimes occured simultaneously. We, therefore, looked for conditions that would selectively effect one process or the other. Selective elimination of sulfur dioxide was carried out with lithium aluminum hydride (LAH) in ether,[4] and this reaction will not be further discussed here. As to the elimination of hydrogen chloride, it was found that this could be accomplished by using either acidic or basic conditions. The use of base, particularly lithium diisopropylamide (LDA), led specifically to thiopyran derivatives from 1 or 2, usually in good yields. The fragmentation of adducts 1 in hydrochloric or hydrobromic acid was somewhat less specific, with ring-enlarged products being obtained over a wide range of yields. However, the formation of functionalized thiopyrones in the latter medium made this reaction synthetically attractive. A description of the acid- or base-induced eliminations as compared to pure thermal fragmentation is given below.

Chart I[a]



1a–h 2a–e 3b–e



4a–h

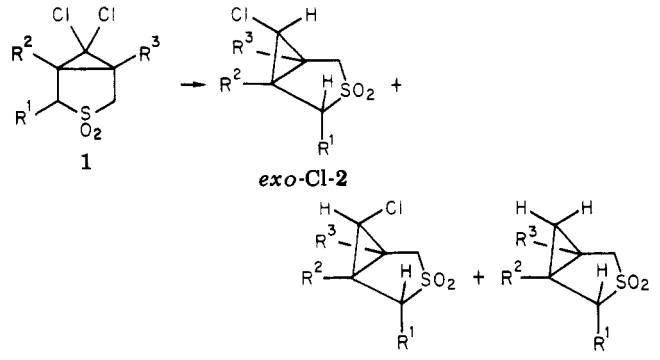
[a] a, $R^1 = R^2 = R^3 = H$; b, $R^1 = R^2 = H$, $R^3 = CH_3$; c, $R^1 = H$, $R^2 = R^3 = CH_3$; d, $R^1 = R^3 = CH_3$, $R^2 = H$; e, $R^1 = R^2 = R^3 = CH_3$; f, $R^1 = H$, $R^2 = C_6H_5$, $R^3 = CH_3$; g, $R^1,R^2 = (CH_2)_4$, $R^3 = H$; h, $R^1,R^2 = (CH_2)_5$, $R^3 = H$; i, $R^1 = R^3 = H$, $R^2 = CH_3$; j, $R^1 = H$, $R^2 = CH_3$, $R^3 = C_6H_5$.

Adducts 1a–h (Chart I) were prepared from the corresponding sulfolenes (4) by reaction with chloroform and aqueous base in the presence of a quaternary ammonium salt catalyst in 60–90% yields. The sulfolenes 4 were either commercially available or prepared from the corresponding 1,3-dienes by reaction with sulfur dioxide.[7] Butadiene sulfone itself (4a) did not yield any dichlorocarbene adduct under the above conditions. Adduct 1a could, however, be prepared in 45% overall yield from the dichlorocarbene adduct 5 of *cis*-1,4-dichloro-2-butene[8] by reaction with sodium sulfide in ethanol and oxidation of crude 6 with hydrogen peroxide in acetic acid.

(1) Mock, W. L. *J. Am. Chem. Soc.* **1970**, *92*, 6918–26 (correction: *Ibid.* **1973**, *95*, 3656).
(2) Gaoni, Y. *Tetrahedron Lett.* **1978**, 3277–8.
(3) Gaoni, Y. *Tetrahedron Lett.* **1976**, 2167–70.
(4) Gaoni, Y. *Tetrahedron Lett.* **1977**, 947–50.
(5) Gaoni, Y. *Tetrahedron Lett.* **1977**, 4521–4.
(6) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970; pp 46–7.
(7) Turk, S. D.; Cobb, R. L. In "1,4-Cycloaddition Reactions"; Hamer, J.; Ed.; Academic Press: New York, 1961; pp 13–45.
(8) Boswell, R. F.; Bass, R. G. *J. Org. Chem.* **1975**, *40*, 2419–20.

0022-3263/81/1946-4502$01.25/0

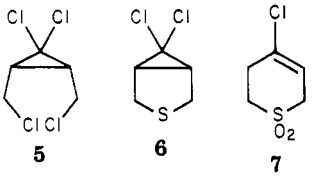
Table I. Reduction of Adducts 1 with LAH in THF



adduct 1	molar equiv of LAH	product (% yield)
1a, $R^1 = R^2 = R^3 = H$	5.3	*exo*-Cl-2a (13), *endo*-Cl-2a (60)
1b, $R^1 = R^2 = H$; $R^3 = CH_3$	1.5	*exo*-Cl-2b (32), *endo*-Cl-2b (34), 3b
	6.0	3b (84)
1c, $R^1 = H$; $R^2 = R^3 = CH_3$	1.5	*exo*-Cl-2c (41), *endo*-Cl-2c (27), 3c
	6.0	3c (82)
1d, $R^1 = R^3 = CH_3$; $R^2 = H$	1.5	*exo*-Cl-2d (44), *endo*-Cl-2d (49)
	6.0	3d (90)
1e, $R^1 = R^2 = R^3 = CH_3$	1.5	*exo*-Cl-2e (47), *endo*-Cl-2e and 3e (30)

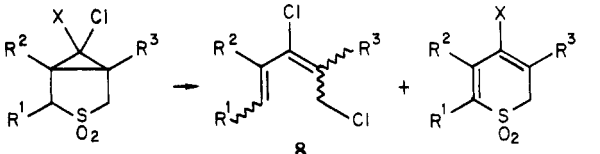
Reduction of adducts 1 to 2 or 3 was achieved through the use of LAH in tetrahydrofuran (THF). Use of a large excess of LAH furnished compounds **3b–d** in over 80% yields. Use of lesser amounts of LAH furnished the monochlorinated products **2a–e** in good yields, accompanied occasionally by a small amount of **3** (Table I). Compounds **2** were obtained as a chromatographically separable mixture of the *exo*- and *endo*-chloro derivatives. Their geometries were determined by observation of the vicinal coupling constants of the cyclopropyl protons ($J_{cis} > J_{trans}$) or by differential thermal fragmentation (see below). It was thus established that in all cases the *exo*-Cl-2 isomer preceded the *endo*-Cl-2 isomer upon chromatographic separation on silica gel.

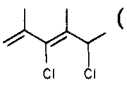
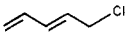
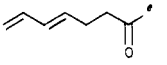
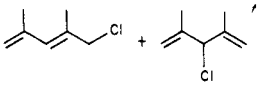
Compound **1a** was exceptional in its reductive behavior in that dechlorinated **3a** could not be obtained under the above conditions. Use of more drastic conditions (e.g., warming) produced **7** as the major product, besides the **2a** isomers.



Thermal Fragmentation of Compounds 1 and 2. The only adduct 1 reported prior to this work, namely, **1a**, has been found to yield only the rearranged chlorinated diene **8a** upon thermolysis.[1] We have, however, found that several other adducts 1 yielded simultaneously a dichloro diene, **8**, and a chlorothiopyran, **9**, and that several monochlorides **2** provided the corresponding dechlorinated analogues. The thermal fragmentations were carried out at 160 °C (145 °C for the **2c** isomers), and their results are summarized in Table II. The formation of **10c** from only one of the two **2c** isomers allowed us to conclude that in this isomer an endo chlorine favored a concurrent elimination of hydrogen chloride, as opposed to the exclusive elimination of sulfur dioxide from the other, exo isomer.

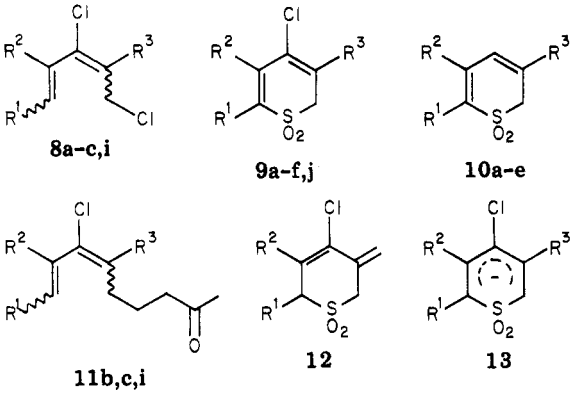
Table II. Thermal Fragmentation of Adducts 1 and 2



adduct	product (% yield)	ketone derivative[a]
1b	8b + 8i (72)	11b + 11i[b]
1c	8c[c] (55), 9c (18–20)	11c
1e	8e +  (75),[d] 9e (10)	
endo-Cl-2a	 (60)	
exo-Cl-2c		
endo-Cl-2c	10c[g,h]	

[a] Obtained by reaction of 8 with acetylacetone.[9] [b] Ketone 11b was obtained as a mixture of two geometrical isomers. Only 11i formed an adduct with dimethyl acetylenedicarboxylate. [c] One geometrical isomer (see ref 10 considering the solvolytic behavior of this compound). [d] The mixture of chlorides was converted into the corresponding trimethylcyclopentenone (Experimental Section). [e] See ref 11. [f] See ref 4. [g] Estimated by ^1H NMR to constitute 30% of the mixture. [h] In addition to the two products shown for *exo*-Cl-2c.

Chart II

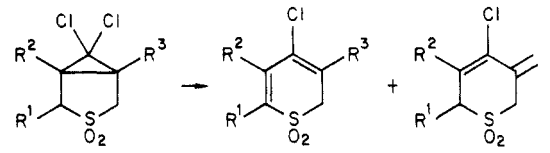


A few of the chloro dienes 8 (Chart II) were characterized by reaction with acetylacetone[9] and formation of the dienylic ketones 11. The *E* geometry of the dienylic chloride derived from **2a** could thus be established (Table II).

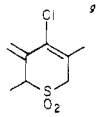
Thiopyran Dioxide and Thiopyrone Derivatives by Ring Enlargement in Acidic Media. (a) Hydrochloric Acid. 2*H*- and 4*H*-Thiopyran-4-ones are compounds of considerable theoretical and practical interest.[12–16] Sul-

(9) Boatman, S.; Hauser, C. R. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V. pp 767–9.
(10) Gaoni, Y. *Tetrahedron Lett.* **1977**, 371–4.
(11) Crombie, L.; Harper, S. H.; Thompson, D. *J. Chem. Soc.* **1951**, 2906–15. Crombie, L.; Hemesley, P.; Pattenden, G. *J. Chem. Soc. C* **1969**, 1016–24.

Table III. Thiopyran Dioxides by Ring Enlargement in Hydrochloric Acid



1 9 12

adduct	products (% yield)
1a [a]	
1b [b]	9b (10), 12 ($R^1 = R^2 = H$; 8.5)
1c	9c (22), 12 ($R^1 = H$, $R^2 = CH_3$; 41) [c,d]
1d [e]	
1e [f]	9e, 12 ($R^1 = R^2 = CH_3$),  [g]
1f	9f, 9j, 12 ($R^1 = H$, $R^2 = Ph$)

[a] No reaction occurred, because of very low solubility of 1a. [b] Ethylene glycol was used as a cosolvent. [c] Separation of the isomers was achieved through base extraction of 9c. [d] A similar equilibrium mixture of 2:1 was obtained from each of the separated isomers under the reaction conditions. [e] The corresponding cyclopentenone was the exclusive product.[2] [f] Either of the 2-*exo*- or 2-*endo*-methyl derivatives were used. [g] Total yield was ca. 90%. The two inseparable type-12 isomers were converted with base to 9e.

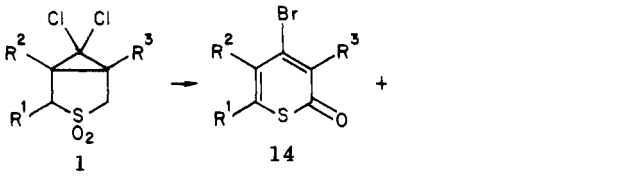
fones 1 and 2 could become a ready source for these compounds through ring enlargement,[17] and conditions for selectively effecting this transformation were sought.

One set of conditions, related to the conversion of adducts 1 into cyclopentenones,[2] consisted of warming them in aqueous acids. Two isomeric thiopyran dioxide derivatives, 9 and 12, were obtained from several adducts 1 by refluxing in 35% hydrochloric acid, the yields being higher for the more substituted sulfones (Table III).

Sulfones 12 could be isomerized to 9 through the highly stabilized anion 13[15,16] by base treatment followed by protonation. A facile prototropic shift in 9 complicated the isolation of well-defined products in the case of unsymmetrically substituted sulfones. Thus, **9b** seemed to be accompanied, at least in solution, by the isomeric **9i**. As to the isomeric **9f** and **9j**, their ^1H NMR spectra differed only in the resonance of the C_2 methylene, all other signals being superimposable. Moreover, mixtures of the two were readily changing in composition under a variety of conditions.[12] A passably pure isomer, showing just one methylene absorption, could be obtained by fractional crystallization from ether. It was assigned structure **9j** on the basis of a bathochromic shift of its UV maximum (285 nm), ascribable to an extended conjugated system, relative to that of a 2:3 mixture of **9f** and **9j** (277 nm).

(b) Hydrobromic Acid. Formation of Thiopyrones. As already mentioned, adduct **1c** was originally decomposed in 47% hydrobromic acid with the hope of converting it directly into a cyclopentenone. Thiopyrone derivatives **14c–16c** were obtained instead,[3] having a reduced sulfur atom and a bromine atom in position 2 of the primary reaction product. Thiopyran **9c** was shown to be an intermediate in this transformation. Other adducts 1 were later found to undergo a similar reaction and so also were thiopyrans 9 and 12, which could replace 1 when it was not reactive (e.g., **1a**) or when it was producing mainly a cyclopentenone (e.g., **1d**, Table IV).

Table IV. Thiopyrones by Ring Enlargement in Hydrobromic Acid

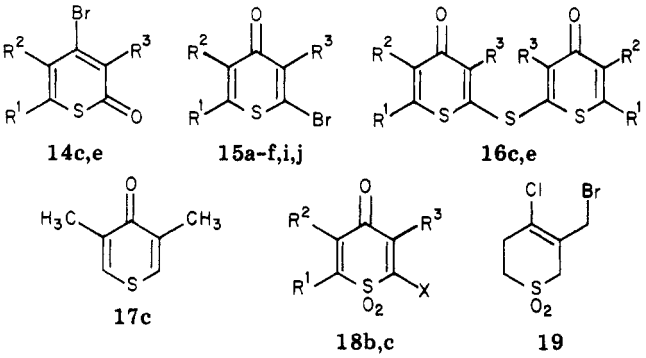


1 14 15 16

adduct	products (% yield)
9a [a]	15a (5)
1b	15i (2–3), 15b (3) [b]
1c [c]	14c (ca. 1), 15c (18–20), 16c (15–18), 9c and 12 ($R^1 = H$, $R^2 = CH_3$)
1d	15d (45)
1e	14e (trace), 15e (23), 16e (3–4) [d]
1f	15f (5), 15j (4), 9 and 12 isomers (12)

[a] 1a was unreactive, being highly insoluble. [b] Sulfone 19 was the major product from this reaction (up to 13%). [c] Similar results were obtained from 9c and 12 ($R^1 = H$, $R^2 = CH_3$). [d] The corresponding trimethylcyclopentenone was also isolated, in 20% yield.

Chart III



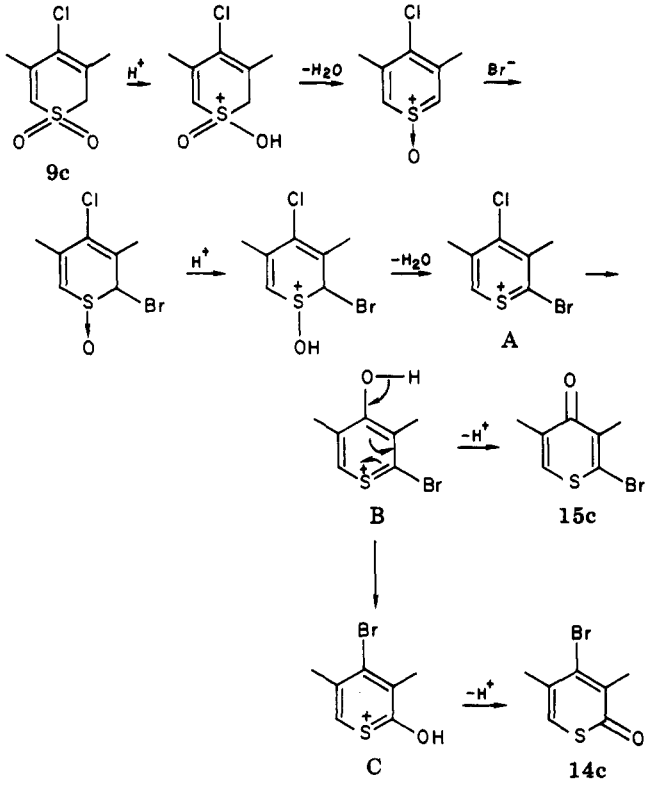
14c,e 15a-f,i,j 16c,e 17c 18b,c 19

Although the total yield of **15c** and **16c** was rather low, their facile preparation in three steps from dimethylbutadiene compensated for this drawback. Up to 7 g of **15c** and 1.2 g of **16c** could be obtained in one batch from **1c** (50 g), and the two compounds could be converted to other 2-functionalized thiopyrones, pyrones, or pyridones.[18,19] An earlier attempt at the preparation of a bromothiopyrone by direct bromination of the thiopyrone nucleus has not been successful.[20]

Compounds **14c–16c** (Chart III) were separated by chromatography and characterized through their analytical and spectral properties and through some chemical

(12) Kharchenko, V. G.; Chalaya, S. N.; Konovalova, T. M. *Chem. Heterocycl. Compd.* **1974**, *10*, 1155–70; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1974**, *10*, 1003–15.
(13) Mayer, R.; Broy, W.; Zahradnik, R. *Adv. Heterocycl. Chem.* **1967**, *8*, 219–76.
(14) Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1979**, *44*, 3144–7 and preceding papers in the series.
(15) Bradamante, S.; Pagani, G. *J. Chem. Soc., Perkin Trans. 2* **1973**, 50–1 and preceding papers in the series.
(16) Janssen, M. J. In "Organic Sulfur Chemistry"; Stirling, C. J. M. Ed.; Butterworths: London, 1975; pp 19–42.
(17) For a review on ring enlargement via dihalocarbene adducts, see: Barlet, R.; Vo-Quang, Y. *Bull. Soc. Chim. Fr.* **1969**, 3729–60.
(18) Greenberg, F. H.; Gaoni, Y. *J. Org. Chem.* **1978**, *43*, 4966–8.
(19) Gaoni, Y.; Greenberg, F. H. *J. Org. Chem.* **1981**, *46*, 74–8.
(20) Pauson, P. L.; Proctor, G. R.; Rodger, W. J. *J. Chem. Soc.* **1965**, 3037–40.

Scheme I



transformations. Thus, reduction of **15c** with hydrogen over palladium catalyst in the presence of magnesium oxide yielded the known **17c**.[21] Oxidation of the latter with *m*-chloroperbenzoic acid (MCPBA) furnished **18c** (X = H), which could be also obtained in high yield from **9c** through oxidation with selenium dioxide in ethanol (similar oxidation of **9b** yielded **18b**, X = H). Oxidation of **15c** itself with MCPBA produced **18c** (X = Br). Sulfide **16c** was obtained from **15c** in good yield through reaction with sodium sulfide in dimethyl formamide (DMF).

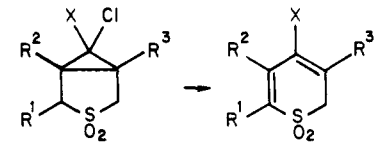
The isomeric **14c** and **15c** are readily distinguishable through their UV spectra, as is commonly practiced with isomeric thiopyran-2- and -4-ones.[18]

The structure of other thiopyrones **14–16** were based on analogy with the **c** series and on common spectral features such as IR and UV spectra. All thiopyran-4-ones showed a characteristic carbonyl absorption in the IR,[22] in agreement with a polarized structure.[13,20] The chemical shift of the carbonyl carbon of **15c** (^{13}C NMR, δ 176.5), as well as the lack of reactivity of this carbonyl toward primary amines,[19] was also indicative of such a structure.

A possible explanation regarding the formation of compounds **15** is based on the presence of bromine next to a reduced sulfur atom. This suggests that a Pummerer-type reaction[23] could have occurred twice through stepwise protonation on oxygen, elimination of two molecules of water, and addition of bromide ion to yield intermediate A, as shown in Scheme I for **9c**. Eventual substitution of the chlorine atom by a hydroxyl group would yield intermediate B, which is protonated **15c**. A certain fraction of A or B might have undergone a stepwise substitution to yield intermediate C, which is protonated **14c**.

(21) Beak, P.; McLeister-Monroe, E *J. Org. Chem.* **1969**, *34*, 589–96.
(22) Tarbell, D. S.; Hoffman, P. *J. Am. Chem. Soc.* **1954**, *76*, 2451–3.
(23) Russel, G. A.; Mikol, J. G. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1968; Vol. 1, pp 157–207.
(24) Molenaar, E.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1047–56.

Table V. Ring Expansion of 1 and 2 with LDA



1, X = Cl
2, X = H

9, X = Cl
10, X = H

compd	product (% yield)	compd	product (% yield)
1a	9a (50–60)	1h	9h (60)
1b	9b, 9i (70)	*endo*-Cl-2a	10a[b]
1c[a]	9c (60)	*endo*-Cl-2b	10b, 10i (39)
1d	9d (61)	*endo*-Cl-2d	10d (68)
1g	9g (70)	2e[c]	

[a] See text for reaction of 1c with butyllithium. [b] Reference 24. [c] No thiopyran was obtained from either of the **2e** isomers under the usual conditions or at lower temperatures.

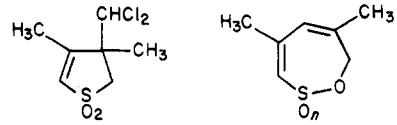
In order to account for the formation of **16**, one has to invoke a reductive fragmentation of one of the intermediate species, with formation of a sulfide ion and reaction with **15**. Bromide **15c** itself was stable under the reaction conditions; it produced **16c** by reaction with sulfide ion under different conditions, as mentioned above.

Ring Expansion Reactions of 1 and 2 under Basic Conditions. The use of base at low temperature to eliminate hydrogen chloride from adducts **1** or **2** was expected to supress a concurrent thermal elimination of sulfur dioxide. The reaction would proceed by abstraction of an acidic proton α to the sulfone, followed by cleavage of the internal cyclopropane bond and elimination of a chloride ion. Concurrent reactions could, however, arise from cleavage of an external cyclopropane bond or from opening of the five-membered ring in a way similar to that observed with the α-sulfonyl anion of sulfolenes.[5] Both types of these side reactions have indeed been observed in two particular cases.

Several basic conditions, including the use of sodium alcoholate, Grignard reagents, butyllithium, and lithium diisopropylamide (LDA), have been tried with various sulfones **1** and **2**. The latter reagent has been found to be of more general use, producing thiopyrans **9** and **10**, usually in 60–70% yields (Table V). Grignard reagents (ethylmagnesium bromide or phenylmagnesium bromide) gave higher yields of **9c** from **1c** but low yields of ca. 20% with most other **1** adducts.

Reaction of **1c** with butyllithium at low temperature produced **9c** in 66% yield relative to unrecovered starting material, but a concurrent fragmentation of the 1,6-bond also furnished **20** in 5% yield.

Reaction of the **2c** isomers with butyllithium produced yet another type of cleavage, leading to a seven-membered sultine, **21**, again with differentiation of the *exo*- and *endo*-chloro isomers. Thus, while *endo*-Cl-**2c** gave **10c** as a sole reaction product, the isomeric *exo*-Cl-**2c** produced also an almost equal amount of **21**. Oxidation of **21** with MCPBA produced the sultone **22**.

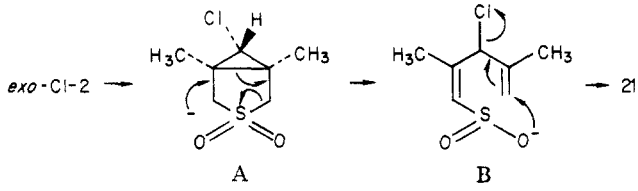


20

21, $n = 1$
22, $n = 2$

The formation of **21** is assumed to proceed via ring cleavage of the first-formed anion A (Scheme II), followed

Scheme II



by an intramolecular S_N2' substitution of the chlorine by the sulfinate anion B.

The formation of **21** from the exo isomer and not from the endo isomer reflects again on the unfavorable position of the exo chlorine for displacement by the electons of the 1,5-bond.

Experimental Section

General Procedures. Melting points were taken on a Fisher-Johns apparatus and were not corrected. Infrared spectra were measured in potassium bromide with a Perkin-Elmer Infracord 137 or 457A grating spectrometer and ultraviolet spectra in ethanol with a Cary 118 spectrophotometer. Proton NMR spectra were measured in deuteriochloroform with a Varian A-60 spectrometer. Fourier transform ^1H spectra were determined on a Varian FT-80A spectrometer and are denoted by "(80)". All chemical shifts are reported in δ units downfield from internal Me_4Si, and the J values are given in hertz. Mass spectra were determined with Atlas MAT 731 or MAT CH4 spectrometers. TLC was done on Merck Kieselgel 60-F254 precoated aluminum plates. The silica gel for column chromatography was Merck Kieselgel 60 (70–230 mesh). Elemental analyses were performed by Mr. R. Heller of the Weizmann Institute of Science, Microanalytical Laboratory.

Preparation of Adducts 1b–h. To a solution of sulfolene **4** (0.15 mol) in chloroform (150 mL) were added benzyltriethylammonium chloride (2 g) and a warm sodium hydroxide solution (ca. 45 °C; from 150 g NaOH and 300 mL of water). The mixture was vigorously stirred for 4 h, while the temperature was controlled at 45–50 °C. Addition of ice and extractive workup with dichloromethane furnished a crude product which was purified by treatment with carbon black or by trituration with cold methanol, followed by recrystallization.

6,6-Dichloro-1-methyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**1b**): mp 154–155 °C (ethanol); 61% yield; NMR δ 1.70 (s, Me), 2.13 (dd, 1, $J^1 = 8.5$, $J^2 = 4$, C_5 H), 3.08 and 3.62 (dAB q, 2, $J_{A,B} = 14.5$, $J_{4A,5} = 8.5$, $J_{4B,5} = 4$, $^4J_{4B,2} = 2$, C_4 H), 3.27 (d, 2, $J_{2,4A} = 2$, C_2 H); IR 1300, 1115 cm^{-1}. Anal. ($C_6H_8Cl_2O_2S$) C, H, Cl, S.

6,6-Dichloro-1,5-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**1c**): mp 138–139 °C (ethanol); 83–89% yield; NMR δ 1.53 (s, 6, 2 Me), 3.38 (m, 4, narrow AA'BB' system); IR 1300, 1100 cm^{-1}. Anal. ($C_7H_{10}Cl_2O_2S$) C, H, Cl, S.

6,6-Dichloro-1,4-*exo*-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**1d**): mp 136–137 °C (methanol); up to 64% yield; NMR δ 1.58 (d, $J = 7$, Me), 1.68 (s, Me), 1.7 (1, partly under Me signal, C_5 H), 3.13 (m, 1, C_4 H), 3.33 (s, 2, C_2 H); IR 1300, 1125, 1110 cm^{-1}. Anal. ($C_7H_{10}Cl_2O_2S$) C, H.

Sulfolene **4e** was obtained as a liquid which did not solidify and which was used as such in the above reaction. A ca. 45% yield of a **1e** adduct could be obtained directly by the above procedure. Chromatography of the residual material (silica gel ×15, elution with ether–hexane, 2:3) furnished a further amount (ca. 10% yield) of the same **1e** isomer besides a minute amount (<1%) of a second **1e** isomer and of recovered **4e** (ca. 20%).

The major isomer was 6,6-dichloro-1,2-*exo*,5-trimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*exo*-**1e**): mp 97–98 °C (ethanol); NMR δ (80) 1.32 (s, Me), 1.46 (d, $J = 7$, Me), 1.50 (s, Me), 3.25 (AB q, 2, $J = 15$, $\Delta\nu = 24$ Hz, C_4 H), 3.28 (q, 1, C_2 H); IR 1310, 1130, cm^{-1}. Anal. ($C_8H_{12}Cl_2O_2S$) C, H.

The minor isomer was 6,6-dichloro-1,2-*endo*,5-trimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*endo*-**1e**): mp 118–119 °C; NMR δ (80) 1.47 (s, Me), 1.50 (s, Me), 1.62 (d, $J = 7$ Hz, Me), 3.63 (AB q, 2, $J = 14$, $\Delta\nu = 27$ Hz, C_4 H), 3.64 (q, 1, C_2 H); IR 1305, 1105 cm^{-1}. Anal. ($C_8H_{12}Cl_2O_2S$) C, H.

6,6-Dichloro-1-methyl-5-phenyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**1f**): mp 136–137 °C (ethanol); NMR δ (80) 1.55 (s, Me), 3.3–3.8 (m, 4), 7.40 (Ph); IR 1313, 1130 cm^{-1}. Anal. ($C_{12}H_{12}Cl_2O_2S$) C, H.

2,2-Dichloro-5-thiatricyclo[4.4.0.0^{1,3}]decane 5,5-dioxide (**1g**): mp 102–103 °C (ethanol); yield 63%; NMR δ 1.5–2.2 (br band, 9, with dd on top due to C_3 H), 2.92 and 3.50 (dAB q, 2, $J_{AB} = 15$, $J_{4A,3} = 9$, $J_{4B,3} = 4$, C_4 H), 3.11 (t, 1, C_6 H); IR 1312, 1300, 1125 cm^{-1}. Anal. ($C_9H_{12}Cl_2O_2S$) C, H.

11,11-Dichloro-8-thiabicyclo[5.4.0.0^{1,10}]undecane 8,8-dioxide (**1h**): mp 117–118 °C (ethanol); yield 77%; NMR δ 1.2–2.4 (br band, 11, with dd on top due to C_{10} H), 3.03 and 3.62 (dAB q, 2, $J_{A,B} = 14$, $J_{9A,10} = 9$, $J_{9B,10} = 4$, C_9 H), 3.30 (br, 1, C_7 H); IR 1310, 1147 cm^{-1}. Anal. ($C_{10}H_{14}Cl_2O_2S$) C, H.

Preparation of 1a. To a solution of **5**[8] (33.5 g, 0.16 mol) in ethanol (350 mL) was added solid sodium sulfide nonahydrate (50 g, 0.2 mol), and the mixture was stirred and warmed at 80 °C for 3.5 h. The volume of liquid was reduced to ca. 100 mL by evaporation at reduced pressure, ether (300 mL) and pentane (200 mL) were added, and the resultant mixture was treated with carbon black and filtered on Celite. The solution was washed with water and with brine, dried, and concentrated to yield 18.3 g (67%) of cyclized product (^1H NMR; see below). The crude product was oxidized in acetic acid (65 mL) by rapid addition of 30% hydrogen peroxide (30 mL) at room temperature (water bath cooling) followed by warming to 70 °C. An exothermic reaction developed after ca. 0.5 h which was controlled by external cooling. Addition of water to the warm solution caused precipitation of **1a** which was filtered, washed with water and methanol, and dried (13.9 g, 43% from **5**). Recrystallized **1a** (ethyl acetate) had no melting point:[1] NMR δ (80) 2.57 (m, 2), 2.98 and 3.51 (complex AB-type pattern, 4). Thermal fragmentation of **1a** gave **8a**.[1]

Pure 6,6-dichloro-3-thiabicyclo[3.1.0]hexane (**6**) was obtained by distillation of the crude product from the reaction of **5** with sodium sulfide: bp 115–116 °C (2.7 kPa); NMR δ (80) 2.57 (m, 2), 3.25 (complex AB-type pattern, 4, $J_{AB} \approx 12$, $\Delta\nu = 22$ Hz); IR ($CHCl_3$) 1345, 1285, 1180, 1033, 973, 898, 822 cm^{-1}. Anal. ($C_5H_6Cl_2S$) C, H.

Monochlorides 2a–e and Dechlorinated 3b–d. The general procedure for obtaining **2** was to add powdered LAH (1.5 mol equiv) all at once to a stirred, ice-cooled solution of **1** in THF (200 mL/0.067 mol of **1**). Stirring was maintained for 1 h in the cold and then at room temperature, usually for 1 h further. TLC plates were developed with sulfuric acid and heat, since most compounds involved would not show in UV light or in iodine vapor. The reaction mixture was cooled with ice, treated dropwise with a saturated sodium sulfate solution until an easily separable precipitate was formed, filtered, and dried (sodium sulfate). The crude product was chromatographed (silica gel ×40) to separate the *exo*- from the *endo*-chloro isomers and from any **3** present.

To get compounds **3**, we used excess LAH (6 molar equiv, or a 1:1 ratio by weight of **1**) with stirring at room temperature for 4 h. Pure **3** was then obtained by direct crystallization of the crude product.

Isomers **2a**: Reduction of **1a** to **2a** needed excess LAH (1:1 by weight) and stirring at room temperature for 5 h.

6-*exo*-Chloro-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*exo*-Cl-**2a**; mp 149–150 °C (dichloromethane–hexane)) was eluted first (4% ethyl acetate in dichloromethane, silica gel ×70): 13% yield; NMR δ (80) 2.13 (m, 2, C_1 H and C_5 H), 3.11 (t, 1, $J_{trans} = 3.0$, C_6 H), 3.22 (AB q, 4, $J = 13.8$, $\Delta\nu = 40$ Hz, C_2 H and C_4 H); IR 1305, 1228, 1110, 930, 828, 816 cm^{-1}. Anal. ($C_5H_7ClO_2S$) C, H.

6-*endo*-Chloro-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*endo*-Cl-**2a**; mp 94–95 °C (ethyl acetate-hexane)) was eluted second, after some mixed fractions: 60% yield (14.5% of mixed fractions); NMR δ (80) 2.14 (m, 2, C_1 H and C_5 H), 3.44 (AB q, 4, $J = 14.5$ $\Delta\nu = 42$ Hz, C_2 H and C_4 H), 3.73 (t, 1, $J_{cis} = 6.8$, C_6 H); IR 1310, 1237, 1115, 825 cm^{-1}. Anal. ($C_5H_7ClO_2S$) C, H.

Reduction of **1a** (5 g, 25 mmol) with LAH (1.5 g, 40 mmol) for 4 h at 55–60 °C and chromatographic separation of the resultant mixture (300 g silica gel, elution with ethyl acetate–hexane, 1:1) yielded a reduced, nonpolar material followed by recovered **1a** (11%), *exo*-Cl-**2a** (14%), **7** (26%), and *endo*-Cl-**2a** (10%).

4-Chloro-5,6-dihydro-2*H*-thiopyran 1,1-dioxide (**7**): mp 140–141 °C (dichloromethane–hexane); NMR δ (80) 3.11 (m, 4), 3.67 (m, 2), 5.79 (t, 1); IR 1280, 1200, 1164, 1100, 980, 950, 880, 838 cm^{-1}; mass spectrum, *m/e* 168 and 166 (M^+), 104, 102, 67. Anal. ($C_5H_7ClO_2S$) C, H.

Isomers **2b** and sulfone **3b**; 6-*exo*-chloro-1-methyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*exo*-Cl-**2b**): mp 73–74 °C (benzene–hexane); yield 32% from **1b**; NMR δ 1.54 (s, Me), 1.73 (m, 1, C_5 H), 2.85–3.85 (m, 5); IR 1305, 1230, 1152, 1110 cm^{-1}. Anal. ($C_6H_9ClO_2S$) C, H.

6-*endo*-Chloro-1-methyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*endo*-Cl-**2b**): mp 62–63 °C (ethanol); yield 34%; NMR δ 1.50 (s, Me), 1.82 (m, 1, C_5 H), 2.8–3.6 (m, 5); IR 1295, 1240, 1150, 1120 cm^{-1}. Anal. ($C_6H_9ClO_2S$) C, H.

Mixtures of the two **2b** isomers with **3b** (ca. 25% yield) were obtained in intermediate fractions. Pure **3b** was obtained from **1b** by using excess LAH.

1-Methyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**3b**): mp 50–51 °C (pentane–ether); yield 84%; NMR δ 0.8–1.1 (m, 2, C_6 H), 1.36 (s, Me), 1.44 (m, 1, C_5 H), 2.8–3.7 (m, 4); IR 1297, 1135 cm^{-1}. Anal. ($C_6H_{10}O_2S$) C, H.

Isomers **2c** and sulfone **3c**; 6-*exo*-chloro-1,5-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*exo*-Cl-**2c**): mp 135–136 °C (benzene–hexane); yield 41%; δ 1.33 (s, 2 Me), 3.27 (AB q, 4, J = 14, $\Delta\nu$ = 18 Hz), 3.45 (s, 1, C_6 H); IR 1325, 1240, 1150, 1100 cm^{-1}. Anal. ($C_7H_{11}ClO_2S$) C, H.

6-*endo*-Chloro-1,5-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*endo*-Cl-**2c**): mp 140–141 °C (ether–hexane); yield 27%; NMR δ 1.45 (s, 2 Me), 3.20 (s, 5, suprimposed C_2, C_4, and C_6 H); IR 1304, 1240, 1140, 1102 cm^{-1}. Anal. ($C_7H_{11}ClO_2S$) C, H.

Mixtures of *exo*-Cl-**2c** with **3c** (ca. 13%) and then pure **3c** (7%) were obtained in intermediate fractions.

1,5-Dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**3c**): mp 106–107 °C (ether–hexane); NMR δ 0.66 and 1.13 (AB q, 2, J = 6, C_6 H), 1.30 (s, 2 Me), 3.20 (narrow AB q, 4); IR 1296, 1150, 990 cm^{-1}. Anal. ($C_7H_{12}O_2S$) C, H.

Reduction of **1c** with excess LAH furnished **3c** in 82% yield.

Isomers **2d**, and sulfone **3d**; 6-*exo*-chloro-1,4-*exo*-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*exo*-Cl-**2d**): mp 92–93 °C (ether–hexane); yield 44%; NMR δ (80) 1.35 (t, 1, J = 3.2, C_5 H), 1.49 (d, J = 7.1, Me), 1.51 (s, Me), 2.91 (m, 1, partly hidden, C_4 H), 3.11 (AB q, 2, J = 15.9, $\Delta\nu$ = 32.6 Hz, C_2 H), 3.21 (d, 1, J_{trans} = 3.2, C_6 H); IR 1310, 1131, 1106 cm^{-1}. Anal. ($C_7H_{11}ClO_2S$) C, H.

6-*endo*-Chloro-1,4-*exo*-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*endo*-Cl-**2d**): mp 104–105 °C (ether–hexane); yield 49%; NMR δ (80) 1.31 (dd, 1, partly hidden, C_5 H), 1.44 (s, Me), 1.54 (d, J = 6.9, Me), 2.85 (dq, 1, C_4 H), 3.11 (s, 2, C_2 H), 3.47 (d, 1, J_{cis} = 7.0, C_6 H); IR 1300, 1213, 1125, 1007 cm^{-1}. Anal. ($C_7H_{11}ClO_2S$) C, H.

1,4-*exo*-Dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**3d**) was obtained in 90% from **1d** by use of excess LAH and crystallization of the crude product from ether–hexane: mp 48–49 °C; NMR δ 0.8–1.2 (m, 3, C_5 and C_6 H), 1.34 (s, Me), 1.48 (d, J = 7.1, Me), 2.85 (m, 1, C_4 H), 3.07 (AB q, 2, J = 13.7, $\Delta\nu$ = 25.4 Hz, C_2 H); IR 1289, 1217, 1137, 1112 cm^{-1}. Anal. ($C_7H_{12}O_2S$) C, H.

Isomers **2e** and sulfone **3e** were obtained by reduction of *exo*-**1e**; 6-*exo*-chloro-1,2-*exo*,5-trimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*exo*-Cl-**2e**): mp 108–109 °C (hexane); yield 47%; NMR δ (80) 1.21 (s, Me), 1.32 (s, Me), 1.42 (d, J = 7.3, Me), 2.84 (q, 1, J = 7.3, C_2 H), 3.11 (AB q, 2, J = 14.0, $\Delta\nu$ = 32.5 Hz, C_4 H), 3.27 (s, 1, C_6 H); IR 1300, 1220, 1125 cm^{-1}. Anal. ($C_8H_{13}ClO_2S$) C, H.

Chloride *endo*-Cl-**2e** and **3e** (total yield ca. 30%) were difficultly separable. Repeated chromatography yielded small amounts of each.

6-*endo*-Chloro-1,2-*exo*,5-trimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (*endo*-Cl-**2e**): mp 85–86 °C (hexane); NMR δ (80) 1.23 (s, Me), 1.40 (s, Me), 1.43 (d, J = 7.2, Me), 3.02 (q, 1, partly hidden, J = 7.2, C_2 H), 3.06 (s, 2, C_4 H), 3.19 (s, 1, C_6 H); IR 1295, 1213 (d), 1120 cm^{-1}. Anal. ($C_8H_{13}ClO_2S$) C, H.

1,2-*exo*,5-Trimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**3e**): mp 58–59 °C (hexane); NMR δ 0.88 (AB q, 2, J = 5.8, $\Delta\nu$ = 26 Hz, C_6 H), 1.19 (s, Me), 1.30 (s, Me), 1.40 (d, J = 7.3, Me), 2.87 (q, 1, J = 7.3, C_2 H), 3.07 (AB q, 2, J = 14.5, $\Delta\nu$ = 22 Hz, C_4 H); IR 1290, 1213, 1115 cm^{-1}. Anal. ($C_8H_{14}O_2S$) C, H.

Thermal Fragmentations of Sulfones 1 and 2: Dienes 8 and Ketones 11. Pyrolyses were carried out at 140–170 °C, either at reduced pressure (2.7 kPa) with distillation of the products or at atmospheric pressure under an inert atmosphere. In the former case, the distillate was taken up in pentane, washed with aqueous sodium bicarbonate, dried, and redistilled, while the residue was purified by chromatography. In the latter case, the total residue was chromatographed.

Sulfone 1b. No residue was observed after pyrolytic distillation. The distillate consisted of a mixture of **8b** and **8i**. The following absorptions were assigned to the isomers from the ^1H NMR spectrum of the mixture. **8b**: δ 2.07 (s, Me), 4.25 (s, CH_2), 5.37 (d, 1, J = 10.5), 5.75 (d, 1, J = 16), 6.75 (dd, 1, J^1 = 16, J^2 = 10.5). **8i**: δ 1.97 (split Me signal), 4.33 (d, 2, J = 7.5, CH_2), 5.20 and 5.62 (2 br s, 2, $=CH_2$), 6.02 (t, 1, J = 7.5).

A mixture of **8b** and **8i** (3.7 g), acetylacetone (2.5 g), anhydrous potassium carbonate (5 g), and absolute ethanol (50 mL) was refluxed for 3 h.[9] The crude ketone mixture (3.75 g) was chromatographed on silica gel (400 g). Elution with 5% ether in hexane yielded 0.96 g of **11b**, 0.32 g of **11i**, and 1.3 g of an unseparated mixture of the two ketones (total yield 61%; ratio of **11b** to **11i** by GC, 2:1).

4-Methyl-3-chloro-1,3-octadien-7-one (**11b**): bp 100–110 °C (bath temperature; 0.13 kPa); NMR δ 1.96 (s, Me), 2.14 (s, Me), 2.55 (s, 4), 5.22 (br d, 1, J = 10), 5.62 (br d, 1, J = 16), 6.75 (dd, 1); a second series of smaller, parallel signals at δ 1.92, 2.59, and 6.70 indicated the presence of a geometrical isomer. Anal. ($C_9H_{13}ClO$) C, H.

2-Methyl-3-chloro-1,3-octadien-7-one (**11i**): bp 100–110 °C (bath temperature; 0.13 kPa); NMR δ 1.95 (br s, Me), 2.13 (s, Me), 2.58 (m, 4), 5.08 (br s, 1), 5.50 (s, 1), 5.80 (m, 1). Anal. ($C_9H_{13}ClO$) C, H.

A mixture of **11b** and **11i** (1.3 g) was refluxed with dimethyl acetylenedicarboxylate (1.0 g) in benzene (40 mL) for 40 h. Chromatography on silica gel (70 g) yielded upon elution with 5% ether in hexane 0.5 g of unreacted **11b**. Further elution with ether–hexane (2:3) furnished 0.8 g of an adduct derived from **11i**. It was characterized by ^1H NMR as dimethyl 4-chloro-3,6-dihydro-5-methyl-3-(3-oxobutyl)phthalate: δ 1.88 (s, Me), 2.10 (s, Me), 2.25 (m, 4, side-chain methylenes), 3.08 (m, 2, ring methylene), 3.50 (m, 1), 3.77 (s, 2 Me). The product aromatized and solidified after several months. It was filtered on silica gel and recrystallized to give dimethyl 4-chloro-5-methyl-3-(3-oxobutyl)phthalate: mp 94–95 °C (hexane); NMR δ 2.16 (s, Me), 2.43 (s, Me), 2.88 (m, 4), 3.88 (s, Me), 3.91 (s, Me), 7.76 (s, 1); mass spectrum, m/e 314, 312 (M^+), 237 (base). Anal. ($C_{15}H_{17}ClO_5$) C, H.

Sulfone 1c. Pyrolytic distillation of **1c** (10 g) at 160 °C yielded a distillate and a residue. Redistillation after washing and drying gave 1,3-dichloro-2,4-dimethyl-2,4-pentadiene (**8c**): bp 74–76 °C (2.7 kPa); yield 4.0 g (56%); NMR δ 1.90 (slightly split Me signal, C_4 Me), 1.97 (s, C_2 Me), 4.17 (s, CH_2), 5.12 (narrow m, $=CH_2$); IR ($CHCl_3$) 1631, 987, 918, 893 cm^{-1}. Anal. ($C_7H_{10}Cl_2$) C, H.

The nonvolatile residue was chromatographed on silica gel (50 g; pentane–ether, 1:1) to yield 4-chloro-3,5-dimethyl-2*H*-thiopyran 1,1-dioxide (**9c**): mp 78–79 °C (hexane); yield 1.68 g (20%); NMR δ 2.16 (two very close Me signals), 3.92 (br s, 2), 6.48 (br s, 1); IR 1321, 1285, 1174, 1111, 994, 889 cm^{-1}; mass spectrum, m/e 194 and 192 (M^+), 162, 157, 146, 144, 129, 128, 127, 113, 93 (base). Anal. ($C_7H_9ClO_2S$) C, H.

Pyrolysis of **1c** (13 g) under atmospheric pressure without distillation followed by chromatography (silica gel, 80 g; pentane then ether–pentane, 3:2) yielded **8c** (5.2 g, 55%) and **9c** (1.9 g, 18%). An unidentified product (0.3 g) was collected in intermediate fractions: mp 160–162 °C (ethanol); mass spectrum, m/e 322, 320 (M^+); calcd for $C_{14}H_{18}Cl_2O_2S$ m/e 322, 320.

Reaction of **8c** with acetylacetone as above yielded 3-chloro-2,4-dimethyl-1,3-octadien-7-one (**11c**): bp 100–110 °C (bath temperature; 0.13 kPa); NMR δ 1.83 (s, Me), 1.90 (br s, Me), 2.14 (s, Me), 2.49 (s, 4), 4.93 and 5.08 ($=CH_2$); IR ($CHCl_3$) 1700, 907 cm^{-1}. Anal. ($C_{10}H_{15}ClO$) C, H.

Sulfone 1e. Pyrolytic distillation of **1e** (11.1 g) at 160 °C yielded a distillate and a residue. The distillate [6.45 g, 78%; δ 1.55 (d, Me), 1.90–1.96 (superimposed Me signals), 4.14 (s, CH_2), 5.0–5.2 (m)] was assumed to consist mainly of 3,5-dichloro-2,4-dimethyl-1,3-hexadiene, containing ca. 10% of **8e** (singlet at δ 4.14). Treatment of this mixture with 80% acetic acid at reflux temperature for 1 h[3] yielded 2,3,5-trimethyl-2-cyclopenten-1-one[25]

in 85% yield; 2,4-dinitrophenylhydrazone, mp 230–231 °C (lit.[25] mp 235–236 °C).

The residue from the above distillation (0.95 g) consisted essentially of **9e** (TLC and ^{1}H NMR; see below).

Sulfone *endo*-Cl-2a. Pyrolysis of *endo*-Cl-**2a** (796 mg) at 160–165 °C under atmospheric pressure caused distillation of the formed product and left no residue. The volatile material was identified as 1-chloro-2,4-pentadiene[11b] (370 mg, 60%). Alkylation with acetylacetone[9] yielded *trans*-1,3-octadien-7-one;[11] 2,4-dinitrophenylhydrazone, mp 80–81 °C (lit.[11a] mp 82–82.5 °C).

Sulfones 2c. The two isomeric **2c** sulfones (0.1 g each) were fragmented at 145 °C during 10 min, and the liquid residues were examined directly by NMR. The product derived from *exo*-Cl-**2c** showed absorptions at δ 1.76 and 1.90 (vinylic methyls), 4.00 and 4.17 (CHCl and CH_2Cl), and 4.80, 4.97, and 5.13 (methenes) ascribable to two isomeric pentadienylic chlorides. The product derived from *endo*-Cl-**2c** also showed, in addition to the same absorptions, signals at δ 2.03, 3.72, 5.92, and 6.18, due to **10c** (see below). The ratio of the signal at δ 2.03 to the two at δ 1.76 and 1.90 was ca. 1:3, indicating 30% of **10c** in the mixture. The presence of **10c** was also shown by TLC, as compared with that of an authentic sample.

Fragmentation of Adducts 1 in Hydrochloric Acid. Adducts **1** were refluxed in 35% hydrochloric acid (10 mL/g) for 1–2 h. A longer reflux time and a cosolvent (ethylene glycol) were needed for **1a** and **1b**, which were much less soluble in the acid than the more highly alkylated adducts. Addition of ice and water and extraction with ethyl acetate furnished a crude product mixture.

Sulfone 1a. Mainly unchanged starting material was observed after several hours, with apparently some **8a** (TLC and ^{1}H NMR).

Sulfone 1b. The crude product (1.2 g, from 3 g of **1b**; 5 h reflux in 30 mL of 35% HCl and 5 mL of ethylene glycol) was triturated with cold pentane to extract an undetermined amount of 2-methyl-2-cyclopenten-1-one[3] and then chromatographed (60 g of silica gel; elution with ether–hexane, 2:3).

4-Chloro-4-methyl-2*H*-thiopyran 1,1-dioxide (**9b**) was eluted first: 0.25 g (10%); mp 77–78 °C (hexane). It seemed to be accompanied in solution by the isomeric 4-chloro-5-methyl-2*H*-thiopyran 1,1-dioxide (**9i**; see **9f** below and ref 12): NMR δ (80) 2.10 (s, Me), 3.92 (s, CH_2), 6.58 (s, 2, vinylic; satellite signals at 2.13 and 3.95 and a multiplet near 6.50 indicated ca. 20% **9i**); IR 1300, 1125 cm^{-1}. Anal. ($C_6H_7ClO_2S$) C, H.

Eluted second was 4-chloro-5,6-dihydro-5-methylene-2*H*-thiopyran 1,1-dioxide (**12**, $R^1 = R^2 = H$): mp 125–126 °C (ethanol); yield 0.21 g (8.5%); NMR δ 3.88 (d, 2, J = 5, C_2 H), 3.97 (br s, 2, C_6 H), 5.47 and 5.92 (2 s, 2, methene), 6.09 (t, 1, J = 5, C_3 H); IR 1300, 1105, 977, 917, 885, 837 cm^{-1}; mass spectrum, m/e 180 and 178 (M^+), 114, 113. Anal. ($C_6H_7ClO_2S$) C, H.

Sulfone 1c. Chromatographic separation of the crude reaction mixture was difficult and gave mainly a mixture of **9c** and **12** (R^1 = H, $R^2 = CH_3$) in 80% yield, besides small amounts of the pure compounds. Complete separation was achieved as follows. A solution of the crude reaction product (3.5 g, from 5 g of **1c**) in ether–dichloromethane (3:1) was extracted with 1 N NaOH (3 × 20 mL). The basic extract was acidified with 5 N H_2SO_4 and extracted with ether to furnish 1.1 g of **9c** (0.92 g from hexane, 22%; mp 78–79 °C). The organic layer was washed with water, dried, and evaporated to yield 2.11 g (1.72 g from ether–hexane, 41%) of 4-chloro-5,6-dihydro-3-methyl-5-methylene-2*H*-thiopyran, 1,1-dioxide (**12**, R^1 = H, $R^2 = CH_3$): mp 115–116 °C; NMR δ 2.05 (br s, Me), 3.83 (br s, CH_2), 3.95 (br s, CH_2), 5.37 and 5.86 (2 br s, methene); IR 1326, 1282, 1176, 1117, 910 cm^{-1}; mass spectrum, m/e 194 and 192 (M^+), 130, 128, 115, 113, 93, 91. Anal. ($C_7H_9ClO_2S$) C, H.

The ratio of the vinylic signals at δ 5.37 and 5.86 relative to the signal at δ 6.48 was used to determine the relative amounts of the two isomers in the reaction mixture and in equilibration reactions.

Fragmentation of **1c** in 24% hydrobromic acid gave results identical with those obtained in concentrated HCl.

Short warming of **12** (R^1 = H, $R^2 = CH_3$) in 2 N NaOH at 60–70 °C gave a red solution from which pure **9c** was obtained upon acidification and extraction with ether, as evidenced by ^{1}H NMR.

Sulfone 1d. Only a mixture of two isomeric cyclopentenones[3] was obtained from **1d** under the usual conditions (2-h reflux).

Sulfones 1e. The 2-*endo*- and 2-*exo*-Me-**1e** isomers gave identical product mixtures according to NMR (94% crude yield). Chromatography separated the **9** isomer from two inseparable **12** isomers:

4-Chloro-3,5,6-trimethyl-2*H*-thiopyran 1,1-dioxide (**9e**): mp 71–72 °C (hexane); yield 51%; NMR δ 2.08 (s, 3 Me), 3.73 (s, CH_2); IR 1300, 1200, 1153, 985, 928 cm^{-1}; mass spectrum, m/e 208 and 206 (M^+), 158, 142, 127, 107, 91. Anal. ($C_8H_{11}ClO_2S$) C, H.

4-Chloro-5,6-dihydro-2,3-dimethyl-5-methylene-2*H*-thiopyran 1,1-dioxide (**12**, $R^1 = R^2 = CH_3$) and 4-chloro-5,6-dihydro-3,6-dimethyl-5-methylene-2*H*-thiopyran 1,1-dioxide were obtained from chromatography as a ca. 6:1 mixture, the composition of which did not change on crystallization from hexane: NMR δ 1.59 (d, J = 7.1, Me), 2.05 (s, Me), 3.78 (s and q, 3), 5.39 (s, 1), 5.90 (s, 1); parallel signals at δ 1.60, 5.29, 5.86.

Sulfone 1f. The crude reaction mixture, showing vinylic proton signals at 5.51, 6.05, and 6.58 (ca. 1:1:2, respectively), was treated in ethanol with 3 N NaOH for 0.5 h at 35 °C. Acidification and extraction with ether gave a solid mixture melting in the range of 90–120 °C and showing one vinylic signal at δ 6.58, two methylene signals at δ 4.00 and 4.15, and one methyl signal at δ 2.23. Crystallization from ether gave a compound which showed only one methylene signal at δ 4.00, while the signal at δ 4.15 was relatively enhanced in the mother liquour.

4-Chloro-5-methyl-3-phenyl-2*H*-thiopyran 1,1-dioxide (**9j**): mp 132–135 °C; NMR δ 2.23 (s, Me), 4.00 (s, CH_2), 6.58 (s, 1), 7.31–7.43 (m, Ph); IR 1306, 1292, 1223, 1120, 1015, 954, 890 cm^{-1}; UV max 285 nm (ε 5400); mass spectrum, m/e 256 and 254 (M^+), 192, 190, 171, 155, 139, 128, 115, 91. Anal. ($C_{12}H_{11}ClO_2S$) C, H.

Reactions of Sulfones 1 and 9 with Hydrobromic Acid. Sulfones **1** or **9** were refluxed in 47% HBr (usually 8 mL/g) for 2–4 h. The mixture was cooled, treated with water, and extracted several times with ether, which did not dissolve dark polymeric material usually formed during the reaction. The ether extract was washed with sodium bicarbonate and with saturated sodium chloride solutions, dried, concentrated, and chromatographed on silica gel (usually 40 g/g of crude; ether–hexane mixtures as eluant).

Sulfone 9a. This sulfone, obtained from **1a** by base-induced elimination, was used rather than the highly insoluble **1a** (1.2 g, 30 mL of acid, 3.5-h reflux). The only well-defined product obtained after chromatography was 2-bromo-4*H*-thiopyran-4-one (**15a**): 5% yield; mp 72–73 °C (hexane or ethanol); NMR δ (80) 7.00 (dd, 1, $J_{5,6}$ = 10.3, $J_{5,3}$ = 1.5, C_5 H), 7.34 (d, 1, $J_{3,5}$ = 1.5, C_3 H), 7.64 (d, $J_{6,5}$ = 10.3, C_6 H); IR 1587, 1515, 1350, 1282, 1125, 923, 856, 830, 783, 710 cm^{-1}; UV max 236 nm (ε 13 200), 284 (inflexion, 15 900), 290 (18 500), 300 (sh, 14 000); high-resolution mass spectrum, m/e 189.9117 and 191.9074; $C_5H_6{}^{79}BrOS$ requires m/e 189.9088, and $C_5H_3{}^{81}BrOS$ requires 191.9068.

Sulfone 1b. The crude reaction product (3 g, from 10 g of **1b**; 100 mL of acid, 1.5-h reflux) was taken in benzene, and an insoluble product was filtered (0.64 g) and recrystallized from ethanol to furnish 3-(bromomethyl)-4-chloro-5,6-dihydro-2*H*-thiopyran 1,1-dioxide (**19**): mp 135–136 °C; NMR δ 3.20 (br s, 4), 3.85 (br s, 2), 4.15 (s, 2); IR 1314, 1295, 1163, 1139, 1120 cm^{-1}; mass spectrum, m/e 262, 260, and 258 (M^+), 225, 223, 181, 179, 161, 159, 143, 117, 115, 113. Anal. ($C_6H_8BrClO_2S$) C, H, S.

Chromatographic separation of the benzene solution furnished further 2-bromo-5-methyl-4*H*-thiopyran-4-one (**15i**): yield 0.27 g (2.8%); mp 101–102 °C (hexane); NMR δ 2.13 (slightly split Me), 7.33 (s, 1, C_3 H), 7.54 (q, 1, $J \approx 1$, C_6 H); IR 1592, 1527, 1270, 1212, 1126, 1016, 898, 874 cm^{-1}; UV max 240 nm (ε 12 000), 294 (16 700), 300 (sh, 15 600); mass spectrum, m/e 206 and 204 (M^+), 178, 176, 166, 164, 125, 97, 85. Anal. (C_6H_5BrOS) C, H, Br, S.

2-Bromo-3-methyl-4*H*-thiopyran-4-one (**15b**): yield 0.30 g (3.1%) mp 116–117 °C (hexane); NMR δ 2.30 (s, Me), 7.00 and 7.67 (AB q, 2, J = 10.5, C_5 H and C_6 H); IR 1592, 1527, 1302, 1182, 1028, 920 cm^{-1}; UV max 240 nm (ε 7540), 293 (13 000), 300 (sh, 11 200); mass spectrum, m/e 206 and 204 (M^+), 178, 176, 125, 97, 71. Anal. (C_6H_5BrOS) C, H, Br, S.

An additional amount (0.23 g) of **19** was then eluted from the column, bringing the total yield of this compound to 7.2% (yields of up to 13% were obtained from similar reactions).

(25) Kienzle, F.; Minder, R. E. *Helv. Chim. Acta* **1976**, *59*, 439–52.

Sulfones 1c and 9c. Chromatographic separation of the crude product (7.8 g from 13 g of **1c**; 3-h reflux) yielded the following compounds.

4-Bromo-3,5-dimethyl-2*H*-thiopyran-2-one (**14c**; eluted with ether–hexane, 1:4): 0.2 g (1.6%); mp 96–97 °C (pentane); NMR δ 2.33 (s, Me), 2.37 (d, $J \approx 1$, Me), 7.12 (br s,1); IR 1590, 1568, 1370, 1273, 1249, 1195, 976, 947, 838 cm^{-1}; UV max 227 nm (ϵ 26000), 233 (27000), 343 (4000); mass spectrum, *m/e* 220 and 218 (M$^+$), 192, 190, 174, 146, 139, 111, 95. Anal. (C_7H_7BrOS) C, H, Br, S.

2-Bromo-3,5-dimethyl-4*H*-thiopyran-4-one (**15c**; same eluant): 2.30 g (18.5%); mp 96–97 °C (hexane); NMR δ 2.14 (d, $J \approx 1$, Me), 2.31 (s, Me), 7.46 (q, 1, $J \approx 1$); ^{13}C NMR δ 17.9, 19.0, 126.7, 131.0, 134.5, 137.5, 176.5; IR 1587, 1364, 1260, 1184, 1026, 978, 915, 869 cm^{-1}; UV max 244 nm (ϵ 9800), 297 (14300), 304 (14200); mass spectrum, *m/e* 220 and 218 (M$^+$), 192, 190, 174, 139, 111, 99, 95. Anal. (C_7H_7BrOS) C, H, Br, S.

A mixture of **9c** and **12** (R^1 = H, R^2 = CH_3) was then eluted (ether–hexane, 1:1; 0.95 g, 7.3%), followed by bis(3,5-dimethyl-4-oxo-4*H*-thiopyran-2-yl) sulfide (**16c**; eluted with ether–hexane, 4:1): 20% yield (on the basis of three molecules of **1c** for one of **16c**); mp 160–161 °C (ethanol); NMR δ 2.17 (d, $J \approx 1$, 2Me), 2.36 (s, 2Me), 7.58 (q, 2, $J \approx 1$); IR 1575, 1362, 1248, 1171, 1024, 969, 923, 867, 843 cm^{-1}; UV max 239 nm (ϵ 24000), 310 (27250); mass spectrum, *m/e* 310 (M$^+$), 295, 293, 277, 262, 249, 242, 210, 197, 183, 177, 172, 171, 140, 111, 99. Anal. ($C_{14}H_{14}O_2S_3$) C, H.

Reaction of a mixture of **9c** and **12** (R^1 = H, R^2 = CH_3) with hydrobromic acid gave similar results to those obtained from **1c**.

Sulfone 9d. Thiopyran **9d** was treated with acid instead of **1d** in order to avoid formation of cyclopentenones. The crude reaction product (0.66 g from 1.03 g of **9d**; 30 mL of acid, 2-h reflux) was chromatographed to yield 2-bromo-3,6-dimethyl-4*H*-thiopyran-4-one (**15d**): yield 0.53 g (45%); mp 109–110 °C (methanol); NMR δ (80) 2.26 (s, Me), 2.31 (d, J = 1.0, Me), 6.77 (br s, 1); IR 1595, 1367, 1330, 903, 887 cm^{-1}; UV max 242 nm (ϵ 11400), 293 (17600), 299 (sh, 17200); mass spectrum, *m/e* 220 and 218 (M$^+$), 192, 190, 140, 139, 111, 100, 99. Anal. (C_7H_7BrOS) C, H.

Sulfone 1e. Chromatographic separation of the crude reaction mixture (7.7 g from 15 g of **1e**; 120 mL of acid, 4-h reflux) gave bromides **14e** and **15e**, each accompanied by 2,3,5-trimethyl-2-cyclopenten-1-one.[25] The ketone (ca. 1.5 g, 20%) was removed by trituration with cold pentane and was identified by ^{1}H NMR and by its 2,4-dinitrophenylhydrazone (see above). The residual solids were then recrystallized to yield the pure bromides.

4-Bromo-3,5,6-trimethyl-2*H*-thiopyran-2-one (**14e**): mp 113–114 °C (pentane); yield 0.02 g (0.14%); NMR δ (80) 2.26 (s, Me), 2.33 (s, 2 Me); IR 1590, 1490, 1366, 1235, 997 cm^{-1}; UV max 232 nm (ϵ 26800), 346 (6200); mass spectrum, *m/e* 234 and 232 (M$^+$), 206, 204, 188, 162, 160, 159, 153, 145, 125, 99, 91, 88. Anal. (C_8H_9BrOS) C, H.

2-Bromo-3,5,6-trimethyl-4*H*-thiopyran-4-one (**15e**): mp 99–100 °C (methanol); yield 3.3 g (23%); NMR δ (80) 2.10, (s, Me), 2.29 (s, 2 Me); IR 1585, 1363, 1335, 1210, 1000, 933, 895, 810, 750 cm^{-1}; UV max 246 nm (ϵ 16800), 295 (14800), 304 (14500); mass spectrum, *m/e* 234 and 232 (M$^+$), 190, 188, 155, 153, 125, 99, 91, 81. Anal. (C_8H_9BrOS) C, H.

Further elution with the same solvent mixture (ether–hexane, 2:3) gave mixtures of **9e** and the corresponding **12** isomers (1.24 g, 10%). Elution with ether–hexane (7:3) then yielded bis(3,5,6-trimethyl-4-oxo-4*H*-thiopyran-2-yl) sulfide (**16e**): mp 183–184 °C (ethanol); yield 0.24 g (3.5%); NMR δ (80) 2.12 (s, 2 Me), 2.29 (s, 2 Me), 2.35 (s, 2 Me); IR 1570, 1360, 1335, 1210, 1030, 988, 755 cm^{-1}; UV max 240 (ϵ 29500), 308 (26500); mass spectrum, *m/e* 338 (M$^+$), 323, 321, 305, 224, 223, 211, 197, 187, 186, 154, 142, 125, 99. Anal. ($C_{16}H_{18}O_2S_3$) C, H.

Sulfone 1f. Considerable polymerization occurred during the reaction (2.54 g of **1f**, 50 mL of acid, 4-h reflux). Chromatography first separated two bromides, **15f,j**.

2-Bromo-3-methyl-5-phenyl-4*H*-thiopyran-4-one (**15f**): mp 136–137 °C (hexane); 0.125 g (5%); NMR δ (80) 2.37 (s, Me), 7.40 (s, Ph), 7.59 (s, 1); IR 1585, 1560, 1350, 1233, 875, 865, 780, 734 cm^{-1}; UV max 241 nm (ϵ 22300), 298 (15340); mass spectrum, *m/e* 282, 281, 280, 279, (M$^+$ and M$^+$ – 1), 236, 235, 201, 173, 172, 171, 134, 129, 128, 115, 102, 99, 89. Anal. ($C_{12}H_9BrOS$) C, H.

2-Bromo-5-methyl-3-phenyl-2*H*-thiopyran-4-one (**15j**): mp 96–97 °C (methanol); yield 0.1 g (4%); NMR δ (80) 2.16 (d, J = 1.2 Hz, Me), 7.34–7.46 (m, Ph and C_6 H); IR 1580, 1363, 1255, 1012, 873, 740 cm^{-1}; UV max 238 nm (ϵ 18600), 295 (15100); mass spectrum, *m/e* 282, 281, 280, 279 (M$^+$ and M$^+$ – 1), 201, 135, 133, 129, 101, 89. Anal. ($C_{12}H_9BrOS$) C, H.

A mixture of the **9** and **12** isomers was then eluted, followed by pure **12** (R^1 = H, R^2 = Ph; total 0.28 g, 12%).

4-Chloro-5,6-dihydro-5-methylene-3-phenyl-2*H*-thiopyran 1,1-dioxide: 125–126 °C (ether–hexane); NMR δ 4.05 (s, 4), 5.51 and 9.05 (2 s, 2, methene), 7.31–7.41 (m, Ph); IR 1290, 1240, 1165, 1100, 910, 885, 760 cm^{-1}; UV max 251 nm (ϵ 19250); mass spectrum, *m/e* 256 and 254 (M$^+$), 192, 190, 156, 155, 154, 153, 152, 129, 128, 127, 115, 102, 91, 89. Anal. ($C_{12}H_{11}ClO_2S$) C, H.

Reduction of 15c: Thiopyrone 17c. Bromide **15c** (0.39 g) was hydrogenated in methanol (10 mL) at normal pressure over 10% palladium on charcoal (0.3 g) in the presence of magnesium oxide (0.3 g). The crude product, practically pure by ^{1}H NMR, was recrystallized from pentane to yield pure **17c** [mp 54–55 °C (lit.[20] 58–60 °C)], corresponding in all spectral data with those described.[20]

Oxidation of 9c with Selenium Dioxide. Sulfone **9c** (0.2 g) was warmed in ethanol (4 mL) with selenium dioxide (70 mg) at 70 °C for 14 h with no apparent change (TLC). Two further portions of the oxidant (2 × 60 mg) were added at 6-h intervals, and warming was continued for another 24-h period. The usual workup and filtration on silica gel (20 g) with ether–hexane (1:1) yielded 3,5-dimethyl-4*H*-thiopyran-4-one 1,1-dioxide (**18c**, X = H); yield 0.15 g (84%); mp 133–134 °C (hexane); NMR δ 2,08 (s, 2 Me), 7.03 (br s, 2); IR 1675, 1652, 1290, 1115, 850 cm^{-1}; UV max 247 nm (ϵ 9550); mass spectrum, *m/e* 172 (M$^+$), 140, 132, 127, 85. Anal. ($C_7H_8O_3S$) C, H.

Oxidation of **17c** (40 mg) with MCPBA (80 mg) in dichloromethane overnight at room temperature yielded dioxide **18c** (X = H), identical in all respects with the product obtained by selenium dioxide oxidation of **9c**.

Oxidation of 15c with MCPBA: Dioxide 18c (X = Br). Bromide **15c** (0.26 g, 1.18 mmol) was oxidized with MCPBA (0.53 g, 2.6 mmol, 85% peracid) in dichloromethane (10 mL) overnight at room temperature. Ammonia was passed over the stirred reaction mixture for 10 min, and the solids were then filtered and washed with dichloromethane. Evaporation of the solvent and crystallization from ether–hexane yielded 2-bromo-3,5-dimethyl-4*H*-thiopyran-4-one 1,1-dioxide (**18c**, X = Br): mp 115 and 123–124 °C; yield 0.202 g (71%); NMR δ 2.13 (d, $J \approx 1$, Me), 2.23 (s, Me), 7.33 (q, 1, $J \approx 1$); IR 1670, 1602, 1337, 1307, 1236, 1175, 1132, 1058, 1030, 928, 840 cm^{-1}; UV max 225 nm (ϵ 13300), 295 (2400). Anal. ($C_7H_7BrO_3S$) C, H.

Preparation of Sulfide 16c from Bromide 15c. Bromide **15c** (0.440 g, 2.0 mmol) was warmed under an inert atmosphere in dimethylformamide (7 mL) with sodium sulfide nonahydrate (0.23 g, 1.06 mmol) at 120 °C for 19 h. Slow addition of water to the warm reaction solution caused precipitation of a solid (0.208 g, 67%), identical in all respects with **16c**.

Oxidation of 9b with Selenium Dioxide. Sulfone **9b** (0.16 g) was refluxed in ethanol (10 mL) with selenium dioxide (0.16 g) for 12 h. Workup and chromatography as above yielded 30 mg (27%) of 3-methyl-4*H*-thiopyran-4-one 1,1-dioxide **18b** (X = H): mp 109–110 °C (hexane); NMR δ 2.06 (d, $J \approx 1$, Me), 6.60 (d, 1, J = 11, C_5 H), 7.0–7.45 (m, 2, C_2 H and C_6 H); IR 1678, 1640, 1337, 1300, 1234, 1150, 1135, 1085, 1017, 890, 842 cm^{-1}; mass spectrum, *m/e* 158 (M$^+$), 129, 126, 118, 113, 110, 94, 86, 85. Anal. ($C_6H_6O_3S$) C, H.

Reactions of Sulfones 1 and 2 with LDA. LDA was prepared according to Gaudemar-Bardone[26] and titrated with diphenyl acetic acid.[27] The LDA solution (2.2 molar equiv) was added to a stirred solution of the sulfone in THF (7 mL/mmol of sulfone), kept under an argon atmosphere, and cooled with ice. The solution was stirred 0.25 h in the cold and 1 h at room temperature and then worked up by quenching with water, evaporation of most of the THF at reduced pressure, acidification with 1 N HCL, and extraction with ether. The crude product

(26) Gaudemar-Bardone, F.; Gaudemar, M. *Synthesis* **1979**, 463–5.
(27) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–80.

was filtered on silica gel to effect separation from isopropylbenzene[26] and then recrystallized.

Sulfone 1a. Longer reaction times (4–6 h) were needed for this sulfone in order to achieve complete conversion to 4-chloro-2*H*-thiopyran 1,1-dioxide (**9a**): mp 102–103 °C (hexane); yield 50–60%; NMR δ (80) 3.97 (d, 2, J = 5.2, C_2 H), 6.30 (t, 1, J = 5.2, C_3 H), 6.60 (s, 2, C_5 H and C_6 H); IR 1308, 1285, 1155, 1110, 1045, 1000, 918, 875, 840, 770 cm^{-1}; UV max 270 nm (ϵ 3060); mass spectrum, m/e 166 and 164 (M^+), 136, 134, 129, 116, 100, 84. Anal. ($C_5H_5ClO_2S$) C, H.

Sulfone 1b. A mixture of **9b** and **9i** was again obtained (see above), in 70% yield.

Sulfone 1c. Compound **9c** was obtained in 60% yield.

Sulfone 1d. There was obtained as one pure isomer in 61% yield 4-chloro-3,6-dimethyl-2*H*-thiopyran 1,1-dioxide (**9d**): mp 71–72 °C (pentane); NMR δ 2.06 (s, C_3 Me) 2.17 (br s, C_6 Me), 3.89 (s, 2, C_2 H), 6.35 (br s, 1, C_5 H); IR 1295, 1150, 1135, 1110, 1020, 980, 930, 900, 852, 800, 740 cm^{-1}; UV max 220 nm (ϵ 3300), 279 (5440); mass spectrum, m/e 194 and 192 (M^+), 144, 129, 127, 115, 113, 94, 93, 91. Anal. ($C_7H_9ClO_2S$) C, H.

Sulfone 1g. There was obtained in 70% yield 5-chloro-2-thiabicyclo[4.4.0]deca-1(6),4-diene 2,2-dioxide (**9g**): mp 70–71 °C (pentane); NMR δ 1.6–1.95 (br, 4), 2.3–2.7 (br, 4), 3.90 (d, 2, J = 5, C_3 H), 6.27 (t, 1, J = 5, C_4 H); IR 1300, 1267, 1170, 1125, 1013, 927, 782, 760 cm^{-1}; mass spectrum, m/e 220 and 218 (M^+), 183, 170, 126, 125, 119, 104, 91. Anal. ($C_9H_{11}ClO_2S$) C, H.

Sulfone 1h. There was obtained in 60% yield 11-chloro-8-thiabicyclo[5.4.0]undeca-1(7),10-diene 8,8-dioxide (**9h**): mp 83–84 °C (pentane); NMR δ 1.4–2.0 (br, 6), 2.6–2.9 (br, 4), 3.88 (d, 2, J = 6, C_9 H), 6.28 (t, 1, J = 6, C_{10} H); IR 1305, 1276, 1140, 1015, 962, 943, 876, 822, 786, 765 cm^{-1}; mass spectrum, m/e 234 and 232 (M^+), 197, 184, 167, 140, 139, 128, 127, 126, 125, 105, 91. Anal. ($C_{10}H_{13}ClO_2S$) C, H.

Sulfone *endo*-Cl-2a. Compound **10a** was obtained in 29% yield; mp 57–58 °C (pentane; lit.[24] 55–57 °C). Spectral data of **10a** corresponded to those published.[24]

Sulfone *endo*-Cl-2b. An inseparable mixture of **10b** and **10i** was obtained in 39% yield; mp 37–39 °C (hexane). Two close methyl signals and two close methylene signals, in a ratio of ca. 1:2, were observed: δ 2.03 and 2.05 (methyls), 3.82 and 3.85 (methylenes), 6.03–6.72 (m, 3, vinylic protons).

Sulfone *endo*-Cl-2d. One isomer was obtained in 68% yield. 3,6-dimethyl-2*H*-thiopyran 1,1-dioxide (**10d**): mp 63–64 °C (ether–hexane); NMR δ 1.98 (s, Me), 2.13 (s, Me), 3.75 (s, 2, C_2 H), 6.09 (br AB q, 2, J = 6.5, $\Delta\nu$ = 30 Hz, C_4 H and C_5 H); IR 1280, 1140, 850, 830 cm^{-1}; UV max 273 nm (ϵ 7550); mass spectrum, m/e 158, 109, 96, 95, 93. 91. Anal. ($C_7H_{10}O_2S$) C, H.

Reaction of 1c with Butyllithium. A solution of n-butyllithium in hexane (0.02 mol) was added dropwise at −78 °C to a suspension of **1c** (4.6 g, 0.02 mol) in THF (60 mL). Stirring was continued for 1 h at that temperature. The reaction was quenched with ammonium chloride solution, and most of the THF was evaporated at reduced pressure. The crude product obtained after the usual workup was chromatographed on silica gel (100 g). Recovered **1c** was eluted first (1.43 g) followed by **9c** (1.76 g, 66% relative to unrecovered **1c**) and then by 3-(dichloromethyl)-3,4-dimethyl-2,3-dihydrothiophene 1,1-dioxide (**20**): yield 0.25 g (8%), mp 140–141 °C (benzene–hexane); NMR δ 1.58 (s, Me), 1.97 (s, Me), 3.43 (AB q, 2, J = 14, $\Delta\nu$ = 40 Hz, C_2 H), 5.87 (s, $CHCl_2$), 6.37 (s, C_5 H); IR 1292, 1110 cm^{-1}; mass spectrum, m/e 230 and 228 (M^+), 193, 166, 164, 145, 129, 117, 79. Anal. ($C_7H_{10}Cl_2O_2S$) C, H.

Reaction of the 2c Isomers with Butyllithium. A solution of n-butyllithium in hexane (1.5 molar equiv) was added to solutions of *exo*-Cl-**2c** or *endo*-Cl-**2c** in THF (25 mL/g) at −78 °C. The cold bath was withdrawn after 0.5 h and the solution allowed to warm to room temperature during 1 h. The crude reaction product from *endo*-Cl-**2c** consisted of **9c** and starting material only (TLC, ^{1}H NMR and chromatographic separation). The crude reaction product from 4 g of *exo*-Cl-**2c** was chromatographed on silica gel (200 g; ether–hexane, 2:3) to yield first 0.68 g (21%) of 4,6-dimethyl-1-oxa-2-thiacyclohepta-3,5-diene 2-oxide (**21**): mp 35–36 °C (pentane); NMR δ 1.73 (br s, C_6 Me) 1.92 (d, $J \approx 1$, C_4 Me), 5.13 (br s, 2, C_7 H), 5.33 (br s, 1, C_5 H), 6.28 (q, 1, $J \approx 1$, C_3 H); IR 1647, 1130, 1105, 930 cm^{-1}; mass spectrum, m/e 158 (M^+), 129, 128, 126, 125, 110, 109. Anal. ($C_7H_{10}O_2S$) C, H.

Thiopyran **9c** was eluted next in 26% yield (0.84 g).

Oxidation of **21** (0.27 g, 1.7 mmol) in dichloromethane (10 mL) with MCPBA (0.31 g, 1.8 mmol), as described above for **15c**, followed by chromatography of the crude product yielded 0.212 g (71%) of a sultone as a distillable oil, 4,6-dimethyl-1-oxa-2-thiabicyclohepta-3,5-diene 2,2-dioxide (**22**): bp 150 °C (bath temperature; 0.013 kPa); NMR δ 1.70 (d, $J \approx 1$, Me), 1.90 (d, $J \approx 1$, Me), 5.24 (s, 2, C_7 H), 5.40 (br s, 1, C_5 H), 6.52 (q, 1, $J \approx 1$, C_3 H); mass spectrum, m/e 174 (M^+), 159, 145, 133, 131, 110, 109, 95, 93, 91. Anal. ($C_7H_{10}O_3S$) C, H.

Reaction of *exo*-Cl-**2d** with butyllithium did not yield any sultine of type **21**.

Registry No. 1a, 30988-35-3; **1b**, 61170-07-8; **1c**, 61170-06-7; *exo*-**1d**, 78655-13-7; *exo*-**1e**, 78655-96-6; *endo*-**1e**, 78592-07-1; **1f**, 78592-08-2; **1g**, 69442-46-2; **1h**, 69442-47-3; *exo*-Cl-**2a**, 78592-09-3; *endo*-Cl-**2a**, 78655-14-8; *exo*-Cl-**2b**, 78592-10-6; *endo*-Cl-**2b**, 78655-15-9; *exo*-Cl-**2c**, 78655-16-0; *endo*-Cl-**2c**, 78655-17-1; *exo,exo*-**2d**, 78592-11-7; *exo,endo*-Cl-**2d**, 78655-18-2; *exo,exo*-**2e**, 78592-12-8; *exo,endo*-Cl-**2e**, 78655-19-3; **3b**, 66463-91-0; **3c**, 63755-66-8; *exo*-**3d**, 78655-20-6; *exo*-**3e**, 78592-13-9; **4b**, 1193-10-8; **4c**, 18214-56-7; **4d**, 10033-92-8; **4e**, 78592-14-0; **4f**, 78592-15-1; **4g**, 42854-47-7; **4h**, 78592-16-2; **5**, 78592-17-3; **6**, 78592-18-4; **7**, 78592-19-5; **8a**, 38412-04-3; **8b**, 61170-15-8; **8c**, 61170-08-9; **8e**, 78592-20-8; **8i**, 61170-14-7; **9a**, 78592-21-9; **9b**, 78592-22-0; **9c**, 61170-09-0; **9d**, 78592-23-1; **9e**, 78592-24-2; **9f**, 78592-25-3; **9g**, 78592-26-4; **9h**, 78592-27-5; **9i**, 61170-19-2; **9j**, 78592-28-6; **10a**, 16805-19-9; **10b**, 28743-50-2; **10c**, 78592-29-7; **10d**, 78592-30-0; **10e**, 78592-31-1; **10i**, 28743-51-3; **11b**, 78592-32-2; **11c**, 78592-33-3; **11e**, 78592-34-4; **12** (R^1 = R^2 = H), 61170-20-5; **12** (R^1 = H; R^2 = Me), 61170-11-4; **12** (R^1 = R^2 = Me), 78592-35-5; **12** (R^1 = H; R^2 = Ph), 78592-36-6; **14c**, 78592-37-7; **14e**, 78592-38-8; **15a**, 78592-39-9; **15b**, 61170-18-1; **15c**, 61170-10-3; **15d**, 78592-40-2; **15e**, 78592-41-3; **15f**, 78592-42-4; **15i**, 61170-17-0; **15j**, 78592-43-5; **16c**, 61170-12-5; **16e**, 78592-44-6; **17c**, 18542-89-7; **18b** (X = H), 61170-21-6; **18c** (X = H), 61170-13-6; **18c** (X = Br), 78592-45-7; **19**, 61170-16-9; **20**, 78592-46-8; **21**, 78592-47-9; **22**, 78592-48-0; chloroform, 67-66-3; dimethyl 4-chloro-3,6-dihydro-5-methyl-3-(3-oxobutyl)phthalate, 78592-49-1; dimethyl 4-chloro-5-methyl-3-(3-oxobutyl)phthalate, 78592-50-4; 3,5-dichloro-2,4-dimethyl-1,3-hexadiene, 78592-51-5; 2,3,5-trimethyl-2-cyclopenten-1-one, 54562-24-2; 2,3,5-trimethyl-2-cyclopenten-1-one 2,4-dinitrophenylhydrazone, 59534-51-9; *trans*-1-chloro-2,4-pentadiene, 78592-52-6; *trans*-1,3-octadien-7-one, 33603-17-7; *trans*-1,3-octadien-7-one 2,4-dinitrophenylhydrazone, 78592-53-7; 2-methyl-2-cyclopenten-1-one, 1120-73-6; 4-chloro-5,6-dihydro-3,6-dimethyl-5-methylene-2*H*-thiopyran 1,1-dioxide, 78592-54-8.