n-butylamine, and 3.75 g of hydrogen sulfide was allowed to react at 100° for 18 hr. Distillation of the product after washing with dilute hydrochloric acid gave **5l** and **5m**: yield 0.55 g (5%); bp 68–69° (45 mm); $n^{20}D$ 1.4799.[26] The nmr spectrum indicates the presence of both *cis* and *trans* isomers of **5l**, although the vpc spectrum shows the presence of 3% **5m**. Vpc analysis does not separate the *cis* and *trans* isomer of **5l**.

The Addition of Hydrogen Sulfide to Diallyl Sulfide. *cis*- and *trans*-2,6-Dimethyldithiane (2a).—Into a solution of 3 g of *n*-dibutylamine and 4.5 g (0.04 mol) of allyl sulfide in 25 ml of benzene was condensed 1.7 g (0.05 mol) of hydrogen sulfide. The solution was heated for 20 hr at 100° in a stainless steel bomb. The product was distilled to give 1.4 g (26%) of **2a**: bp 87° (13 mm); $n^{20}D$ 1.5411.[27]

A vpc spectrum shows two close peaks in a proportion of 34:66, the shorter retention time is assumed to be due to the *trans* isomer. The nmr spectrum supports structure **2a** with two doublets for CH_3 groups at 1.20 and 1.42 ppm in $CDCl_3$, corresponding to six protons.

The Reaction of Hydrogen Sulfide with Pentadiene-1,4.—Under conditions described above, approximately 1% of **3e** was obtained as shown by vpc analysis. The isomeric product **3d** was not observed.

The Reaction of Ethylenimine with Hexadiene 1,5-Monoepisulfide (5o). 2-Methyl-5-aziridinylmethyltetrahydrothiophene (11) and 2-Aziridinylmethyl-1-thiacyclohexane (12).—To a solution of 6.0 g (0.14 mol) of ethylenimine in 25 ml of benzene was added 11.4 g (0.1 mol) of hexadiene episulfide with stirring at 65°. The solution was kept at 65° for 17 hr, then decanted from polymeric residue, and distilled to give 4.7 g of product: bp 50° (0.004 mm); $n^{20}D$ 1.521. Gas chromatographic analysis shows the two components **11** and **12** in a proportion of 50:50 (±2).

Anal. Calcd for $C_8H_{15}NS$: C, 61.09; H, 9.61; N, 8.91; S, 20.39. Found: C, 61.01; H, 9.69; N, 9.13; S, 20.13.

The nmr spectrum of the mixture of **11** and **12** in deuteriochloroform shows a doublet for the methyl group at 1.27 ppm corresponding to 1.5 protons and suggesting the presence of **11** and **12** in equal proportions. Two doublets at 2.27 and 2.17 corresponding to 2.0 protons are assigned to the exocyclic CH_2N group.

Registry No.—**1**, 16728-39-5; **1a**, 16728-40-8; **1b**, 16728-45-3; **1c**, 16728-38-4; **2**, 16728-41-9; **2a** (*cis*), 16728-42-0; **2a** (*trans*), 16727-98-3; **2b**, 16728-43-1; **3a**, 16728-44-2; **3d**, 1613-51-0; **3e**, 1795-09-1; **4**, 16728-25-9; **5a**, 16728-26-0; **5b**, 16728-27-1; **5f** or **g**, 16728-28-2; **5l** (*cis*), 5161-13-7; **5l** (*trans*), 5161-14-8; **5m**, 5161-16-0; **5o**, 6766-70-7; **6**, 16728-32-8; **6a**, 16728-33-9; **7**, 16742-80-6; **11**, 16728-34-0; **12**, 16728-35-1; **14**, 16728-36-2; sulfur dichloride, 10545-99-0.

Acknowledgment.—The author is greatly indebted to the National Research Council, Ottawa, for supporting part of this project, and to D. Johnson and S. Rae for technical assistance.

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[27] F. J. Glavis, L. L. Ryden, and C. S. Marvel, *J. Amer. Chem. Soc.*, **59**, 707 (1937).

The Reaction of Sulfur Dichloride with Cyclic Polyolefins

F. LAUTENSCHLAEGER

Dunlop Research Centre, Sheridan Park, Ontario, Canada

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Sulfur dichloride additions to cyclic polyolefins lead to novel sulfur-containing ring systems. The reaction with cyclooctatetraene, cycloheptatriene, and 1,5,9-cyclododecatrienes was investigated. Intramolecular addition products were obtained in moderate yield to give novel bicyclic sulfides. Of interest are rearrangment reactions of the sulfoxides and sulfones derived from the addition product of sulfur dichloride and cycloheptatriene.

The recently reported addition of sulfur dichloride to cyclic diolefins[1–5] was extended to cyclic tri- and tetraolefins and provides a general synthesis for several unsaturated bicyclic *β,β′*-dichlorosulfides. The observation that bicycloheptadiene leads to a transannular addition product in preference to products resulting from Wagner-Meerwein rearrangement[1] indicated that the reaction could be extended to conjugated cyclic polyolefins, such as cycloheptatriene and cyclooctatetraene. Intramolecular addition was observed in both cases. Results were summarized earlier[4] and details are reported here.[6] The formation of intramolecular addition products from conjugated ring systems in the reaction with sulfur dichloride again emphasizes the unique role of this inorganic sulfenyl chloride in comparison with its organic homologs such as alkylsulfenyl chlorides. For example, the reaction of sulfenyl chlorides with cyclooctatetraene was reported[7] and, although the product was insufficiently characterized, the structure **1** was assumed in analogy to products resulting from addition reactions of cyclooctatetraene involving skeletal rearrangements.[8]

Additions to cyclooctatetraene which proceed partially or predominantly without rearrangement of the carbon skeleton are still exceptions. Examples of this are the addition of cyanoimidogen,[9] carbene,[10] and dicyanocarbene,[11] the epoxidation with peracetic acid,[7,12] and the 1,2 cycloaddition of 1,1-dichloro-2,2-difluoroethylene.[13] Furthermore, the significant studies of Huisgen[14] demonstrated that, in the particular case of the addition of bromine to cyclooctatetraene, the reaction proceeds at −55° without skeletal rearrangement to give a 1,2-addition product, and that ring

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[1] F. Lautenschlaeger, *J. Org. Chem.*, **31**, 1679 (1966).

[2] E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966).

[3] E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

[4] F. Lautenschlaeger in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, p 73; F. Lautenschlaeger, The Princeton University Conference on the Chemistry of Sulfides, June 29, 1966.

[5] F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966).

[6] In an independent investigation just prior to the submission of this paper the reaction of 1 and 2 mol of sulfur dichloride with cyclooctatetraene was reported and the resulting structures were determined on the basis of their nmr spectra: P. Y. Blanc, P. Diehl, H. Fritz, and P. Schlapfer. *Experientia*, **23**, 896 (1967).

[7] H. Brintzinger and M. Langheck, *Ber.*, **86**, 557 (1953); H. Brintzinger and H. Ellwanger, *ibid.*, **87**, 300 (1954).

[8] See, for example, W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

[9] A. G. Anastassiou, *J. Amer. Chem. Soc.*, **87**, 5512 (1965).

[10] T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964); E. Vogel, *Angew. Chem.*, **74**, 829 (1962).

[11] E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

[12] A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **80**, 5505 (1958).

[13] G. Schroder and Th. Martini, *Angew. Chem. Intern. Ed. Engl.*, **6**, 806 (1967).

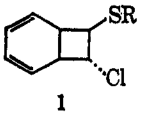
[14] G. Boche and R. Huisgen, *Tetrahedron Lett.*, No. 23, 1769 (1965); R. Huisgen, G. Boche, W. Hechtle, and H. Huber, *Angew. Chem. Intern. Ed. Engl.*, **5**, 585 (1966).

constriction occurs at 0° or in the presence of aluminum trichloride to form a bicyclic dibromide. Thus it was unambiguously demonstrated that tautomerization of cyclooctatetraene to bicyclo[4.2.0]octa-2,4,7-triene is not the initial reaction in addition reactions which ultimately proceed *via* rearrangement.

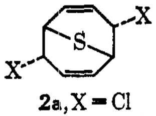
In our investigations of the reaction products which could conceivably consist of a number of novel ring systems, structural assignments were primarily based on nuclear magnetic resonance spectra and on the shielding effect of the sulfoxide oxygen in the spectrum of the derived sulfoxides and sulfones.

Sulfur dichloride reaction with cyclooctatetraene and cycloheptatriene is essentially one of equimolar proportion of reagents. At −10° in methylene chloride as solvent, only a 0.04 molar equiv of cyclooctatetraene remains unreacted. This suggests that unidentified polymeric products arise from an equimolar addition and that by-products corresponding to a reaction of sulfur dichloride with 2 molar equiv of tetraene analogous to the addition of sulfuryl chloride[7] contribute only to a negligible proportion.

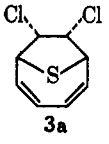
The intramolecular reaction product **2a** is obtained in a yield of 31%. When the addition reaction was carried out at 30°, no isomeric product was obtained as evidenced by gas chromatographic analysis, although, in several cases of repeated additions, evidence for a second product with very close retention time and in a yield of less than 2% was observed. The symmetrical structure **2a** for the major reaction product is suggested by the observation that a single sulfoxide was obtained on oxidation with hydrogen peroxide and that the same sulfoxide was recovered after attempted inversion with triethyloxonium fluoroborate,[5,15] suggesting the symmetrical structure **4**. This structure is further supported by the nuclear magnetic resonance spectrum, where two multiplets with centers 0.22 ppm apart represent protons CHCl, of which the signal at higher field (4.81 ppm) corresponds to the chemical shift of that proton in the sulfide **2a**. This suggests deshielding of only one of the protons H_c and rules out the isomeric structures **3a** and **3b**. As anticipated, in the sulfone **5** the protons H_c are again identical but only 0.11 ppm downfield from their positions in the sulfide **2a**. This deshielding effect is smaller than in the oxidized derivatives of the earlier reported bi- and tricyclic β,β'-dichlorosulfides.[1,5]



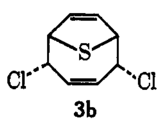
1



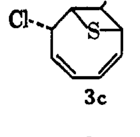
2a, X = Cl
b, X = OH
c, X = H



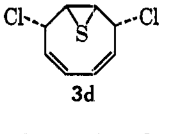
3a



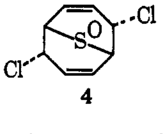
3b



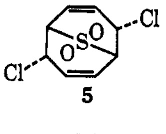
3c



3d



4



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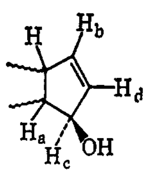
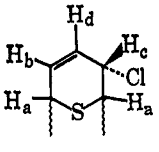
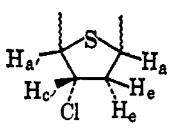


6a



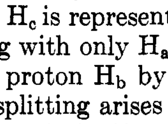
6b



6c

For the configurational assignments of **2a** and its hydrolysis product **2b**, a comparison with the nuclear magnetic resonance spectrum of the ring structure **6a** is of interest.[16] In the latter system, H_c is of opposite configuration with respect to H_a than it is in the six-membered section **6b** of structures **2a** and **2b**. Consequently, the spectrum of **6a** shows a quartet for H_c, resulting from coupling of H_c with H_a and H_d, a quartet for H_d, and a doublet for H_b. In the opposite configuration as shown in **6b**, H_c is represented by a doublet, resulting from coupling with only H_a. Proton H_d is represented by one and proton H_b by two perturbed doublets, whereby the splitting arises from coupling of H_b with both H_a and H_d. A significant difference between the ring system **6a** and the system **6b** is shown by the relative chemical shift of the olefinic protons. Whereas H_d is downfield from H_b in the ring system **6a**, inversion of these positions occurs in **6b** as the result of the proximity of the sulfur atom, which affects H_b to a larger extent than H_d.

Cycloheptatriene leads to the intramolecular addition product **7a** in a yield of 35%. In the nuclear magnetic resonance spectrum, the olefinic and allylic protons in **7a** and its hydrolysis product **7b** resemble those of product **2a** and **2b**. In addition, a sextet pattern observed for $H_{c'}$ at 4.32 ppm corresponding to a single proton suggests the nonequivalence of both CHCl groups and rules out the hypothetical isomeric structures **17** and **18**. The magnetic equivalence of protons H_e[17] explains the sextet pattern for $H_{c'}$ which was also observed on a similar ring system **6c**.[3] This result supports the *trans* configuration of the chlorine with respect to the sulfur atom in the five-membered ring of structure **7a**, which is further supported by a coupling of 4.5 cps between $H_{c'}$ and the bridgehead proton $H_{a'}$.



7a, $X_1 = X_2 = Cl$
b, $X_1 = X_2 = OH$
c, $X_1 = OH$; $X_2 = Cl$

Nucleophilic substitution occurs very readily on the β,β'-dichlorosulfides **2a** and **7a**, although the products are obtained in lower yield than would be expected on the basis of the reaction of similar saturated cyclic chlorosulfides.[1-5] Substitution occurs without rearrangement as demonstrated by the isolation of **2b** and **7b**. The structure **7b** for the diol is supported by the characteristic pattern for the olefinic protons in the nmr spectrum for both dihydroxysulfides **2b** and **7b** and the chlorohydroxysulfide **7c**. The nonidentity of both groups CH–O, indicated by two doublets for these protons at 4.81 and 4.91 ppm, further supports the structure **7b** in preference to an isomeric symmetric structure. Reduction of the dichlorosulfide **2a** with lithium aluminum hydride leads to the novel olefinic sulfide **2c** in low yield.

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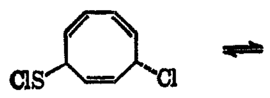
(15) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

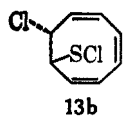
(16) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, p 86.

(17) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

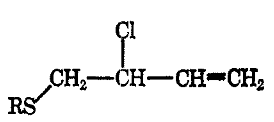
The *trans* or *endo* configuration for the allylic chlorine atom can be rationalized by the assumption of an intermediate episulfonium ion following from the stereochemistry of previously reported additions of sulfur dichloride to cyclic diolefins. The ease of conversion of the diols **2b** and **7b** to the corresponding dichlorides and vice versa supports the involvement of the sulfur atom in these replacement reactions. The stereospecificity of the sulfur dichloride addition and subsequent replacement reactions was particularly remarkable in the products obtained from cyclohexadiene-1,4[3] where in substitution reactions the nucleophile has to approach from the *endo* side of the bicyclic molecule. This is further emphasized on our ring systems **2** and **7**, where the episulfonium intermediate could conceivably compete with an allylic carbonium ion. Participation of such open ions would be expected to yield contribution of products resulting from an *exo* approach of the chloride ion, which was not observed. It is of interest to consider the various episulfonium ions which could be involved in the reaction with cyclooctatetraene and cycloheptatriene. After formation of the intermediates **13a** and **b** in the first addition step, the central location of the sulfur atom of the sulfenyl group in the eight-membered ring could in the second addition step lead to various intermediate ions. These ions can be envisaged by inspection of structures **2a** and **3a** to **3d** after removal of one chloride ion. In each case, the corresponding episulfonium ion or the open allylic carbonium ion are alternative possibilities. The probability of contributions of these various ions would be affected predominantly by the steric requirements of the carbon–sulfur bonds.[18] The formation of product **2a** suggests that the contribution of these intermediates is negligible. It is apparent that the strain required for the sulfur containing ring in the majority of these intermediates is not compensated by the conjugation of the remaining double bonds. Furthermore, it is of interest that, on the basis of the observed product, it cannot be decided whether the reaction of sulfur dichloride with cyclooctatetraene involves two consecutive 1,2 additions or two 1,4 additions *via* **13a** or **13b**, respectively. Our observation, that 1,2 addition proceeds with butadiene-1,3 to give **14**, suggests the first alternative to be more likely. This is further supported by the addition product from cyclooctadiene-1,3[2] for which the structure **15** was established, and which can only result from two consecutive 1,2 additions. The preference for the addition of sulfur dichloride to conjugated olefins in such a manner that the chlorine atom is located in the allylic position is also supported by the product **14** obtained from butadiene-1,3, which consists almost exclusively of the structure shown in preference to the isomeric 1,4 addition product.



13a

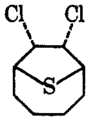


13b



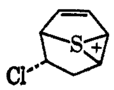
$RSCH_2-CH(Cl)-CH=CH_2$

14

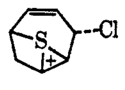


15

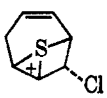
The ambiguity of 1,4 *vs.* 1,2 addition does not exist in the addition to cycloheptatriene, where the alternative episulfonium intermediates should be different. Structures **16a** and **16c** result from two consecutive 1,2 additions and **16b** from an initial 1,4 addition to a terminal double bond. A more strained intermediate, **16d**, results from an initial 1,4 addition to the central double bond of the triene. Therefore, the product can only be explained to result from 1,2 additions. Furthermore, the product obtained from cycloheptatriene can only be rationalized by an initial addition to the terminal olefinic site in preference to addition to the central double bond. Gas chromatographic analysis suggests the formation of isomeric products in a yield of less than 2%. Contributions of structures **17** and **18** could therefore only be small.



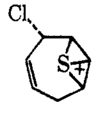
16a



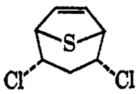
16b



16c



16d



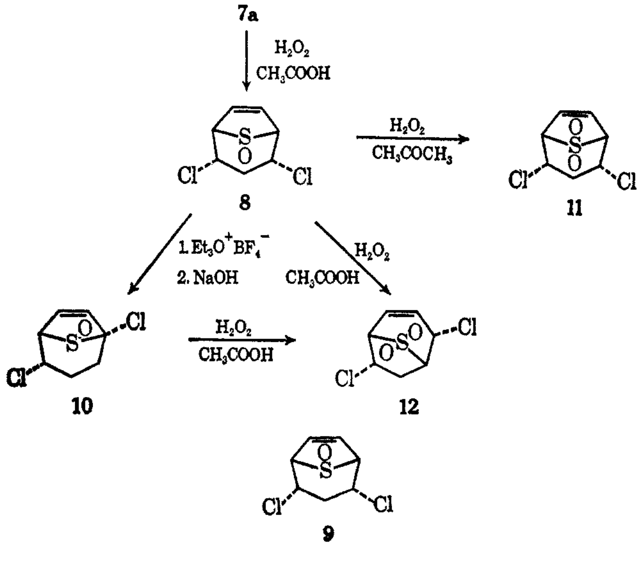
17

18

A sequence of unexpected rearrangements is observed in the series of oxidation products obtained from **7a** (Scheme I). Oxidation of the dichlorosulfide **7a** with hydrogen peroxide in glacial acetic acid leads to the rearranged sulfoxide **8** as the exclusive product in a yield of 97%. No evidence for the presence of an isomeric product was obtained. The structure of **8** is evident from its nuclear magnetic resonance spectrum, which shows a doublet for the olefinic protons at 5.63 ppm corresponding to two protons. A narrow multiplet of a half-width of 8 cps for both groups CHCl is exhibited at 4.99 ppm. The downfield chemical shift for these protons suggests their exposure to the deshielding by the sulfoxide group and therefore supports the sulfoxide configuration as shown in **8**.

Inversion of **8** with triethyloxonium fluoroborate is again accompanied by rearrangement and leads to **10** as the only isolated product. No evidence for the isomeric product **9** was observed. The structure of **10** is

Scheme I



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(18) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620 (1968).

evident from its nuclear magnetic resonance spectrum which resembles **7a** except for the shielding and deshielding introduced by the sulfoxide group (Table I). The CHCl group in allylic position has shifted from 4.71 ppm in **7a** to 5.37 ppm in **10**. This deshielding of H_c is in opposite direction but of comparable magnitude as reported earlier in a similar bicyclic system.[1] In contrast, the effect on H_b is only 0.09 ppm, although both represent β hydrogens with respect to the sulfur atom. The large effect on H_c suggests the pseudo-axial position of that hydrogen and supports the assigned configuration of **7a**. Although the carbon atoms bearing protons H_b and H_c are nearly equidistant to the sulfoxide group, the different spatial arrangement of the carbon–hydrogen bonds leads to large differences in the deshielding of these protons. The largest deshielding is exhibited by H_d, which is spatially closest to the oxygen atom of the sulfoxide group. For the assignment of the position of the sulfoxide group, it is significant that chemical shifts for H_e and $H_{c'}$ in structure **10** are nearly identical with **7a**. The orientation of the S=O bond in isomer **10**, which is on the side of the olefinic unsaturation after inversion of isomer **8**, supports the opposite assignment of the S=O bond in **8**. The small deshielding actually observed on $H_{c'}$, which is located in line but on the back side of the sulfoxide bond, will be confirmed on a later example in this paper.

TABLE I

CHEMICAL SHIFTS OF DICHLORO-8-THIABICYCLO[3.2.1]OCTENE AND DERIVATIVES[a]

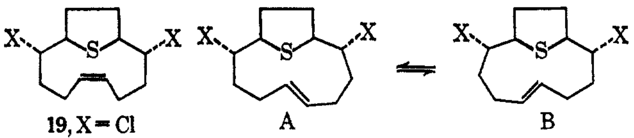
	H_b	H_d	H_c	H_c'
Dichlorosulfide **7a**	5.72	5.18	4.71	4.32
Dihydroxysulfide **7b**[b]	5.92	5.47	4.78	
Dichlorosulfoxide **8**	5.63		4.99	
Dichlorosulfone **11**	5.88		5.17	
Dichlorosulfoxide **10**	5.83	6.16	5.37	4.50
Dichlorosulfone **12**	5.98		5.32	4.91

[a] Values in parts per million downfield from tetramethylsilane, recorded on a Varian A-60 spectrophotometer in deuteriochloroform as solvent. [b] Pyridine as solvent.

Further rearrangement is observed on oxidation of **8** to the oxidation state of the sulfone. If the oxidation is carried out with hydrogen peroxide in glacial acetic acid, an identical sulfone is obtained from both sulfoxides **8** and **10**, but oxidation with hydrogen peroxide in acetone leads to the nonidentical sulfones **11** and **12**, respectively. Although **11** is only isolated in a yield of 51%, **12** is obtained quantitatively from both sulfoxides.

The rearrangement of **7a** on oxidation and its exclusive formation provides a further example of rearrangement of carbon–sulfur bonds arising from steric interaction with electronegative substituents. In earlier examples, the β substituent was either an acetoxy group[19] or a chlorine group, for example, on oxidation of 2,5-chloromethyltetrahydrothiophene.[18] It is of interest that in the case of both ring systems substitution of the β substituent proceeds without rearrangement, whereas oxidation of the sulfides does involve it. In the rearrangement of **7a** to **8**, the predominant factor appears to be the repulsion of the peroxide molecule by the olefinic double bond, which prevents the formation of a sulfoxide with the sulfur–oxygen bond on the side of the olefinic double bond. The rearrangement on inversion of **8** to **10** suggests that the interaction with the olefinic site is partially relieved in **10**. The unusual aspect of this over-all reaction sequence is that the isolation of the sulfone **12** from its sulfide **7a** occurs *via* two rearrangements. These rearrangements are distinctly different from the base-catalyzed isomerizations of β-unsaturated sulfones to their α-unsaturated isomers.[20]

The reaction of sulfur dichloride with cyclic nonconjugated triolefins leads to bicyclic β,β'-dichlorosulfides in which the remaining unsaturation provides substances of synthetic interest. *trans,trans,cis*-Cyclododecatriene-1,5,9 leads to **19** in a yield of 69%, whereas the corresponding *trans,trans,trans* isomer leads to **20** in a yield of 41%. The structure of the products was assigned by analogy to the product obtained from the addition of sulfur dichloride to hexadiene-1,5, where of the possible five-, six- or seven-membered sulfur-containing ring the smallest possible ring system was formed.[18] Addition across the two *trans* bonds of the trienes is therefore assumed to lead to the 2,5-substituted tetrahydrothiophene structure as shown in **19** and **20**. The presence of the *cis* double bond in **19** and the *trans* double bond found in **20** follows from the infrared absorption spectra, which show the characteristic absorption for the remaining *trans* double bond in **20** at 980 cm^{-1} and for the *cis* unsaturation in **19** at 728 cm^{-1}. Substitution reactions proceed readily on the dichlorosulfides and products **21** and **22** were isolated by using the appropriate nucleophiles. The structure of the product **22** is further supported by its nuclear magnetic resonance spectrum which shows a single signal for both acetoxy groups, indicating that both groups are in identical environment whereby this identity arises from free rotation of the olefinic site to include the conformations A and B.



19, X = Cl
21, X = CN

A

B

20, X = Cl
22, X = OCOCH$_3$

In structures such as **2a** in which two olefinic sites are available for further addition reactions, a second intramolecular addition of sulfur dichloride was achieved and the addition product was obtained in a yield of 20%.[6] For the resulting product three tricyclic structures can be envisaged, with a further multiplicity arising from the various possible configurations of the carbon–chlorine bonds. The structure is evident from considerations of the resulting sulfoxides. A single monosulfoxide is formed by oxidation with hydrogen peroxide in acetic acid, indicating the formation of **23** or **24** and also that the four six-membered rings are of identical configuration. Such a configuration results from two consecutive *trans* additions, in agreement with the mechanism of addition of sulfenyl chlorides and sulfur dichloride to olefinic sites. However, the isolation of a single sulfoxide does not permit us to distinguish between these alternative ring systems **23** and **24**. The

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(19) J. Hora and J. Czerny, *Collect. Czech. Chem. Commun.*, **25**, 711 (1960); *Chem. Abstr.*, **54**, 13113*h* (1960).

(20) R. C. Krug and D. E. Boswell, *J. Heterocycl. Chem.*, **4**, 309 (1967).

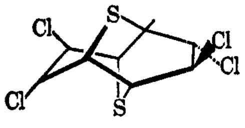
Table II

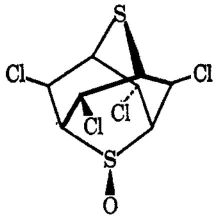
Chemical Shifts of Tetrachlorodithiaadamantane and Derivatives[a]

Compound	CHCl		$\mathrm{CH_a\overset{O}{S}CH_{a'}}$	$\mathrm{CH_aSCH_{a'}}$
Sulfide **24**	5.68 (4)[b]		. . .	3.04 (4)
Monosulfoxide **25**	5.88 (1), 5.68 (2), 5.11 (1)		4.15 (2)	3.32 (1), 3.13 (1)
Disulfoxide **26**	5.95 (2)	5.14 (2)	4.27 (1), 4.16 (1), 4.07 (1)	

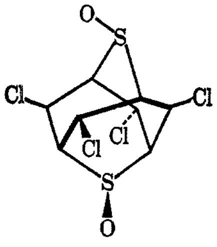
[a] Values are in part per million downfield from tetramethylsilane, recorded on a Varian HA-100 spectrophotometer in deuterioacetic acid as solvent at 27.5° ($\delta \pm 0.01$ ppm). [b] Numbers in parentheses indicate the number of protons as shown by integration values.

further observation that a single disulfoxide is formed confirms the stereochemical conclusions evident from the monosulfoxide and in addition can only be explained on the basis of the highly symmetrical structure **24**. In addition, the nuclear magnetic resonance spectra of the sulfide **24**, the monosulfoxide **25**, and the disulfoxide **26** are readily interpreted by the aid of shielding and deshielding effects of the sulfoxide groups and reliable quantitative data of this effect can be obtained from the spectra of these rigid tricyclic structures (Table II). In the sulfide **24**, the protons adjacent to sulfur ($\mathrm{H_a}$ and $\mathrm{H_{a'}}$) are represented by a multiplet at 3.04 ppm and protons adjacent to chlorine (CHCl) by a multiplet at 5.68 ppm. On conversion to the monosulfoxide **25**, one of the protons adjacent to chlorine is shifted upfield by 0.57 ppm, in very good agreement with that shielding effect on a similar rigid tricyclic system[1] where a shift of 0.53 ppm was observed. In the same monosulfoxide **25** a proton corresponding to a second CHCl group, which is located in line with the sulfoxide group behind the sulfur atom, is deshielded to a smaller extent (0.20 ppm). The remaining two CHCl protons remain unaffected if their chemical shift is compared with the corresponding sulfide **24**, since both are not located within the range of the magnetic anisotropy of the sulfoxide group.


23

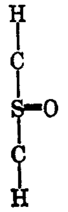

24

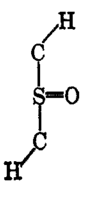
In the disulfoxide **26** the nuclear magnetic resonance spectrum shows similar symmetry as in that of **24**.


26

Two groups CHCl are shielded by 0.54 ppm compared with their position in **24** and the remaining two groups CHCl which are located in line with the sulfoxide group behind the sulfur atom are shielded by 0.27 ppm in good agreement with the observation on **25**.

Further evidence for structure **24** in preference to isomeric structures results from the inspection of the hydrogen atoms in α position with respect to sulfur.


Ia


Ib

Molecular models indicate that only in the dithiaadamantane structure **24** these hydrogen atoms are in a W-shaped relationship within the group HCSCH and are therefore symmetrically oriented with respect to the sulfoxide bond (Ia). In the alternative transannular sulfur dichloride addition products **23**, both groups of HCSCH are arranged as shown in Ib, where one of these hydrogens is *syn* with respect to the sulfoxide group and the second is *anti*. As a consequence, one proton should be in the region of deshielding of the sulfoxide group in structures containing the arrangement as shown in Ib. Therefore, these protons should be nonidentical in the nuclear magnetic resonance spectrum. Although structures **24**–**26** are clearly evident from previous considerations, it was observed that the protons of the group CHSCH in **25** and of both groups CHSOCH in **26** are magnetically nonequivalent (Table II). Inspection of molecular models indicates that this nonidentity arises from a deshielding of one of these protons within these groups by the sulfoxide oxygen atom attached to the nonadjacent sulfoxide group. The magnitude of this effect is remarkable when one considers the fact that the deshielded proton is attached to a carbon in γ position with respect to this sulfoxide group.

The study of the magnetic anisotropy of the sulfoxide group in these polycyclic sulfides provides a convenient method for structural analysis of polycyclic products obtained from sulfur dichloride additions to cyclic polyolefins.

Experimental Section

Nucler magnetic resonance spectra were recorded on a Varian A-60 instrument; chemical shifts are measured downfield from tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 422 grating instrument in potassium bromide pellets. Gas chromatography spectra were obtained on a Perkin-Elmer Model 800 chromatograph. Melting points were measured on a Hallenkamp block and are uncorrected.

The Reaction of Sulfur Dichloride with Cyclooctatetraene. 2,6-Dichloro-9-thiabicyclo[3.3.1]3,7-nonadiene (2a). A.—A solution of 103 g (1 mol) of freshly distilled sulfur dichloride dissolved in 500 ml of methylene chloride was added with stirring to a solution of 104 g (1 mol) of cyclooctatetraene at an internal temperature of −20 to −10°. The solution was kept at −20° for 12 hr. Gas chromatographic analysis indicated the presence of 0.04 mol of unreacted tetraene although a test for sulfenyl chloride was negative. Evaporation of the solvent and distillation yielded 44% of crude product **2a** which partially turns into a tarry material. Recrystallization from hexane yielded an analytical sample, mp 101–102°, in a yield of 31%. *Anal.*

Calcd for $C_8H_8Cl_2S$: C, 30.99; H, 2.60; Cl, 45.73; S, 20.68. Found: C, 31.15; H, 2.65; Cl, 45.65; S, 20.50. The ir spectrum of **2a** shows strong absorption at 1043, 796, 724, 714, 737, and 703 cm^{-1}.

B. From 2b and Hydrogen Chloride.—A solution of 0.17 g (0.001 mol) of **2b** was dissolved in 10 ml of concentrated hydrochloric acid. Precipitation occurred at once. Filtration of the crystalline product after 30 min, drying over calcium chloride, and sublimation provided 0.07 g (36%) of **2a**, mp 101–102°, identified by mixture melting point and its ir spectrum.

2,6-Dihydroxy-9-thiabicyclo[3.3.1]nonadiene-5 (2b).—A suspension of 3 g of the dichlorosulfide **2a** in 50 ml of water containing 6.0 g of sodium carbonate was stirred rapidly at 80° for 5 min, traces of tarry material were filtered off and the aqueous solution was continuously extracted with diethyl ether to give 1.15 g of diol **2b**, mp 176–179°. *Anal.* Calcd for $C_8H_{10}O_2S$: C, 56.47; H, 5.93; S, 18.87. Found: C, 56.30; H, 5.99; S, 18.70. The ir spectrum of **2b** shows major absorption peaks at 3280, 1035, 1011, and 839 cm^{-1}.

Bicyclo-9-thia[3.3.1]2,6-nonadiene (2c).—A solution of 10.3 g (0.05 mol) of **2a** in diethyl ether was refluxed with 1.14 g (0.03 mol) of lithium aluminum hydride until a gas chromatogram indicated the absence of starting material. The suspension was treated with 50 ml of dilute sulfuric acid and filtered; the organic layer was taken up with 20 ml of benzene, washed with water, dried ($MgSO_4$), and evaporated to give 4.6 g of product. Distillation at 75° (0.02 mm) gave 1.0 g of **2c**, $n^{20}D$ 1.5742. *Anal.* Calcd for $C_8H_{10}S$: C, 69.57; H, 7.30; S, 23.19. Found: C, 69.40; H, 7.59; S, 22.86.

The ir spectrum shows strong absorption at 3020, 2880, 1641, 1422, and 700 cm^{-1} and the nmr spectrum ($CDCl_3$) shows four olefinic protons in the region of 5.4–6.3 ppm and the protons due to the groups CHS are represented as a multiplet at 3.40 ppm.

2,6-Dichloro-9-thiabicyclo[3.3.1]nonadiene 9,9-Dioxide (5).—To a solution of 0.72 g (0.0035 mol) of **2a** in 20 ml of glacial acetic acid was added 0.6 g of 50% aqueous hydrogen peroxide. The solution was allowed to evaporate at room temperature to 5 ml and 0.15 g of product was filtered off. The mother liquor on complete evaporation gave another 0.75 g of product. Sublimation of both products provided a pure material, mp 143–145°. *Anal.* Calcd. for $C_8H_8Cl_2O_2S$: C, 40.2; H, 3.38; S, 13.38; Cl, 29.7. Found: C, 40.4; H, 3.42; S, 13.30; Cl, 29.7.

2,6-Dichloro-9-thiabicyclo[3.3.1]nonadiene 9-Oxide (4).—Sulfide **2a** (3 g, 0.0145 mol) was allowed to react with 1 g of 50% aqueous hydrogen peroxide as described under the preparation of **5**. Sulfoxide (3.1 g) was obtained which was purified by recrystallization from water until mp 131.5–133.5° was obtained. *Anal.* Calcd for $C_8H_8Cl_2OS$: C, 43.08; H, 3.62; Cl, 31.80; S, 14.3. Found: C, 43.06; H, 3.64; Cl, 31.86; S, 14.4.

Attempted Inversion of 4 with Triethyloxonium Fluoroborate.—To a solution of 0.22 g (0.001 mol) of **4** in 5 ml of methylene chloride was added 0.19 g (0.001 mol) of triethyloxonium fluoroborate. After the solution had been kept at room temperature for 12 hr, the solvent was partially evaporated to 2 ml to give 0.17 g of adduct, mp 133° dec. On further evaporation, another 0.13 g of product was obtained. *Anal.* Calcd for $C_{10}H_{13}BCl_2F_4O$: C, 35.43; H, 3.86. Found: C, 35.61; H, 3.61.

To a solution of 0.25 g of sodium hydroxide in 5 ml of water was added 0.125 g of the adduct. After stirring for 5 min, the crystalline product was filtered off, washed with water, and air dried to give 0.06 g of **4**, mp 133.5–135°. The product was identified by mixture melting point and by its infrared absorption.

The Reaction of Sulfur Dichloride with Cycloheptatriene. 2,6-Dichloro-8-thiabicyclo[3.2.1]3-octene (7a). A.—Solutions of 257.6 g (2.8 mol) of freshly distilled cycloheptatriene and 288.4 g (2.8 mol) of sulfur dichloride in 500 ml of methylene chloride were allowed to react by approximately equivalent addition into 500 ml of methylene chloride, which was maintained at −20°. After the reaction was complete, gas chromatographic analysis showed 6% of the cycloheptatriene to be unreacted. After evaporation of solvent, gas chromatographic analysis on the residue showed 41% product **7a**. Distillation at 86–88° (0.003 mm) gave 191 g (35%) of **7a**, which slowly crystallizes at room temperature. Recrystallization from hexane increased the melting point to 47.5–49°.

B.—To 30 ml of concentrated hydrochloric acid was added 0.9 g (0.006 mol) of diol **7b**. The mixture was stirred for 1 hr, kept at +5° for 12 hr, and filtered to give 0.85 g of **7a**, mp 46–48.5°. Sublimation did not increase the melting point of the product. *Anal.* Calcd for $C_7H_8Cl_2S$: C, 43.10; H, 4.13; S, 16.41; Cl, 36.36. Found: C, 43.13; H, 4.27; S, 16.32; Cl, 36.21.

In the nmr spectrum (deuteriochloroform) the perturbed quartet arising from H_b is located at 5.72 ppm and the doublet corresponding to H_d at 5.12 ppm. A small coupling of approximately 1 cps is observed on H_b and H_c.

2,6-Dihydroxy-8-thiabicyclo[3.2.1]3-octene (7b).—An amount of 40 g of the crude reaction product of sulfur dichloride and cycloheptatriene, which contained 41% **7a**, was added in] 5-g portions to a boiling solution of 38.2 g of sodium carbonate in 500 ml of water. After high-speed stirring for 15 min, the suspension was allowed to cool and then shaken with 200 ml of diethyl ether to extract ether soluble portions of the separated oily layer. Subsequently, the decanted aqueous solution was continuously extracted for 24 hr with diethyl ether to give, after evaporation, 6.0 g of **7b**, mp 179–181°. Recrystallization from chloroform increased the melting point to 188.5–190°. *Anal.* Calcd for $C_7H_{10}O_2S$: C, 53.16; H, 6.37; S, 20.23. Found: C, 53.37; H, 6.50; S, 20.22.

In the nmr spectrum of **7b** (pyridine) the perturbed quartet of H_b is located at 5.92 ppm and the doublet due to H_d at 5.47 ppm.

2-Hydroxy-6-chloro-8-thiabicyclo[3.2.1]3-octene (7c).—From the water-insoluble portion of the hydrolysis of **7a** described above, 1.2 g of **7c** was obtained by extraction with 250 ml of hexane, and chilling of the extract, mp 95.5–98°. Sublimation did not increase the melting point further. *Anal.* Calcd for C_7H_9ClOS: C, 47.6; H, 5.14; S, 18.12; Cl, 20.8. Found: C, 47.61; H, 5.78; S, 17.76; Cl, 19.82.

In the nmr spectrum of **7c** (deuteriochloroform) the perturbed doublet due to H_b is located at 5.80 ppm and the doublet for H_d at 4.49 ppm.

Oxidation of 2,6-Dichloro-8-thiabicyclo[3.2.1]3-octene with Hydrogen Peroxide. 2,4-Dichloro-8-thiabicyclo[3.2.1]6-octene 8-Oxide (8).—To a solution of 4.4 g (0.0225 mol) of **7a** in 25 ml of glacial acetic acid was added 1.6 g (0.0225 mol) of hydrogen peroxide (50%). The solution was allowed to evaporate to give 4.6 g (97%) of product, mp 90–95°. Recrystallization from heptane increased the melting point to 102–103.5°. *Anal.* Calcd for $C_7H_8Cl_2OS$: C, 39.82; H, 3.82; Cl, 33.59; S, 15.28. Found: C, 40.49; H, 3.73; Cl, 33.38; S, 15.29.

The ir spectrum shows major bands at 1223, 1058, 792 and 773 cm^{-1} and is identical in detail in both the crude oxidation product of **7a** and the purified sample **8**. The nmr spectrum of **8** (hexachlorobutadiene, 80°) shows a doublet for the olefinic protons at 5.63 ppm, multiplets for the groups CHCl at 4.99 ppm, for CHS at 3.7 ppm and for the methylenic protons at 2.75 ppm, each corresponding to two protons.

2,6-Dichloro-8-thiabicyclo[3.2.1]3-octene 8-Oxide (10).—To a solution of 4.4 g (0.02 mol) of **8** in 50 ml of methylene chloride was added 3.8 g (0.02 mol) of triethyloxonium fluoroborate. After standing at room temperature for 5 hr, the solution was evaporated to 25 ml and chilled to −20°; 2.5 g of adduct A, mp 138° dec, was filtered off. *Anal.* Calcd for $C_9H_{13}BF_4Cl_2OS$: C, 33.03; H, 3.98; S, 9.79; Cl, 21.71. Found: C, 32.88; H, 4.04; S, 10.25; Cl, 22.09. On complete evaporation of the solvent, another 5.0 g of adduct was obtained (B).

A.—A suspension of 2.0 g (0.005 mol) of A was stirred for 2 min with 25 ml of 5% aqueous sodium hydroxide. The suspension was filtered and air dried to give 1.0 g (94%) of crude **10**, mp 103–107°. Recrystallization from 80 ml of water increased the melting point to 115–116°. *Anal.* Calcd for $C_7H_8Cl_2OS$: C, 39.82; H, 3.82; Cl, 33.59; S, 15.28. Found: C, 39.56; H, 3.41; Cl, 33.63; S, 15.40.

The infrared spectrum shows major peaks at 1068 cm^{-1} for the sulfur–oxygen stretching mode and 794 and 776 cm^{-1} for the carbon–chlorine stretching mode. Medium intensity peaks are observed at 1300, 887, 874, and 703 cm^{-1}.

B.—A suspension of 5.0 g of B in 50 ml of 5% aqueous sodium hydroxide was stirred for 5 min, filtered, the residue washed with water and air dried to give 2.3 g of product, mp 85–100°. The nmr spectrum of the crude product showed only signals due to **10**. The ir spectrum of the crude product is identical with that of the purified material.

2,6-Dichloro-8-thiabicyclo[3.2.1]3-octene 8,8-Dioxide (12). A.—To a solution of 0.42 g (0.002 mol) of **10** in (20 ml) glacial acetic acid was added 0.3 g of hydrogen peroxide (45% in water). The solution was kept at 60° for 24 hr and was then evaporated to 10 ml to give 0.1 g of **12**, mp 140–142°. Complete evaporation of the mother liquor yielded another 0.35 g of **12**, mp 141–142°, total yield 99%. *Anal.* Calcd for $C_7H_8O_2Cl_2S$: C, 37.00; H, 3.55; Cl, 31.24; S, 14.12. Found: 37.24; H, 3.41; Cl, 31.27; S, 14.04. The compound shows strong infrared absorption at 1320, 1183, 1112, and 792 cm^{-1}. In the nmr spectrum ($CDCl_3$) the olefinic protons are represented by a narrow multiplet at 5.98 ppm, the allylic CHCl group signal (doublet) is located at 5.32 ppm and the second CHCl group at 4.91 ppm.

B.—To a solution of 0.42 g (0.002 mol) of **8** in 20 ml of glacial acetic acid was added 0.3 g of hydrogen peroxide (45% in water). The solution was heated at 60° for 10 hr and evaporated to dryness and the residue, 4.5 g, mp 123–126°, was recrystallized from ethanol to give a product of mp 138–139.5°. Sublimation provided an analytical sample, mp 142–143°.

The ir spectrum of the purified material is in detail identical with that of the crude reaction product. Mixture melting point with the product obtained from **10** is not depressed.

2,4-Dichloro-8-thiabicyclo[3.2.1]-6-octene 8,8-Dioxide (11).—To a solution of 0.42 g (0.002 mol) of **8** in 20 ml of acetone was added 0.3 g of hydrogen peroxide, the solution was refluxed for 4 hr and then evaporated to dryness to give 0.45 g of partially crystalline material, which was stirred with water, filtered, dried over phosphorus pentoxide, and showed mp 96–99°; the yield was 0.22 g (51%). Sublimation produced an analytical sample, mp 102–103°. *Anal.* Calcd for $C_7H_8Cl_2O_2S$: C, 37.00; H, 3.55; Cl, 31.24; S, 14.12. Found: C, 37.17; H, 3.40; Cl, 31.35; S, 14.00. The infrared spectrum shows major absorption peaks at 1020, 1108, 840 cm^{-1} with medium intensity peaks at 1490, 1425, 1271, 1225, 1158 and 928 cm^{-1} and is not identical with **12**.

The Reaction of Sulfur Dichloride with Butadiene-1,3 (14).—Into a 2-l. round-bottom flask containing 800 ml of dry methylene chloride and cooled to −60 to −70° was condensed 378 g (7 mol) of butadiene. An amount of 348 g (3.38 mol) of sulfur dichloride was added dropwise, maintaining the internal temperature at −60°. After standing at −20° for 12 hr the volatile portions were evaporated to give 670 g (94%) of product. *Anal.* Calcd for $C_8H_{12}Cl_2S$: C, 45.50; H, 5.69; Cl, 33.63; S, 15.16. Found: C, 45.45; H, 5.55; Cl, 33.69; S, 15.30.

The nmr spectrum of **14** shows 2.0 protons for the group CH_2S, 1.95 protons for the group CH=CH, and 0.9 protons for CHCl in close agreement with the proposed structure **14**.

2,9-Dichloro-13-thiabicyclo[8.2.1]-5-tridecene (*cis*) (19).—To a solution of 810 g (5 mol) of *trans,trans,cis*-cyclododecatriene in 2000 ml of methylene chloride was added a solution of 103 g (1 mol) of sulfur dichloride in 500 ml of methylene chloride at −20° with stirring. After the addition was complete, the suspension was allowed to reach room temperature, insoluble product was filtered off and the filtrate was distilled to remove solvent and unreacted triolefin. Recrystallization of the residue from hexane gave 182 g (69%) of **19**, mp 139.5–141.5°. *Anal.* Calcd for $C_{12}H_{18}Cl_2S$: C, 54.34; H, 6.79; S, 12.07; Cl, 26.8. Found: C, 54.42; H, 6.68; S, 12.02; Cl, 26.7.

2,9-Dicyano-13-thiabicyclo[8.2.1]-5-tridecene (*cis*) (21).—To a solution of 9.0 g (0.2 mol) of potassium cyanide in 150 ml of 95% ethanol was added 10.1 g (0.038 mol) of **19** over a period of 30 min at an internal temperature of 40–45°. The solution was treated with 500 ml of water and filtered to give 8.0 g (87%) of crude **21**, mp 134–147, which was washed with pentane and recrystallized from alcohol to give a sample of mp 153–155.5°. *Anal.* Calcd for $C_{14}H_{18}N_2S$: C, 68.29; H, 7.32; N, 11.38; S, 13.01. Found: C, 68.17; H, 7.37; N, 11.42; S, 13.31. The ir spectrum shows strong absorption peaks at 3005, 2920, 2235, 1445, 727, and 695 cm^{-1}.

2,9-Dichloro-1,3-thiabicyclo[8.2.1]-5-tridecene (*trans*) (20).—Under conditions described for the synthesis of **19**, a yield of 41% of **20** was obtained, mp 108–109°. *Anal.* Calcd for $C_{12}H_{18}Cl_2S$: C, 54.34; H, 6.79; S, 12.07; Cl, 26.8. Found: C, 54.48; H, 6.85; S, 12.18; Cl, 26.9. The ir spectrum shows strong absorption at 2965, 2920, 1428, 979, 653, and 638 cm^{-1}.

2,9-Diacetoxy-1,3-thiabicyclo[8.2.1]-5-tridecene (*trans*) (22).—To a solution of 2.65 g (0.01 mol) of **19** in 100 ml of glacial acetic acid was added 1.8 g (0.022 mol) of sodium acetate. The solution was heated on the steam bath for 1 hr and then poured into 1 l. of water. After standing at room temperature for 8 hr the product was filtered off and allowed to dry to give 2.5 g (80%) of **22**, mp 97–99°. After sublimation, mp 104–106° was obtained. *Anal.* Calcd for $C_{16}H_{24}O_4S$: C, 61.5; H, 7.74; S, 10.26. Found: C, 61.7; H, 7.25; S, 10.14. The nmr spectrum ($CDCl_3$) shows a single peak for the group $OCOCH_3$ at 2.0 ppm.

3,5,7,9-Tetrachloro-1,10-dithiaadamantane (24).—To a solution of 10.4 g (0.05 mol) of **2a** in 100 ml of benzene was added a solution of 7.8 g (0.075 mol) of sulfur dichloride and the solution was refluxed until the red color of sulfur dichloride disappeared. After evaporation of benzene the residue crystallized partially. Recrystallization from acetic acid gave 3.1 g of **24** (20%). Sublimation afforded an analytical sample, mp 224–225°. *Anal.* Calcd for $C_8H_8Cl_4S_2$: C, 31.0; H, 2.60; Cl, 45.73; S, 20.68. Found: C, 31.35; H, 2.62; Cl, 45.50; S, 20.58. The ir spectrum shows strong absorptions at 1320, 801, 686, 594, and 380 cm^{-1} and medium-intensity bands at 1270, 1253, 1221, and 939 cm^{-1}.

3,5,7,9-Tetrachloro-1,10-dithiaadamantane 1-Oxide (25).—To a solution of 0.31 g (0.001 mol) of **24** in 75 ml of warm acetic acid was added 1 molar equiv of hydrogen peroxide (45% in water). After 48 hr at 60° the solution had evaporated to 20 ml and 0.07 g of unchanged **24** was filtered off. Complete evaporation of the solvent left 0.23 g of a crystalline product, which was dried over phosphorus pentoxide and recrystallized from heptane to give an analytical sample, mp 215–216° (hot stage). *Anal.* Calcd for $C_8H_8Cl_4OS_2$: C, 29.47; H, 2.47; Cl, 43.49; S, 19.66. Found: C, 29.46; H, 2.22; Cl, 43.14; S, 19.58.

The ir spectrum is distinguished from that of the sulfide **24** by strong absorption peaks at 822, 1058 and 1084 cm^{-1}. The spectrum of the purified product is identical with the crude reaction product's spectrum before recrystallization and suggests therefore the absence of isomeric products.

3,5,7,9-Tetrachloro-1,10-dithiaadamantane 1,10-Dioxide (26).—To a solution of 0.5 g (0.0016 mol) of **24** in 100 ml of warm acetic acid was added with rapid stirring 0.243 g (0.00322 mol) of hydrogen peroxide (45% in water). The solution was kept at 70° for 12 hr and was then allowed to evaporate to half volume, 0.25 g of crude **26** was filtered off, mp 140° dec. Complete evaporation and drying of the residue afforded another 0.3 g of product.

An analytical sample, mp 258°, was obtained by sublimation of the crude material. *Anal.* Calcd for $C_8H_8Cl_4O_2S_2$: C, 28.08; H, 2.36; Cl, 41.46; S, 18.74. Found: C, 28.10; H, 2.35; Cl, 41.50; S, 18.70.

The ir spectrum is distinguished from that of the monosulfoxide **25** and sulfide **24** by the absence of an intense peak at 802 cm^{-1} and the presence of strong peaks at 820 and 1076 cm^{-1}, arising from the carbon–chlorine and sulfur–oxygen stretching frequency. The spectrum is identical with that of the crude reaction product obtained by evaporation of the reaction mixture.

Registry No.—**2a**, 16831-97-3; **2b**, 16831-98-4; **2c**, 16831-99-5; **4**, 16832-00-1; **4** adduct, 12271-16-8; **5**, 16832-01-2; **7a**, 16832-02-3; **7b**, 16832-03-4; **7c**, 16832-04-5; **8**, 16832-05-6; **10**, 16832-06-7; **10** (adduct A), 12271-15-7; **11**, 16832-07-8; **12**, 16832-08-9; **14**, 16832-09-0; **19**, 16832-10-3; **20**, 16832-16-9; **21**, 16832-11-4; **22**, 16832-12-5; **24**, 16832-15-8; **25**, 16832-13-6; **26**, 16832-14-7; sulfur dichloride, 10545-99-0.

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