(m, four protons of two methylene groups), 7.97 (s, three protons of the acetoxy methyl group), 7.35 (s, broad, two bridgehead protons), 7.17 (d, $J = 7.2$ Hz, proton on mercury-bearing carbon), 5.94 (s, broad, bridge proton), 5.17 (d, $J = 7.2$ Hz, proton on acetoxy-bearing carbon).

Anal. Calcd for $C_9H_{12}O_2HgClBr$: C, 23.09; H, 2.58; Hg, 42.85; Cl, 7.57; Br, 17.07. Found: C, 23.04; H, 2.57; Hg, 42.69; Cl, 7.82; Br, 16.94.

Effects of Sodium Acetate Addition.—A solution of III (0.075 g, 0.00050 mol) and mercuric acetate (0.159 g, 0.00050 mol) in 1.0 ml of absolute methanol was allowed to stand overnight, poured into 10 ml of sodium chloride solution ($\sim$0.5 *M*), and extracted with six 5-ml portions of methylene chloride. After drying over calcium chloride and evaporating to dryness the product weighed 0.06 g (30% yield). The infrared spectrum showed a carbonyl peak at 5.8 μ which, by comparison with the 3.4-μ absorption both in this product and in pure VIII, indicated about 30% VIII in the product. When this experiment was repeated with 0.1 *M* sodium acetate in the methanol, the crude product had a spectrum identical with that of the product obtained in acetic acid. When this latter experiment (0.1 *M* NaOAc) was carried out with norbornene, the reaction was very fast (complete in 10 min) and the product contained about 60% acetate and 40% methoxymercurial. This ratio was obtained by comparing the infrared spectrum of the product with those of various mixtures of 3-*exo*-chloromercuri-2-*exo*-norbornyl acetate and 3-*exo*-methoxy-2-*exo*-norbornylmercuric chloride.[11a]

Both III and norbornene were oxymercurated in the presence of 0.1 *M* sodium acetate at the same concentrations given above but using 50 vol. % water–tetrahydrofuran as solvent. The results corresponded rather closely to those obtained in methanol. Thus, the product from III was almost pure VIII but that from norbornene contained 40–50% hydroxymercurial.

Registry No.—III, 16487-05-1; VII, 10309-50-9; IX, 16487-07-3; X, 16487-08-4.

Acknowledgment.—We are grateful to the National Institutes of Health for a fellowship (T. T. T.) and to the National Science Foundation for an equipment grant (GP-2137) and other support (Grant GP-2829).

The Reaction of Sulfur Dichloride with Linear Diolefins. Stereochemical Aspects in the Formation of Cyclic Sulfides[1]

F. LAUTENSCHLAEGER

Dunlop Research Centre, Sheridan Park, Ontario, Canada

Received January 9, 1968

Additions of sulfur dichloride to linear diolefins, such as pentadiene-1,4, hexadiene-1,5, diallyl sulfide, and diallyl ether, which lead to cyclic β,β'-dichlorosulfides is reported. Only in one case an alternative synthesis had been reported previously. Stereochemical aspects of that addition are discussed, which are characterized by the predominant formation of the *cis* products in that reaction. The addition reaction is compared with the hydrogen sulfide addition to several linear diolefins. An outstanding feature of the reaction is the influence of steric effects on the reaction products, which cause the formation of predominantly anti-Markovnikov products. In one example, ring expansion from a tetrahydrothiophene ring system to a thiacyclohexane system occurs both during oxidation and reduction of the sulfur dichloride addition product. An alternative synthesis to the cyclic β,β'-dichlorosulfides is provided by the addition of chlorine to the corresponding olefinic episulfides.

Although sulfur monochloride and 2,3-dimethylbutadiene were reported to give 3,4-dichloro-3,4-dimethyltetrahydrothiophene in a yield of 1%[2] and although transannular additions of sulfur dichloride to cyclic diolefins occur readily, the possibility that cyclic derivatives may result in reactions of sulfur dichloride with linear diolefins has not been investigated. This reaction is an approach to a variety of cyclic sulfides. In the absence of special geometric arrangements of the olefinic double bonds, which would favor such an intramolecular addition, the use of high dilutions of equimolar amounts of reagents is required to reduce the yield of intermolecular addition which leads to polymer formation.[3-6] In this report, only monomeric components of the addition reaction are investigated, which consist exclusively of cyclic β,β'-dichlorosulfides.

The products of that addition reaction are of mechanistic and stereochemical interest with respect to the size of the resulting heterocyclic ring system and the configuration of its substituents. In principle, three possible ring systems can be envisaged to result from that reaction with linear diolefins, which differ in the number of atoms in the sulfur-containing ring (Scheme I). In addition, and contrary to the reaction of sulfur dichloride with cyclic diolefins[3-6] where only a single stereoisomer was obtained, the reaction with linear diolefins could conceivably lead to two stereoisomers, one *meso* (*cis*) and a *dl* pair (*trans*). With one exception, the products described here have not been reported in the earlier literature.

Results and Discussion

The addition reaction of sulfur dichloride was investigated on seven diolefins. The structures of the isolated addition products were primarily assigned on the basis of their nuclear magnetic resonance spectra, specifically on the relative proportion of CH_2Cl and CHCl *vs.* CH_2S and CHS protons, which distinguishes the various ring systems.

Additional support for several of the assigned structures results from the reduction of the cyclic dichlorosulfides to known sulfides with lithium aluminum hydride. In addition, several of these sulfides can be synthesized in low yield by the reaction of hydrogen sulfide with the corresponding linear diolefins.[7,8]

The addition of sulfur dichloride to diallyl ether leads to 1 in a yield of 42%. No isomeric products of differ-

---

[1] Presented in part at the Intra-Science Research Symposium, Santa Monica, Calif., Nov 30, 1967.

[2] H. J. Backer and J. Strating, *Rec. Trav. Chim.*, **54**, 52 (1935).

[3] E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, **31**, 1669 (1966).

[4] (a) F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966); (b) F. Lautenschlaeger, The Princeton University Conference on the Chemistry of Sulfides, June 29, 1966.

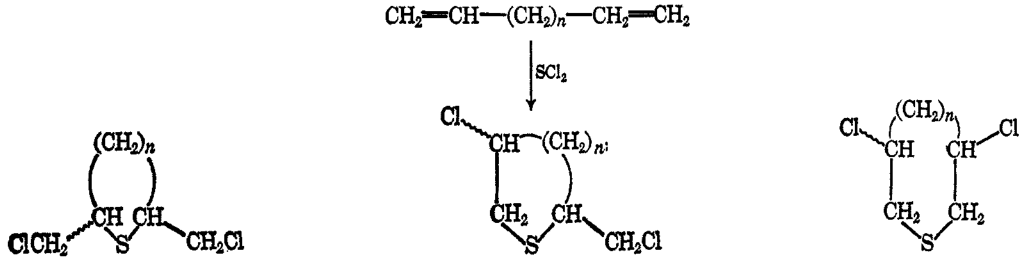
[5] E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1679 (1966).

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

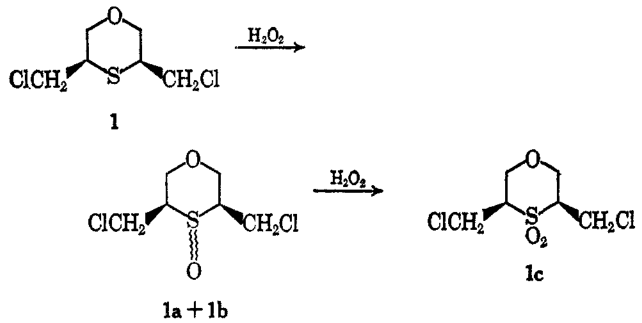
[7] D. Harman and W. E. Vaughn, *J. Amer. Chem. Soc.*, **72**, 631 (1950).

[8] C. S. Marvel and E. D. Weil, *ibid.*, **76**, 61 (1954).

SCHEME I

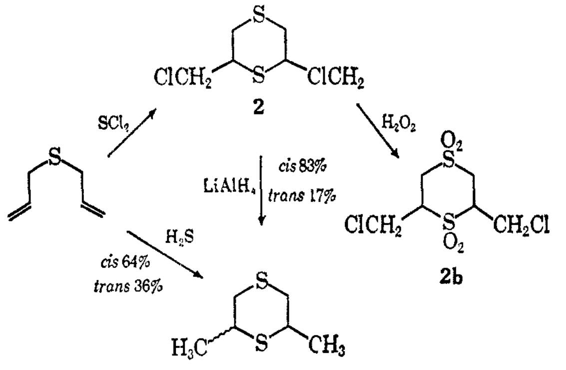


ent ring size were observed as evidenced by gas chromatographic analysis. The *cis* configuration for the dichlorosulfide **1** is suggested on the basis of the formation of two sulfoxides **1a** and **1b** on oxidation with hydrogen peroxide in glacial acetic acid, as shown by chromatographic analysis. Oxidation of a mixture of both sulfoxides leads to a single sulfone **1c** in a yield of 85%.

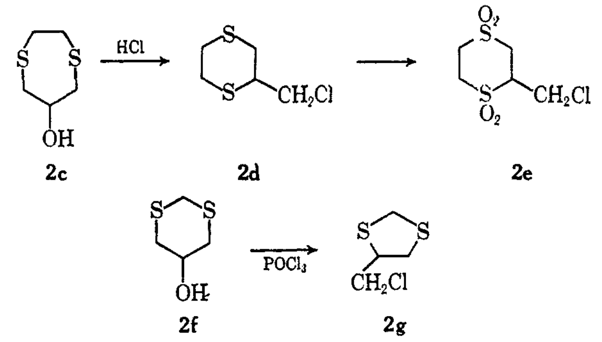


The dithian derivative **2** is obtained from diallyl sulfide in a yield of 44% (Scheme II). The isolation of that ring system is of interest since this corresponds to the head-to-head dimer of 3-chloropropylene sulfide. The dimerization of that episulfide has not been reported and, since only the head-to-tail isomer has been isolated from the dimerization of 3-chloropropylene oxide,[9] the formation of **2** from 3-chloropropylene sulfide would not be expected. The unsubstituted sulfide **2a** was obtained by the addition of hydrogen sulfide to diallyl sulfide. This addition in the presence of a secondary amine follows the rule of Markovnikov, which leads predominantly to the formation of a secondary carbon-sulfur bond in preference to the primary bond and, consequently, leads to the same ring system as the anti-Markovnikov addition of sulfur dichloride to the corresponding diolefin, as demonstrated in Scheme II. The only difference of these two approaches to **2a** appears in the *cis/trans* ratio of the two pathways, with the hydrogen sulfide addition showing an increased contribution of the *trans* isomer with a proportion of *cis/trans* of 64:36, whereas reduction of the dichlorosulfide **2** with lithium aluminum hydride leads to the *cis* and *trans* isomer of **2a** in a proportion of 83 *vs.* 17%. The predominance of the *cis* isomer in the reduction product suggests the *cis* configuration for **2**.

SCHEME II



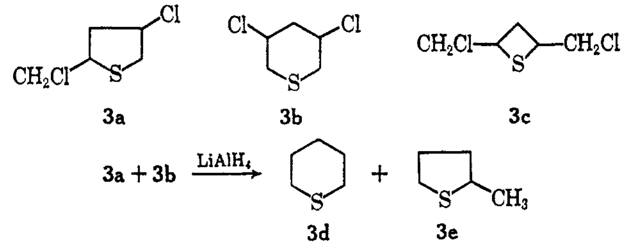
2a



The reaction of sulfur dichloride with pentadiene-1,4 leads to **3a** and **3b** in a proportion of 65:35 in a total yield of 39%. A gas chromatogram indicates the presence of both isomers of **3a** and **3b** by the appearance of two pairs of poorly separated peaks. Spinning-band distillation separates one isomer of **3a** of undetermined configuration.

Reduction of a mixture of **3a** and **3b** in a proportion of 74:26 with lithium aluminum hydride yields the sulfides **3e** and **3d** in a proportion of 82:18 and a total yield of 33% (Scheme III). In contrast, hydrogen sulfide addition to pentadiene-1,4 leads to **3e** exclusively, although only in a yield of approximately 1%, demonstrating that the initial addition of hydrogen sulfide to that terminal olefin proceeds to form the Markovnikov adduct, 4-mercaptopentene-1. This addition in the presence of amine is in contrast to the benzoyl peroxide catalyzed cyclization of 5-mercaptopentene-1, which, as expected from homolytic additions, leads predominantly to the anti-Markovnikov product **3d** (57–76%)

SCHEME III

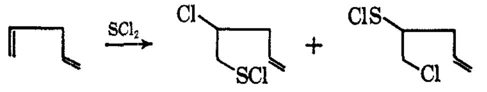


---

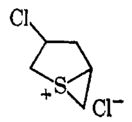
[9] J. D. McClure, U. S. Patent 3,140,296 (1964); *Chem. Abstr.*, **61**, P8318*d* (1964).

in preference to **3e** (15–42%).[10] Further examples in the report of these internal additions of olefinic mercaptans indicate the large steric effect on the mode of this cyclization reaction under homolytic conditions. These results indirectly support our conclusions derived from the sulfur dichloride addition, that steric factors play a dominant role in the formation of the alternative cyclic sulfides.

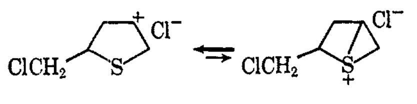
Whereas exclusively anti-Markovnikov products are isolated from the addition of sulfur dichloride to diallyl ether and diallyl sulfide, the formation of the corresponding anti-Markovnikov product **3c** in the reaction of pentadiene-1,4 is excluded for steric reasons. The first addition step would involve the formation of **3f** and **3g**, in analogy to the addition of sulfenyl chlorides to terminal olefins.[11] Intramolecular addition *via* the episulfonium intermediate **3h** is unlikely because of the steric requirements of that ion. The intermediate is therefore better represented by the open ion **3j**, which leads to **3a** and together with **3b** could also be obtained from **3i** or its open ion.



3f **3g**

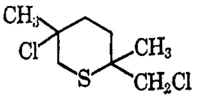


3i

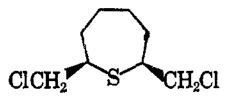


3j **3h**

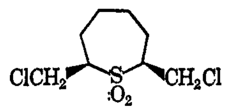
From a complex mixture of monomeric products, obtained from sulfur dichloride and 2,5-dimethylhexadiene-1,5 in a yield of 69%, product **4** was isolated in a yield of only 6%. The formation of several addition products indicates that even in the addition to this diolefin contribution from anti-Markovnikov additions are obtained.



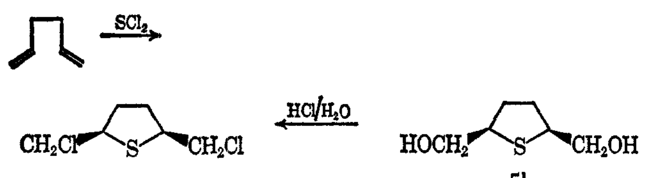
4



6

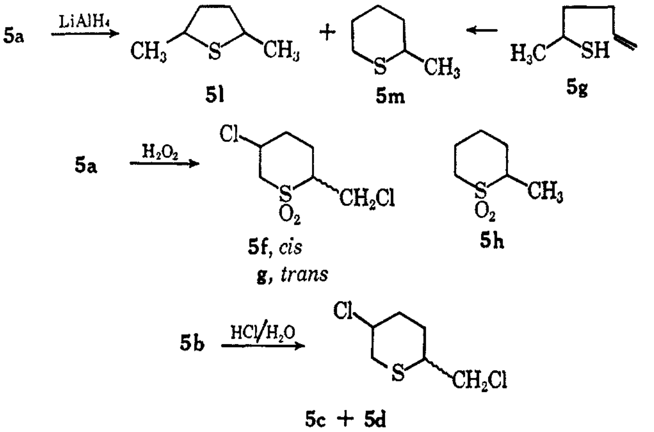


6a



5a **5b**

SCHEME IV



In contrast, the addition of sulfur dichloride to hexadiene-1,5 leads to **5a** as the only product. The formation of **5a** is surprising in view of the reported formation of its isomeric ring system **5c** and **5d** by the treatment of the *cis* and *trans* isomers of **5b** with concentrated hydrochloric acid.[12] According to these earlier reports, both stereoisomers of **5b** were isolated from the reduction of the diethyl esters of *cis*- and *trans*-tetrahydrothiophene-2,5-dicarboxylic acid. It was reported that conversion of these diols to the dichlorosulfides **5c** and **5d** occurs by treatment with concentrated hydrochloric acid. In the light of our observation, this conclusion seems doubtful, although rearrangements of substituted cyclic sulfides are common. For example, this postulated ring rearrangement has analogies in the ring contraction of 3-hydroxy-1,5-dithiacycloheptane (**2c**) to 2-chloromethyl-1,4-dithiane (**2d**) in the presence of hydrochloric acid,[13] and also in the ring contraction of 2-phenyl-1,3-dithian-5-ol (**2f**) to 4-chloromethyl-2-phenyl-1,3-dithiolane (**2g**) with phosphorous chloride in the presence of pyridine.[14] These rearrangements proceed during substitutions of the β-carbon atom of the sulfides and therefore can be assumed to involve the intermediate episulfonium ion. Against this background, it is conceivable that both nonidentical chlorides **5c** and **5d** could be obtained from **5b** on treatment with hydrochloric acid and that oxidation with monoperphthalic acid leads to the sulfones **5f** and **5g** as has been claimed.[12] The products of the assumed structures **5f** and **5g** were converted into the known thiane dioxide **5h** by hydrogenation over Raney nickel[12] (Scheme IV). The six-membered cyclic structures **5c** and **5d** were suggested for the sulfides only on the basis of the isolation of **5h**. In contrast to this, we have observed that the five-membered cycle **5a** represents the addition product of the sulfur dichloride to hexadiene-1,5 and that the corresponding diol **5b** can be obtained from **5a** with aqueous sodium carbonate. Furthermore, treatment of the diol **5b** with hydrochloric acid leads to **5a** without rearrangement. In contrast to earlier reports, we observe that oxidation of **5a** with hydrogen peroxide proceeds *via* rearrangement to the ring-expanded six-membered ring system **5f** or **5g**, the configuration of which we have not assigned. The fact that rearrangement with ring expansion occurs during oxidation and

---

(10) J. M. Surzur, M. P. Crozet, and C. Dupuy, *C. R. Acad. Sci., Paris Ser. C*, t264 (Feb 13, 1967).

(11) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966).

(12) J. Cerny and J. Hora, *Collect. Czech. Chem. Commun.*, **25**, 711 (1960); *Chem. Abstr.*, **57**, 13113*h* (1960).

(13) R. C. Fuson and A. J. Speziale, *J. Amer. Chem. Soc.*, **67**, 155 (1945.)

(14) E. Atkinson, R. J. S. Beer, D. Harris, and D. J. Royal, *J. Chem. Soc., Sect., C*, 638 (1967).

not during the treatment with hydrochloric acid, as had been suggested, is not surprising in view of the observation of these authors,[12] that the oxidation of the diacetate of **5b** leads to a ring-expanded diacetoxy sulfone.

Furthermore, although the same authors[12] suggest the involvement of an episulfonium intermediate in the conversion of the *trans*- and *cis*-diol **5b** to the rearranged sulfides **5c** and **5d**, it was suggested that this conversion is stereospecific in that both the *cis*- and *trans*-diol **5b** lead to either the *cis*- and *trans*-dichlorides **5c** and **5d**. If an episulfonium intermediate is assumed, this would be a common intermediate for both the *cis* and *trans* products and identical products should be expected. Therefore, either the nonidentity of the resulting postulated products **5c** and **5d** or the isolated products **5f** and **5g** or the episulfonium intermediate should be questioned. Spectroscopic data of products **5f** and **5g** as well as **5c** and **5d** were not reported. Physical constants of both **5c** and **5d** as well as their derivatives are nearly identical and do not permit distinguishing between them.

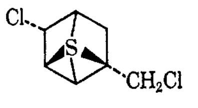
We assume that the ring expansion observed on **5a** on oxidation is due to the steric crowding of the β substituents and the oxygen attached to the sulfur atom, which is particularly critical if these substituents are *cis* with respect to one another. In this case, the sulfur–oxygen bonds in the sulfone would restrict the free rotation of the equatorial CH_2Cl groups. That this is not the only factor is evident from the absence of these rearrangements on ring systems **1**, **2**, and **4**.

The *cis* configuration is also assumed for the diol **5b** on the basis of its infrared absorption, which shows a band at 3630 cm^{-1} for the free O-H stretching frequency and a second band at 3580 cm^{-1} due to intramolecular hydrogen bonding in high dilution. Molecular models suggest that intramolecular hydrogen bonding can only be explained on the basis of a *cis* configuration. Although intramolecular bonding to the sulfur atom can be considered,[15] the characteristic frequency for that absorption had been observed at longer wavelength near 3524 cm^{-1}.

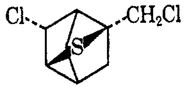
More significant stereochemical differences between the two approaches to the cyclic sulfide, the hydrogen sulfide addition and the sulfur dichloride addition with subsequent reduction, result in the reaction sequence arising from hexadiene-1,5. In both approaches, 2,5-dimethyltetrahydrothiophene **5l** and 2-methylthiacyclohexane **5m** are obtained in various proportions. It is interesting that, although only the tetrahydrothiophene ring system **5a** is isolated from the sulfur dichloride addition, reduction of that product leads to **5l** and **5m** in a proportion of 67 and 33%, indicating that ring expansion is not restricted to oxidation of **5a** but occurs also during reduction. The proportion of five- and six-membered-ring structure is not identical from both approaches; addition of hydrogen sulfide to hexadiene-1,5 favors the five-membered-ring system **5l** with a distribution of 97 *vs.* 3%. Also significant is the *cis/trans* ratio of **5l** obtained from the diolefin with hydrogen sulfide, which is 64:36 compared with the formation of only the *cis* isomer from the reduction of **5a**, which again suggests the *cis* configuration for **5a**. The larger predominance of the *cis* isomer in the reductions of both **5a** and **2** is therefore the most characteristic feature of the two alternative routes, the hydrogen sulfide and the sulfur dichloride addition to the diolefin. In comparison, ring closure of 2,6-dichlorohexane, obtained from hexadiene-1,5, leads to a smaller preponderance of the *cis* over the *trans* isomer of **5l**; a proportion of 58:42 was obtained.

A cyclic addition product from octadiene-1,7 is obtained only in 13% yield. The structure **6** is suggested for the product on the basis of its nuclear magnetic resonance spectrum. Oxidation with hydrogen peroxide leads to the corresponding unrearranged sulfone **6a**.

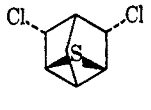
The reaction with methylenenorbornene may lead to four intramolecular addition products. The structure **7** for the sulfide was tentatively assigned on the basis of the presence of a signal for a chloromethyl group in the nuclear magnetic resonance spectrum and on the basis of the unsymmetric shielding of the S=O group in the isomeric sulfoxides derived from **7**,[4b] which rules out the isomeric structure **8**. The formation of **7** is analogous to the reaction of sulfur dichloride with bicyclo[2.2.1]heptadiene in which the thietane ring system **9** was formed.



7



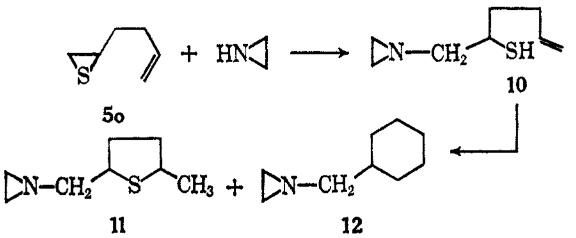
8



9

Studying the base-catalyzed formation of cyclic sulfides further, it was assumed that intramolecular addition of an olefinic mercaptan as proceeding in the hydrogen sulfide addition to linear diolefins should also result from the addition of a primary or secondary amine to an olefinic episulfide. Addition of ethyleneimine to the episulfide **5o** involves the formation of the intermediate mercaptan **10** which closes to the two isomeric sulfides **11** and **12** in a proportion of 50:50 and a total yield of 30% (Scheme V). This reaction shows, as expected, a larger contribution of the Markovnikov product **11**. In comparison with the cyclization of 4-mercaptopentene-1 in the presence of benzoyl peroxide, in which of the two alternative five- and six-membered-ring systems, the six-membered ring is predominant.[10] The formation of the methyleneaziridyl derivatives **11** and **12** in preference to products in which the aziridinyl group is attached to the thiane or tetrahydrothiophene ring suggests the opening of the episulfide group on the terminal carbon atom, as expected from the observations on the opening of propylene sulfide

SCHEME V



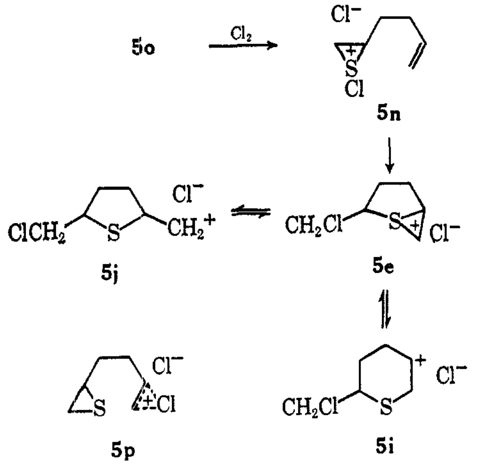
---

[15] A. Lüttringhaus, S. Kabuss, H. Prinzbach, and F. Langenbucher, *Ann.*, **653**, 195 (1952).

with secondary amines.[16,17] The presence of only a single doublet in the nuclear magnetic resonance spectrum for the methyl group in **12** suggests the formation of a single isomer in that cyclization reaction.

An alternative synthesis to several cyclic β,β'-dichlorosulfides is suggested by the assumption that the intermediate **5n** in the addition of chlorine to the episulfide **5o** should be identical with that obtained from sulfur dichloride and an olefinic compound (Scheme VI).

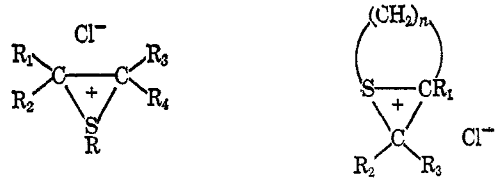
SCHEME VI



Consequently, in the case of an episulfide of such a diolefin in which intramolecular addition of sulfur dichloride occurs, the addition of chlorine should lead to the formation of a cyclic β,β'-dichloromonosulfide, identical with the sulfur dichloride addition product to the diolefin, and in contrast to the reported chlorine additions to episulfides,[18] which give β,β'-dichlorodisulfides, exclusively. This was indeed observed, addition of chlorine to **5o** leads to **5a** in a yield of 66%. Similarly, addition of chlorine to 1,5-cyclooctadiene monoepisulfide **13**[19] leads to the earlier[6] reported cyclic sulfide **14**. In the addition of chlorine to unsaturated episulfides, the product does not permit distinguishing between the initial approach of the chloronium ion to the sulfur atom as in **5m** or to the unsaturation as shown in **5p** because both lead to identical products.

Transannular additions to unsaturated sulfides should therefore provide a convenient synthesis to ring systems related to structures obtained by the addition of sulfur dichloride to diolefins.

If both the addition of sulfur dichloride to the diolefin and the intramolecular addition of the resulting unsaturated β-chlorosulfenyl chloride followed the rule of Markovnikov, the largest possible ring system would be formed in all cases of reactions with terminal diolefins. Such a product was detected only as a minor component in one case (**3b**). This observation is interesting in view of earlier studies on the stereochemical nature of sulfenyl chloride additions to unsaturated compounds. In these addition reactions, the assumption of an intermediate episulfonium ion has generally become accepted.[20] However, the possibility of contributions of open ions was not ruled out.[21] This becomes particularly relevant if the carbon–sulfur bonds in the three-membered ring are not symmetrical with R_1 to R_4 being nonidentical (I), either because of



I

stabilization of the carbonium ion by electronic effects of the various substituents or because of steric requirements. Both influences would favor a contribution of an open ion and could even act against the formation of an episulfonium ring structure. This steric influence is different from the steric approach effect, which affects the mode of opening of an unsymmetric episulfonium ion by an approaching nucleophile. Rearrangements of sulfenyl chloride addition products to olefins are therefore not surprising since kinetically and thermodynamically favored products could result, as demonstrated in the significant study of Mueller and Butler on the addition of sulfenyl chlorides to 1-alkenes,[11] which showed that predominantly anti-Markovnikov products are obtained at low temperatures, and rearrangement to Markovnikov addition products occurred at room temperature. Also, mixtures of both isomers were obtained by the addition of alkenesulfenyl chlorides to acrylic acid derivatives.[22]

Whereas the factors leading to these varying modes of additions are not yet understood, it is obvious from the observed additions of sulfur dichlorides to diolefins that steric factors appear to dominate and determine the product distribution. Specifically, the deciding factor is the formation of the five-membered sulfur-containing cycle in preference to the four- or six-membered isomer in case of **3a**, **3b**, and **5a**. The exclusive formation of the seven-membered ring in preference to the eight- or nine-membered ring in **6** and the exclusive formation of the six-membered in preference to the seven- or eight-membered ring in **1** and **2**, follow from similar considerations. In addition, the formation of the ring systems, **1**, **2**, **3a**, **5a**, **6**, and **7**, is further favored by the approach of the chloride ion from the least hindered site, although in view of the absence of **3c** this cannot be considered the overriding factor. These results become plausible if a contribution of open ions of the episulfonium intermediates are considered, in which case it is anticipated that the three carbon–sulfur bonds of the episulfonium ring structure are sterically nonequivalent and that steric effects determine which of the two possible ions, for example, **5i** and **5j**, predominates. The bicyclic episulfonium intermediate (I) would open and locate the carbonium ion in less strained ring system, whereby it could be anticipated that a contribution of such an episulfonium ion becomes smaller or negligible if n of $(CH_2)_n$ (I) approaches 1.

The significance of these steric factors becomes particularly apparent in a comparison of the products ob-

---

[16] N. S. Isaacs, *Can. J. Chem.*, **44**, 395 (1966).

[17] (a) S. D. Turk, R. P. Loutham, R. L. Cobb, and C. R. Bresson, *J. Org. Chem.*, **29**, 974 (1964). (b) A more recent investigation in the opening of episulfides was carried out by N. V. Schwartz, *ibid.*, in press.

[18] J. M. Stewart and H. P. Cordts, *J. Amer. Chem Soc.*, **74**, 5880 (1952).

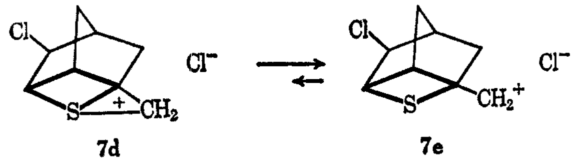
[19] French Patent 1,428,686 (to Dunlop Rubber Co. Ltd.) (1965).

[20] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71**, 2724 (1949).

[21] A. Streitwieser, *Chem. Rev.*, **56**, 571 (1958).

[22] K. D. Gundermann and R. Huchting, *Chem. Ber.*, **95**, 2191 (1962).

tained from pentadiene-1,4 and methylenenorbornene. Whereas steric considerations exclude the formation of the thietane system **3c**, on the basis of similar considerations, the formation of the thietane system **7** should be favored in the reaction with strained bycyclic systems such as methylenenorbornene. It could be argued that, in the latter case, a large contribution of the open ion **7e** *vs.* the episulfonium intermediate **7d** is involved, since a symmetric episulfonium ion would require the two carbon–sulfur bonds of the three-membered cyclic ion to be of equivalent length, which is sterically impossible and may rule out such a cyclic intermediate.



7d **7e**

The isolation of only the *cis* isomer in case of **1**, **2**, and **5a** follows from thermodynamic considerations, which requires isomerization *via* the episulfonium intermediate to the thermodynamically most stable ring system. The latter is expected to be the *cis* isomer in analogy to observations on 1,3-disubstituted cyclohexanes, for which the less stable isomer was shown to be a *dl* pair and therefore *trans*.[23] The increased stability of the *cis*-1,3 isomer results from the possibility of the *cis* isomer to exist in the favored diequatorial conformation, whereas the *trans* isomer would necessarily be equatorial-axial.[24] Isomerization through the episulfonium intermediates such as **5e** would readily allow the formation of the more stable product.

Experimental Section

Gas chromatographic analysis was carried out on a 3-, 6-, or 12-ft Apiezon column between 75 and 175° on a Perkin-Elmer 800 instrument. Infrared spectra were recorded on a Perkin-Elmer 422 spectrophotometer either neat or in potassium bromide pellets. Nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument. Melting points were determined in a Gallenkamp block and are uncorrected.

2,6-Chloromethyl-1,4-oxathiane (1).—Solutions of 107 g (1.1 mol) of allyl ether and 103 g (1 mol) of sulfur dichloride were allowed to react as described previously[4a] to give 42% of **1** as shown by vpc analysis, which also indicates the presence of a single product. Separation from polymeric product by molecular distillation gave 60 g (30%) of crude product, which crystallized partially at room temperature. After sublimation, a product of mp 36–37.5° was obtained.

The product shows strong ir bands at 1106, 896, and 730 cm^{-1}. The nmr spectrum in carbon disulfide solution shows integration values of 2:2:1 for multiplets centered near 3.84, 3.55, and 2.84 ppm in agreement with the assigned structure **1**.

Anal. Calcd for $C_6H_{10}OCl_2S$: C, 35.8; H, 5.01; Cl, 35.3; S, 15.9. Found: C, 35.7; H, 4.99; Cl, 35.0; S, 15.8.

2,6-Chloromethyl-1,4-oxathiane Oxide (1a + b).—A solution of 2.9 g (0.04 mol) of 47% hydrogen peroxide and 8.04 g (0.04 mol) of **1** in 60 ml of acetone was allowed to stand at room temperature for 12 hr. The solution was evaporated to give 8.4 g (97%) of product, mp 60–92°. An analytical sample of the mixture of the isomers was obtained by sublimation at 60° (0.1 mm). Vpc analysis shows the absence of unchanged sulfide **1**.

Anal. Calcd for $C_6H_{10}O_2Cl_2S$: C, 33.18; H, 4.64; Cl, 32.67; S, 14.77. Found: C, 32.87; H, 4.34; Cl, 32.60; S, 14.74.

2,6-Chloromethyl-1,4-oxathiane 4,4-Dioxide (1c).—A solution of 0.5 g of the mixture of sulfoxides **1a** and **b** in 50 ml of glacial acetic acid was allowed to stand at 25° for 64 hr. The solution was then evaporated to 5 ml to give 0.25 g of **1c**, mp 129–130.5°. On complete evaporation, another 0.2 g of product was obtained: mp 128–129.5°; total yield 85%.

Anal. Calcd for $C_6H_{10}Cl_2O_3S$: C, 30.91; H, 4.32; S, 13.75; Cl, 30.43. Found: C, 31.26; H, 4.36; S, 13.91; Cl, 30.69.

2,6-Chloromethyl-1,4-dithiane (2).—The product was obtained as described for **1** and was purified by recrystallization from ethanol and subsequent sublimation. An analytical sample showed mp 49–51°.

The nmr spectrum shows four protons centered at 3.63 ppm for the group CH_2Cl and six protons centered at 2.97 ppm for the groups CH_2S and CHS. In the ir spectrum, major absorption bands are observed at 1412, 732, 690, and 670 cm^{-1}.

Anal. Calcd for $C_6H_{10}Cl_2S_2$: C, 33.2; H, 4.67; Cl, 32.62; S, 29.58. Found: C, 33.4; H, 4.72; Cl, 32.03; S, 29.53.

2,6-Chloromethyl-1,4-dithiane 1,1,4,4-Tetroxide (2b).—Oxidation of 1 g of **2** with hydrogen peroxide as described above gives 1.2 g (93%) of **2b**, mp 204–206°, soluble in hot acetic acid, hot hexachlorobutadiene, and cold pyridine. Recrystallization from acetic acid increased the melting point to 250° dec.

Anal. Calcd for $C_6H_{10}Cl_2O_4S_2$: C, 25.62; H, 3.58; S, 22.81; Cl, 25.22. Found: C, 25.97; H, 3.54; S, 23.05; Cl, 25.05.

The Reaction of Sulfur Dichloride with Pentadiene-1,4. 2-Chloromethyl-4-chlorotetrahydrothiophene and 3,5-Dichlorothiacyclohexane (3a and b).—Solutions of 50 g (0.735 mol) of pentadiene-1,4 and 75.7 g (0.735 mol) of sulfur dichloride in 500 ml of dry pentane were allowed to drop into 1 l. of dry pentane over a period of 2 hr. The reaction proceeded at room temperature. After 12 hr the solution was decanted from 50.1 g of insoluble product A. On evaporation of the solvent, 73.1 g of oily product B was obtained. Vpc analysis of B showed two components in a proportion of 65:35 which were further separated into four peaks at decreased column temperature. Fractionation of 60 g of B at 0.05 mm through a 10-in. Vigreux column gave following fractions: (1) bp 48–52°, 5.2 g; (2) bp 52–62°, 15.8 g, $n^{20}D$ 1.5545; (3) bp 62°, 13.7 g, $n^{20}D$ 1.5560; (4) bp 64–84°, 7.0 g.

Fraction 1 shows an isomer ratio of 16:1; fraction 4 of 2:3 by vpc analysis. Fractions 1 and 4 show similar elemental compositions.

Anal. Calcd for $C_5H_8Cl_2S$: C, 35.10; H, 4.71; Cl, 41.46; S, 18.74. Found: C, 35.52; H, 4.67; Cl, 41.03; S, 18.17.

Fractionation on a spinning-band column separated a single stereoisomer of **3a** of unidentified configuration: bp 47° (0.05 mm); $n^{20}D$ 1.5558.

Reduction of 3a and b with Lithium Aluminum Hydride (3d and e).—To a solution of 5.22 g (0.03 mol) of **3a** and **b** (of a proportion of 74:26) in 100 ml of diethyl ether was added 0.75 g (0.02 mol) of lithium aluminum hydride. After refluxing with stirring for 64 hr, the suspension was acidified with dilute sulfuric acid; the ether solution washed with water, dried ($MgSO_4$), and distilled to give 1.0 g of a mixture of **3d** and **e** (18:82), 33%, bp 40–41.5° (25 mm), $n^{20}D$ 1.4893. The components were identified by comparison of their vpc retention times with those of authentic materials.[25]

2-Chloromethyl-2,5-dimethyl-5-chlorothiacyclohexane (4).—Solutions of 92.5 g (0.84 mol) of 2,5-dimethylhexadiene-1,5 and 81.5 g (0.84 mol) of sulfur dichloride in 500 ml of pentane were allowed to react at room temperature by adding the solutions over a period of 30 min. After 12 hr, the solution was decanted from polymeric material and evaporated to give 123.4 g (76%) of product. Vpc analysis shows eight major products which only partially could be separated by distillation.

Fractionation through a 5-in. Vigreux column of 100 g of product at 0.001 mm gave following fractions: (1) bp 40–60°, 9.2 g; (2) bp 60–68°, 11.1 g; (3) bp 69–72°, 12.0 g; (4) bp 72–78°, 6.0 g; (5) bp 78–88°, 9.5 g; (6) bp 88–104°, 19 g.

Repeated crystallization of fraction 5 from hexane gave a sample of **4**, mp 65.5–67°.

Anal. Calcd for $C_8H_{14}Cl_2S$: C, 45.01; H, 6.67; Cl, 33.30; S, 15.05. Found: C, 45.02; H, 6.51; Cl, 32.83; S, 14.89.

The nmr spectrum of **4** shows two AB patterns for the groups CH_2Cl at 3.53 ppm (J_{AB} = 11 cps) and CH_2S at 2.77 ppm (J_{AB} = 15 cps) each corresponding to two protons. The nonequivalence of the two methyl groups is indicated by single peaks at 1.69 and 1.18 ppm.

---

(23) M. Mousseron and R. Granger, *Bull. Soc. Chim. Fr.*, [5] **5**, 1518 (1938).

(24) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(25) E. V. Whitehead, R. A. Dean, and F. A. Fiedler, *J. Amer. Chem. Soc.*, **73**, 3632 (1951).

2,7-Chloromethyl-1-thiacycloheptane (6).—Solutions of 82.7 g (0.75 mol) of octadiene-1,7 and 76.0 g (0.75 mol) of sulfur dichloride in 250 ml of hexane were added to 3 l. of hexane under stirring at 50° over a period of 3 hr. After an additional 8 hr at room temperature, the clear solution was decanted and evaporated to give 52.5 g (33%) of syrupy product. Vpc analysis indicates a total yield of 13% of **6**. Molecular distillation at 100° separated 17.2 g of volatile material, from which 7 g of **6** were separated by fractionation: bp 92–94° (0.1 mm); $n^{20}\text{D}$ 1.5432. Vpc analysis shows a single peak for that product.

Anal. Calcd for $C_8H_{14}Cl_2S$: C, 45.05; H, 6.62; Cl, 33.29; S, 15.02. Found: C, 45.90; H, 6.41; Cl, 32.86; S, 15.25.

The nmr spectrum for **6** shows four protons corresponding to CH_2Cl between 3.4 and 4.1 ppm in carbon disulfide solution.

2,7-Chloromethyl-1-thiacycloheptane 1,1-Dioxide (6a).—To a solution of 0.53 g of **6** (2.5 mmol) in 20 ml of acetone was added 0.34 g (5.6 mmol) of 47% aqueous hydrogen peroxide. After 12 hr the solution was allowed to evaporate, the crude crystalline material was washed with 10 ml of methanol to give 0.2 g of sulfone, mp 121–125°. After recrystallization from glacial acetic acid, mp 127–129° was obtained. Evaporation of the mother liquor gave another 0.2 g of product.

Anal. Calcd for $C_8H_{14}Cl_2O_2S$: C, 39.19; H, 5.76; S, 13.08; Cl, 28.92. Found: C, 38.87; H, 5.56; S, 13.08; Cl, 28.78.

The nmr spectrum in hexachlorobutadiene at 100° shows four protons corresponding to the groups CH_2Cl in the region between 3.4 and 4.2 ppm, two protons for the groups CHS between 2.8 and 3.4 ppm, and eight protons for the methylenic protons as a wide multiplet centered at 1.93 ppm.

2,5-Chloromethyltetrahydrothiophene (5a). A.—Solutions of 103 g (1 mol) of sulfur dichloride and 98 g (1.2 mol) of hexadiene-1,5 were allowed to drop into 2 l. of pentane over a period of 30 min at room temperature. After 8 hr the solution was decanted from 29 g of insoluble product. Evaporation of solvent gave 147 g (79.5%) of crude product. Vpc of the crude reaction product showed a single peak for **5a** in a yield of 61%.

Distillation through a Vigreux column at 0.1 mm gave following fractions: (1) bp 86–88°, 41.5 g; $n^{20}\text{D}$ 1.5504; (2) bp 88–93°, 26.2 g; (3) bp 93–97°, 19.2 g; $n^{20}\text{D}$ 1.5504.

Anal. Calcd for $C_6H_{10}Cl_2S$: C, 38.92; H, 5.39; Cl, 38.31; S, 17.32. Found: C, 38.93; H, 5.52; Cl, 38.19; S, 17.28.

Fraction 1 shows an nmr spectrum (in CS_2) in agreement with structure **5a**, with four protons due to the groups CH_2Cl between 3.3 and 4.2 ppm, two protons for the groups CHS centered at 2.8 ppm, and four protons for the methylenic hydrogens between 1.6 and 2.5 ppm.

No difference was obtained in the nmr spectrum of fractions 1 and 3 although fraction 3 shows additional weak peaks in its ir spectrum at 865, 788, 773, and 512 cm^{-1}.

B.—An amount of 2.95 g (0.02 mol) of the diol **5b** was dissolved in 50 ml of concentrated hydrochloric acid. The clear solution turned cloudy after several min, and was then extracted with pentane after 2 hr. The pentane solution was washed with water, dried ($MgSO_4$), and evaporated to give 3.7 g (100%) of dichlorosulfide **5a**, identified by its ir and vpc spectra.

C.—Into a solution of 10.4 g (0.09 mol) of hexadiene monoepisulfide dissolved in 50 ml of methylene chloride was passed 7.1 g (0.1 mol) of chlorine at −35° with rapid stirring. The solution was evaporated to give 17 g (97%) of crude product; vpc shows 66% **5a**. Distillation produced 10.8 g (61%) of **5a**, identified by its ir absorption.

Hexadiene 1,5-monoepisulfide (5o) was obtained from the corresponding epoxide by treatment with potassium thiocyanate[26] in a yield of 50%: $n^{20}\text{D}$ 1.4920; bp 62° (24 mm).

Anal. Calcd for $C_6H_{10}S$: C, 63.09; H, 8.83; S, 28.07. Found: C, 63.90; H, 8.69; S, 28.03.

2-Chloromethyl-5-chlorothiacyclohexane 1,1-Dioxide (5f or g).—To a solution of 3.7 g (0.02 mol) of **5a** in 50 ml of acetone was added 3.4 g (0.05 mol) of 50% aqueous hydrogen peroxide. The solution was allowed to stand for 5 days at room temperature and was then evaporated to give a partially crystallized product, which was suspended in 5 ml of methanol to give 1.7 g of crude product, mp 110–114°. Recrystallization increased this to 118–121° (lit.[12] mp 119.5–120°). Evaporation of the methanol solution produced an oily fraction, virtually identical by ir analysis with the purified sulfone. Crystallization of the oil from 10 ml of chloroform–hexane in a proportion of 1:1 at −20° yielded another 0.8 g of product: mp 110–117°; total yield 57%.

The nmr spectrum of the sulfone in $CDCl_3$ shows three protons arising from the groups CHCl and CH_2Cl between 3.4 and 4.5 ppm with the multiplet for CHCl at 4.32 ppm. Three protons due to groups CH_nSO_2 are observed between 3.4 and 3.6 ppm and four methylenic protons in the region of 1.8–2.5 ppm support the structure **5f** or **g**.

2,5-Hydroxymethyltetrahydrothiophene (5b).—A suspension of 9.25 g of **5a** (0.05 mol) in 100 ml of water containing 10.6 g (0.1 mol) of anhydrous sodium carbonate was stirred at 90° with a high-speed mechanical stirrer until a clear solution had formed after approximately 10 min. Extraction with diethyl ether (500 ml) and distillation after drying with magnesium sulfate gave 4 g of **5b**: bp 108° (0.1 mm); $n^{20}\text{D}$ 1.5459.[12]

The nmr spectrum in pyridine shows 4.0 protons corresponding to CH_2OH at 3.85 ppm, 4.0 methylenic protons at 2 ppm, and two protons at 2.85 ppm, corresponding to the group CHS.

The ir spectrum of **5b** was recorded on a Perkin-Elmer 421 instrument in an undetermined low concentration, obtained by stirring the alcohol with carbon tetrachloride and subsequent centrifugation. Further dilution did not affect the absorption peaks at 3630 and 3580 cm^{-1}. A neat sample shows strong absorption at 1020 and 3300 cm^{-1}.

Reduction of 2,5-Chloromethyltetrahydrothiophene.—To a solution of 5.55 g (0.03 mol) of **5a** in 100 ml of tetrahydrofuran was added 0.75 g (0.02 mol) of lithium aluminum hydride. After refluxing for 12 hr the vpc spectrum showed the absence of starting material. The suspension was poured into 1 l. of water, extracted with two portions of 100 ml of pentane, the pentane was washed with water and dried ($MgSO_4$). The vpc spectrum shows **5l** and **5m** in a proportion of 67:33. Distillation yielded 2.0 g of the mixture of **5l** and **5m**: bp 49° (38 mm); $n^{20}\text{D}$ 1.4788. The products were identified by comparison of their vpc retention times and physical constants[26] with those of authentic samples.

2,6-Dichloro-9-thiabicyclo[3.3.1]nonane (14). From Cyclooctadiene 1,5-Monoepisulfide.—Into a solution of 2.3 g (0.016 mol) of 1,5-cyclooctadiene monoepisulfide dissolved in 200 ml of methylene chloride was passed 1.14 g (0.016 mol) of chlorine at −40°. The solution was allowed to warm to room temperature and the solvent evaporated to give 3.45 g of semicrystalline material. Sublimation of 0.5 g of the crude product gave 0.47 g of **14** (94%), mp 80–87°. A sample was purified by crystallization as described earlier[6] to give a pure sample of mp 100–101° and was identified by mixture melting point and ir spectrum as identical with a product obtained from sulfur dichloride and *cis,cis*-cyclooctadiene-1,5.

13 **14**

***exo,exo*-2-Chloromethyl-5-chloro-9-thiatricyclo[2.2.1.1^{2,6}]octane (7).**—2-Methylene-5-norbornene (220 g, 2.07 mol) and 206 g (2 mol) of sulfur dichloride were allowed to react in hexane as described before[4] at −40°. While still at this temperature, the solution was decanted, the solvent evaporated to give 220 g (53%) of syrupy product. A portion of 42 g was distilled through a 2-in. Vigreux column to give 17 g of product, bp 87° (0.09 mm). Alternatively, the pure product can be obtained in comparable yield by steam distillation of the crude reaction product. An analytical sample was obtained by recrystallization from methanol and shows mp 44–46.5°.

Anal. Calcd for $C_8H_{10}Cl_2S$: C, 45.94; H, 4.82; Cl, 33.90; S, 15.33. Found: C, 45.89; H, 4.90; Cl, 33.99; S, 15.62.

2,5-Dimethyltetrahydrothiophene (5l) from 2,5-Dichlorohexane and Sodium Sulfide.—The reported procedure[26] was followed on a mixture of *meso*- and racemic 2,5-dichlorohexane, obtained by the addition of hydrogen chloride to diallyl. From 9.3 g (0.06 mol) of the dichloride, 4.1 g of **5l**, 59%, bp 53–54° (30 mm), $n^{20}\text{D}$ 1.4766, was obtained. The nmr spectrum in $CDCl_3$ shows the presence of two doublets for methyl groups at 1.33 and 1.31 ppm in a proportion of 58:42, whereby the lower field doublet is due to the *cis* isomer, as demonstrated by adding an authentic sample.

The Addition of Hydrogen Sulfide to Hexadiene-1,5 (5l and 5m).—A solution of 8.2 g of hexadiene-1,5 (0.1 mol), 1 g of di-

---

[26] H. R. Snyder, J. H. Stewart, and J. B. Ziegler, *J. Amer. Chem. Soc.*, **69**, 2672 (1947).

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); $n^{20}\mathrm{D}$ 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); $n^{20}\mathrm{D}$ 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); $n^{20}\mathrm{D}$ 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.

---

[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

Received February 29, 1968

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

---

[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 Suldes, 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).