SO_4, this material appeared to be mainly styrene containing some of the episulfide.

These results were reproducible within narrow limits in further experiments.

1,2-Epithio-4-pentene.—The reaction flask was charged with 260 g of sodium sulfide and heated to 80°, and the system was evacuated to 5 Torr. A 105-g sample of sulfur monochloride–1,4-pentadiene adduct (see Table IV, footnote *c*) was added dropwise over a period of 1.5 hr. The temperature was maintained at 80° for 0.5 hr after the addition was completed. At the end of this period, the ice-cooled trap contained 8.0 g of an organic liquid with n^{20}_{D} 1.5578, and the Dry Ice–acetone cooled trap contained 33.2 g (36.5%) of 1,2-epithio-4-pentene, n^{20}_{D} 1.4990. The latter material was 98.2% pure episulfide according to glpc analysis. The impurities were 0.8% 1,4-pentadiene and 1% higher boiling material. The product was identified by comparison of its infrared spectrum, boiling point, and refractive index with those of an authentic sample prepared from the corresponding epoxide and thiourea.[29]

Cyclopentene Sulfide.—A 1-l. three-necked flask containing 110 g of coarsely powdered sodium sulfide was fitted as in the previous examples. The reaction flask was heated by an oil bath at 80° and the system was evacuated to 20 Torr. A 45-g sample of a cyclopentene–sulfur monochloride adduct was then added dropwise to the stirred sodium sulfide. When all the adduct had been added, the temperature of the oil bath was raised to 120° and the pressure was reduced to 10 Torr. When the contents of the reaction flask appeared dry, heating was discontinued. There was obtained 10 g of product with n^{20}_{D} 1.5235 and 20.6 g of product with n^{20}_{D} 1.530. These two fractions were combined and distilled under reduced pressure to yield 15.6 g (47%) of cyclopentene sulfide, n^{20}_{D} 1.5230. The infrared spectrum was identical with that of an authentic sample of cyclopentene sulfide.

Addition of Sulfur Dichloride to Propylene.—To a solution of 84 g (2 mol) of propylene in 100 ml of methylene chloride was added a solution of 25.75 g (0.25 mol) of sulfur dichloride in 50 ml of methylene chloride with cooling at an internal temperature of −40°, over a period of 30 min. The solution was allowed to stand at this temperature for 3 hr, and the volatile portions was evaporated to give 45 g (96%) of product, bp 56–60° (0.5 mm).

The nmr spectrum of the undistilled product shows one doublet for CH_3CHCl at 1.48 ppm and a second for CH_3CHS– at 1.30 ppm of equal intensity, suggesting equal contributions from both isomeric structures.

Addition of Sulfur Monochloride to Propylene Sulfide.—To a solution of 13.5 g (0.1 mol) of sulfur monochloride in 50 g of methylene chloride was added 14.8 g (0.2 mol) of propylene sulfide with stirring at an internal temperature of −40°. An additional 0.7 g of sulfide was required to obtain a negative test for sulfenyl chloride, indicating that polymerization of episulfide occurs to a small extent. After evaporation of volatiles, the nmr spectrum of the crude reaction product showed a proportion of 34:66 for the two isomeric structures **8** and **9** with doublets at 1.68 and 1.42 ppm ($CDCl_3$).

Mono-, di-, and trisulfide analyses of the sulfur chloride addition products to propylene were carried out by glpc. The analysis of the addition product of cyclohexene was obtained by liquid–solid chromatograpy on neutral alumina and chloroform as solvent for developing and elution. Under these conditions, di- and polysulfides together with free sulfur were eluted. The value of the monosulfide percentage was obtained by difference.

Warning.—Some of the β-chloroalkyl monosulfides formed as by-products in the addition of sulfur monochloride to olefins are vesicants, especially those from ethylene, propylene, allyl chloride, and allyl bromide. We have encountered no difficulty in working with the adducts from other olefins, but they should all be handled with caution.

Registry No.—Sulfur monochloride, 10025-67-9.

Acknowledgment.—The authors are greatly indebted to Professor N. Kharasch and Dr. R. T. Wragg for their helpful discussions and to M. Myhre, K. Edwards, and G. Takaki for technical assistance.

---

[29] C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, **282** (1949).

---

endo-2,3-Epithio-5-norbornene. Formation of an Episulfide from the Adduct of Bicycloheptadiene and Sulfur Dichloride

F. LAUTENSCHLAEGER

Dunlop Research Centre, Sheridan Park, Ontario, Canada

Received January 14, 1969

The treatment of *exo,exo*-3,5-dichloro-8-thiatricyclo$[2.2.1.1^{2,6}]$octane (**1**) with potassium cyanide in aqueous ethanol gave, not the expected substitution product, but a 30% yield of an elimination product, *endo*-2,3-epithio-5-norbornene (**2**). Oxidation of **2** with potassium periodate and treatment of **1** with aqueous sodium carbonate both gave **4**, the *exo* sulfoxide corresponding to **2**. Oxidation of **4** with hydrogen peroxide gave the sulfone; addition of chlorine to **2** gave **1**.

Within the series of sulfur dichloride additions to diolefins, we had reported the reaction with bicycloheptadiene.[1] Although it is generally observed that substitution on β,β'-dichloro sulfides proceeds smoothly, as has been demonstrated on cyclic and bicyclic structures of this type,[1-4] a series of unusual rearrangements is observed in the case of the strained bicyclic ring system **1** for which there is no analogy in the reported chemical reactions of cyclic sulfides. Part of this work was reported earlier[4a] and details are reported here.

Results and Discussion

During attempts to replace chloro groups on *exo,exo*-3,5-dichloro-8-thiatricyclo$[2.2.1.1^{2,6}]$octane (**1**),[1] we have observed that attempted substitution reactions lead to unexpected products. Although the reaction with potassium cyanide was shown to proceed to give the corresponding β,β'-dicyano sulfides from other bicyclic dichloro sulfides,[2] extension of this reaction to **1** leads to dechlorination and affords the product **2** in a yield of 30%. A similar reduction of a dichloroalkyl sulfide has not been reported and therefore provides a unique route to an olefinic episulfide.

It is of interest that the analogous epoxide **2a** has been obtained on oxidation of bicycloheptadiene in very low yield[5] and that the corresponding nitrogen-containing heterocycle has only been reported as its phenylsulfonyl

---

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

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

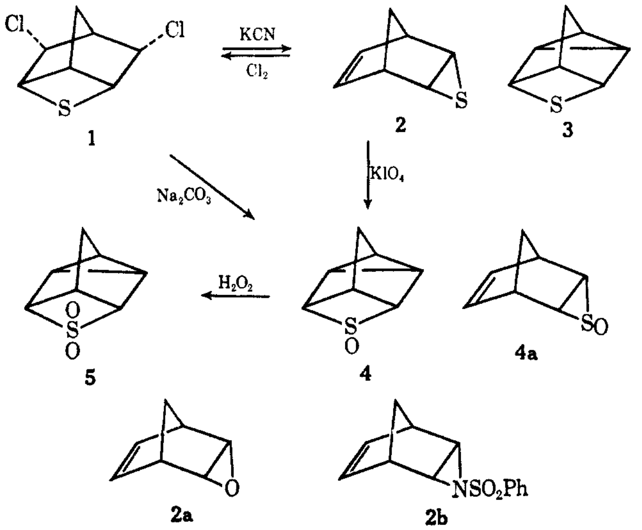
[3] E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

[4] (a) F. Lautenschlaeger in "The Chemistry of Sulfides," A. V. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, p 73; (b) F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966).

[5] J. T. Lumb and G. H. Whitham, *J. Chem. Soc.*, 1189 (1964).

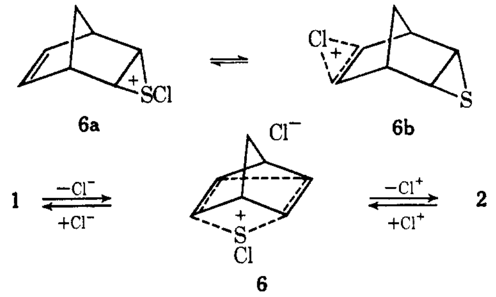
derivative **2b**.[6] The approach to **2** *via* its epoxide, a route most commonly chosen for the synthesis of episulfides, is therefore of little synthetic value.

For structural identification of the reaction product, two isomeric structures **2** and **3** had to be considered. That the isolated compound has structure **2**, rather than the alternative structure **3**, is evident from the following spectral data. The infrared spectrum shows the olefinic unsaturation at 1633 and 730 cm^{-1} and indicates the episulfide structure by strong absorption peaks at 1030 and 645 cm^{-1}. In the nuclear magnetic resonance spectrum, recorded on a Varian HA-100 instrument, the olefinic protons H_d are observed at 5.73 ppm in deuteriochloroform, which is 1.02 ppm upfield from the positions of these protons in bicycloheptadiene.[7] The *exo* hydrogens H_a attached to the three-membered ring are found at 3.28 ppm. The two nonidentical methylenic protons H_c and $H_{c'}$ show a 12-line pattern centered at 2.08 ppm, and the remaining protons are observed at 5.73 (H_d), 3.28 (H_a), and 3.02 ppm (H_b).

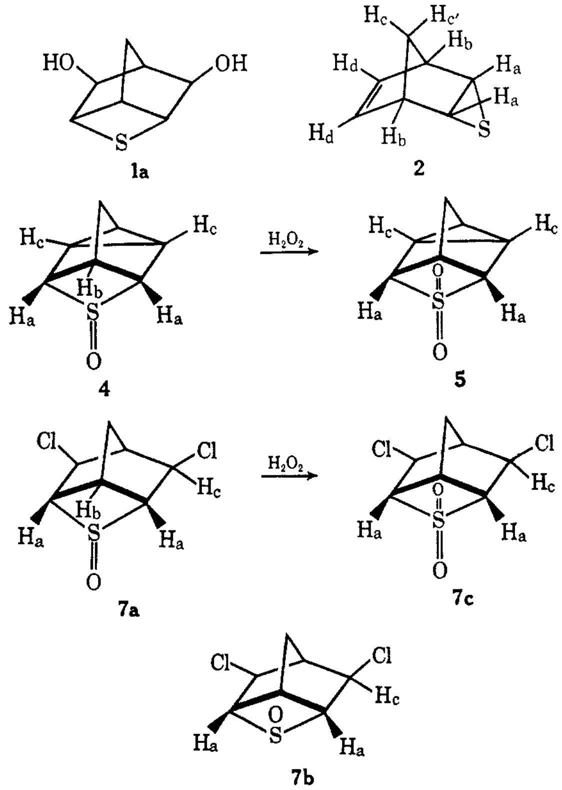


The ultraviolet spectrum shows a weak absorption at 265 mμ (ε 40) which does not permit distinguishing between the two isomeric structures **2** and **3**, since absorptions for thianes and episulfides are observed at similar wavelengths.[1,8,9] The small bathochromic shift of the absorption maximum of **2** in comparison with aliphatic episulfides might indicate homoallylic conjugation between unsaturation and the episulfide ring. The mass spectrum of **2** shows the molecular ion as the predominant product. A major fragmentation product results from the loss of sulfur and another from the loss of acetylene, which can readily be interpreted on the basis of structure **2**.

Reactions of the episulfide **2** do not permit distinguishing between the isomeric structures **2** and **3**. For example, addition of chlorine to **2** leads to the original dichloro sulfide **1** in nearly quantitative yield. This reaction provides another example of additions of chlorine to unsaturated episulfides, in which the same episulfonium intermediate would result from additions of chlorine to episulfide as from the addition of sulfur dichloride to olefins.[10] The structure of the isolated product does not allow a conclusion as to whether initial addition of chlorine occurs to the sulfur atom (**6a**) or to the olefinic site (**6b**), since transannular rearrangement could lead to the common intermediate **6c**. Furthermore, although triphenyl phosphine desulfurizes episulfides,[11] and thus provides a means of identification of episulfides, **2** is recovered unchanged with the formation of only 2% bicyclo[2.2.1]heptadiene as desulfurization product.



Another example for the ambiguity of structure analysis for **2**, if based on the structure of reaction products, is provided by the oxidation of **2**. W have recently reported several oxidations of substituted cyclic sulfides, where the oxidation reactions are accompanied by rearrangements.[10,12] The oxidation of **2** provides another example in that series. Oxidation with potassium periodate leads to the sulfoxide **4** as the only isolated isomer in a yield of 60%. Gas chromatographic analysis of the crude reaction product indicates the formation of additional products of similar retention time. The formation of isomeric products cannot, therefore, be excluded.



---

(6) A. C. Oelschlager and L. H. Zalkow, *Chem. Commun.*, **1**, 5 (1966).

(7) "Varian Catalogue of NMR Spectra," Vol. 2, Varian Associates, New York, N. Y., 1900.

(8) R. E. Davis, *J. Org. Chem.*, **23**, 216, 1380 (1958).

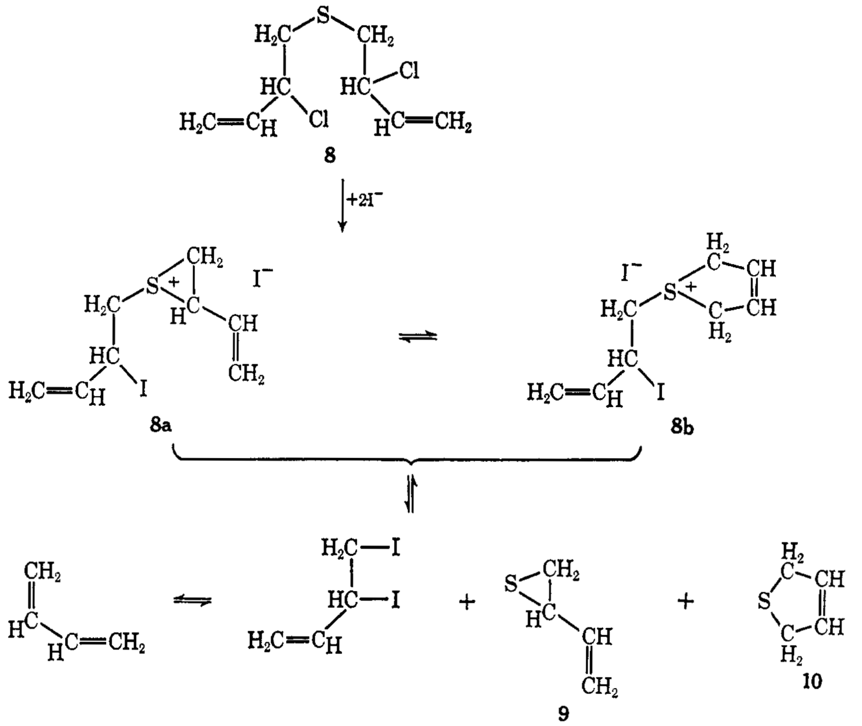
(9) J. F. McGhie, W. A. Ross, F. J. Julietti, B. E. Grimwood, G. Usher, and N. M. Waldron, *Chem. Ind.* (London), 1980 (1962); K. Takeda and T. Komeno, *ibid.*, 1793 (1962).

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

(11) For a review of desulfurization reactions of episulfides, see M. Sander, *Chem. Rev.*, **66**, 297 (1966).

(12) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2627 (1968).

SCHEME I



The configuration of the oxygen atom in **4** could either be *exo* or *endo*. For this assignment, the similarity of **4** with the sulfoxide **7a** and its isomeric sulfoxide **7b** was considered, for which we accept the configuration proposed recently.[13] That the configuration of the oxygen atom in **4** is *exo* rather than *endo* can be ascertained by comparing the change of the chemical shift values of the protons of **4** on conversion to its sulfone **5** with its change in the *exo* sulfoxide **7a** on conversion to its corresponding sulfone **7c** (Table I).

TABLE I

CHEMICAL SHIFT CHANGES[a] ON CONVERSION OF SULFOXIDE **4** TO SULFONE **5** (A) AND SULFOXIDE **7a** TO SULFONE **7c** (B)

A	B
H_a, $+0.60$	H_a, $+0.57$
H_b, -1.54	H_b, -1.39
H_c, $+0.14$	H_c, $+0.19$

[a] In parts per million with deuteriochloroform as solvent. Positive values correspond to downfield displacements.

It is observed that this effect is virtually identical in both ring systems, although initially the chemical shifts of the affected protons are significantly different. For **4**, proton H_b is found at 4.20, H_a at 3.16, and H_c at 1.69 ppm. In the spectrum of **5** these protons are located at 2.66, 3.76, and 1.83 ppm. These differences (Table I) of -1.54, $+0.60$, and $+0.14$ ppm compare with $+0.57$, -1.39, and $+0.19$ ppm observed on conversion of the *exo* sulfoxide **7a** to its sulfone **7c**. We suggest that this surprising similarity in direction and magnitude of chemical shift changes supports a similar configuration of the sulfoxide group in both ring systems. Medium-intensity infrared absorption bands at 893 cm^{-1} in **4** and 875 cm^{-1} in **5**, which have been assumed to be characteristic for such cyclic systems,[14] and the absence of bands due to olefinic unsaturation in both the infrared and nuclear magnetic resonance spectrum provide evidence for the presence of a nortricyclene structure.

For mechanistic considerations, it is significant that on treatment of **1** with aqueous sodium sulfide, a small yield of the dihydroxy sulfide **1a** is obtained. Also, treatment of **1** with aqueous sodium carbonate leads to the sulfoxide **4** in 39% yield.

Attempts to extend the reaction of potassium cyanide to other β,β'-dichloroalkyl sulfides have been less successful. Treatment of **8** with potassium cyanide in glycerol leads to both 2,5-dihydrothiophene (**10**) and 3,4-epithio-1-butene (**9**) in a yield of <5%. It was assumed that such elimination would be more facile if the chloro group is substituted by an iodo group. Indeed, on treatment of **8** with sodium iodide, formation of iodine, butadiene (48%), and **10** (35%), as well as polymeric product, was observed.

For the mechanistic interpretation of the formation of **2**, it is suggested that either an episulfonium ion such as **6** may be reduced to episulfide by the elimination of Cl$^+$, or addition of a nucleophile such as Cl$^-$ may lead to the formation of β,β'-disubstituted product. In our example, potassium cyanide initiates the replacement of the chloride ion from **1** *via* the intermediate **6** and also acts as scavenger for the eliminated chlorine.

The reaction of **8** with potassium iodide follows an analogous mechanistic pattern. The sulfonium ion **8a** could rearrange to **8b** prior to dissociation into sulfides and 3,4-diiodo-1-butene with subsequent formation of butadiene-1,3 and iodine (Scheme I). The reverse reaction, the addition of alkyl iodide to episulfide, was reported earlier.[15]

It is of interest to compare the reaction of **1** with potassium cyanide with the reaction of **1** in aqueous sodium carbonate, in which an efficient scavenger for positive chlorine is absent. In this case, initial elimination

---

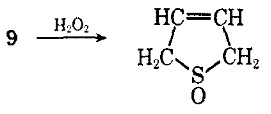
(13) C. R. Johnson, *Tetrahedron Lett.*, in press.

(14) G. E. Pollard and D. D. Phillips, *Spectrochim. Acta*, **18**, 837 (1962).

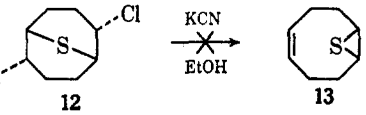
(15) G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **25**, 1754 (1960).

of chlorine leads to the oxidation of the sulfide **2**. That such rearrangement during the oxidation may occur has been demonstrated in the reaction of **2** with potassium metaperiodate.

In analogy to the oxidation of **2** with periodate, oxidation of **9** with hydrogen peroxide in acetone leads to rearranged product, 2,5-dihydrothiophene 1-oxide (**11**), in a yield of 25% as the only isolated distillable product. These reactions provide additional examplesin a series of rearrangements of olefinic sulfides during oxidation reactions.[12]



11



12 13

Attempts to isolate the olefinic episulfide **13**[16] from 2,6-dichloro-9-thiabicyclo[3.3.1]nonane (**12**)[4,6] and potassium cyanide failed, indicating the absence of a tendency for **12** to dehalogenate under these conditions. This is further evidenced by the high yield of the conversion of **12** to the corresponding dihydroxy compound with sodium bicarbonate,[4,6] in contrast to the behavior of **1**. This suggests that the formation of episulfide by the reduction of β,β'-dichloroalkyl sulfides is not a general reaction.

Experimental Section

Melting points were recorded on a Hallenkamp block and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 521 instrument and nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument unless otherwise noted.

***endo*-2,3-Epithio-5-norbornene (2).**—A solution of 214 g (1.1 mol) of **1** and 180 g of sodium cyanide in 3 l. of 85% ethanol was heated to 65° for 2 hr. The suspension was diluted with 3 l. of water and extracted with chloroform. The chloroform solution was washed with water, dried with anhydrous magnesium sulfate, and distilled under reduced pressure. A fraction boiling between 35 and 50° (0.5 mm) was steam distilled to give 41 g of **2**, mp 45–47°.[17]

Anal. Calcd for C_7H_8S: C, 67.7; H, 6.4; S, 25.8. Found: C, 68.1; H, 6.5; S, 25.6.

The product is extremely volatile and can readily be sublimed at atmospheric pressure. The product shows strong infrared absorption bands at 2980, 1330, 1240, 1038, 801, 772, 730, and 654 cm^{-1}. The bending frequency of the group CH_2 shows two peaks at 1451 and 1443 cm^{-1}.

Attempted Desulfurization of 2 with Triphenylphosphine.—A solution of 0.2 g of **2** and 0.5 g of triphenylphosphine in 5 ml of carbon disulfide was allowed to stand at room temperature for 5 days, after which time gas chromatographic analysis showed 2% of norbornadiene and unchanged **2**. Evaporation of solvent and sublimation at atmospheric pressure gave a 90 % yield of **2**, identified by its infrared spectrum.

A similar reaction with carbon tetrachloride as solvent was carried out at 80° and showed 5% desulfurization after 3 hr.

Formation of 1 by Addition of Chlorine to 2.—To a solution of 2.5 g (0.02 mol) of **2** in 25 ml of methylene chloride, chlorine was added at −20° until a positive test with potassium iodide was obtained. The solution was allowed to warm to ambient temperature and the solvent was evaporated to give 3.8 g (100%) of crystalline product. Infrared and gas chromatographci analysis identified the product as **1**. Sublimation of 3.3 g of this material at 30° (0.4 mm) gave 2.8 g (84%) of **1**, mp 43–45°, identified by its infrared spectrum and mixture melting point on comparison with those of an authentic sample of **1**.

***exo,exo*-2,6-Dihydroxy-8-thiatricyclo[2.2.1.1^{2,6}]octane (1a).**—To a solution of 17.6 g of sodium sulfide (0.33 mol, assuming 34% water content), 58.5 g (0.3 mol) of **1** was added at 80°. After the solution was stirred at high speed for 1 hr, gas chromatographic analysis showed the absence of starting material. Polymeric product (15 g) was filtered and the aqueous solution was continuously extracted with diethyl ether. The ether solution was washed with water and evaporated to give 11.2 g of crystalline product, from which an analytical sample of **1a** was obtained on crystallization from 80 ml of benzene–ethyl acetate (1:1 v/v), mp 183–195° dec.

Anal. Calcd for $C_7H_{10}O_2S$: C, 53.20; H, 6.38; S, 20.25. Found: C, 53.56; H, 6.30; S, 20.58.

The nmr spectrum (pyridine) shows a narrow multiplet at 1.98 ppm (CH_2), a multiplet for the three protons of the thietane ring at 2.98 ppm, the second bridgehead proton at 3.67 ppm, CHOH protons at 6.02 ppm, and OH protons at 4.42 ppm (singlet).

8-Thiatetracyclo[2.2.1.1^{2,6}.0^{3,5}]octane 8-Oxide (4). A. By Oxidation with Potassium Periodate.—To a solution of 1.24 g (0.01 mol) of **2** in 25 ml of aqueous methanol (1:1), 2.40 g (0.01 mol) of potassium metaperiodate was added with stirring at 25°. The solution was allowed to stir for 60 hr, after which time gas chromatographic analysis showed the absence of **2**. After filtration, the solution was extracted with five portions of chloroform (5 ml each). The combined dried extracts were washed with two portions of water (5 ml each) and dried over anhydrous magnesium sulfate. After evaporation of solvent, the partially crystalline residue was recrystallized from pentane to give 0.88 g (63%) of **4**, mp 76–77°.

Anal. Calcd for C_7H_8OS: C, 59.99; H, 5.75; S, 22.84. Found: C, 59.97; H, 5.73; S, 22.82.

The infrared spectrum shows major absorption bands at 1270, 1130, 1045 (S=O), and 815 cm^{-1} and low-intensity absorptions at 3050, 3025, 3010, and 2945 cm^{-1} in the range of the CH stretching frequency.

B. By Treatment of 1 with Aqueous Sodium Carbonate.—Into a solution of 63.6 g (0.6 mol) of sodium carbonate in 750 ml of water, 58.5 g (0.3 mol) of **1** was added with high-speed stirring and an internal temperature of 90–100°. The suspension was allowed to cool, a syrupy product was separated with diethyl ether, and the aqueous solution was continuously extracted with diethyl ether to give 18.6 g (39%) of **4**, mp 70–75°, identified by infrared analysis and mixture melting point of the purified product. Recrystallization from heptane raised the melting point to 75–77°. Another fraction (1.0 g) of a noncrystallizable product was obtained which was not identified.

Oxidation of 2 with Hydrogen Peroxide. 8-Thiatetracyclo[2.2.1.1^{2,6}.0^{3,5}]octane 8,8-Dioxide (5).—To a solution of 1.4 g (0.01 mol) of **2** in 10 ml of glacial acetic acid, 0.64 g (0.01 mole) of a 50% aqueous solution of hydrogen peroxide was added. After evaporation of the solvent at normal pressure, 1.5 g (96%) of a crystalline residue remained. Recrystallization from 15 ml of benzene and carbon tetrachloride (1:4 v/v) gave a first fraction of 0.7 g, mp 135° dec. On complete evaporation and sublimation of the residue, another 0.7 g of **5** was obtained, mp 230° dec.

Anal. Calcd for $C_7H_8O_2S$: C, 53.82; H, 5.16; S, 20.52. Found: C, 53.96; H, 5.40; S, 20.45.

The infrared spectrum of **5** shows major absorption peaks at 2175, 1172, 1093, 809, 568, and 500 cm^{-1}. The nmr spectrum ($CDCl_3$) shows protons H_e at 1.62 (singlet, $W_{1/2}$ = 3 cps), H_a at 3.76, H_b at 2.66, H_d at 2.1, and H_c at 1.83 ppm.

Oxidation of 3,4-Epithio-1-butene with Hydrogen Peroxide. 2,5-Dihydrothiophene 1-Oxide (11).—To a solution of 1.72 g (0.02 mol) of butadiene episulfide[18] in 25 ml of acetone, 1.28 g (0.02 mol) of a 50% solution of hydrogen peroxide in water was added with stirring. After 12 hr, the solution was evaporated and the residual oil was distilled to give 0.50 g (25%) of **10**, bp 51.5–52° (0.01 mm), n^{20}_D 1.5370.[19] The product was identical

---

[16] F. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969).

[17] Gas chromatographic analysis indicated that no change of the material occurred during steam distillation.

[18] C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 278 (1949).

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

with a substance obtained by oxidation of 2,5-dihydrothiophene with hydrogen peroxide[19] by infrared analysis.

Reaction of a Sulfur Dichloride Addition Product of 1,3-Butadiene with Potassium Cyanide (8).—To a suspension of 195.3 g (3 mol) of potassium cyanide in 200 ml of glycerol, which was heated to 120°, 105.5 g (0.5 mol) of a sulfur dichloride addition product of 1,3-butadiene[12] was added with vigorous stirring. The system was maintained at a pressure of 10 mm during the addition, and volatile portions were collected in a liquid nitrogen cooled trap. Gas chromatographic analysis of the resulting product (1.5 g) showed the presence of both **9** and **10** in a proportion of 12:1.

Reaction of 8 with Sodium Iodide. A. In Acetone.—To a solution of 2.2 g (0.01 mol) of **8** in 15 ml of acetone, 4.6 g (0.031 mol) of sodium iodide was added. The suspension was heated to reflux temperature for 10 min, which led to the elimination of iodine, evidenced by discoloration of a sample by thiosulfate. Quantitative gas chromatographic analysis showed the formation of 0.63 g (72%) of dihydrothiophene (**10**) as well as a trace amount of vinyl thiirane (**9**). Separation of the insoluble reaction products by filtration yielded 0.225 g of polymeric product after exhaustive extraction with water.

B. In Glycerol.—Into a suspension of 50 ml of glycerol and 23 g (0.153 mol) of sodium iodide in a three-necked flask equipped with stirrer, dropping funnel, and internal thermometer, 10.55 g (0.05 mol) of the sulfur dichloride addition product of 1,3-butadiene (**8**) was added. The addition was carried out over a period of 5 min at an internal temperature of 90–105° with stirring. Frothing indicated the formation of gaseous product, which was collected in two Dry Ice–acetone traps and identified by its boiling point (−4.5°) and infrared spectrum as 1,3-butadiene, yield 1.3 g (48%).

The remaining reaction product was then further degassed at a pressure of 100–120 mm, which led to the isolation of 1.5 g (35%) of crude **10**, identified by its gas chromatographic retention time and its infrared spectrum.

Registry No.—**1a**, 22061-72-9; **2**, 22061-73-0; **4**, 22061-74-1; **5**, 22061-75-2.

The Reaction of Selenium Monochloride with Diolefins

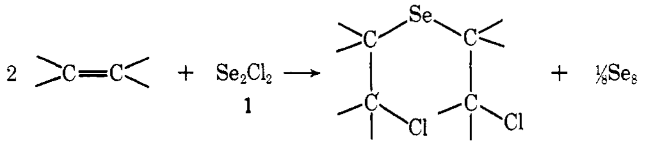
F. LAUTENSCHLAEGER

Dunlop Research Centre, Sheridan Park, Ontario, Canada

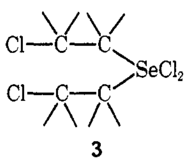
Received March 20, 1969

The addition of selenium monochloride to olefins is known to lead to bis(β-chloroalkyl) selenides and free selenium. This reaction has now been studied on a variety of diolefins. Thus, cyclic selenides were obtained from linear diolefins, whereas bi- and tricyclic products were isolated from cyclic and bicyclic diolefins. Significant differences between the addition of selenium monochloride and sulfur dichloride were only apparent in reactions with conjugated olefins. The isolated products represent novel selenium-containing ring structures. The reaction provides a convenient synthesis of β,β′-substituted selenides for which, in most cases, no alternative synthesis is conceivable.

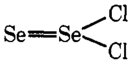
Attempts to add selenium monochloride **1** to olefinic hydrocarbons have been reported [1-5] to lead to the separation of free selenium and the formation of bis(β-chloroalkyl) selenides of the general structure **2**. By-products of the type **3** resulted from the chlorination of the initial addition products. The proportion of **2** and **3** depends on the mode of addition, whereby the addition of the selenium chloride to the olefin favors the formation of **2**. The separation of one of the two selenium atoms of the reagent was interpreted to result from the existence of selenium monochloride in the unsymmetrical structure **4a** in preference to the linear structure **4b**. This is in contrast to recent reports, which favor the linear structure for the homologous sulfur monochloride.[6] Furthermore, in earlier investigations yields of the isolated addition products were not reported and products were only identified by determination of their chlorine content.



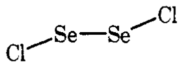
2



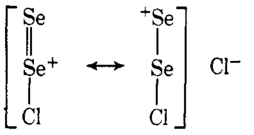
3



4a



4b



5a 5b

Investigations of the reactions of selenium tetrachloride **6** with chlorinated olefins[7a] in the presence of selenium showed that products can be obtained which correspond to the addition products obtained from selenium monochloride. It was therefore concluded that selenium dichloride would exist in equilibrium with selenium tetrachloride and selenium (eq 1). However,

$$\mathrm{SeCl_4 + Se \rightleftharpoons 2SeCl_2} \qquad (1)$$

in the absence of free selenium, the addition of selenium tetrachloride to olefins leads to β, β′-dichloroalkylselenium dichlorides **3**.[7a] Applying the combination of selenium tetrachloride and selenium, the addition of the elements of selenium dichloride was achieved to vinyl chloride. However, the presence of aluminum chloride was required to affect the addition to halogen substituted olefins. Significantly, attempts to carry out substitution reactions on these addition products with methanolic potassium hydroxide have led to dehydro-

---

(1) C. E. Boord and F. F. Cope, *J. Amer. Chem. Soc.*, **44**, 395 (1922).

(2) E. S. Gould and J. D. McCullough, *ibid.*, **73**, 1105 (1951).

(3) F. H. Heath and W. L. Semon, *J. Ind. Eng. Chem.*, **12**, 1101 (1920).

(4) H. W. Bausor, C. S. Gibson, and W. J. Pope, *J. Chem. Soc.*, **117**, 1453 (1920).

(5) E. H. Harvey and H. A. Schuette, *J. Amer. Chem. Soc.*, **50**, 2837 (1928).

(6) (a) E. Hirota, *Bull. Chem. Soc., Jap.*, **31**, 130 (1958); (b) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

(7) (a) H. Brintzinger, K. Pfannstiel, and H. Vogel, *Z. Anorg. Chem.*, **256**, 75 (1948); (b) D. M. Yost and C. E. Kircher, *J. Amer. Chem. Soc.*, **52**, 4680 (1930).