by the uv method. The recovery of benzoic acid from the peracid was over 95% by means of uv analysis. The results are listed in Table I.

Rate Measurements.—The oxidation was started by adding a peracid solution to a thermostated solution containing aldehyde and buffer. Aliquots were taken out at appropriate intervals of time and the remaining peracid was determined by iodometry. No apparent difference in rates was observed for the reactions in air and under nitrogen atmosphere. The spontaneous decomposition of perbenzoic acid was negligible in most runs, but when it became significant in comparison with its reaction with aldehyde, the rate constants were corrected.

Registry No.—Perbenzoic acid, 93-59-4.

The Synthesis of Episulfides from Olefins and Sulfur Monochloride

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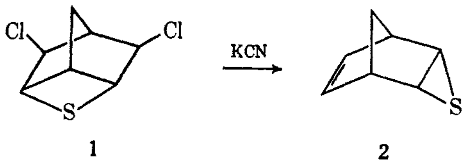
The addition of sulfur monochloride to an excess of many alkenes gives practical yields of β-chloroalkyl disulfides, which are readily reduced and dehydrohalogenated by sodium sulfide to give stereochemically pure episulfides.

The principal synthetic approaches to episulfides have been reviewed recently.[1] Since the publication of these reviews, several new approaches have been disclosed: the reaction of ketohydrazones with sulfur,[2] the synthesis of *trans*-3,4-diphenyl-1,2-epithiocyclobutane in a yield of 34% by short irradiation of *cis*,-*trans*-β-phenylvinyl sulfide[3] as the first synthesis of a cyclobutene episulfide, the pyrolysis of aryl- or alkyl-2-hydroxyethyl thiolcarbonates,[4] the reduction of 2-hydroxyethyl disulfide with phosphines and secondary phosphine oxides,[5] and the reduction of the sulfide **1** to the unsaturated episulfide **2**.[6]

The most significant approaches may be classified into two groups. First, olefins can be oxidized with sulfur, leading to episulfides directly.[7] Second, olefinic compounds can be raised to the desired oxidation state and the resulting epoxides, dihalides, or chlorohydrins can be converted to episulfides by a variety of sulfur-containing reagents, such as potassium thiocyanate or thiourea in the case of epoxides. Related to the first group would be the reaction of the hypothetical thiohypochlorous acid, HSCl, with olefins. Although hypochlorous acid is readily prepared and effectively used in the synthesis of epoxides, the sulfur analogs HSBr and HSCl were only suggested as intermediates in the reaction of hydrogen sulfide with bromine or chlorine.[8] It can be doubted, however, that these sulfur analogs could be used effectively in view of their anticipated behavior as oxidizing agents and the ease of oxidation of the resulting halomercaptans to bis(β-haloalkyl) disulfides.

Whereas the first synthetic approach, the addition of sulfur to olefins, is still only of theoretical interest, the second path represents the almost exclusively used route for laboratory synthesis. This latter approach has several limitations. The conversion of cyclopentene oxide to the corresponding episulfide with thiourea or potassium thiocyanate is unsatisfactory [9] Furthermore, the formation of episulfides from sulfur-containing olefins such as 2,5-dihydrothiophene (**3**) *via* oxidative routes would necessarily involve oxidation of the sulfur atom; and as a consequence, a direct route to an episulfide such as **4** has not been available.

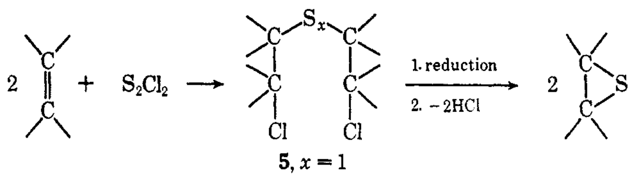


1 **2**

3 **4**

We now report a novel, two-step synthesis of episulfides from the corresponding olefins. Sulfur monochloride is added to the olefin in the first step to form mixtures of β-chloroalkyl mono-, di-, and trisulfides (**5**–**7**). The adducts **6** and **7** are then converted to the episulfide by means of sodium sulfide or aluminum amalgam (Scheme I).

SCHEME I



5, $x = 1$

6, $x = 2$

7, $x = 3$

Results and Discussion

Addition of Sulfur Monochloride to Olefins.—Although the addition of sulfur monochloride to olefins was reported as early as 1860,[10] the synthetic value of

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[1] D. D. Reynolds and D. L. Fields in "Heterocyclic Compounds with Three- and Four-Membered Rings," Interscience Publishers, New York, N. Y., 1964, p 576; M. Sander, *Chem. Rev.*, **66**, 297 (1966); L. Goodman and E. J. Reist in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966.

[2] N. Latif, I. Fathy, N. Mishriky, and B. Haggag, *Can. J. Chem.*, **44**, 629 (1966).

[3] E. Block, Ph.D. Thesis, Harvard University, 1967.

[4] D. L. Fields and D. D. Reynolds, U. S. Patent 3,247,225 (1966).

[5] M. Grayson and C. F. Farley, *Chem. Commun.*, **16**, 831 (1967).

[6] F. Lautenschlaeger in "The Chemistry of Sulfides," A. Tobolsky, Ed., Interscience Publishers, New York, N. Y., 1968, pp 73–81; *J. Org. Chem.*, **34**, 3998 (1969).

[7] P. Fowles, M. de Sorgo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1352 (1967). For a review, see H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

[8] M. Schmidt in "Inorganic Polymers," F. G. Stone and W. A. Graham, Ed., Academic Press, New York, N. Y., 1962, Chapter 3.

[9] See, *e.g.*, (a) E. E. van Tamelen, *J. Amer. Chem. Soc.*, **73**, 3444 (1951); (b) L. Goodman and B. R. Baker, *ibid.*, **81**, 4924 (1959).

[10] A. Niemann, *Ann.*, **113**, 288 (1860).

this reaction appeared limited in view of the reported elimination of hydrogen chloride from the reaction products **5**–**7** with the formation of tars and up to 70% β-chloroalkyl monosulfides (**5**). Since the latter cannot be converted to episulfide, the amount of **5** formed in the addition of sulfur chloride to the olefin must be minimized to achieve an optimum yield of episulfide.

The following equations present some of the possibilities of the formation of **5** and **7** in the addition of sulfur monochloride to an olefin.

$$S_2Cl_2 \rightleftharpoons SCl_2 + {}^1/_8S_8 \qquad (1)$$

$$S_2Cl_2 + {}^1/_8S_8 \rightleftharpoons S_3Cl_2 \qquad (2)$$

$$2S_2Cl_2 \rightleftharpoons SCl_2 + S_3Cl_2 \qquad (3)$$

$$RS_2R + S_2Cl_2 \longrightarrow RSCl + RS_3Cl \ (R = \beta\text{-chloroalkyl}) \qquad (4)$$

$$RSCl + CH_3CH{=}CH_2 \longrightarrow \underset{\mathbf{5}}{RSR} \qquad (5)$$

$$RS_3Cl + CH_3CH{=}CH_2 \longrightarrow \underset{\mathbf{7}}{RS_3R} \qquad (6)$$

Coffey[11] reported the formation of tars and long-chain polysulfides from the addition of ethylene to sulfur monochloride, during which the sulfur monochloride was present in excess throughout the reaction. The formation of these products was ascribed to the action of free sulfur on the intermediate β-chloroalkylsulfenyl chloride,[11] the free sulfur being eliminated from sulfur monochloride according to eq 1.[12] Compounds of types **5** and **7** could also result from attack of sulfur monochloride on initially formed **6** according to eq 4–6.[13,14] If this type of reaction contributes to the formation of large amounts of **5**, then, by adding sulfur monochloride to a large excess of olefin, the attack of sulfur monochloride on the adduct should be minimized. Indeed, when the addition of carefully distilled, commercial grade sulfur monochloride to propylene was carried out in sealed ampoules at room temperature and with excess olefin present as a diluent, a quantitative yield of adduct was obtained. Although the addition of sulfur monochloride to cyclic olefins can readily be achieved at room temperature, the addition to less reactive, terminal olefins, such as propylene, is quite slow but can be accelerated by the addition of small amounts of pyridine. By fractional distillation and by glpc analysis, the adduct was found to consist only of nearly equimolar amounts of **5**, **6**, and **7**. No free sulfur β-chloropropyl polysulfides with more than three sulfurs in the chain, or chlorinated products were detected in the crude adduct. This suggests that tar and polysulfide formation in the earlier work may be due to the mode of addition. The absence of chlorinated products in our propylene–sulfur monochloride adducts also indicates that the chlorinating effect of sulfur monochloride on unsaturated hydrocarbons is negligible.

Disproportionation of the sulfur monochloride into sulfur dichloride and dichlorotrisulfane as in eq 3 must also be considered as a possible source of **5**. This disproportionation may depend on the pressure of catalytic amounts of impurities in the sulfur monochloride. Commercial sulfur monochloride probably contains traces of ferric ion among other impurities, since ferric ion is used to catalyze the reaction of sulfur with chlorine.[15] If the redistilled commercial sulfur monochloride is replaced by sulfur monochloride, prepared from highly pure sulfur and chlorine, in the addition to propylene, the amount of **5** in the adduct in reduced from *ca.* 30 to 14%, although not consistently. Furthermore, the addition of dichloropolysulfanes, obtained by heating sulfur monochloride with excess sulfur,[15] to propylene further reduces the amount of **5** formed to 3% (Table I). These results can be interpreted as an indication that an equilibrium such as in eq 3 exists and that inorganic impurities might affect it.

TABLE I
EFFECT OF VARIOUS SULFUR CHLORIDES ON YIELDS OF β-CHLOROALKYL MONOSULFIDES

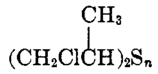
Type of sulfur chloride	Yield of β-chloroalkyl monosulfide, %[a] With propylene	With cyclohexene
SCl_2	...	95
S_2Cl_2	30–35	22–31
S_xCl_2 (x = 4.6[b])	13	14
S_xCl_2 (x = 6.6[b])	3	1

[a] Yields of 97–100% were obtained in these addition reactions. [b] Such a polysulfur chloride contains free sulfur. The number shown indicates the average number of sulfurs in the chain, including the free sulfur present.

In the addition of sulfur chlorides to unsymmetrically substituted olefins, the possibility of positional isomers in the adducts arises. Thus, for example, in the addition of sulfur monochloride to propylene, the resulting disulfide adduct could be 2-chloro-1-propyl disulfide (**8**, n = 2) or 1-chloro-2-propyl disulfide (**9**) or a mixture of

$(CH_3CHClCH_2)_2S_n$

8



$(CH_2ClCH(CH_3))_2S_n$

9

both structures. Since both isomers can be converted to the same episulfides, the isomer distribution is not important in determining the yield of episulfide obtainable in the case of simple olefins, but it does give an indication of the mechanism of the addition and could affect the product distribution obtainable from allyl derivatives. It is found that, in the case of propylene, a mixture of the isomers **8** and **9** is obtained in a ratio of *ca.* 1:1. It is of interest to compare this isomer distribution with that obtained from the addition of chlorine to propylene sulfide[16] and the isomer distributions of the adducts of alkyl- and arylsulfenyl chlorides with olefins,[17] both of which types of reactions are postulated to proceed *vis* episulfonium ion intermediates. Table II summarizes the isomer distributions from the additions of chlorine and sulfur monochloride to propylene sulfide and of sulfur dichloride and sulfur monochloride to propylene. In all cases, the isomer distribution is similar, although not identical, and would indicate a common type of intermediate; *viz.*, the episulfonium ion with varying numbers of sulfur atoms attached to the

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[11] S. Coffey, *J. Chem. Soc.*, **119**, 95 (1921).

[12] (a) J. B. Conant, E. B. Hartshorn, and G. O. Richardson, *J. Amer. Chem. Soc.*, **42**, 585 (1920); (b) W. J. Pope and J. L. B. Smith, *J. Chem. Soc.*, **119**, 397 (1921).

[13] R. C. Fuson, D. M. Burness, R. E. Foster, and R. D. Lipscomb, *J. Org. Chem.*, **11**, 499 (1946).

[14] R. C. Fuson, C. C. Price, and D. M. Burness, *ibid.*, **11**, 475 (1946).

[15] See "Gmelins Handbuch der Anorganischen Chemie," System-Nummer 9, Schwefel, Teil B, Verlag Chemie, Weinheim, Germany, 1963.

[16] N. V. Schwartz, *J. Org. Chem.*, **33**, 2895 (1968), and references cited therein.

[17] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

Table II

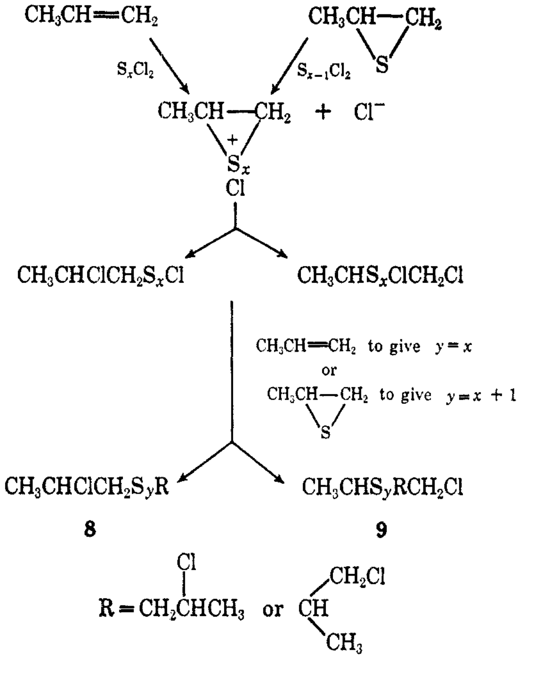
Isomer Distribution of Products Formed in Reactions Which May Proceed by a Common Episulfonium Intermediate[a]

Reaction[a]	Av no. of sulfur atoms[a] (y) in **8** or **9**	Distribution of isomeric groups, %		Chemical shift of CH_3 signal in nmr[b]	
		9	**8**	**9**	**8**
Propylene + SCl_2	1	50	50	1.30	1.48
Propylene + S_2Cl_2	2	42	58	1.35	1.56
Propylene sulfide + Cl_2	2	55[c]	45[c]	1.35	1.56
Propylene sulfide + S_2Cl_2	4	66	34	1.42	1.68

[a] See Scheme II. [b] In deuteriochloroform at 35°, in τ, parts per million, downfield from tetramethylsilane. [c] See ref 16.

sulfonium sulfur causing the observed differences (Scheme II). These isomer distributions were determined from the nmr spectra of the crude reaction products. The chemical shifts of the methyl protons of the various isomers are also shown in Table II. These chemical shifts show distinct differences and also indicate a significant influence of the sulfur chain length on the position of the methyl protons.

Scheme II



In the case of addition of sulfur monochloride to allyl derivatives, the isomer distribution in the adduct can affect the nature of the cyclic sulfide obtained. Scheme III shows the possibilities for additions to allyl chloride, allyl bromide, and allyl acetate. If Markovnikov addition takes place (path A) to give **11a**, **11b**, or **11c**, subsequent reduction and dehydrohalogenation could give from **10a** either **12a** or **13** or a mixture of both, depending on the relative ease of 1,2 *vs.* 1,3 displacement, and from **10b** either **12b** or **13** or a mixture of both, but no **12a**. Similarly, Markovnikov addition of S_2Cl_2 to **10c** should result in **12c** or **13** or a mixture of both but no **12a**. If anti-Markovnikov addition takes place to give **14a**, **14b**, or **14c**, then reduction and dehydrohalogenation should give only **12a** from **10a** and either **12a** or **12b** or a mixture of both from **10b**, and **12c** or **12a** or a mixture of both from **10c**, depending on relative ease of displacement of the functional groups. Determination of the isomer distributions by nmr from addition of sulfur monochloride to **10a**, **10b**, and **10c** carried out at ambient temperature in excess olefin shows the adducts to be exclusively anti-Markovnikov (Table III), *i.e.*, **12a**, **12b**, and **12c**. Thus, treatment of both the allyl chloride and allyl bromide–sulfur monochloride adducts with aluminum amalgam yields only **12a**, while only **12c** is obtained from allyl acetate.

Table III

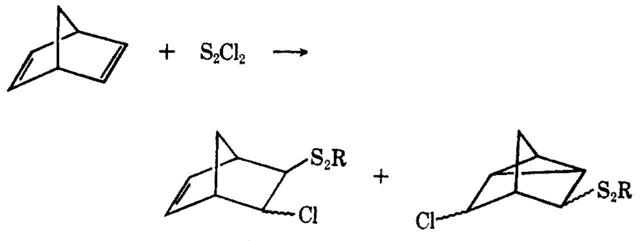
Isomer Distribution of the Addition of Sulfur Monochloride to Allyl Derivatives

$CH_2=CHCH_2X$	CHS[a]	Numbers of protons for groups $CH_2Cl + CH_2X$
X = Cl	1.0	4.0
X = Br	1.0	4.0
X = $OCOCH_3$	1.0	4.0
X = CN	...	(2.0)[b]

[a] CHS is observed in the range of 3.0–3.5 ppm, and CH_2Cl and CH_2X are unresolved in the range of 3.5–4.5 ppm. [b] Incomplete separation of CH_2CN and CHS protons permits only evaluation of CH_2Cl.

If we consider preparing episulfides from conjugated dienes, the question arises as to whether sulfur monochloride adds predominantly 1,2 or 1,4 to these compounds. We have recently reported that sulfur dichloride adds exclusively 1,2 to 1,3-butadiene,[18] while methane- and benzenesulfenyl chlorides have also been shown to add predominantly 1,2 to a variety of conjugated dienes.[19] Thus, it is not surprising to find that sulfur monochloride reacts with 1,3-butadiene to give 95% 1,2 adduct **15a**, which can be converted to the episulfide, along with 5% 1,4 adduct **16a**. It was found that the 1,2 adduct **15a** as well as the corresponding 1,2 adduct **15b** from butadiene and sulfur dichloride are readily rearranged to the 1,4 adducts **16a** and **16b** by heating with anhydrous zinc chloride in benzene (see Scheme IV).

Although sulfur monochloride and sulfur dichloride give similar adducts with butadiene, they behave quite differently toward norbornadiene. Addition of sulfur dichloride to norboradiene gives compound **1**, in which 1 mol of sulfur dichloride has added to both double bonds of norbornadiene.[20] On the other hand, the addition of sulfur monochloride to norbornadiene leads to a reaction of 2 mol of diolefin/1 mol of sulfur chloride. Structures **17** and **18** are in agreement with the nmr spectrum of the resulting 1:2 adduct. The nmr spectrum indicates 64% olefinic unsaturation, which



17 **18**

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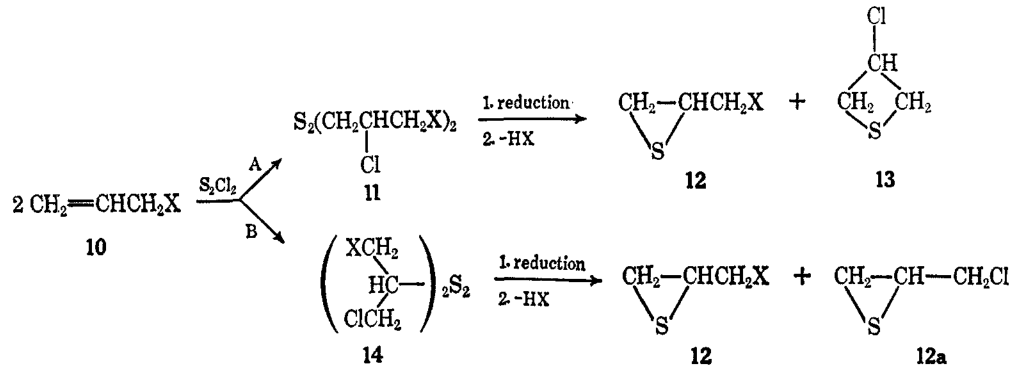
(18) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2627 (1968).

(19) W. H. Mueller and P. E. Butler, *ibid.*, **33**, 2642 (1968).

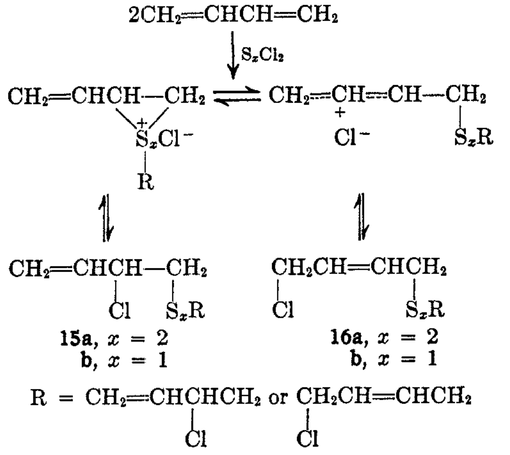
(20) F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966).

SCHEME III



10–12, 14a, X = Cl
b, X = Br
c, X = OAc

SCHEME IV



probably arises from structures of the type **17**, although other products cannot be excluded.

Whereas the addition of sulfur monochloride to excess 1,3-butadiene or norbornadiene leads almost exclusively to 1:2 addition products **15a**, **17**, and **18**, addition to nonconjugated dienes such as 1,4-pentadiene, 1,5-hexadiene, and 1,7-octadiene leads to mixtures of 1:1 and 1:2 addition products. This indicates the decreased reactivity of the remaining unsaturation in **17** and **18** toward further addition of sulfur monochloride, while nonconjugated dienes react statistically at either one or both of the double bonds with sulfur monochloride, whereby addition at both double bonds leads to polymer formation.

Conversion of Sulfur Monochloride Adducts to Episulfides.—For the reduction of the olefin–sulfur monochloride adducts, various procedures could be applied to give β-chloroalkanethiols, which on treatment with base would yield the desired episulfides, but reductionof the adducts in basic media would be particularly advantageous, since episulfides would be formed directly.

A general mode of reduction was found in the reaction with aluminum amalgam. Although such a reduction was reported on the addition products of halogen-substituted olefins to yield mercaptans,[21] the formation of the corresponding episulfide was not observed in that reaction. We have found, however, that episulfides are the major products isolated from the aluminum amalgam treatment of the sulfur monochloride adducts of a variety of olefins (Table IV). Small amounts of β-chloroalkanethiols are produced sometimes as by-products. Although chlorothiols are probably intermediates in the reaction, conversion to the corresponding episulfides occurs through dehydrochlorination by aluminum hydroxide, which is produced during the reaction. Polysulfide polymers have been cleaved using aqueous sodium sulfide, sodium hydrogen sulfide, or mixtures of sodium hydrogen sulfide and sodium sulfite,[22] and we have found that sodium sulfide or sodium sulfide–sodium sulfite mixtures are excellent reagents for converting the sulfur monochloride–olefin adducts to episulfides directly. An additional advantage is that it can be used in the absence of solvents. In most cases the episulfide is obtained in high purity, except in cases of thermally unstable episulfides, when olefins arising from the desulfurization of the episulfide under the conditions of the reaction may make up a portion of the product.

The effect of varying the quantity of sodium sulfide on the yield of propylene sulfide from β-chloropropyl disulfide is shown in Table V. It is apparent from comparing reactions 2 and 3 that a large molar excess of sodium sulfide is required to obtain the optimum yields of episulfide. In the absence of such an excess, the presence of sodium sulfite in the reaction mixture markedly improves the yield of episulfide (reaction 4). Increasing the excess of sodium sulfide further improves the yield, but this is less significant, as shown in reaction 1. From the stoichiometry of the reaction between sodium sulfide and disulfide, it is obvious that sodium sulfite is required as a sulfur acceptor, although in its absence, excess sodium sulfide serves to remove the sulfur formed.

It was observed that the commercially available fused sodium sulfide, which contains approximately 38% water, gives the best yields of episulfides. If an aqueous solution of sodium sulfide or the nonahydrate is used, the yield of episulfide is decreased and the product is also contaminated with varying amounts of unreacted starting material (Table V, reactions 5 and 6). Sodium hydrogen sulfide proved to be less effective than the

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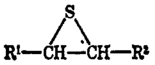
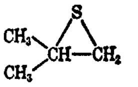
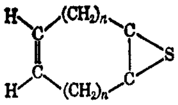
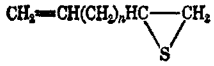
[21] (a) I. L. Knunyants and E. G. Bykhovskaya, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 852 (1955); (b) L. I. Zakharkin and V. V. Korneva, *ibid.*, 852 (1958).

[22] E. M. Fettes and H. Mark, *J. Appl. Polym. Sci.*, **5**, 7 (1961).

TABLE IV

EPISULFIDES OBTAINED FROM SULFUR MONOCHLORIDE ADDITION PRODUCTS OF OLEFINS

Registry no.	R^1	R^2	Bp, °C (mm)	n^{20}D	Yield on reduction, % — With aluminum amalgam	With sodium sulfide
						
420-12-2	H	H	55–56 (760)	1.4945	...	75^a
1072-43-1	H	CH_3	74 (760)	1.4752	35	65 88^a
3221-15-6	H	CH_2Cl	55 (28)	1.5280	41	29
22138-98-3	H	$CH_2CH(CH_3)_2$	40 (13)	1.4688	27^b	...
4468-63-7	H	n-C_4H_9	43 (0.16)	1.4718	25^b	...
13383-38-5	H	n-C_7H_{15}	57 (0.1)	1.4722	20^b	...
13748-26-0	H	n-C_8H_{17}	57 (0.02)	1.4720	41^b	...
1078-74-6	H	n-$C_{10}H_{21}$	80 (0.02)	1.4721	37^b	...
13785-70-1	H	$CH_2C_6H_5$	60 (0.1)	1.5780	23^b	...
19858-15-2	H	CH_2OAc	65 (6)	1.4828	31^b	...
1498-99-3	H	C_6H_5	30 (0.01)	1.6015	...	44
5954-71-2	CH_3	CH_3 (*cis*)	51 (130)	1.4775	...	64
5955-98-6	CH_3	CH_3 (*trans*)	88–89 (760)	1.4640	...	62
						
3772-13-2			84–86 (760)	1.4660	...	58
						
285-75-6		$n = 3$	74 (16)	1.5230	37	47
286-28-2		$n = 4$	30 (1)	1.5310	46	29
						
13785-72-3		$n = 1$	69 (10)	1.5647	16^{b,c}	...
13785-73-4		$n = 2$	44 (0.3)	1.5551	15^{b,c}	...
						
5954-75-6		$n = 0$	45 (80)	1.5227	...	16^c
6766-73-0		$n = 1$	84 (30)	1.4990	...	36.5^{b,c}
6766-70-7		$n = 2$	62 (24)	1.4927	...	41^{b,c}
14122-59-9		$n = 4$	33 (0.5)	1.4892	...	29^{b,c}
						
19858-20-9			45 (0.1)	...	41^b	...

[a] This yield was obtained from a pure sample of β-chloroalkyl disulfide. Other yields are from the crude olefin–S_2Cl_2 adduct. [b] New compound. Satisfactory elemental analysis was obtained. References to other episulfides can be found in ref 1. [c] This yield was obtained from a sulfur chloride–diolefin addition product of a molar ratio of 1:10 and is based on the amount of S_2Cl_2 used.

TABLE V

CONVERSION OF β-CHLOROPROPYL DISULFIDE TO PROPYLENE SULFIDE

Reaction	Form of Na_2S	Molar ratio of reactants, disulfide/ Na_2S/Na_2SO_3	Yield of episulfide, %
1	62%	1:4:4	88
2	62%	1:4:0	82
3	62%	1:2:0	38
4	62%	1:2:2	65
5	$Na_2S\cdot 9H_2O$	1:4:4	59 (+ 20% disulfide)
6	Na_2S (1 *M* solution)	1:4	30
7	NaSH	1:3:4	35

more basic sodium sulfide in the conversion of β-chloropropyl disulfide to propylene sulfide (reaction 7).

The synthesis of episulfides from olefins *via* their sulfur monochloride adducts is stereospecific. The only episulfide formed from *cis*-2-butene is *cis*-2-butene episulfide. None of the *trans* isomer was detected by glpc analysis. Similarly, *trans*-2-butene leads exclusively to the corresponding *trans*-episulfide. Sulfur monochloride must, therefore, add *trans* to olefins, as alkyl- and arylsulfenyl halides have been shown to do.[23] Episulfonium ion intermediates are probably intermediates in both cases. In the subsequent conversion of the olefin–sulfur monochloride adduct to episulfide,

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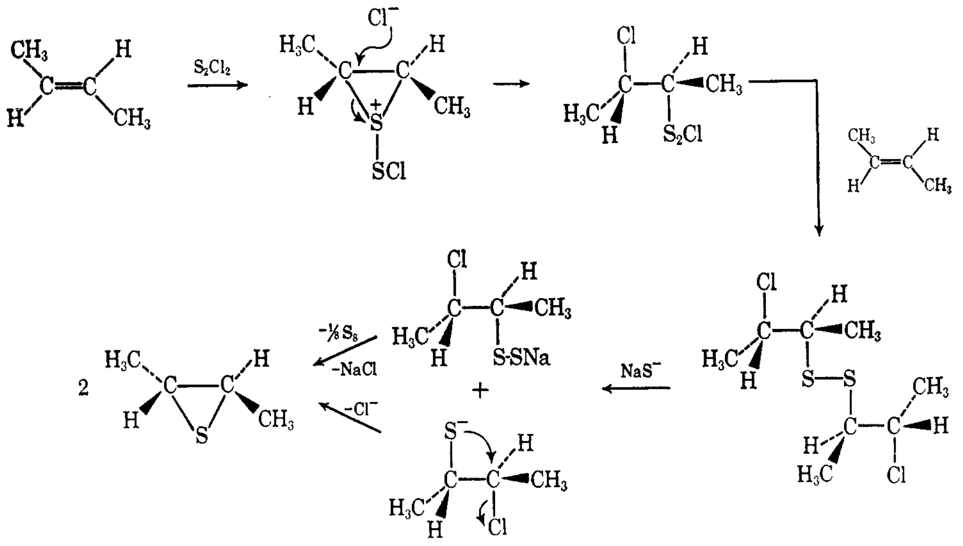
[23] G. H. Schmid and M. V. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).

Scheme V



backside attack by the sulfur on the β carbon with elimination of chloride ion takes place. Scheme V illustrates this for *trans*-2-butene.

In conclusion, the addition of sulfur monochloride to olefins followed by reduction of the adduct with sodium sulfide provides a convenient, inexpensive route to a large number of episulfides.

Experimental Section

Gas chromatographic analyses of the reaction products of sulfur chloride and propylene were carried out on a Model 800 Perkin-Elmer gas chromatograph containing a 3-ft Apiezon L column at 175° with helium as carrier gas. Nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument and infrared spectra were recorded on a Perkin-Elmer 521 grating instrument. Sulfur monochloride was obtained from the Hooker Chemical Co. and was redistilled from charcoal before use or prepared from sulfur and chlorine. Spectrographically pure (99.999+%) sulfur was obtained from the American Smelting and Refining Co., South Plainfield, N. J. All sodium sulfide used was technical grade, flake material which contains approximately 62% Na_2S.

Preparation of Sulfur Monochloride.—Spectrographically pure sulfur was heated to 165°, and high-purity (>99.99%) chlorine was passed through the melt until all sulfur remained dissolved if the solution was cooled to room temperature. The product was then fractionated and the material with bp 40° (22 mm) was identified as sulfur monochloride by its infrared spectrum.[24]

Reaction of Sulfur Monochloride with Sulfur.—A solution of 64 g of sulfur in 135 g (1 mol) of sulfur monochloride was refluxed for 5 days and then volatitles were evaporated at 1-mm pressure until the infrared spectrum of the remaining solution showed the absence of free sulfur monochloride absorptions.[24] The remaining polysulfur chloride shows infrared absorptions at 7.93 (m), 9.35 (m), 10.4 (s), 11.0 (s), and 11.75 μ (s). Reactive sulfenyl groups were determined in reactions with excess cyclohexene, which showed that up to 280 g of the sulfur halide is required to react with 2 mol of cyclohexene.

Reaction of Polysulfur Chloride with Propylene.—Into a Pyrex high-pressure tube was placed 26 g of a polysulfur chloride as prepared above, and 30 g of propylene was condensed into the tube at the temperature of liquid nitrogen. The tube was sealed under vacuum and allowed to warm to room temperature. After 7 days, a colorless solution had formed. After the container was cooled and opened and the excess of olefin was removed, 32.2 g of addition product was obtained containing 3% β-chloropropyl monosulfide as shown by distillation and gas chromatography of the volatile portion. The major product has essentially the same infrared spectrum as a product from sulfur monochloride.

Reaction of Propylene with Sulfur Monochloride. A.—Into a Pyrex tube was placed 9.3 g (0.07 mol) of sulfur monochloride, and 20 g (0.48 mol) of propylene was condensed into the tube at the temperature of liquid nitrogen. The tube was sealed under vacuum, allowed to warm to room temperature, and kept at this temperature for 7 days, after which time the solution had become colorless. The tube was opened at −70°, excess propylene was evaporated, and the pale yellow residue, 15.3 g (100%), was analyzed by vapor phase chromatography to contain 35% β-chloropropyl monosulfide. In a repeat experiment under the same conditions, a 34% yield monosulfide was obtained. The evaporating propylene was free of acid when tested with wet indicator paper.

B.—To a solution of 5.9 g (0.043 mol) of sulfur monochloride in 10 g (0.24 mol) of propylene was added 0.5 g (0.006 mol) of dry pyridine. After 8 hr at room temperature in the dark, a pale yellow solution and a yellow precipitate were obtained. After 8.5 g of product was decanted, the solid residue was washed with pentane and the solution was evaporated to give another 0.8 g (97%) of product. The solid residue was found to be water soluble. Gas chromatographic analysis showed the presence of 15% β-chloropropyl sulfide.

C.—If the reaction described under A was carried out with 5.8 g (0.043 mol) of a commercial grade sulfur monochloride fractionated at 40° (22 mm) and 14.2 g (0.34 mol) of propylene, 9.2 g (97%) of a colorless product was obtained. Distillation of 4.7 g of the product through a 3-in. Vigreux column at 0.01 mm and from an oil bath at a maximum temperature of 160° produced two fractions, 3.2 g, bp 36–67°, and 1.5 g, bp 67–105°. Both fractions were mixtures of β-chloropropyl mono-, di-, and trisulfide. No residue was obtained.

Reaction of Cyclohexene with Sulfur Monochloride.—Into a 3-l. three-necked round-bottom flask equipped with reflux condenser, stirrer, and dropping funnel was placed 900 g (11 mol) of freshly distilled cyclohexene. The funnel contained 675 g (5.0 mol) of sulfur monochloride. Under an atmosphere of dry nitrogen, approximately 50 g of the sulfur monochloride was allowed to drop into refluxing cyclohexene. The solution was heated for 30 min and cooled, and a negative test with potassium iodide indicated the absence of sulfur chloride. The solution was then cooled in an ice–water bath and the remaining sulfur chloride was added over a period of 2 hr at an internal temperature of 25–30°. The solution was stirred overnight until a negative test with potassium iodide was obtained. The excess of olefin was distilled off, leaving 1505 g (99%) of a syrupy product. Gas chromatographic analysis showed the absence of chloro- and dichlorocyclohexane, and solutions of the addition product in acetone did not separate free sulfur on standing for several weeks.

Additions of sulfur monochloride to the remaining hydrocarbon olefins were carried out under similar conditions. The corresponding products were obtained in nearly quantitative yield.

Addition of Sulfur Monochloride to Allyl Derivatives.—To a 10 *M* excess of allyl chloride, allyl bromide, allyl acetate, and allyl cyanide was added sulfur monochloride, and the solutions were stirred at room temperature for 7 days, after which nega-

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[24] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950).

tive tests for sulfenyl halides were obtained. On evaporation of excess olefin, quantitative yields of addition products were obtained.

Addition of Sulfur Monochloride to *cis*- and *trans*-2-Butene.—The adducts of both *cis*- and *trans*-2-butene were prepared by condensing 56 g (1 mol) of the pure olefins into a crown-capped pressure bottle containing 25 g (0.185 mol) of freshly distilled sulfur monochloride. Pyridine (0.2 ml) was added and the sealed bottles were allowed to stand at room temperature for 50 hr. The addition product was obtained in a yield of 96% in both cases after evaporation of excess olefin.

Addition of Sulfur Monochloride to 1,3-Butadiene.—Into a stainless steel bomb equipped with a glass liner was condensed 227 g (4.2 mol) of 1,3-butadiene. At −20°, 93 g (0.69 mol) of purified sulfur monochloride was added. The solution was stirred with a magnetic stirrer. After 16 hr at room temperature, the excess olefin was allowed to evaporate to give 167 g (98.8%) of product.

Anal. Calcd for $C_8H_{12}Cl_2S_2$: H, 4.95; Cl, 26.6; S, 26.27. Found: H, 5.18; Cl, 26.6; S, 26.32.

The infrared spectrum shows the characteristic vinyl absorption bands at 1870, 1640, and 925 cm^{-1}. The nmr spectrum ($CDCl_3$) shows signals at 2.6–3.2 (2 H, CH_2S) and 4.85–5.85 ppm (2.95 H, olefinic H). A multiplet at 4.25 ppm (0.95 H, CHCl) further supports the observation that **15a** is the predominant reaction product.

Isomerization of Sulfur Monochloride Addition Product of 1,3-Butadiene.—A solution of 9.8 g (0.04 mol) of **15a** in 50 ml of benzene containing 0.5 g of anhydrous zinc chloride was refluxed for 14 days, after which a conversion to the isomerized product **16a** was obtained to an extent of 95% as shown by its nmr spectrum ($CDCl_3$).

Isomerization of Sulfur Dichloride Addition Product of 1,3-Butadiene.—A solution of 10.6 g (0.05 mol) of **15b** with 0.2 g of anhydrous zinc chloride was refluxed in 50 ml of benzene for 21 days, yielding an isomeric mixture of **15b** and **16b** in a proportion of 2:98.

Reaction of Sulfur Monochloride with 1,5-Hexadiene.—To a solution of 207 g (2.5 mol) of 1,5-hexadiene was added 34 g (0.25 mol) of sulfur monochloride in one portion. The solution was stirred at room temperature for 64 hr, after which a negative test with potassium iodide was obtained. On evaporation of excess diolefin, 58.6 g of a pale yellow liquid was obtained.

Anal. Calcd for $(C_6H_{10}Cl_2S_2)_n$: C, 33.2; H, 4.6; Cl, 32.8; S, 29.6. Calcd for $C_{12}H_{20}Cl_2S_2$: C, 48.1; H, 6.7; Cl, 23.8; S, 21.4. Found: C, 40.9; H, 5.6; Cl, 27.6; S, 26.2.

The additions of sulfur monochloride to 1,4-pentadiene and 1,7-octadiene were carried out under similar conditions and elemental analyses indicated that mixtures of products arising from both 1:1 and 2:1 additions of diolefin and sulfur monochloride were obtained.

Anal. Calcd for $(C_5H_8Cl_2S_2)_n$: C, 29.6; H, 3.9; Cl, 35.0; S, 31.5. Calcd for $C_{10}H_{16}Cl_2S_2$: C, 44.4; H, 5.9; Cl, 26.2; S, 23.6. Found: C, 38.1; H, 4.7; Cl, 30.11; S, 26.5.

Addition of Sulfur Monochloride to Norbornadiene. Formation of 17 and 18.—To 792.3 g (8.5 mol) of norbornadiene was added 540 g (4 mol) of sulfur monochloride in 10-ml portions. The second portion was added after complete reaction of the first was achieved. The reaction temperature was maintained at 25° by external cooling. On completion of the reaction, a small excess of diolefin was distilled off to give 1250 g (97%) of the addition product.

Anal. Calcd for $C_{14}H_{16}Cl_2S_2$: C, 42.07; H, 5.05; Cl, 22.21. Found: C, 42.10; H, 5.00; Cl, 22.45.

The infrared spectrum of the product shows major absorption bands at 2980–2960, 1453, 1330, 1290, 1275, 902, 812, 740, and 708 cm^{-1}, with absorptions due to olefinic unsaturation at 3065 and 708 cm^{-1}. The nmr spectrum (CS_2) shows signals at 6.10 (1.28 H, olefinic H), 2.4–1.2 (3.37 H, $-CH_2-$ and nortricyclene H), and 4.3–2.6 ppm (3.3 H, complex pattern for CHCl, CHS, and bridgehead H).

Reduction of Sulfur Monochloride Addition Products. Reduction with Aluminum Amalgam. Cyclohexene Episulfide.—In 1 l. of diethyl ether was dissolved 152 g (0.5 mol) of an addition product of sulfur monochloride to cyclohexene, and 50 g of amalgamated aluminum[25] was added. Addition of 100 ml of water to the mechanically stirred suspension over a period of 2 hr caused smooth refluxing and complete reaction of the amalgam. The suspension was filtered and the residue was washed with ether. The combined filtrates were washed with water, dried with magnesium sulfate, and distilled to give 47 g (33%) of cyclohexene episulfide, $n^{20}D$ 1.5310.[26] Other episulfides obtained by this method from aluminum amalgam are shown in Table IV.

Under identical conditions, 41% chloropropylene sulfide was obtained by reduction of the allyl bromide–sulfur monochloride addition product. The product was identified by its infrared spectrum and its refractive index. Gas chromatographic analysis indicated the absence of alternative products.

Reduction with Sodium Sulfide. General.—The apparatus used for the reaction of olefin–sulfur monochloride adducts with sodium sulfide consisted of a three-necked flask equipped with a dropping funnel with pressure-equalization arm and a stainless steel stirrer. The third neck was equipped with a 60° bend which led through a vacuum take-off adapter to an ice–water cooled flask. This, in turn, was connected through a Dry Ice–acetone cooled trap to a vacuum pump. The flask was charged with 4 equiv of ground, technical grade, fused sodium sulfide and was heated to 80–85° in an oil bath. The system was evacuated to between 10 and 100 Torr for low-boiling episulfides or to less than 1 Torr for high-boiling episulfides such as styrene episulfide. The olefin–sulfur monochloride adduct was then added dropwise to the stirred sodium sulfide over a period of 1–1.5 hr. The reaction was stopped after another 15–30 min. In the case of low-boiling episulfides, the ice–water-cooled trap contained small amounts of starting material, while the episulfide was isolated along with water in the Dry Ice cooled trap. High-boiling episulfides were usually trapped in the ice–water-cooled flask.

Propylene Sulfide.—The reaction flask was charged with 12.5 g (0.1 mol) of sodium sulfide and 12.6 g (0.1 mol) of sodium sulfite which had been intimately ground together into a homogeneous powder. The system was evacuated to 10 Torr. When the temperature in the oil bath had reached 80°, 5.0 g (0.023 mol) of β-chloropropyl disulfide adduct was added dropwise to the stirred solid mixture. The temperature of the oil bath was allowed to rise to 100° over a period of 1 hr. At the end of this period, the Dry Ice cooled trap was found to contain 3 g (88%) of propylene sulfide along with about 5 ml of water. The propylene sulfide, after separation from the water and drying ($MgSO_4$), was found to have $n^{22}D$ 1.4760. The infrared spectrum of this material was identical with that of an authentic sample and a glpc analysis showed it to be more than 99% pure. Yields of propylene sulfide averaging 65% were obtained by this procedure when crude propylene–sulfur monochloride adducts were used.

***trans*-2-Butene Episulfide.**—Treatment of 42 g (0.17 mol) of the sulfur monochloride addition product of *trans*-2-butene with 120 g (0.95 mol) of sodium sulfide as described in the general procedure at 95–100° and 80 mm yielded 18.6 g (62%) of *trans*-2-butene episulfide, $n^{20}D$ 1.4640 (lit.[27] $n^{20}D$ 1.4624). A glpc analysis showed the product to be about 99% pure with no detectable amount of the *cis* isomer present.

***cis*-2-Butene Episulfide.**—The conversion of 42 g of the addition product of *cis*-2-butene and sulfur monochloride to the episulfide was carried out under the same conditions used for the *trans* isomer and gave 19.1 g (64%) of *cis*-2-butene episulfide, $n^{20}D$ 1.4775 (lit.[27] $n^{20}D$ 1.4765). A glpc analysis showed the product to be 99% pure and showed none of the *trans* isomer to be present.

Styrene Episulfide.—The 60° bend of the apparatus described above was wrapped with a heating tape and this part of the apparatus was heated to about 60–70°. The reaction flask was charged with 120 g of sodium sulfide and the flask was heated to 80° in the oil bath. The system was evacuated to 0.75 Torr and 40 g of a styrene sulfur monochloride adduct was added dropwise to the stirred solid during 1.5 hr. The episulfide collected in the ice–water cooled trap as the addition proceeded. The reaction flask was heated for a further 15 min after the addition had been completed. The ice–water cooled trap contained 14 g (44%) of styrene episulfide with very little water. After drying over $MgSO_4$, the product had $n^{20}D$ 1.6015 and the infrared spectrum was identical with that of an authentic sample of the episulfide.[28] The Dry Ice–acetone cooled trap contained 7.0 g of an organic liquid along with some water. After drying over Mg-

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[25] A. I. Vogel, "Textbook of Practical Organic Chemistry," 3rd ed, Longmans Green and Co., London, 1957, p 119.

[26] L. Goodman, A. Benitez, and B. R. Baker, *J. Amer. Chem. Soc.*, **80**, 1680 (1958).

[27] N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959).

[28] C. O. Guss and D. L. Chamberlain, *ibid.*, **74**, 1342 (1952).

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.

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

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

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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

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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] (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).