for the *equatorial* CH_3O *groups*, and 6.48 (J_{HP} = 10.8 cps) for the *apical* CH_3O *group*. The spectra were also examined in $CDCl_3$ from 30 to −70°.

Registry No.—**14**, 21309-22-8; **15**, 21309-23-9.

Acknowledgment.—We are grateful to Dr. L. A. Wilson of Varian Application Laboratories, Springfield, N. J., for his instruction and personal assistance which made possible the ^1H nmr measurements below −100°.

Allylic Sulfenyl Chlorides. A New Synthesis of Substituted 1,4-Dithianes

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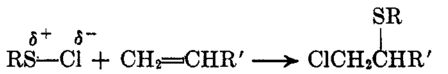
Received April 4, 1969

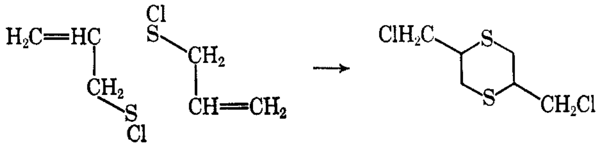
Allylsulfenyl chloride and methallylsulfenyl chloride are proposed as reactive intermediates formed from the chlorination of the corresponding disulfides. Subsequent reactions of these intermediates produce 2,5-bis-(chloromethyl)-1,4-dithianes in good yield.

Simple aliphatic sulfenyl chlorides react with terminal olefins to preferentially produce β-chloro thio ethers with chlorine on the terminal carbon (*anti*-Markovnikov addition, eq 1).[2] This preferred direction of addition



$$\overset{\delta^+}{\mathrm{RS}}\text{—}\overset{\delta^-}{\mathrm{Cl}} + \mathrm{CH_2{=}CHR'} \longrightarrow \mathrm{ClCH_2\overset{SR}{\overset{|}{C}}HR'} \qquad (1)$$

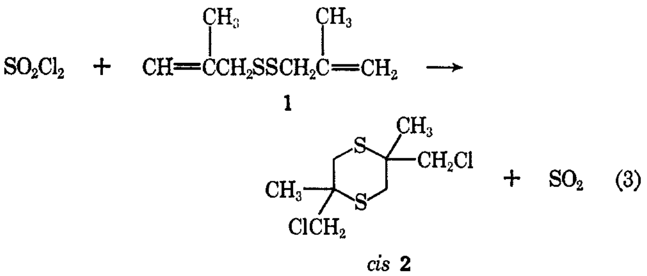
generally occurs in the absence of certain special substituents which reverse the direction of episulfonium ion ring opening and tend to favor Markovnikov addition.[3] Allylic sulfenyl halides are unusual in the sense that they contain both a sulfenyl chloride group and a reactive olefin site in the same molecule, and as such could exist only as transient reaction intermediates. However, both the sulfenyl chloride and olefinic portions of such a molecule are analogous to the simple sulfenyl chloride–olefin system and should behave in the expected manner. Under the proper conditions, therefore, reaction of allylic sulfenyl halides should produce cyclic dithiane derivatives (eq 2).



(2)

Results and Discussion

Chlorination of dilute solutions of allylic disulfides provides a convenient synthesis of 1,4-dithiane containing $ClCH_2$– groups in the 2 and 5 positions of the ring. The reaction of methallyl disulfide (**1**) with sulfuryl chloride produced a dimer or methallylsulfenyl chloride in good yield (eq 3) along with a minor amount of oligomer. Elemental analysis and molecular weight determination were consistent with the molecular formula $C_8H_{14}S_2Cl_2$. Because of a difference in solubility in chloroform, enriched fractions of the 2,5-bis(chloromethyl)-2,5-dimethyl-1,4-dithiane (**2** and **3**) isomers could be obtained and identified by nmr analysis.

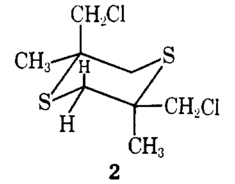


(3)

cis **2**

trans **3**

The nmr spectra of **2** and **3** have peaks (in a 2:2:3 ratio) characteristic for isolated methylene groups next to both sulfur and chlorine and for a tertiary methyl group adjacent to sulfur.[4] The axial and equatorial protons of the ring methylene groups are chemically shifted (see Figure 1) owing to their different magnetic environments and appear as a pair of AB doublets. The methylene protons next to chlorine are likewise nonequivalent owing to their proximity to the asymmetric center and also comprise an AB system. The isolated tertiary methyl groups are three-proton singlets as expected. Taken together with the physical and chemical evidence, the nmr data provide convincing evidence for the isomeric dithiane structures for **2** and **3** (Table I).



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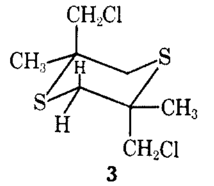

3

Table I

Nmr Data for 2 and 3[a]

Compd	Protons	Chemical shift, δ (ppm)	Designation (Figure 2)	Multiplicity (*J*, cps)
2	CH_3	1.46 (3H)		s
	CH_2S	2.97 (1 H)	H_e	d (J_g = 14.5)
		2.80 (1 H)	H_f	d
	CH_2Cl	3.56 (1 H)	H_h	d (J_g = 10.8)
		3.98 (1 H)	H_g	d
3	CH_3	1.31 (3 H)		s
	CH_2S	ax 2.97 (1 H)	H_c	dd (J_g = 14.5, ^4J = 1.3)
		eq 2.80 (1 H)	H_d	d
	CH_2Cl	n 3.58 (1 H)	H_a	d (J_g = 10.6)
		x 4.46 (1 H)	H_b	dd

[a] s, singlet; d, doublet; t, triplet; n, *endo;* x, *exo;* ax, axial; eq, equatorial.

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[1] To whom inquiries should be directed.

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

[3] W. A. Thaler, W. H. Mueller, and P. E. Butler, *ibid.*, **90**, 2069 (1968).

[4] P. E. Butler, W. H. Mueller, and J. J. R. Reed, *Environ. Sci. Tech.*, **1**, 315 (1967).

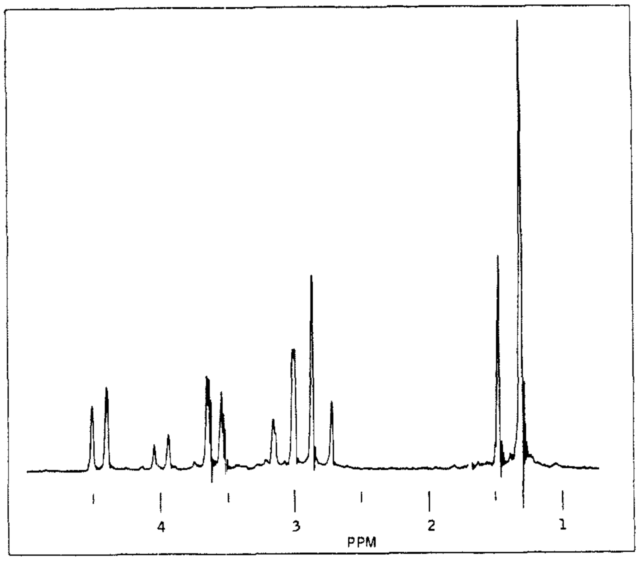
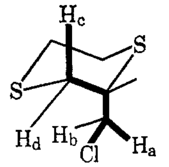


Figure 1.—The 100-Mcps nmr spectrum of *cis*- and *trans*-2,5-dichloromethyl-2,5-dimethyl-1,4-dithiane.

The stereochemical assignment (*cis* for **2**, *trans* for **3**) is based on the observation of a stereospecific long-range coupling through four σ bonds observed in the spectrum (see Figure 2) of the *trans* isomer which implies a preferred conformation with the chloromethylene groups axial [this coupling is absent in the averaged (ea $\rightleftharpoons$ ae) *cis* isomer]. The ^4J coupling of 1.3 cps between the methylene proton next to chlorine (H_a) and the methylene proton next to sulfur (H_c) in **3** can only operate when these two groups are in a *trans* diaxial arrangement with the protons in an extended zigzag or "W" conformation.[5] Furthermore, it is apparent from the specificity of the coupling that the preferred conformation of the *exo*-methylene group is such that chlorine atom is lined up so that the direction of its dipole moment is *trans* coplanar to the direction of the C–S bond. In this position, stereospecific coupling with only one of the methylene protons is possible (the magnitude of the coupling is somewhat larger than that expected for ^4J coupling between a freely rotating methyl group and an axial proton[6]), as indicated by the well-known dependence of long-range coupling on the dihedral angle between the coupling protons.[7]



Another unusual feature of the spectrum of the *trans* isomer **3** is the rather large paramagnetic shift ($\sim$0.9 ppm) experienced by one of the methylene protons (H_b) of the axial chloromethylene group. From a study of the Dreiding model of **3** it is seen that this proton lies under the plane of the ring in close proximity to both sulfur atoms. Compared with the *trans* isomer **3**, a similar downfield shift but of smaller magnitude ($\sim$0.2 ppm) is observed for the methyl group of the *cis* isomer **2**, one of whose methyl groups resides in the axial position (in reality an average chemical shift is observed for this methyl group so that the magnitude of the downfield shift is reduced).

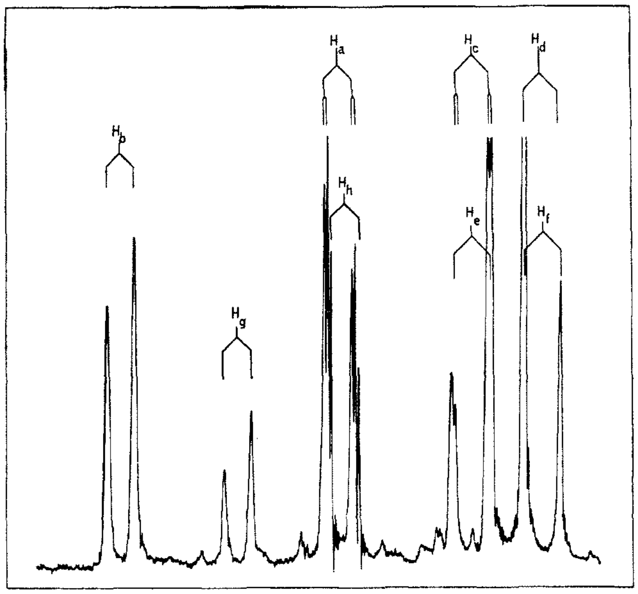


Figure 2.—Partial 100-Mcps nmr spectrum of the methylene proton region.

As a result of the rapid flipping of the ring between the two most stable conformations (ae $\rightleftharpoons$ ea) in the *cis* isomer, an averaged spectrum results. In this situation spectral features peculiar to axial substituents such as the long-range coupling and the low field shift of protons under the ring are "averaged out" by ring inversion. No long-range coupling is resolved although the line widths of the pertinent protons are somewhat broad. It is apparent from the low field shift of one of the chloromethylene protons (H_g) that the chlorine group when in the axial position opposes the C–S dipole in analogy to the *trans* isomer.

The proton assignments and long-range couplings were confirmed by several frequency sweep decoupling experiments. Irradiation of H_a collapsed H_b to a singlet and also eliminated the long-range coupling with H_c which produced an AB doublet of equal intensity to H_d. Conversely, irradiation of H_c eliminated the long-range coupling in H_a. In regard to the *cis* isomer, mutual coupling between the AB systems of the ring methylene protons (H_e and H_f) and between the chloromethylene protons (H_g and H_h) were confirmed by spin decoupling experiments.

Treatment of allyl disulfide with sulfuryl chloride leads to a mixture of the isomeric dithianes (**4**). The 60-Mcps nmr spectrum of the mixture is quite complicated owing to the overlapping of the two ABCXY systems. This problem is not resolved at 100 Mcps. However, in analogy with assignments to **2** and **3**, the low field absorptions for a chloromethylene proton are in the axial position and are not intense which is good evidence that the major isomer has both chloromethyl groups in the equatorial positions (*trans*-2,5-bis(chloromethyl)-1,4-dithiane). At 100 Mcps, the minor low field absorption appears as a double quartet consistent with a vir-

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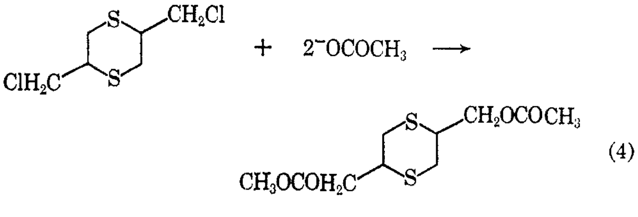
[5] (a) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); (b) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962); (c) A. Rassat, C. W. Jifford, J. M. Lehn, and B. Waegell, *Tetrahedron Lett.*, 233 (1964).

[6] M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

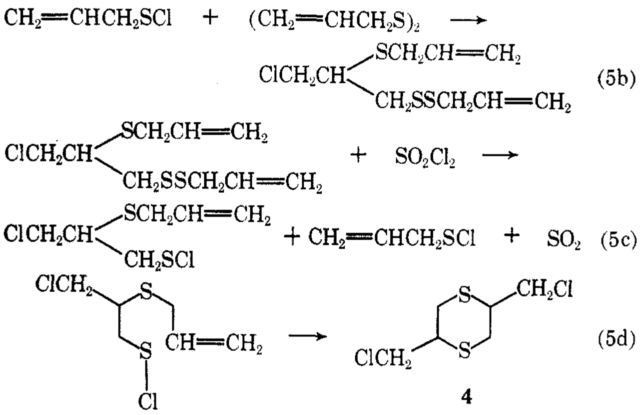
[7] (a) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); (b) K. L. Williamson and W. S. Johnson, *ibid.*, **83**, 4623 (1961).

tually coupled proton next to chlorine in the (ea ⇌ ae) *cis* isomer. This isomer mixture was converted into the corresponding diacetate derivative (eq 4) whose 100-Mcps gave additioual support to the above assignments; however, it should be pointed out that these assignments are tentative.


(4)

Although the chemistry observed from the addition of SO_2Cl_2 to dilute solutions of allylic disulfide can be adequately explained by the dimerization of two allylic sulfenyl chloride molecules (eq 1), it is more likely that the allylic sulfenyl chloride reacts with the allylic disulfide which is present in higher concentrations under these reaction conditions (eq 5a and 5b). Subsequent chlorinolysis of the disulfide followed by intramolecular addition of the sulfenyl chloride intermediates to the double bond would produce the 1,4-dithiane system (eq 5c and 5d). Conditions such that both the sulfuryl chloride and disulfide were added simultaneously to the reaction medium were not tried, but could conceivably have favored reaction by two molecules of the allylic sulfenyl halide. However, distinction between the two possible pathways (eq 1 or eq 5) would not be possible. The longer lifetime of the allylic sulfenyl chloride under these conditions would, however, enhance the possibility of unimolecular reaction (eq 6). If such episulfides were formed they would undoubtedly be consumed by subsequent reaction with sulfuryl chloride and sulfenyl chloride. A third alternative, the addition of disulfide to sulfuryl chloride, also presents difficulties, since chlorination of the double bond by the excess chlorinating agent can also take place.

$$(CH_2{=}CHCH_2S)_2 + SO_2Cl_2 \longrightarrow 2CH_2{=}CHCH_2SCl \quad (5a)$$

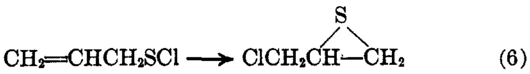


$$CH_2{=}CHCH_2SCl + (CH_2{=}CHCH_2S)_2 \longrightarrow ClCH_2CH{<}^{SCH_2CH{=}CH_2}_{CH_2SSCH_2CH{=}CH_2} \quad (5b)$$

$$ClCH_2CH{<}^{SCH_2CH{=}CH_2}_{CH_2SSCH_2CH{=}CH_2} + SO_2Cl_2 \longrightarrow ClCH_2CH{<}^{SCH_2CH{=}CH_2}_{CH_2SCl} + CH_2{=}CHCH_2SCl + SO_2 \quad (5c)$$

(5d)

4


(6)

Dilute solutions were used throughout this work to favor cyclization over polymerization, and no attempt was made to ascertain the influence of concentration on the relative yield of dithiane and oligomer.

Dithianes produced in this study contain reactive chlorine substituents β to a thio ether group and are useful for the preparation of difunctional products *via* nucleophilic displacements (eq 4).

Experimental Section

2,5-Bis(chloromethyl)-2,5-dimethyl-1,4-dithiane.—Sulfuryl chloride (64 g, 0.5 mol) was added dropwise to a stirred solution of 87.2 g (0.5 mol) of methallyl disulfide in 2500 ml of methylene chloride containing 1.0 g of $CaCO_3$. The reaction was maintained at −20° during the addition and stored at −15° overnight. The solution was filtered and the solvent was removed by means of a rotary evaporator, yielding 118 g (96%) of crude product. Sublimation at high vacuum (diffusion pump) gave a 73% yield of a semisolid product.

Anal. Calcd for $C_8H_{14}S_2Cl_2$: C, 39.18; H, 5.75; S, 26.15; mol wt, 245. Found: C, 38.88; H, 5.62; S, 26.62 mol wt, 268.

A small quantity of the crude product mixture was filtered to obtain solid product and the liquid filtrate was then distilled giving a solid distillate and a clear glassy residue. The liquid filtrate is apparently composed of dithiane and higher oligomer. Analyses are given in Table II.

TABLE II

	Analyses, %				
	C	H	S	Cl	Mol wt
$C_8H_{14}S_2Cl_2$	39.19	5.75	26.15	28.92	245
Filtered solid	39.11	5.80	26.23	29.13	239
Filtrate	39.07	5.90	26.22	29.30	360
Distilled filtrate	39.01	5.91			241
Glassy residue	38.43	5.75			462

2,5-Bis(chloromethyl)-1,4-dithiane.—To a stirred solution of 73.1 g (0.5 mol) of allyl disulfide in 2500 ml of methylene chloride containing 1.0 g of $CaCO_3$, 67.5 g (0.05 mol) of sulfuryl chloride was added dropwise while the temperature was maintained at −20°. The reaction mixture was stored overnight at −15° at which time the solution was colorless. The solution was filtered and methylene chloride was stripped off yielding 108 g (99%) of crude product.

Anal. Calcd for $C_6H_{10}S_2Cl_2$: C, 33.18; H, 4.64; Cl, 32.66; S, 29.53; mol wt, 217. Found: C, 33.47; H, 4.68; S, 29.98; mol wt, 288.

A portion of the crude product (19.5 g) was distilled at 0.025-mm pressure. The first fraction (bp 103–110°) weighed 12.35 g, the second fraction (bp 110°) weighed 1.01 g (69% yield), and the remaining residue weighed 3.38 g.

Anal. Found for fraction 1: C, 33.59; H, 3.65; Cl, 32.58; S, 29.43; mol wt, 220. Found for fraction 2: C, 33.06; H, 4.78; Cl, 32.54; S, 29.05; mol wt, 225.

2,5-Bis(acetoxymethyl)-1,4-dithiane.—A solution of 10.9 g (0.05 mol) of 2,5-bis(chloromethyl)-1,4-dithiane in 25 ml of acetic acid was stirred with 12.3 g (0.15 mol) of sodium acetate for 20 hr at 60°. The acetic acid was removed on a rotary evaporator, and 2 *N* NaOH solution was added to the cooled product until the excess acidity was neutralized. The aqueous solution was extracted with methylene chloride, dried, and filtered, and the solvent was evaporated yielding 10.9 g (82%) of crude product. Distillation [125–130° (0.01 mm)] gave a 76% yield of product.

Anal. Calcd for $C_{10}H_{16}O_4S_2$: C, 45.45; H, 6.10; S, 24.22. Found: C, 45.86; H, 6.21; S, 24.41.

Registry No.—2, 21273-20-1; 3, 21273-21-2; 4 (*cis*), 21273-22-3; 4 (*trans*), 21273-46-1; 2,5-bis-(acetoxymethyl)-1,4-dithiane (*cis*), 21273-23-4; 2,5-bis-(acetoxymethyl)-1,4-dithiane (*trans*), 21273-47-2.

Acknowledgment.—We are grateful to Professor L. M. Jackman for helpful discussions and to Mr. J. J. Werner for technical assistance.