Stereochemistry of Desulfurization of Thietane Derivatives

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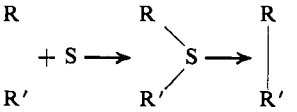
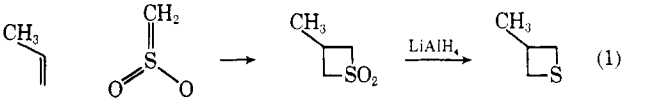
Abstract: The preparation of thietanes by pyrolysis of the sodium salt of 1-thiocyanato-3-hydroxypropanes is described. Stereochemistry of fragmentation of the sulfone (induced by pyrolysis) and sulfonium salts (induced by organolithium treatment) to cyclopropanes has been investigated. Both show net crossover, *i.e.*, *cis*-2,4-dimethyl derivatives producing mainly *trans*-1,2-dimethylcyclopropane and *trans*-2,4-dimethyl derivatives producing mainly *cis*-1,2-dimethylcyclopropanes. Mechanisms of these reactions are discussed with respect to trimethylene diradicals. The utility of these reactions for cyclopropane synthesis is considered.

The use of sulfur in organic syntheses has attracted the attention of many investigators. In particular, the ability to link two units together followed by desulfurization with concomitant carbon–carbon bond formation, as shown schematically, has



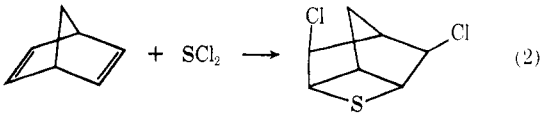
proven to have great utility in many instances where other techniques failed.[1] If R and R′ are connected by a chain, the net result is ring formation. Common techniques for the desulfurization step involve conversion of the sulfide to a sulfone followed by either (1) thermal or photochemical decomposition[1,2] or (2) bromination and base treatment (Ramberg–Backlund reaction).[3] Eschenmoser[1b] developed a most elegant method to synthesize corrins and porphyrins involving linking two pyrrole derivatives *via* a sulfur atom followed by subsequent desulfurization of a presumed episulfide intermediate by an organophosphorus species. We have undertaken a series of studies designed to explore further these techniques and to develop new ones. In this paper, we wish to report our studies directed toward techniques of desulfurization of thietanes to form cyclopropanes. In particular, this paper reports a new synthetic route to thietanes, the first preparation of thietanonium salts, a novel reaction of thietanonium salts, and the stereochemistry of elimination of thietane sulfones.

Preparation of Thietanes. Thietanes have been prepared by a variety of techniques.[4] Perhaps the most direct method involves cycloaddition of sulfenes followed by lithium aluminum hydride reduction of the resultant sulfone (eq 1).[5] A novel reaction leading to a thietane was the addition of sulfur dichloride to norbornadiene (eq 2).[6] Unfortunately, addition to other



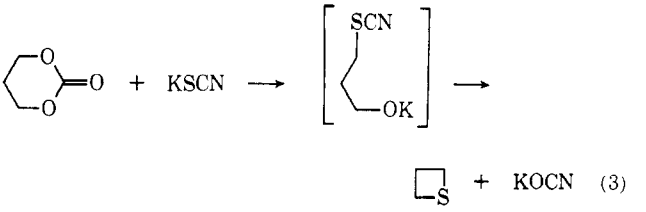
(1)

1,4-dienes did not produce similar results. The most



(2)

general technique available consists of a 1,4 elimination of a suitably constituted thiol. Several approaches to the requisite thiols exist. Alkylation of thiourea or thiocyanate by a 1,3-dihalide followed by hydrolysis has been employed.[7] A simple one-step procedure involved the thermal condensation of a cyclic carbonate with potassium thiocyanate (eq 3); however, the yields are



(3)

not high.[8] A more general approach appeared to be that developed by Dodson and coworkers and is outlined in Scheme I for the case of 2,4-dimethylthietane.[9] Addition of thiolacetic acid to 3-penten-2-one produced 4-thioacetoxypentan-2-one (I). Reduction of the thioacetate with lithium aluminum hydride generated the hydroxythiol (II), which could not be converted into the thiol chloride (III) nor any derivative which converted the hydroxyl group to a good leaving group. In the belief that our problems were related to the presence of a free sulfhydryl, we attempted to prepare 2-hydroxy-4-thioacetoxypentane (IV) by selective reduction of the ketone of I. Unfortunately, the only isolated product from sodium borohydride reduction of I proved to be 2-acetoxy-4-thiolpentane (V). Apparently, acetyl migration in the desired compound IV to produce the thermodynamically more stable acetate V occurred. All attempts to isolate IV failed. To circumvent these problems, we modified our approach as outlined in Scheme II. Conversion of the thiol (II) to the hydroxy-

(1) (a) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969), and references therein; (b) Y. Yamada, D. Miljkovic, P. Wehrli, B. Golding, P. Löliger, R. Keese, K. Müller, and A. Eschenmoser, *Angew. Chem., Int. Ed. Engl.*, **8**, 343 (1969).

(2) F. Vögtle, *Chem. Ber.*, **102**, 1449, 3077 (1969); F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **8**, 274 (1969); R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.*, 1197 (1970); V. Boekelheide and J. L. Mondt, *ibid.*, 1203 (1970); V. Boekelheide and P. H. Anderson, *ibid.*, 1207 (1970).

(3) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969); F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *ibid.*, **90**, 429 (1968).

(4) For a review, see M. Sander, *Chem. Rev.*, **66**, 341 (1966).

(5) P. L. F. Chang and D. C. Dittmer, *J. Org. Chem.*, **34**, 2791 (1969), and references therein.

(6) F. Lautenschlager, *ibid.*, **31**, 1679 (1966).

(7) J. D. Downer and J. E. Colchester, *J. Chem. Soc.*, 1528 (1965).

(8) S. Searles, Jr., H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, **27**, 2828 (1962).

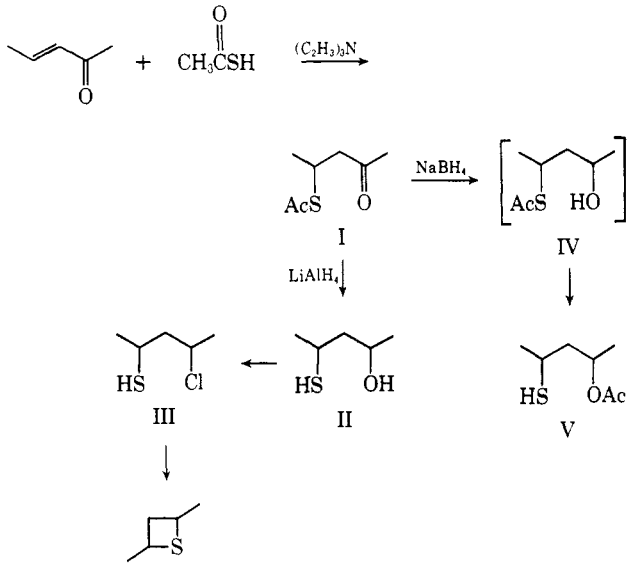
(9) R. M. Dodson and G. Klose, *Chem. Ind. (London)*, 450 (1963).

Table I. Chemical Shifts of Thietanes and Their Derivatives[a]

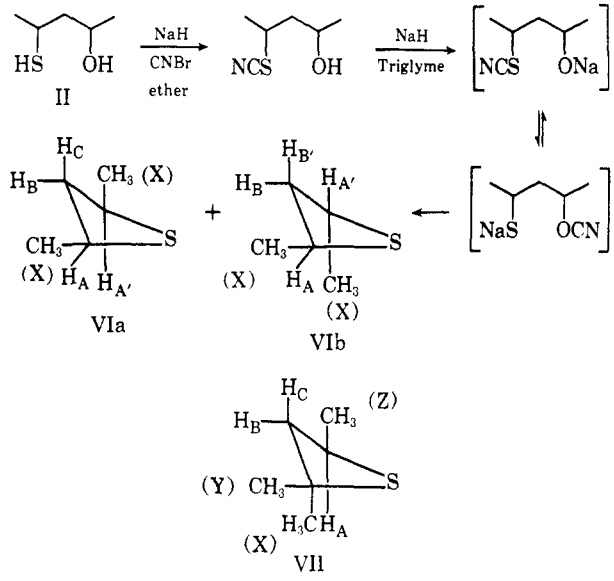
Compd	Ring protons A	B	C	D	C-Methyls X	Y	Z	S-Methyl
VIa[b]	3.58	2.99	2.15		1.35			
VIb[b]	3.62	2.61			1.45			
VII[b]	3.61	2.68	2.35		1.57	1.43	1.38	
VIIIa[b]	4.15	1.13	2.45		1.38			
VIIIb[b]	4.19	1.85			1.43			
IX[b]	4.17	1.42	2.10		1.52	1.45	1.40	
Xa[c]	4.29	3.31	2.51		1.64			3.17
Xb[c]	4.63	3.98	3.19	2.77	1.68	1.51		2.94
XI[c]	3.67	2.67	2.28		1.35–1.54			2.75, 2.82

[a] All chemical shifts are expressed in parts per million downfield from internal TMS. [b] Determined as a solution in carbon tetrachloride. [c] Determined as a solution in deuterioacetonitrile.

Scheme I. Attempted Synthesis of Thietane

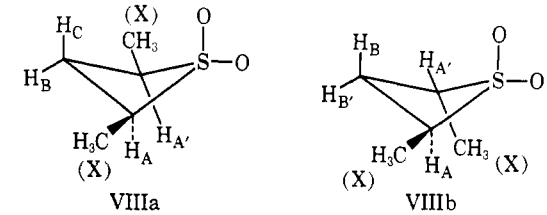


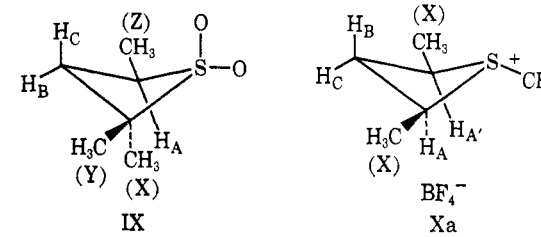
Scheme II. Synthesis of Thietanes

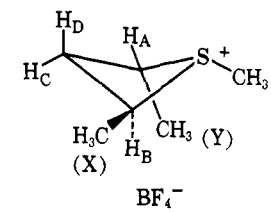


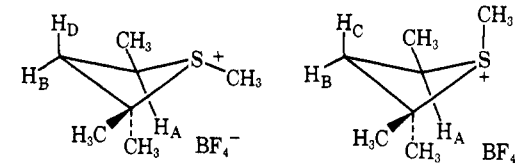
thiocyanate proceeds in high yield by first conversion to the thiolate and then subsequent cyanation. Treatment of the crude thiocyanate with a second mole of sodium hydride followed by pyrolysis generated the dimethylthietanes with elimination of sodium cyanate. In this way, *cis*- and *trans*-2,4-dimethylthietanes (VIa and b), and 2,2,4-trimethylthietane (VII) were produced in up to 70% yields.

Preparation of Thietane Derivatives. Oxidation of the thietanes with peracetic acid in acetic acid at reflux generated the corresponding sulfones VIIIa and b and IX.[9,10] Alkylation of the thietanes with trimethyloxonium fluoroborate at −30° in methylene chloride produced the corresponding *S*-methylthietanonium salts (Xa, Xb, XI) as white crystalline solids which were unstable in the solid state at room temperature over a period of time.









Spectral Properties. The nmr data of the thietanes and their derivatives are summarized in Tables I and II.[11] The coupling constants and chemical shifts clearly

(10) M. Sander, *Monatsh. Chem.*, **96**, 896 (1965).

Table II. Coupling Constants of Thietanes and Their Derivatives[a]

Compd	Ring couplings						Methyl coupling
	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}	
VIa	7.4	8.4		11.1			6.5
VIb	6.9						6.6
VII	7.5	8.2		11.2			6.3
VIIIa	9.3	9.3		11.2			7.0
VIIIb	8.0						7.0
IX	9.4	9.4		11.3			6.8
Xa	9.0	9.5		12.5			7.0
Xb		8.9	5.0	8.7	8.6	12.8	7.0, 7.0

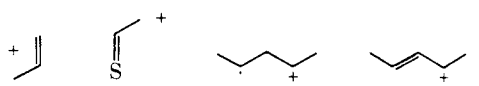
[a] All coupling constants are expressed in hertz.

support a nonplanar structure for all the derivatives; however, an examination of the coupling constants suggests that the sulfone ring appears to have flattened out considerably compared to the thietanes or their *S*-methyl salts. It is most interesting that pseudoequatorial 2,4-methyl groups of both the sulfides (VIa, VII) and sulfones (VIIIa, IX) are more shielded than their pseudoaxial counterparts (VII, IX). The chemical shifts of the methyl groups of the *trans*-sulfide and sulfone (VIb, VIIIb) are approximately the arithmetic mean of the pseudoaxial and pseudoequatorial shifts—a fact in agreement with these compounds being an equimolar mixture of two rapidly interconverting conformers. The high-field shift of the pseudoequatorial methyl groups arises from shielding due to the eclipsing of these groups by two lone pairs of electrons and two oxygens in the sulfide and sulfone, respectively. Nevertheless, the trend is reversed in the sulfonium salts (Xa, Xb) in which the pseudoequatorial methyl comes at lower field than the pseudoaxial one. In this case, the anisotropy of the sulfonium group provides better deshielding of the pseudoequatorial alkyl groups. For both the sulfides and sulfonium salts, the pseudoaxial hydrogen at C_3 appears at higher field than the pseudoequatorial one. This differential shielding presumably originates in the 1,3 hydrogen–lone pair interaction. In the sulfone, there is a large upfield shift of the β-pseudoequatorial proton. From the above data, it appears that the anisotropy of the sulfone group causes a strong shielding of groups anti to the oxygens and in a plane containing the $^{\alpha}$C–S–$^{\alpha}$C and bisecting these oxygens. The fact that the chemical shifts of H_B for VIb and VIIb approximate the mean of the pseudoaxial and pseudoequatorial hydrogens supports the previous contention that these compounds are equimolar mixtures of rapidly equilibrating conformers.

The nmr spectra of the thietanonium salts provide further support for the folded conformation. With both the *cis*- and *trans*-2,4-dimethylthietanes, only one geometric isomer was produced in each case as indicated by the appearance of relatively clean nmr spectra and a single sharp singlet for the *S*-methyl groups. The appearance of two absorptions for the *S*-methyl groups in the approximate ratio of 1:1 for the trimethylthietanonium salt suggests both possible isomers are present in this case. The *trans*-dimethyl salt Xb is fixed in the conformation depicted above. The appearance of two clean doublets for the *C*-methyl groups and of two different α-methine groups clearly attests to this fact. Assignment of the higher field methine to the pseudoaxial hydrogen derives from its trans coplanar orientation with respect to the electron pair at sulfur.[12] The 1,3-diaxial H–CH_3 interaction also provides some net shielding (see also the trimethylsulfonium salt spectrum).

The high-field absorption of the α-methine hydrogens of the cis salt Xa suggests its stereochemistry to be exclusively as shown. Heating to 80° failed to cause any broadening of the *C*- or *S*-methyl groups. The lack of any change demonstrates that inversion at sulfur in the thietanonium salts does not occur. Thus, the four-membered ring considerably slows the inversion process compared to the acyclic salts.[13] Attempts to go higher in temperature were frustrated by the rapid thermal decomposition of the salt above 80°.

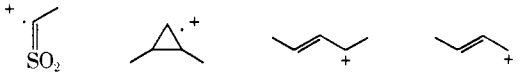
The mass spectra of the *cis*- and *trans*-dimethylthietanes are virtually superimposable. They show loss of methyl and cleavage of the four-membered ring into XI and XII (base peak). This fragmentation may be considered an allowed retro $\sigma^2s + \sigma^2s$ cycloaddition.



XI XII XIII XIV

A most interesting fragment appears at *m/e* 69, which presumably is represented by XIV. Loss of sulfur from the molecular ion to generate XIII should be allowed. Rapid hydrogen loss to produce the stable allylic cation is expected to be fast.

The mass spectra of the corresponding *cis*- and *trans*-sulfones are also virtually superimposable. Neither exhibit a molecular ion. A retro 2 + 2 cycloaddition to produce ions XI and XVI is prominent. The most intense peaks corresponding to XVII, XVIII, and XIX arise from sulfur dioxide loss. The fact that the base



XVI XVII XVIII XIX

peak appears at *m/e* 55 (*i.e.*, XIX) strongly suggests that 1,2-dimethylcyclopropane radical cation represents the ion at *m/e* 70.

Sulfone Pyrolyses. During the course of our investigations, the groups of King and de Mayo reported the thermal decomposition of thietane sulfones at >900°.[14] Two major processes occurred—the first involving sulfur dioxide extrusion to give cyclopropane and the second involving formation of olefin and sulfene. Earlier, Dodson and Klose[9] reported the nonstereospecific fragmentation of *cis*- and *trans*-2,4-diphenylthietane 1,1-dioxide to the corresponding cyclopropanes. The presence of the phenyl substituents is highly undesirable in trying to determine the stereo-

(11) For other discussions of the nmr spectra of thietanes and their derivatives, see (a) W. D. Keller, T. R. Lusebrink, and C. H. Sederholm, *J. Chem. Phys.*, **44**, 782 (1966); (b) C. R. Johnson and W. D. Siegl, *Tetrahedron Lett.*, 1879 (1969); (c) R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 5644 (1969).

(12) For similar effects in N-heterocycles, see J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967), and references therein.

(13) D. Darwish, S. H. Hui, and R. Tomilson, *ibid.*, **90**, 5631 (1968); R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967); D. Darwish and G. Tourigny, *J. Amer. Chem. Soc.*, **88**, 4303 (1966).

(14) J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. de Mayo, *Chem. Commun.*, 31 (1969); C. L. McIntosh and P. de Mayo, *ibid.*, 32 (1969).

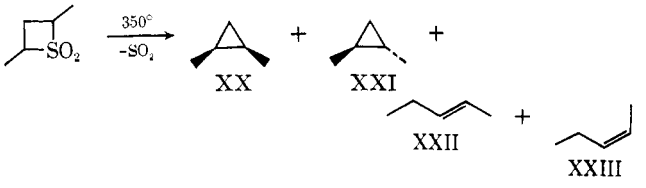
chemical course of the reaction. In pyrazoline decompositions, the phenyl-substituted isomers behave differently than the other substituted pyrazoline derivatives. We found that pyrolysis through a Pyrex or preferably Vycor column at temperatures between 350 and 450° completely consumed starting materials. To avoid thermal isomerizations of the cyclopropanes, all pyrolyses were carried out at 350° with contact times much less than 1 min. The hydrocarbon products accounted for approximately 60% of the starting material. In the case of the *trans*-sulfone, 19% of starting material was recovered at 350°, but none in the case of the *cis*-sulfone. The results are summarized in Table III. In

Table III. Hydrocarbon Products from Sulfone Decompositions[a]

Starting sulfone	*T*, °C	% XX	% XXI	% XXII	% XXIII	XX/XXI
VIIIa	350	33.8	40.1	16.3	9.8	0.84
VIIIb	350	39.2	32.9	16.4	11.5	1.19

[a] All results are the average of two or more runs. The errors are estimated to be ±0.3.

each case, the products are a mixture of *cis*- and *trans*-



1,2-dimethylcyclopropane in yields up to 50% and *cis*- and *trans*-2-pentenes in yields up to 12%. Higher temperatures increased the amount of pentenes relative to cyclopropanes. It is interesting to note that there is appreciable crossover of stereochemistry in both pyrolyses. As the temperature of the pyrolysis was increased, the selectivity seemed to decrease. However, the ratios of XX/XXI were not reproducible and decomposition of the product cyclopropane did occur to some extent at the higher temperature end. Attempts to study the photolytic cleavage led only to recovered starting material either by direct photolysis or in the presence of sensitizer.

Thietanonium Salt Decompositions. In 1954, Bordwell and his coworkers reported the *n*-butyllithium-induced decomposition of thietane.[15] In this reaction, they found lithium *n*-butylmercaptide and a gas assumed to be cyclopropane. In ancillary work, various groups reported the reactions of sulfonium salts with organolithium.[16] Bornstein[17] observed formation of thioanisole in the phenyllithium-induced decomposition of 2-methyl-1,3-dihydroisothianaphthenylium iodide but failed to find any of the product derived from *o*-xylylene as an intermediate. In this reaction, the major products derived from proton abstraction.

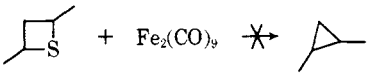
We investigated the fragmentation of thietanes and their salts as a method of formation of cyclopropanes.

(15) F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Amer. Chem. Soc.*, **76**, 1982 (1954).

(16) B. M. Trost, R. LaRochelle, and R. C. Atkins, *ibid.*, **91**, 2175 (1969); Y. H. Khim and S. Oae, *Bull. Chem. Soc. Jap.*, **42**, 1968 (1969); V. Franzen, H. I. Joschek, and C. Mertz, *Justus Liebigs Ann. Chem.*, **654**, 82 (1962); V. Franzen and C. Mertz, *ibid.*, **643**, 24 (1961).

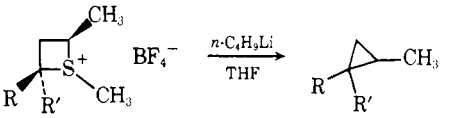
(17) J. Bornstein, J. E. Shields, and J. H. Supple, *J. Org. Chem.*, **32**, 1499 (1967).

In the reaction of 2,4-dimethylthietane with *n*-butyllithium, vpc analysis indicated the absence of cyclopropanes. This reaction was not investigated further. The reaction of the thietanes with diiron nonacarbonyl also failed to produce any C_5 hydrocarbons. It had



been reported that episulfides were desulfurized with this reagent.[18] We had found that these desulfurizations indeed proceed in high yields and with high stereospecificity.[19]

Although the thietanes themselves proved to be poor substrates for desulfurization, the thietanonium salts served very well. Increasing the electronegativity of sulfur facilitates nucleophilic attack at sulfur by the organolithium to induce fragmentation. The hydrocarbon products consisted mostly of cyclopropanes (in yields of approximately 25%) and traces of olefins (in



R = CH_3; R′ = H
R = H; R′ = CH_3
R = R′ = CH_3

approximately 1% yields). The yields of cyclopropanes do not vary with the degree of substitution. The reaction proceeds with a remarkably high degree of stereospecificity (see Table IV).

Table IV. Stereochemistry of Fragmentation of Thietanonium Salts

Compd	Temp, °C	% cis XX	% trans XXI	XX/XXI
Xa	−30	10.0	90.0	0.11
Xa	−78	8.5	91.5	0.09
Xb	−30	86.9	13.1	6.63
Xb	−78	88.6	11.4	7.77

Discussion

Desulfurization of thietanes as a route to cyclopropanes has met with only moderate success. Sulfone pyrolysis produces higher yields of cyclopropanes but the hydrocarbon fraction is appreciably contaminated by pentenes and the reaction has no appreciable stereospecificity. On the other hand, the thietanonium salt decomposition produces much lower yields of cyclopropanes, but the stereospecificity is high and the yields of pentenes are low.

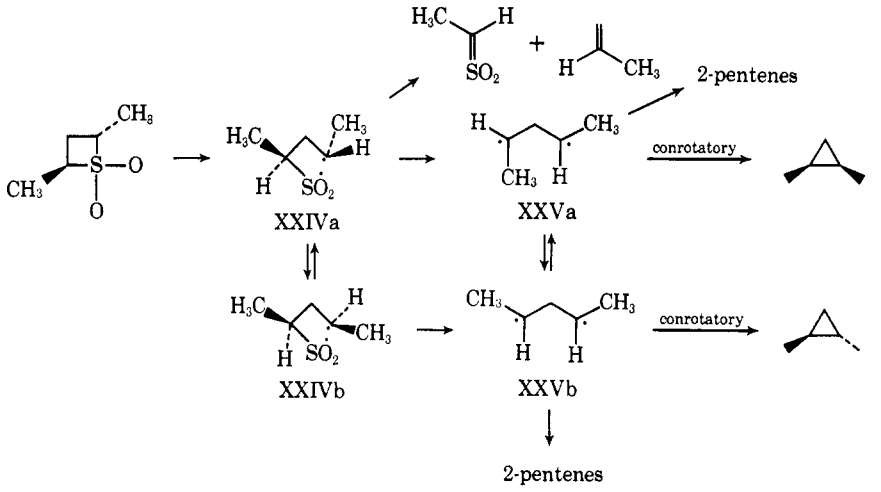
The mechanisms of these reactions, especially the latter, are of great interest, especially as they relate to the π cyclopropane problem.[20] Two competing processes exist in the thietane sulfone pyrolysis as evidenced by the formation of both C_5 hydrocarbons and C_3 hydrocarbons and sulfur-containing products.[14] Scheme III presents a unifying mechanistic picture to account for these observed results. Initial single bond homolysis

(18) R. B. King, *Inorg. Chem.*, **2**, 326 (1963).

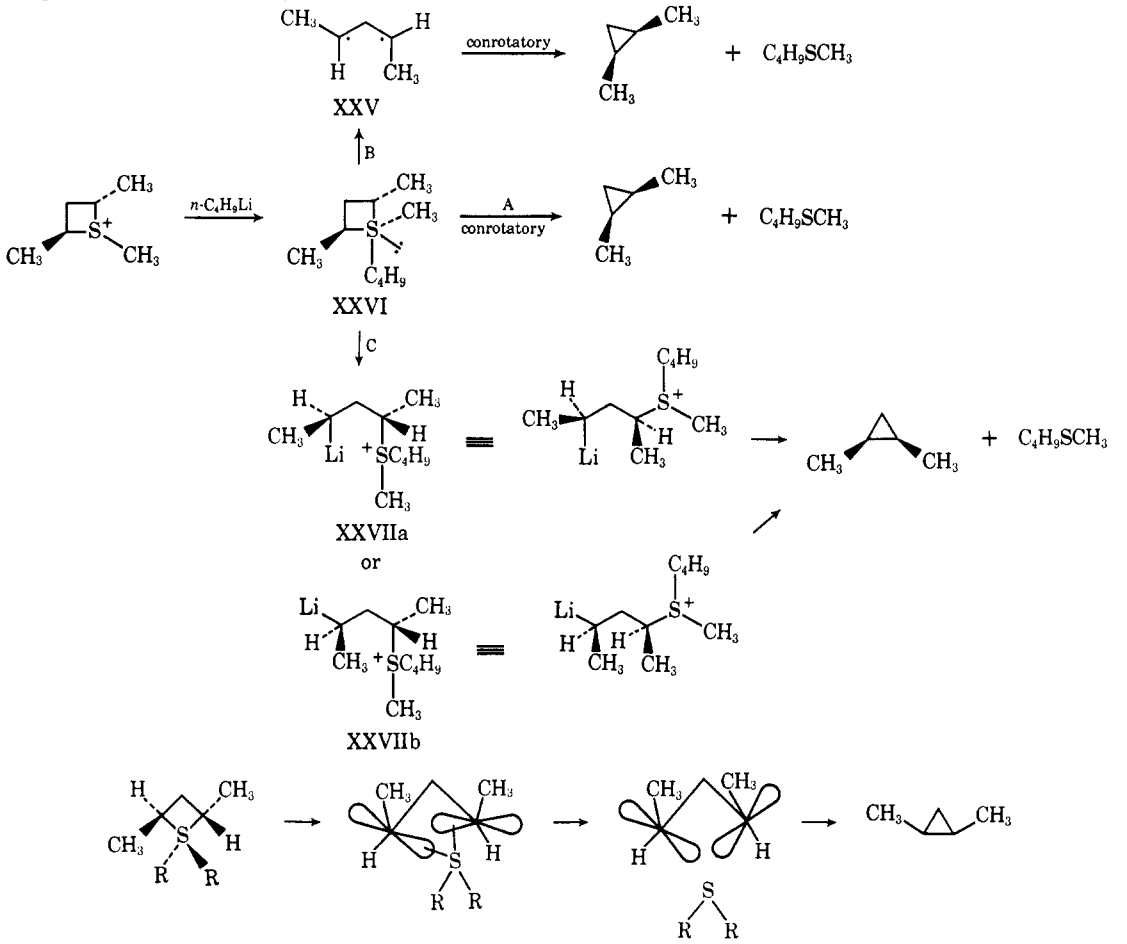
(19) S. Ziman, unpublished observations in these laboratories.

(20) For an excellent discussion, see R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

Scheme III. Mechanistic Considerations in Sulfone Pyrolysis



Scheme IV. Organolithium-Induced Fragmentation of Thietanonium Salts



produces the 1,4-diradical XXIVa which can undergo (1) fragmentation to sulfene and olefin, and (2) loss of SO_2 to produce trimethylene XXV. The lack of a very high energy of formation for sulfur dioxide compared to molecular nitrogen rationalizes sulfone pyrolyses as a two-step process *vs.* a one-step two-bond homolysis for azo decompositions of symmetrically substituted substrates. Interconversion of XXIVa and XXIVb appears to be slow relative to its decomposition, since there is appreciable memory in the formation of the cyclopropane products and there is no loss of stereochemistry in recovered thietane sulfone. Decomposition to π cyclopropane XXV followed by cyclization predicts the net inversion obtained. Hoffman's extended Hückel calculations suggest that the antisymmetric state of π cyclopropane is of lower energy than the symmetric state for CCC bond angles greater than 100°.[21] This result suggests the 1,3-diradical should close predominantly in a conrotatory sense to produce cyclopropane of inverted geometry. Experimental verification of these theoretical conclusions arises mainly in the work of Crawford in his studies of pyrazoline decompositions.[22] The selectivity ratios for cyclopropane for-

(21) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).
(22) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).

mation of 0.84 and 1.19 for the *cis*- and *trans*-1,2-dimethylthietane sulfones, respectively, is considerably lower than the values of 0.50 and 2.86 that Crawford obtained in the pyrazoline decomposition. Two reasons may account for the discrepancy. First, sulfone decompositions require approximately 150° higher in temperature than pyrazoline decompositions. Second, some stereochemical loss may occur prior to trimethylene formation by leakage of XXIVa to XXIVb. The formation of pentenes also supports the intermediacy of XXV; disproportionation by 1,2-hydrogen shift competes with recombination. The higher temperatures of sulfone pyrolyses account for the higher yields compared to pyrazoline decompositions.

The available data do not exclude other mechanistic schemes. However, Scheme III represents the simplest scheme with the minimum number of intermediates.

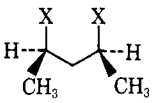
Scheme IV summarizes the mechanistic possibilities for cyclopropane formation from the thietanonium salts. All of the routes assume the initial formation of the pentacoordinated sulfur species XXVI. Evidence for such species as intermediates in other organosulfur reactions derives from our work and others which will not be reviewed here.[16,23] The products of the fragmentation reaction demand such a species as a transition state or intermediate. Of the three most reasonable paths for product formation, outlined in Scheme IV, paths A and B require XXVI as an intermediate. The driving force in each case is the conversion of decet sulfur to its much more stable octet valence state.

The most direct path for cyclopropanation is the symmetry allowed conrotatory expulsion of dialkyl sulfide from XXVI (path A) as envisioned at the bottom of Scheme IV. This screw motion method of fragmentation was considered as a possibility in pyrazoline decomposition as well.[20] Nevertheless, the great strain energy that must be associated with such motions makes path A highly unlikely.

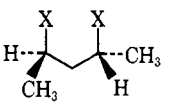
Formation of trimethylene XXV (path B) and ligand expulsion (path C) are the most reasonable alternatives. Path C warrants more detailed attention. Ligand expulsion to form a zwitterion must be occurring with a high degree of stereospecificity to account for the result summarized in Table IV. If ring opening occurred with retention of configuration (to XXVIIa), exo-sickle elimination[24] (assuming that displacement occurs with inversion of configuration at the carbon bearing the leaving group) produces cyclopropane of inverted configuration. Alternatively, ring opening with inversion to yield XXVIIb requires W elimination to produce inverted cyclopropanes.

Several lines of evidence mitigate against path C as the mechanism of cyclopropane formation. First, the yields of cyclopropane appear independent of the degree of substitution. If an elimination from XXVIIa or b were involved, yields of cyclopropane might have been expected to decrease as the degree of alkyl substitution increases. Second, comparison of the thietanonium salt reaction with a second 1,3 elimination suggests the unlikelihood of path C. In particular, the formation of cyclopropanes from 2,4-dibromopentanes and *n*-butyllithium was investigated.

Following the method of Pritchard and Volmer,[25] we converted the *meso*- (XXVIIIa) and *dl*- (XXIXa) glycols into the corresponding bromides utilizing phos-



XXVIII



XXIX

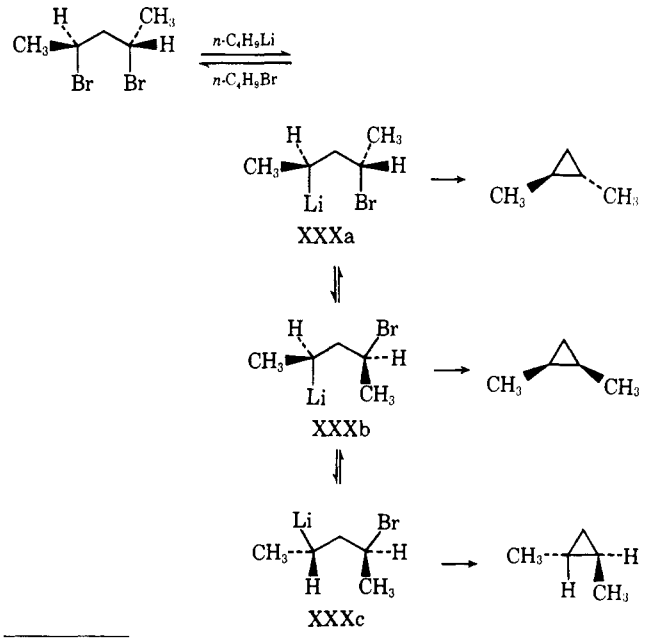
a, X = OH
b, X = Br

phorus pentabromide. In our hands, the *meso*-glycol produced *meso*-dibromide (XXVIIIb) contaminated by 8.6% *dl*-dibromide (XXIXb), whereas the *dl*-glycol produced *dl*-dibromide (XXIXb) essentially uncontaminated by *meso*-dibromide. For all subsequent reactions, vpc-collected samples of pure isomers were employed. Each dibromide was allowed to react under the conditions of the thietanonium salt decomposition. Table V summarizes the relevant data. That metal–halogen exchange has occurred extensively under these conditions is evidenced by the isolation of 2-bromopentane as a major product of the reaction. It arises by protonation of the initially formed 2-lithio-4-bromopentane (see Scheme V). That initial metal–halogen

Table V. Reactions of 2,4-Dibromopentane with *n*-Butyllithium

Starting isomer	Temp, °C	% XX	% XXI
meso	−30	82.2	17.8
meso	−78	90.4	9.6
dl	−30	24.3	75.7
dl	−78	16.5	83.5

Scheme V. Cyclopropanes from 2,4-Dibromopentanes

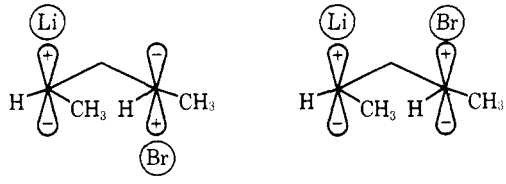


(23) K. K. Anderson and N. E. Papanikolaow, *Tetrahedron Lett.*, 5445 (1966); E. N. Givens and H. Kwart, *J. Amer. Chem. Soc.*, **90**, 378 (1968); W. A. Sheppard, *ibid.*, **84**, 3058 (1962); E. Winterfeldt, *Chem. Ber.*, **98**, 1581 (1965); C. R. Johnson and J. J. Rigan, *J. Amer. Chem. Soc.*, **91**, 5398 (1969); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969).

(24) The nomenclature suggested by A. Nickon and N. H. Werstink [*J. Amer. Chem. Soc.*, **89**, 3914 (1967)] is employed.

(25) J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

exchange occurs with a high degree of retention of configuration is supported by previous work and the data here.[26] At low temperatures in particular the reaction proceeds with a high degree of stereospecificity, indicating that the stereochemistry of the starting dibromide is being relatively faithfully translated into the stereochemistry of the product. Exo-Sickle elimination (from XXXb) cannot account for the stereochemistry of the products. Thus, the 1,3 elimination must proceed either by double retention (from XXXa) or double inversion (from XXXc). To the extent that this reaction represents an intramolecular SN2 displacement the double inversion process appears the most likely. Bordwell and his group recently demonstrated a double inversion process for a 1,3 elimination in a modification of the Ramberg–Bäcklund reaction.[27] The preference for double inversion may also be related to the trimethylene problem. The transition state for the double inversion may be considered as resembling the antisym-



metric state of trimethylene, whereas the transition state for double retention may be considered as resembling the symmetric state of trimethylene. The greater stability of the antisymmetric state *vs.* the symmetric state of trimethylene would thus predict that the double inversion process be of lower energy. The high preference for W over exo-S elimination is somewhat baffling. The possibility that such a 1,3 orientation plays a special role in determining the course of the reaction is being investigated. In particular, we might ask whether a trimethylene species plays a role even in such intramolecular alkylations.

Several aspects of the dibromide reaction mitigate against a similar intramolecular displacement (*i.e.*, path C) from occurring in the thietanonium salt decomposition. Considering that bromide is a better leaving group than dialkyl sulfide, the yields of cyclopropane and the degree of stereospecificity should be higher (or at least comparable) in the bromide cases than in the case of the thietanonium salts. The opposite is obtained. Furthermore, the isomer ratio for the thietanonium reactions is practically independent of temperature in our operating range, whereas for a dibromide reaction there is such a dependence. This observation too is the opposite of that anticipated for mechanism C.

Path B remains the only route consistent with all available evidence. The least motion cleavage of XXVI to XXV followed by the well-documented conrotatory closure predicts *trans*-2,4-dimethylthietane produces *cis*-1,2-dimethylcyclopropane. The selectivity factors are considerably higher than in either sulfone or pyrazoline pyrolyses. The fact that reaction temperatures between 200 and 400° lower than in the pyrolyses are employed readily accounts for this observation. Further support for trimethylene XXV arises in the formation of *cis*- and *trans*-2-pentenes concurrent with cyclopropanes under the reaction conditions.

(26) R. L. Letsinger, *J. Amer. Chem. Soc.*, **72**, 4842 (1950); H. O. House and R. S. Zo., *ibid.*, **80**, 182 (1958); B. M. Trost and S. Ziman, *Chem. Commun.*, 181 (1969).

(27) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968).

Experimental Section[28]

Preparation of 4-Thioacetoxypentan-2-one. To 6 l. of dry ether (freshly distilled from lithium aluminum hydride) was added a solution of 201.6 g (2.4 mol) of 3-penten-2-one and 262.8 g (2.6 mol) of triethylamine in 1 l. of dry ether. The mixture was heated to reflux and 196.5 g (2.58 mol) of thiolacetic acid in 500 ml of dry ether was added dropwise over 4.5 hr. The mixture was then refluxed 48 hr after which it was transferred to a separatory funnel and washed with ten 100-ml portions of 3 *N* hydrochloric acid, two 100-ml portions of 0.5 *N* sodium hydroxide solution, and two 100-ml portions of H_2O. All aqueous layers were combined and extracted with two 200-ml portions of ether. These ether extracts were then washed with 100 ml of 3 *N* hydrochloric acid, two 100-ml portions of 0.5 *N* sodium hydroxide solution, and 100 ml of H_2O. All ether solutions were combined, and, following drying over magnesium sulfate overnight, the ether was removed by distillation. The crude product was distilled at reduced pressure through a Vigreux column to yield 321 g (84% of theory) of 4-thioacetoxypentan-2-one with bp 121–125° (25 mm).

At a column temperature of 120°, this material had a vpc retention time of 11.0 min.[29] Its infrared spectrum[30] exhibited carbonyl absorptions at 1680 (thio ester) and 1710 cm^{-1} (saturated ketone). The nmr spectrum[31] exhibits a doublet (3 H, J = 7.0 Hz) at δ 1.30, a singlet (3 H) at 2.10, a singlet (3 H) at 2.25, the MN part of a AMN pattern (2 H) with δ_M = 2.74 and δ_N = 2.63 (J_{AM} = 8.77 Hz, J_{AN} = 4.73 Hz, and J_{MN} = 9.0 Hz), and the A part of the AMN system also coupled to a methyl group at 3.79.

Anal. Calcd for $C_7H_{12}O_2S$: C, 52.5; H, 7.5; S, 20.0. Found: C, 52.6; H, 7.5; S, 19.9.

Preparation of 4-Thioacetoxy-4-methylpentan-2-one. As described above, 9.8 g (0.10 mol) of mesityl oxide, 8.4 g (0.11 mol) of thiolacetic acid, and 11 g (0.11 mol) of triethylamine in 550 ml of ether was reacted. Distillation of the crude product produced 3.1 g (31% recovery) of mesityl oxide and 11 g (96% yield based upon recovered starting material) of colorless liquid boiling at 95° at 20 mm which proved to be the desired Michael adduct. Its infrared spectrum[30] exhibited carbonyl absorption at 1720 (saturated ketene) and 1685 cm^{-1} (thio ester). Its nmr spectrum[31] shows four singlets at δ 3.10, 2.25, 2.13, and 1.53 in the ratio of 2:3:3:6.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.12; H, 8.10; S, 18.41. Found: C, 55.17; H, 8.06; S, 18.32.

Preparation of 2-Hydroxy-4-thiolpentane. To 91.1 g (2.4 mol) of lithium aluminum hydride in 6 l. of dry ether (freshly distilled from lithium aluminum hydride), 330.6 g (2.1 mol) of 4-thioacetoxypentan-2-one in 500 ml of dry ether was added dropwise over a 2-hr period. After refluxing the solution overnight, the reaction was stopped by the dropwise addition of *ca.* 200 ml of H_2O, followed by 4 l. of 4 *N* hydrochloric acid. When all the inorganic salts had dissolved, the ether layer was separated and the aqueous layer was extracted with four 250-ml portions of ether. The ether extracts were combined and dried over magnesium sulfate, and the ether was removed by distillation through a Vigreux column. The crude product was distilled under reduced pressure through a Vigreux column to yield 220.5 g (87.7% of theory) of 2-hydroxy-4-thiolpentane boiling at 88–92° (20.0 mm).

The infrared spectrum[31] showed no S–H absorption but did show strong hydroxyl absorptions at 3640 and 3410 cm^{-1}. The nmr spectrum[31] clearly shows that a mixture of *threo*- and *erythro*-

(28) Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectra were taken on a CEC 103C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent. Vpc analyses were performed on Aerograph Model 90P and Hewlett-Packard Model 5750 gas chromatographs.

(29) A 5-ft × 0.25 in. column packed with 20% SE-30 on Chromosorb W was employed.

(30) Determined as a solution in chloroform.

(31) Determined as a solution in carbon tetrachloride.

hydroxythiols are present. It shows three sets of methyl doublets at δ 1.14 (J = 6.2 Hz), 1.16 (J = 6.2 Hz), and 1.36 (J = 6.8 Hz), a methylene multiplet centered at 1.51, a methine multiplet centered at 3.0, and a methine multiplet centered at 3.89.

Anal. Calcd for $C_5H_{12}OS$: C, 50.0; H, 10.1; S, 26.7. Found: C, 50.1; H, 10.1; S, 26.6.

Preparation of 2-Hydroxy-4-methyl-4-thiolpentane. Reduction of 4-thioacetoxy-4-methylpentan-2-one (7.0 g, 0.045 mol) by 2.0 g (0.060 mol) of lithium aluminum hydride in 200 ml of dry ether was performed as described above. Distillation of the residue after work-up generated 5.1 g (85% yield) of desired product as a colorless oil boiling at 40° (0.6 mm). Its infrared spectrum[30] showed the absence of carbonyl absorptions and the presence of hydroxyl absorption at 3420 cm^{-1} and weak sulfhydryl absorption at 2560 cm^{-1}. The nmr spectrum showed a complex multiplet at δ 4.14 for the methine proton adjacent to hydroxyl, a broad absorption at 2.60 for the hydroxyl peak (washes out rapidly when sample shaken with D_2O), a broad absorption at 1.88 for the thiol proton (washes out slowly when sample shaken with D_2O), a methylene multiplet at 1.78, two methyl singlets at 1.48 and 1.45 for the nonequivalent methyl groups at quaternary carbon, and a methyl doublet (J = 6.2 Hz) at 1.22.

Anal. Calcd for $C_6H_{14}OS$: C, 53.66; H, 10.52; S, 23.90. Found: C, 53.71; H, 10.60; S, 23.96.

Sodium Borohydride Reduction of 4-Thioacetoxypentan-2-one. A suspension of 2.96 g (78.3 mmol) of sodium borohydride in 210 ml of 1,2-dimethoxyethane (freshly distilled from lithium aluminum hydride) was added to 2.87 g (17.9 mmol) of 4-thioacetoxypentan-2-one in 170 ml of dry 1,2-dimethoxyethane. After stirring the mixture for 8 hr at room temperature, 25 ml of glacial acetic acid was added dropwise and the mixture stirred 1 additional hr. Most of the 1,2-dimethoxyethane was removed under reduced pressure and the residue dissolved in 100 ml of ether. The ether layer was washed three times with sodium carbonate and then with water until neutral to litmus. After drying the solution and evaporation of solvent, the resultant oil distilled at 90–91° (25 mm) to yield 1.38 g (47.5% yield) of colorless liquid.

The spectral data clearly identify this compound as 4-acetoxypentane-2-thiol. In particular its infrared spectrum[30] shows no hydroxyl absorption, weak thiol absorption centered at 2420 cm^{-1}, and strong acetate carbonyl at 1720 cm^{-1}. The nmr spectrum[31] is quite complex because a mixture of diastereomers is present. A series of methyl doublets appear at δ 1.15 (J = 6.2 Hz), 1.20 (J = 6.5 Hz), and 1.31 (J = 6.9 Hz); a methyl singlet appears at 1.98; a complex absorption for 2 H is centered at 1.58; and methine absorptions are centered at 2.92, 3.92, and 4.98.

Anal. Calcd for $C_7H_{14}O_2S$: C, 51.8; H, 8.7; S, 19.8. Found: C, 51.6; H, 8.8; S, 19.9.

Preparation of 2-Hydroxy-4-thiocyanatopentane. A suspension of 20.45 g (0.0853 mol) of sodium hydride in 1000 ml of ether was prepared. To this rapidly stirred mixture was added 100.02 g (0.0853 mol) of 2-hydroxy-4-thiopentane dropwise over 0.5 hr. When hydrogen evolution slowed, the mixture was refluxed for 1 hr and then cooled, after which 92.33 g (0.870 mol) of cyanogen bromide in 200 ml of ether was slowly added. Subsequent to this addition, the mixture was refluxed for 2.5 hr, then cooled and rapidly stirred for 15 min with 200 ml of 1.5 *N* hydrochloric acid. The ether layer was separated and washed successively with 150 ml of 1.5 *N* sodium hydroxide solution, 75 ml of 1.5 *N* hydrochloric acid, 150 ml of saturated sodium bicarbonate solution, and finally by two 150-ml portions of H_2O. The ether solution was dried by stirring over magnesium sulfate for 0.5 hr and the ether was removed *in vacuo* to yield 120 g of 2-hydroxy-4-thiocyanatopentane as a honey-colored oil. This material was used in the next step without furthur purification. Attempted distillation caused considerable decomposition.

A sample was collected from vpc for characterization.[32] Its infrared spectrum[31] showed hydroxyl absorptions at 3630 and 3460 cm^{-1} and thiocyanate absorption at 2160 cm^{-1}. Its nmr spectrum[31] was quite complex due to the presence of both threo and erythro isomers.

Anal. Calcd for $C_6H_{11}NOS$: C, 49.6; H, 7.6; N, 9.6; S, 22.1. Found: C, 49.7; H, 7.7; N, 9.6; S, 22.1.

Preparation of 2,4-Dimethylthietanes. A solution of 14.5 g (0.1 mol) of crude 2-hydroxy-4-thiocyanatopentane in 100 ml of dry triglyme was prepared under nitrogen. Addition of 4.4 g (0.1 mol) of sodium hydride was accompanied by some gas evolution. After this gas evolution ceased, the temperature was raised slowly to 175–195° as a slow stream of nitrogen swept through the solution. The products were collected in two low-temperature (liquid nitrogen) traps. Simple distillation of the collected material produced 2.0 g (20% yield) of a mixture of *cis*- and *trans*-2,4-dimethylthietanes. The yields are quite variable and have been as high as 70%. Each isomer was obtained pure by collection from a vpc column.[33] The spectral characteristics appear in the Results.

Anal. Calcd for $C_6H_{12}S$: C, 58.8; H, 9.9; S, 31.3. Found (*cis*-dimethylthietane): C, 59.0; H, 10.0; S, 31.2. (*trans*-2,4-Dimethylthietane): C, 58.7; H, 9.9; S, 31.3.

Preparation of 2,2,4-Trimethylthietane. To a stirred mixture of 50 ml of freshly distilled triethylene glycol dimethyl ether (triglyme) and 0.96 g of sodium hydride as a 57% dispersion in mineral oil (20 mmol of active hydride) was added a solution of 2.7 g (20 mmol) of 2-hydroxy-4-methyl-4-thiolpentane in 10 ml of triglyme at 25°. When hydrogen evolution ceased, a solution of 2.2 g (20 mmol) of cyanogen bromide in 10 ml of triglyme was added dropwise. Heat evolution occurred. The mixture was stirred 1 hr during which time the mixture was allowed to cool to room temperature. A second equivalent (0.96 g of 57% mineral oil dispersion, 20 mmol of active hydride) of sodium hydride was added. When hydrogen gas evolution ceased, the mixture was slowly heated to 170–190° while a slow stream of nitrogen was passed through the solution and into a trap cooled by liquid nitrogen. There was obtained 400 mg (18% yield) of 2,2,4-trimethylthietane as colorless liquid. Its spectral properties are summarized in the Results.

Anal. Calcd for $C_6H_{12}S$: 116.06597. Found: 116.06599.

Preparation of 2,4-Dimethylthietane 1,1-Dioxide. To a solution of 200 mg (2.0 mmol) of *cis*-2,4-dimethylthietane in 2 ml of glacial acetic acid was added 2.5 ml of 40% peracetic acid in acetic acid. The mixture was refluxed for 1 hr, cooled, diluted with 75 ml of saturated aqueous ammonium sulfate, and extracted with three 25-ml portions of aqueous sodium bicarbonate solution. The aqueous washings were back-extracted with ether. After drying the solution and removing the solvent, the crude material was isolated by preparative vpc to yield 180 mg (55% yield) of pure colorless oil. The infrared spectrum showed strong sulfone bands at 1330, 1310, 1159, and 1120 cm^{-1}. Its other spectral properties are listed in the Results.

Anal. Calcd for $C_5H_{10}O_2S$: C, 44.8; H, 7.5; S, 23.6. Found: C, 45.0; H, 7.6; S, 23.9.

In an identical fashion 228.6 mg (2.24 mmol) of *trans*-2,4-dimethylthietane was treated with peracetic acid to yield 176.5 mg (48% yield) of colorless oil. The infrared spectrum[31] shows strong sulfone absorptions at 1320 and 1120 cm^{-1}. The other spectral data are summarized in the Results.

Anal. Calcd for $C_5H_{10}O_2S$: C, 44.8; H, 7.5; S, 23.6. Found: C, 44.9; H, 7.4; S, 23.7.

Preparation of 2,2,4-Trimethylthietane 1,1-Dioxide. In a fashion identical with the dimethylthietane 1,1-dioxide preparations, 54.2 mg (0.466 mmol) of 2,2,4-trimethylthietane was oxidized with 0.185 ml (0.935 mmol) of 40% peracetic acid in acetic acid. Collection from vpc produced 31.7 mg (39% yield) of colorless sulfone. The infrared spectrum[31] showed strong sulfone bands at 1300 and 1110 cm^{-1}. The nmr spectrum is discussed in the Results.

Anal. Calcd for $C_6H_{12}SO_2$: 148.05579. Found: 148.05581.

Pyrolysis of 2,4-Dimethylthietane 1,1-Dioxides. The pyrolysis column consisted of a 700 × 25 mm Pyrex or Vycor tube fitted with male and female 24–40 joints and a thermocouple well in the middle. The column was filled with 5-mm Pyrex beads and was heated by closely wound nichrome wire wrapped the length of the column and successively covered by insulating layers of porcelain cement, Pyrex "glass wool," and asbestos sheeting. The power was supplied by Variacs. The samples, dissolved in benzene, were injected through a septum-capped, side-armed gas inlet tube, and the products collected in a liquid nitrogen cooled microtrap. Cyclohexane was added as an internal standard and the products were analyzed by vpc.[33] The results are summarized in Table III.

Preparation of Thietanonium Salts. A slurry of 126.8 mg (0.857 mmol) of trimethyloxonium fluoroborate in 0.3 ml of dry methylene chloride was cooled to −30°. Addition of 76.4 mg (0.748 mmol) of *trans*-2,4-dimethylthietane occurred dropwise. The mixture was allowed to stand with periodic shaking for 1.5 hr after which time the solvent was removed under reduced pressure at −30°

(32) An 8 ft × 0.25 in. column packed with 20% Dow Corning 710 silicone oil on Chromosorb W.

(33) A 20 ft × 0.25 in. column packed with 25% β,β'-oxydipropionitrile–phenylacetonitrile was employed.

to produce a white crystalline solid. The solid material was kept cold, since upon warming decomposition occurred. It was identified by its spectral characteristics (see Results) and was employed in subsequent reactions without further purification. In identical fashion, *cis*-2,4-dimethylthietane and 2,2,4-trimethylthietane were converted to their corresponding *S*-methyl sulfonium salts.

***n*-Butyllithium-Induced Decomposition of Thietanonium Salts.** To the white crystalline thietanonium salt prepared from 76.4 mg (0.748 mmol) of *trans*-2,4-dimethylthietane was added 0.4 ml of dry tetrahydrofuran at −30°. To the resultant slurry, 0.48 ml (1.5 mmol) of 20% *n*-butyllithium in tetrahydrofuran was added slowly by syringe. After standing with periodic shaking for 1.5 hr, the reaction was quenched by addition of 6.7 μl of water. The volatiles were distilled into a Dry Ice trap and analyzed by vpc[33] after addition of 2-methyl-2-butene as an internal standard. All products were identified by direct comparisons with authentic samples. In identical fashions, thietanonium salts prepared from *cis*-2,4-dimethylthietane and 2,2,4-trimethylthietane were treated with *n*-butyllithium and the products analyzed. On our column,[33] the order of elution of products was *trans*-1,2-dimethylcyclopropane, *trans*-2-pentene, *cis*-1,2-dimethylcyclopropane, *cis*-2-pentene, and finally *n*-butyl methyl sulfide. The results are summarized in Table IV. All results are the average of two or more runs.

Preparation of 2,4-Pentanediol. 2,4-Pentanediol was prepared by the method of Pritchard and Vollmer.[25] From 50.04 g (0.50 mol) of 2,4-pentanedione we obtained 45.92 g (90% yield) of colorless oil boiling at 112–113° (23 mm) (lit.[25] bp 65° (2 mm)).

Preparation of Cyclic Sulfite Esters of 2,4-Pentanediol. By the method of Pritchard and Vollmer,[25] we obtained 53.80 g (91% yield) of a mixture of meso and racemic sulfites, bp 82–83° (15 mm), from 40.92 g (0.40 mol) of 2,4-pentanediol. The isomers were separated by distillation on a Nester-Faust 60-cm Teflon spinning band column with the fraction boiling at 63–64° (6 mm) (lit.[25] bp 72° (12 mm)) being pure meso (vpc[34] retention time 15 min) and the fraction boiling at 72–74° (lit.[25] bp 82° (12 mm)) being the pure racemic isomer (vpc[34] retention time 23 min). The nmr spectrum[31] of the racemic isomer shows two methyl doublets at δ 1.33 and 1.53, the methylene group centered at 2.00 and two methine absorptions at 4.39 and 4.99. The nmr spectrum[31] of the meso isomer shows one methyl doublet at 1.23, the methylene protons centered at 1.72, and the methine protons at 4.99.

Saponification of Cyclic Sulfite Esters. *meso*-2,4-Pentanediol cyclic sulfite (5.66 g, 0.141 mol) was saponified as described by Pritchard and Vollmer[25] to produce 6.81 g (94% yield) of *meso*-2,4-pentanediol. The nmr spectrum[31] of our sample matched the published spectrum. *dl*-2,4-Pentanediol cyclic sulfite (5.72 g, 0.143 mol) was saponified as described by Pritchard and Vollmer[25] to yield 5.93 g (87% yield) of *dl*-2,4-pentanediol.

Preparation of 2,4-Dibromopentanes. *meso*-2,4-Pentanediol (3.34 g, 33 mmol) was converted into 2.0 g (26% yield) of *meso*-2,4-dibromopentane contaminated by 8.6% *dl* isomers as determined by vpc analysis by the method of Pritchard and Vollmer.[25] The nmr spectrum[31] shows the methyl doublet at δ 1.72, the methylene protons centered at 2.31, and the methine protons at 4.16. Its mass spectrum shows molecular ion peaks at 228, 230, and 232 in the ratio of 1:2:1 as well as abundant peaks at 151, 149, 109, 107, 70, 55, 53, 51, 44, 43, and 42. *dl*-2,4-Pentanediol (5.11 g, 50 mmol) was converted into 6.52 g (57% yield) of pure *dl*-2,4-dibromopentane as described by Pritchard and Vollmer.[25] Its nmr spectrum[31] exhibits a methyl doublet at δ 1.78, methylene hydrogen absorption at 2.07, and methine hydrogen absorptions at 4.32. Its mass spectrum was essentially superimposable upon that of the meso isomer.

Reaction of 2,4-Dibromopentanes with *n*-Butyllithium. A solution of 42.4 mg (0.184 mmol) of *dl*-2,4-dibromopentane in 0.2 ml of dry tetrahydrofuran was cooled to −30°. To this solution 0.12 ml (0.368 mmol) of cold 20% *n*-butyllithium in tetrahydrofuran was added by syringe. The mixture was maintained at −30° for 2.5 hr and then quenched by addition of 20 μl of water. All volatiles were distilled *in vacuo* into a Dry Ice cold trap. The products were analyzed by vpc using 2-methyl-2-butene and *p*-xylene as internal standards.[33] The results are summarized in Table V.

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(34) A 10 ft × 0.25 in. column packed with 25% Carbowax 20M on Chromosorb P was employed.