The Decomposition of Thiirane 1,1-Dioxides (Episulfones)

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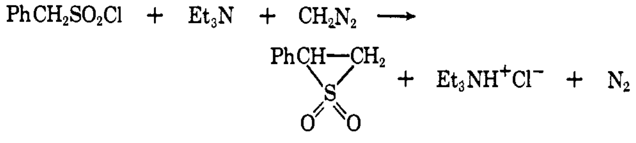
Abstract: The first-order rates of decomposition of the episulfones, 2-phenylthiirane 1,1-dioxide (**1**), *trans*-2,3-diphenylthiirane 1,1-dioxide (**2**), and *cis*-2,3-diphenylthiirane 1,1-dioxide (**3**) (to alkene and sulfur dioxide), were found to correlate surprisingly well with the ionizing power of the medium. The rates were found to be accelerated by alkoxide ion and were first order in alkoxide ion when the concentration was sufficiently high. Solvolytic decomposition of **2** gave *trans*-stilbene stereospecifically and **3** gave *cis*-stilbene stereospecifically, but *trans*-stilbene was obtained from **3**, as well as from **2**, when alkoxide ion was present. Deuterium exchange experiments showed that in the presence of methoxide ion **3** underwent exchange, with retention of configuration, at a rate considerably faster than its rate of epimerization to **2**. The solvolytic decompositions of **1–3** are represented as occurring by way of diradical intermediates; a diradical anion intermediate is assumed for the alkoxide ion promoted reactions. The latter reaction is believed to involve addition of methoxide ion to the sulfone grouping.

Methods are now available for the preparation of both symmetrical and unsymmetrical thiirane 1,1-dioxides (episulfones). Staudinger and Pfenninger found that diphenyldiazomethane and sulfur dioxide gave tetraphenylthiirane 1,1-dioxide;[2] this method has since been applied to prepare the parent heterocycle,[3a] and its 2,3-diaryl-2,3-diethyl,[3b] 2,3-dimethyl,[4] and 2,3-diphenyl[5,6] derivatives. Recently Opitz and Fischer have shown that a variety of unsymmetrical thiirane dioxides can be obtained from the reaction of sulfenes and diazomethane.[7]

Most thiirane 1,1-dioxides decompose near room temperature to give alkenes and sulfur dioxide.[2-7] For *cis*- and *trans*-2,3-dimethylthiirane 1,1-dioxides and *cis*-2,3-diphenylthiirane 1,1-dioxide the decompositions occur stereospecifically with retention of configuration of the alkene.[4-6] The present study was initiated to determine the effect of base on the rate and stereochemistry of episulfone decompositions. This has been accomplished and, in addition, information pertinent to the mechanism of these decompositions has been obtained.

Phenylthiirane 1,1-dioxide (**1**) was prepared by the method of Opitz and Fischer.[7]



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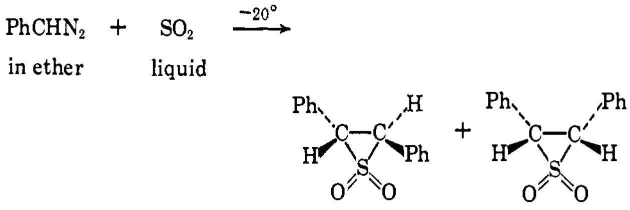
Application of Staudinger's method[2] to phenyldiazomethane using a temperature below −20° gave a low yield of a mixture consisting of about 55% *trans*- and 45% *cis*-2,3-diphenylthiirane 1,1-dioxides (**2** and **3**, respectively).



2 (55%) 3 (45%)

The composition of the mixture is based on the proportions of *trans*- and *cis*-stilbenes obtained on thermal decomposition. The *cis* isomer **3** was obtained in a purity of about 95% by warming a methylene chloride solution containing **2** and **3** for about 10 min, which caused most of the **2** present to decompose, followed by precipitation of **3** with pentane. The **3** obtained in this way decomposed stereospecifically to *cis*-stilbene in agreement with previous reports.[5,6,8]

First-Order Decompositions. At 0° the rate of decomposition of **2** was faster than that of **3** by an amount sufficient to allow spectrophotometric determination of the individual rates using a mixture of isomers. At 25° the decomposition of **3** interfered with the determination of the infinity absorbance for **2**, but the rate for **2** could be obtained by the Guggenheim method. The rates varied appreciably with solvent, as is brought out in Table I.

Examination of Table I shows that the rate of decomposition of the three episulfones (to alkene and sulfur dioxide) increases markedly (over 1000-fold) with increasing ionizing power of the medium. A plot of log k/k_0 for **1** against Grunwald-Winstein Y values for the solvolysis of *t*-butyl chloride[9] gave a surprisingly good line for the aqueous dioxane runs [Figure 1; slope (m) $\cong$ 0.5]. The rate in water, obtained by extrapolation, was 1.4 sec^{-1}. Plots of log k for **1** *vs.* volume per cent water for aqueous dioxane, acetonitrile, and dimethyl sulfoxide solutions gave a series of curves which converged with increasing water content. The rate in pure water, obtained by extrapolation, was about 1 sec^{-1}.

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(1) National Institutes of Health Predoctoral Fellow, 1964–1966.

(2) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

(3) (a) G. Hess, E. Reichold, and S. Majumdar, *ibid.*, 90, 2106 (1957); (b) L. V. Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942).

(4) (a) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); (b) N. P. Neureiter, *ibid.*, **88**, 558 (1966).

(5) L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965).

(6) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

(7) G. Opitz and H. Fischer, *Angew. Chem. Intern. Ed. Engl.*, **4**, 70 (1965).

(8) The relative instability of **2** ($t_{1/2}$ = 2.8 min in chloroform at 25° as compared to 89 min for **3**) no doubt accounts for its presence going undetected previously.

(9) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846 (1948); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

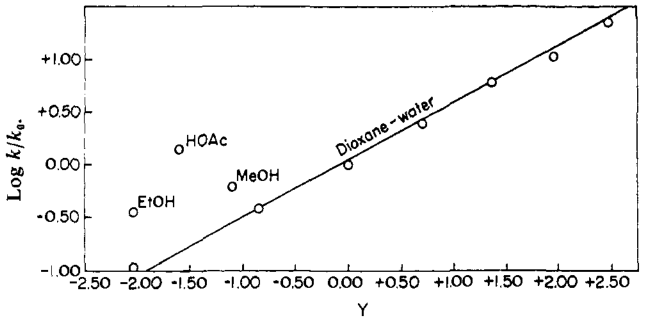

Figure 1. A plot of log k/k_0 decomposition rates for 2-phenylthiirane 1,1-dioxide (**1**) in various solvents plotted against Grunwald–Winstein Y values (k_0 is taken as the rate in 70% dioxane-H_2O, where Y is close to zero).[9]

The variation in rate for **1** in pure solvents also correlates surprisingly well with the ionizing power of the solvent, as judged by comparison with the solvolysis rates for *p*-methoxyneophyl tosylate[10] in various solvents. It will be observed (Figure 2) that a log–log plot of decomposition rates *vs.* solvolysis rates gives a reasonably good line. The increase in rate of **1** in tetrahydrofuran (THF) with added lithium perchlorate is also expected for an ionic process. Note, however, that the addition of lithium perchlorate does not produce the large salt effect observed for the solvolysis of *p*-methoxyneophyl tosylate in nonpolar solvents.[11] In the decomposition of **1** in THF b, from the equation $k = k_0(1 + b[\text{salt}])$, is *ca.* 14 as compared to 482 for the ionization of *p*-methoxyneophyl tosylate in this solvent.[11a]

Table I. Effect of Solvent on the Rates of Decomposition of 2-Phenylthiirane 1,1-Dioxide (**1**) and of *trans*- and *cis*-2,3-Diphenylthiirane 1,1-Dioxides (**2** and **3**, respectively) in Various Solvents at 25°

	k,[a] sec^{-1}		
Solvent	**1**	**2**	**3**
Benzene	...	1.7×10^{-3}	1.2×10^{-4}
Dioxane	2.5×10^{-4}	2.8×10^{-3}	1.1×10^{-4}
Tetrahydrofuran	2.5×10^{-4}	...	...
Tetrahydrofuran[b]	3.2×10^{-4}	...	...
Acetonitrile	6.4×10^{-4}	...	...
Chloroform	8.3×10^{-4}	3.9×10^{-3}	1.3×10^{-4}
Dimethyl sulfoxide	3.0×10^{-3}	...	...
Ethanol	5.2×10^{-3}	...	...
2-Methyl-2-propanol	5.3×10^{-3}	...	...
2-Propanol	5.4×10^{-3}	...	...
Methanol	9.4×10^{-3}	2.4×10^{-2}	3.6×10^{-4}
Acetic acid	2.0×10^{-2}	2.4×10^{-2}	4.1×10^{-4}
Formic acid	...	...	2.7×10^{-2}
Water	~ 1[c]	~ 1.2[c]	$(\sim 3 \times 10^{-2})$[c]

[a] Average of at least two runs; rates were reproducible to ±10%. [b] Containing 0.0125 M $LiClO_4$; with 0.036 M $LiClO_4$ the rate was 3.8×10^{-4} sec^{-1} and with 0.096 M $LiClO_4$ it was 6.5×10^{-4}. [c] Obtained by extrapolation of a plot of log k *vs.* per cent water in dioxane (v/v).

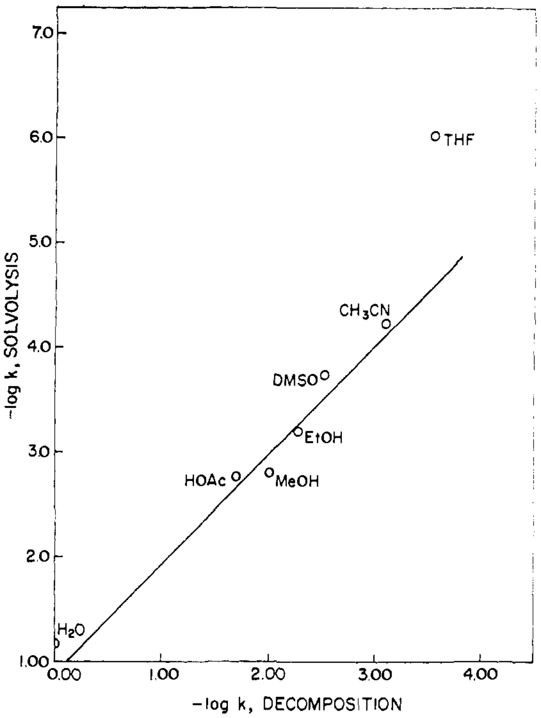

Figure 2. A plot of log k for the solvolysis of *p*-methoxyneophyl tosylate in various solvents[10] against log k for the decomposition of 2-phenylthiirane 1,1-dioxide (**1**) in these same solvents.

Similar trends for the decomposition rates for **2** and **3** with solvent variation were observed (Table I). The relatively slower decomposition of **3** allowed measurements to be made also in formic acid; **1** and **2** decomposed too rapidly in formic acid at 25° to permit rate determinations by the method used for **3**. Activation parameters for the rates of decomposition of **1**, **2**, and **3** in chloroform and in methanol are summarized in Table II.

Table II. Activation Parameters for the Decomposition of Phenylthiirane 1,1-Dioxide (**1**) and *trans*- and *cis*-2,3-Diphenylthiirane 1,1-Dioxides (**2** and **3**) at 25°

Compd	Solvent	E_a, kcal/mole[a]	$\Delta S^{\ddagger}$, eu
1	$CHCl_3$	17.5	−16
2	$CHCl_3$	17	−14.5
3	$CHCl_3$	21	−8
1	CH_3OH	18.5	−9
2	CH_3OH	19	−5
3	CH_3OH	21	−6

[a] Calculated from a plot of log k *vs.* $1/T$ (10° temperature differentials).

The decompositions for **2** and **3** were stereospecific; **2** gave *trans*-stilbene, whereas **3** gave *cis*-stilbene.[5,6]

Second-Order Decompositions. For **1**, **2**, and **3** the rates of decomposition in methanol are accelerated in the presence of sodium methoxide. Variation of the methoxide ion concentration showed that the reactions are first order in methoxide ion and, therefore, presumably second order. The rate of methoxide ion reaction for **2** was nearly the same as for **1** at 25°. Surprisingly enough, the rates for **2** and **3** were found to be *identical.* A product study for the reaction of **3** provided an explanation. Whereas **3** decomposes stereospecifically in methanol solution to give *cis*-stilbene, the product in the presence of sodium methoxide *is almost entirely trans-stilbene.* This fact, plus the

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(10) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(11) (a) S. Winstein, S. Smith, and D. Darwish, *ibid.*, **81**, 5511 (1959); (b) S. Winstein, E. C. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964).

identity of the rates for **2** and **3**, can be explained by a rapid epimerization of **3** to **2** followed by a rate-determining, methoxide-promoted decomposition. This mechanism was confirmed by deuterium exchange studies (*vide infra*). The kinetic data are summarized in Table III.

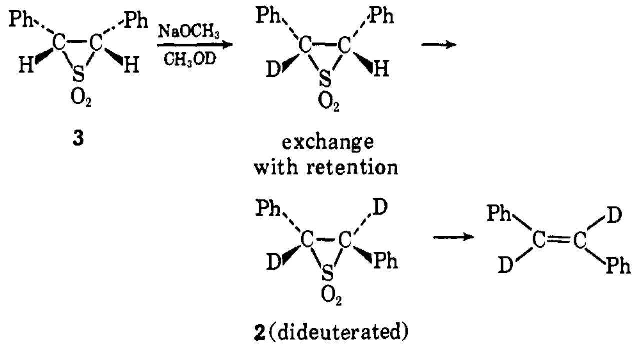
Table III. Kinetic Data for the Decomposition of 2-Phenylthiirane 1,1-Dioxide (**1**) and *trans*- and *cis*-2,3-Diphenylthiirane 1,1-Dioxides (**2** and **3**) with Dilute Methanolic Sodium Methoxide

Thiirane 1,1-dioxide	Temp, °C	[MeO⁻], M	k, M^{-1} sec^{-1}	E_a, kcal/mole	$\Delta S^{\ddagger}$ (25°), eu
2-Phenyl (**1**)	15.0	2.62×10^{-3}	1.6	18	+3
	15.0	1.31×10^{-2}	1.7		
	15.9	2.35×10^{-3}	1.7		
	24.9	2.62×10^{-3}	4.6		
	35.2	2.62×10^{-3}	12.4		
trans-2,3-Diphenyl (**2**)	0.0	2.62×10^{-3}	2.4×10^{-1}	21	+12
	8.9	1.85×10^{-3}	8.5×10^{-1}		
	8.9	1.31×10^{-2}	8.6×10^{-1}		
	25.0	1.88×10^{-3}	5.5		
cis-2,3-Diphenyl (**3**)[a]	0.0	1.88×10^{-3}	2.3×10^{-1}	21	+12
	0.0	1.88×10^{-2}	2.4×10^{-1}		
	25.0	1.88×10^{-3}	5.5		

[a] Deuterium exchange studies indicate that **3** is epimerizing to **2** prior to decomposition.

Comparison of the rates in Tables I and III shows that methoxide ion produces a definite effect on the decomposition rate. For **1** at 25° a methoxide ion concentration of 0.0029 M (at equal concentrations of MeO^- and **1**) will make the half-life of the methoxide-promoted reaction equal to that of the methanolysis reaction; for **2** the methoxide concentration required is 0.0066 M. For **3**, which has a considerably slower methanolysis rate ($t_{1/2}$ = 1920 sec *vs.* 29 sec for **2** at 25°) a concentration of methoxide ion of 10^{-5} M is sufficient to make the half-lives of the first-order and second-order decompositions equal.

Deuterium Exchange Experiments. Decomposition of **1** in CH_3OD with sodium methoxide at 0° gave styrene containing about 5% of styrene-d_1. Under similar conditions **3** gave 5.5% *trans*-stilbene-d_1 and 94.5% *trans*-stilbene-d_2. A mixture of **2** (~50%), **3** (~40%), and *trans*-stilbene (~10%) (ultraviolet and vpc analyses) gave 46.5% *trans*-stilbene-d_0, 23.2% *trans*-stilbene-d_1, and 30.3% *trans*-stilbene-d_2. From this result it would appear that somewhat less than one-half of the molecules of **2** are exchanging a single deuterium atom prior to decomposition; few, if any, molecules are exchanging two deuterium atoms prior to decomposition. This places the rate of exchange for **2** as being about one-third the rate of methoxide ion promoted decomposition (0.23 M^{-1} sec^{-1} at 0°). The exchange rate for **3** must be considerably faster (steric acceleration) than that of **2** in order that both hydrogen atoms of **3** be exchanged prior to decomposition. Furthermore, the rate of exchange for **3** must be considerably faster than the rate of epimerization or else an appreciable quantity of the product would have been *trans*-stilbene-d_1. This requires that **3** exchange with *retention of configuration*.



3

2 (dideuterated)

Discussion

Mechanisms for Episulfone Decompositions. The facile and stereospecific decompositions of *cis*-2,3-dimethylthiirane 1,1-dioxide to *cis*-2-butene,[4b] and of *trans*- and *cis*-2,3-diphenylthiirane 1,1-dioxides (**2** and **3**) to *trans*- and *cis*-stilbenes, respectively, are remarkable in that the Hoffmann–Woodward symmetry selection rules for intermolecular cycloadditions (and their reversals) appear to exclude a concerted thermal decomposition of thiirane 1,1-dioxides.[12] The success of the rules in predicting the behavior of the analogous five-membered ring systems[12b] lends some confidence to their extension to three-membered rings, and there are several other lines of evidence that make a concerted decomposition unlikely. The most important of these is the sensitivity of the decompositions to solvent ionizing power (Table I, Figures 1 and 2). An even greater sensitivity to solvent effects has been observed in the (nonconcerted) 2 + 2 cycloadditions of tetracyanoethylene to electron-rich alkenes, such as *t*-butyl vinyl sulfide, which are believed to occur by a dipolar ion mechanism.[13] These cycloadditions are often, but not always, stereospecific.[13] In contrast, the rate of the (concerted) Diels–Alder reaction between 1,3-diphenylbenzo[*c*]furan and acrylonitrile is relatively insensitive to solvent effects[14] ($k_{MeOH}/k_{C_6H_6}$ = 2.3 *vs.* 14 for **2** and 5.3 for **3**: k_{MeOH}/k_{CHCl_3} = 0.35 *vs.* 11 for **1**, 6.2 for **2**, and 2.8 for **3**).[15]

A second bit of evidence favoring a nonconcerted mechanism is the near-identity of the rates of decomposition of **1** and **2** in solvents of good ionizing power (Table I) and the near-identity of their activation energies in chloroform and in methanol (Table II). This suggests that only *one* of the phenyl groups in **2** is providing conjugative stabilization in the transition state.[16] The slower rate, higher activation energy, and lower sensitivity to increased solvent ionizing power of **3**, as compared to **1** and **2**, point to less effective conjugation in the transition state, presumably caused by steric interference between the *cis*-phenyl groups. Al-

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(12) (a) R. W. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965). (b) See W. L. Mock, *ibid.*, **88**, 2857 (1966), and S. D. McGregor and D. M. LeMal, *ibid.*, **88**, 2858 (1966), for evidence with respect to the concerted nature of 1-thiacyclopent-3-ene 1,1-dioxide decompositions. (c) J. P. Freeman and W. H. Graham, *ibid.*, **89**, 1761 (1967), have recently questioned the applicability of the rules to three-membered rings.

(13) S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966).

(14) M. Gillois and P. Rumpf, *Bull. Soc. Chim. France*, 1823 (1959).

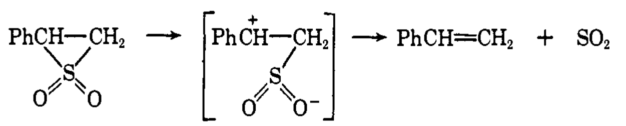
(15) It will be interesting to examine the effect of solvent on the rate of decomposition of 2,5-dihydrothiophene 1,1-dioxides in this regard.

(16) From the data on heats of hydrogenation (see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 78-80) the stabilization energies of the C=C bonds in *trans*-stilbene and styrene are 10.2 and 5.1 kcal/mole, respectively (relative to ethylene).

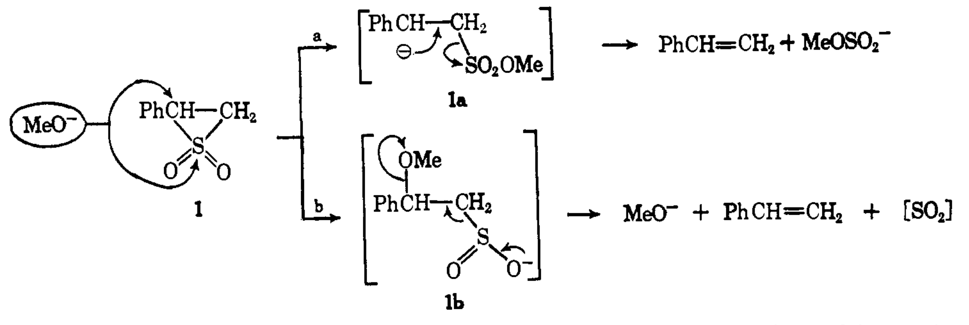
though the transition state for **3** is stabilized to a lesser degree by conjugation, it does allow important relief of ground-state strain, which shows up as a more positive entropy of activation (by 6–8 eu). The 4-kcal/mole difference in activation energy for **2** *vs.* **3** in chloroform (Table II) would have resulted in a rate difference of over 10^4-fold (instead of 30-fold), if the entropies had been the same. These effects are leveled somewhat in methanol; the entropies of activation are now comparable, and **3** has only a 2–3-kcal/mole higher activation energy.

Two final points favoring a nonconcerted mechanism are the acceleration of the reaction by methoxide ion (Table III)[17] and the observation that **1**, **2**, and **3** decomposed to the extent of 80–90% at −78° under ultraviolet irradiation (in agreement with Hoffmann–Woodward predictions[12a]), whereas in the absence of irradiation the episulfones decomposed to an extent of less than 20%.

Assuming that a concerted mechanism can be ruled out, a dipolar ion mechanism and a diradical mechanism remain to be considered. The dipolar ion mechanism is attractive because it will accommodate very nicely the observed rate acceleration accompanying increasing ionizing power of the medium (Figures 1 and 2).

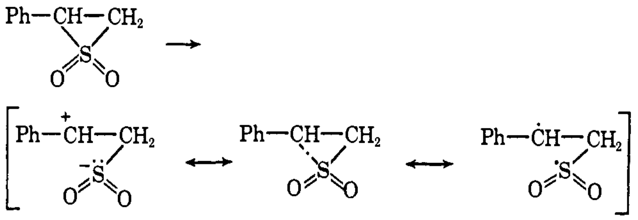


The relatively small salt effect (*vide supra*) does not seem to be consistent with the dipolar ion mechanism, but one might argue that this was associated in some way with the opening of the strained three-membered ring. There are at least two other objections to this mechanism, however. Firstly, in analogous SN1-type reactions solvent participation involves considerable bonding of the solvent to carbon in the transition state. By analogy, one would expect in the present instance that bonding of the solvent to carbon would lead to the formation of at least some of the corresponding substitution products, $PhCH(OCH_3)CHPhSO_2H$ (from **2** or **3**) or $PhCH(OCH_3)CH_2SO_2H$ (from **1**). Secondly, in the reaction promoted by methoxide ion the dipolar ion mechanism becomes an anion mechanism. One can visualize attack at sulfur or at carbon to give anionic intermediates **1a** or **1b**.

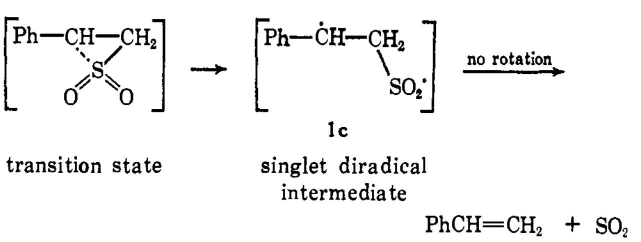


Path a is unattractive, however, in that the rate of proton abstraction by the intermediate **1a** should be extremely fast, and elimination of $MeOSO_2^-$ from the resulting sulfonate, $PhCH_2CH_2SO_2OMe$, would be expected to be very slow.[18] Path b also seems unlikely, since salts of β-methoxy-β-phenylethanesulfinate (**1b**) are known, and would appear to be stable under conditions whereby **1** is converted rapidly to styrene.[19] Thus these anion mechanisms are suspect, and this casts further doubt on the dipolar ion mechanism.

The distinction between a dipolar ion mechanism and a diradical mechanism is subtle. The transition state can be looked on either as a dipolar ion or as a diradical with dipolar character.



It is only after the bond is broken completely and the atoms move apart that we can distinguish between these mechanisms by designating a dipolar ion or diradical *intermediate*. This intermediate must lose sulfur dioxide more rapidly than rotation occurs around the C–C bond in order to satisfy the observed stereochemistry of the reaction.



The transition state leading to **1c** can be assumed to have dipolar character. In fact, as mentioned above, the *same* representation could be used for a transition state leading to a dipolar ion intermediate. The rate acceleration effect of solvents with good ionizing power (Figures 1 and 2) therefore can be rationalized. Tuleen, Bentrude, and Martin[20] have described a homolysis reaction which responds in a similar manner to changes in solvent ionizing power. The line they obtained in a plot comparable to Figure 2 has a slope of 1.6 as com-

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[17] It will be of interest in this regard to see whether or not the decomposition of 2,5-dihydrothiophene 1,1-dioxides is promoted by alkoxide ions.

[18] Bäcklund (Doctoral Dissertation, University of Uppsala, Sweden, 1945) observed the formation of small amounts of 1- and 2-propane sulfonates in the reaction of chloromethyl ethyl sulfone with hydroxide ion. These must have arisen by hydroxide ion attack on the sulfur atom of methylthiirane 1,1-dioxide (alkyl analog of **1**) to form two isomeric carbanions analogous to **1a**, which then abstracted a proton from the solvent. We have not observed the formation of sulfonates in the reaction of **1** or **2** with bases, but a comparable reaction to form a sulfonate does occur with 2,3-diphenylthiirene 1,1-dioxide.[5]

[19] W. Kirmse and L. Horner, *Ann.*, **614**, 4 (1958).

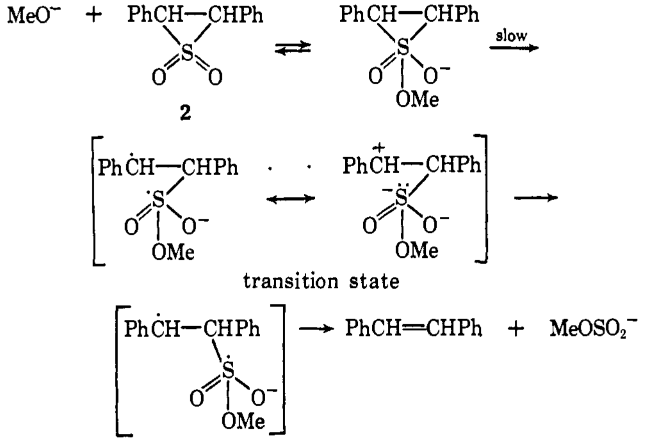
[20] D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 1938 (1963).

pared to 1.1 for the line in Figure 2. Their salt effect is somewhat larger (b = 76 *vs.* 14).

The principal weakness of this (or any stepwise) mechanism is that it does not readily accommodate the observed stereospecificity of the decomposition. The elegant work of Montgomery, Schueller, and Bartlett[21] has demonstrated that the diradicals formed in 2 + 2 cycloadditions of $F_2C{=}CCl_2$ to 1,3-dienes undergo rotation prior to collapse to product. By analogy, one might expect the decomposition of **2**, **3**, and *cis*- and *trans*-2,3-dimethylthiirane 1,1-dioxides[2] to be nonstereospecific. On the other hand, there is evidence to indicate that in the gas phase the loss of an iodine atom from the radical $MeCHI\dot{C}HCH_3$ and of NO from the (allylic) radical $CH_2{=}CH\dot{C}HCH(CH_3)NO$ is in each instance considerably faster than bond rotation.[22] In view of these results it seems possible that loss of SO_2 from the (eclipsed) singlet diradical **1c** might be more rapid than rotation. It may be significant in this respect that loss of SO (which should be a poorer leaving group than SO_2) from *cis*- and *trans*-2,3-dimethylthiirane 1-monoxides is not stereospecific.[23] This may represent a borderline situation where bond rotation and loss of the leaving group are competitive.

One other bit of evidence that may be construed to favor a radical-type decomposition is the observation that stored samples of episulfones always give some polysulfone.[2]

The methoxide ion promoted decompositions of **1** and **2** are pictured as involving a preliminary addition of methoxide ion to the sulfone grouping. Here the rapid epimerization of **3** to **2** prior to decomposition precludes determination of the stereochemistry, but with 2,3-dimethylthiirane 1,1-dioxides (which are not epimerized by hydroxide ion[2]) the stereochemistry was the same in the presence or absence of hydroxide ion.[2]



There appears to be no evidence in the literature for addition to the S=O bond of a sulfone. It would be expected by analogy with the behavior of cyclopropanones,[24] however, that episulfones, such as **1** and **2**, would be unusually prone to undergo such additions.[25,26] Presumably the adduct would have a somewhat weaker C–S bond, and would decompose by way of the diradical anion intermediate shown. Again, the similarity in rates and activation parameters for **1** and **2** (Table III) is consistent with only one of the phenyl groups participating in conjugation in the transition state for the decomposition. It is interesting that the increased rates for the methoxide-promoted decompositions of **1** and **2**, as compared to their methanolyses, are caused primarily by an increase in activation entropies. This is perhaps a consequence of the lesser degree of solvent reorganization required for a reaction in which the charge is merely dispersed in the transition state as compared to one where two charges of opposite sign are generated.

Exchange and Epimerization. The deuterium exchange data for **2** indicate a rate of exchange roughly one-third the rate of decomposition, or about 7×10^{-2} M^{-1} sec^{-1} at 0° in methanol with sodium methoxide. The appreciably slower rate for **1** can be attributed to the absence of the inductive effect of the second phenyl group and the statistical factor of two. The appreciably faster rate for **3** can be attributed to steric acceleration.[27] The rate of exchange per hydrogen atom of $PhCD_2SO_2CD_2Ph$ in methanol with sodium methoxide is about 4×10^{-2} M^{-1} sec^{-1} at 0°.[28] When this rate is corrected for the isotope effect (factor of perhaps 5–10), it will be several times as great as the rate for **2**. While benzyl sulfone is not a perfect model, this comparison does show that the presence of the three-membered ring has not introduced either a *large* accelerating or decelerating effect on the rate.[29]

In an earlier section evidence was presented to show that with sodium methoxide in methanol-O-d_1 **3** underwent deuterium exchange with retention of configuration at a rate considerably faster than it underwent epimerization to **2** (followed by decomposition to *trans*-stilbene). Retention of configuration in deuterium exchanges involving α-sulfonyl carbanions is not unusual,[30] but to our knowledge has not been reported previously for a cyclic sulfone.[31] This result is of particular interest, since removal of a proton from a comparable conformation in an acyclic sulfone would have given a symmetric α-sulfonyl carbanion, if such ions are effectively planar.[30] It seems likely that in this instance the three-membered ring is responsible for the maintenance of configuration.

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(21) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

(22) (a) S. W. Benson, K. W. Egger, and D. M. Golden, *ibid.*, **87**, 468 (1965); (b) K. W. Egger and S. W. Benson, *ibid.*, **87**, 3314 (1965).

(23) G. E. Hartzell and J. N. Page, *J. Org. Chem.*, **32**, 359 (1967).

(24) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966); **89**, 1028 (1967).

(25) O. R. Zaborsky and E. T. Kaiser, *ibid.*, **88**, 3084 (1966), have observed a very large rate acceleration in the alkaline hydrolysis of five-membered ring sultones relative to open-chain analogs; addition of hydroxide ion may be involved here.

(26) Examples wherein sulfur is joined to atoms by more than four covalent bonds (*e.g.*, SF_6) are, of course, well documented, although they are not numerous. See W. A. Sheppard, *ibid.*, **84**, 3064 (1962), for a recent example.

(27) H. C. Brown, *Science*, **103**, 385 (1946).

(28) J. M. Williams, Jr., Ph.D. Dissertation, Northwestern University, Aug 1966.

(29) In a somewhat analogous system H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960), found that the acidities of isopropyl phenyl sulfone and cyclopropyl phenyl sulfone were about the same in tetrahydrofuran and in hydrocarbon solvents. See also A. Ratajczak, F. A. L. Anet, and D. J. Cram, *ibid.*, **89**, 2072 (1967).

(30) See D. J. Cram, R. D. Trepka, and P. St. Janiak, *ibid.*, **88**, 2749 (1966), and papers cited therein for examples and discussions.

(31) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Letters*, 515 (1962), observed that decarboxylation of optically active 2-carboxy-2-methylbenzothiophene 1,1-dioxide gave racemic sulfone, presumably *via* an α-sulfonyl carbanion. See also D. J. Cram and T. A. Whitney, *J. Am. Chem. Soc.*, **89**, 4651 (1967).

Experimental Section

2-Phenylthiirane 1,1-Dioxide (1). 2-Phenylthiirane 1,1-dioxide was prepared in the manner described by Opitz.[7] Cooling below -20° was necessary to obtain crystalline material. The yield of the product was raised sharply (from 40 to 90%) by isolating the episulfone at low temperature (*viz.* -50°) without a significant change in the purity of the product (mp $\sim 34^\circ$ in each instance).

***trans*- and *cis*-2,3-Diphenylthiirane 1,1-Dioxides (2 and 3).** To a solution containing 1.96 g (36.3 mmoles) of sodium methoxide in 90 ml of dry pyridine was added 10.0 g (36.3 mmoles) of benzaldehyde *p*-tosylhydrazone.[32] This mixture was stirred at 55–60° for 30 min and poured into 300 ml of ice water. The resulting mixture was extracted with four 100-ml portions of cold pentane. The pentane fractions were combined and washed ten times with 60-ml portions of ice water and five times with 100-ml portions of ice water. After drying over anhydrous sodium sulfate overnight at 0°, the pentane solution was cooled to -80° and filtered. The resulting filtrate was kept between -40 and -60° and stirred while liquid sulfur dioxide was added dropwise. A precipitate formed immediately. After the color of phenyldiazomethane had been discharged, the slightly yellow precipitate was collected quickly on a filter and washed with a few milliliters of cold pentane. (The solid turned bright yellow after standing at room temperature for a short time.) The solid (500 mg, 6%) was transferred immediately to a vial and this was cooled to -196° with liquid nitrogen and kept at -196° until just prior to its use. A similar preparation in which the sulfur dioxide addition step was carried out at -20° gave essentially the same result.

The melting point of the initial precipitate was 78–86.5° dec; subsequent recrystallizations (methylene chloride–pentane) raised the melting point to 86–88° dec. The stilbenes resulting from the melting of the episulfones were shown by vpc (5 ft, 0.25 in. o.d. column, 12% SE-30 gum rubber on 50–80 mesh Chromosorb W at 190° [33]) to be 55% *trans*-stilbene and 45% *cis*-stilbene. Subsequent low-temperature recrystallizations (dissolving the solid at *ca.* 10° in methylene chloride, cooling to -78°, adding pentane, and cooling the solution with liquid nitrogen to induce crystallization if necessary) did not significantly change the ratio of *cis*- to *trans*- stilbene formed by the thermal decomposition of the solid. That the solid was not merely a mixture of the *cis*-episulfone **3** and *trans*-stilbene was apparent from kinetic data, which showed that *trans*-stilbene as well as *cis*-stilbene was being formed on decomposition. Careful low-recovery recrystallization always gave a mixture of the *trans*- and *cis*-episulfones **2** and **3**, except where higher temperatures (*ca.* 40°) were used. Warming a mixture of **2** and **3** in methylene chloride for *ca.* 10 min and then adding pentane with cooling gave the *cis* compound **3** in about 95% purity, mp 86–88° dec (lit.[7] mp 85–86° dec). This last method of recrystallization gave a low recovery of the *cis* isomer **3**.

Treatment of 2-Phenylthiirane 1,1-Dioxide (1) with Methoxide Ion in Methanol-O-*d*. To a solution containing 350 mg of sodium metal dissolved in 30 ml of methanol-O-*d* (0.5 *M* in methoxide ion) was added 100 mg (0.6 mmole) of **1**. This mixture was stirred at 0° for 5 hr, quenched in water, and thoroughly extracted with ether. Removal of the ether *in vacuo* gave 55 mg (88%) of styrene as analyzed by vpc (5 ft, 0.25 in. o.d. column, 12% SE-30 gum rubber on 60–80 mesh Chromosorb W at 70°). A pmr spectrum of this styrene sample did not indicate the presence of any deuterium. Mass spectral analysis revealed the presence of *ca.* 5% styrene-d_1 and less than 0.5% styrene-d_2. Repetition of this experiment at room temperature gave the same result.

Treatment of *cis*-2,3-Diphenylthiirane 1,1-Dioxide (3) with Sodium Methoxide in Methanol-O-*d*. About 200–250 mg of a mixture of **2** (*ca.* 55%) and **3** (*ca.* 45%) was dissolved in 3 ml of methylene chloride. The solution was held at reflux, adding additional methylene chloride as needed to keep the volume at about 2 ml, for about 10 min. The solution was cooled to -78° (Dry Ice–acetone) while *ca.* 5 ml of pentane was added slowly. The resulting mixture was filtered quickly, and the precipitate of **3** was washed with cold pentane. The solid, except for about 5 mg which was saved for later analysis, was transferred quickly to a flask containing 350 mg of sodium metal dissolved in 30 ml of methanol-O-*d*. This mixture was held at 0° with stirring for 3 hr. It was then quenched with water and the resulting mixture was extracted with ether. The resulting product was shown by vpc analysis to be *trans*-stilbene (<3% *cis*-stilbene).[34] A pmr spectrum of the resulting solid indicated little or no vinyl hydrogens present. Mass spectra analysis showed d_0, 0%; d_1, 5.5%; d_2, 94.5%.

The 5-mg sample of **3** set aside for analysis was decomposed thermally in boiling methanol. Analysis by vpc showed the resulting mixture to be 95% *cis*-stilbene and 5% *trans*-stilbene.

Treatment of a Mixture of 2 and 3 with Sodium Methoxide in Methanol-O-*d*. The mixture of **2** and **3** was recrystallized from methylene chloride–pentane at -78°. A small portion of the sample was decomposed thermally and shown by vpc analysis to be 60% *trans*-stilbene and 40% *cis*-stilbene. An ultraviolet spectrum of the initial solid showed it to be contaminated with *ca.* 10% *trans*-stilbene.[35] The remainder of the solid was treated with 0.5 *M* sodium methoxide in methanol-O-*d* at 0° as before and the resulting *trans*-stilbene isolated as before. Duplicate mass spectral analysis showed d_0, 46.5%, 46.1%; d_1, 23.2%, 23.5%; d_2, 30.3%, 30.4%.

Photolysis of 2-Phenylthiirane 1,1-Dioxide (1). An immersion lamp was placed in a vessel containing 100 mg of **1** (0.60 mmole) dissolved in 200 ml of anhydrous ether, and the whole apparatus was submerged in a dewar flask cooled with Dry Ice–acetone. The mixture was irradiated for 10 hr, and the ether was then removed *in vacuo* at *ca.* -10°. An infrared spectrum (CCl_4) of the resulting liquid showed the absence of sulfone bands (7.5 and 8.7 μ). Vpc analysis gave 50 mg (80%) of styrene.

A reference blank was run in the above manner except that the ultraviolet light was omitted. The results showed that **I** could be recovered in about 80% yield, the remaining 20% being styrene.

Photolysis of 2 and 3. In the same manner as above, 150 mg of a mixture of 55% **2** and 45% **3** gave 60% *cis*-stilbene and 40% *trans*-stilbene in 90% over-all conversion. A blank run without ultraviolet light led to less than 20% loss of the episulfones.

Kinetic Procedures. The rates were followed by the appearance of styrene at 247 mμ in the case of **1**, *trans*-stilbene at 320 mμ in the case of **2**, *cis*-stilbene at 280 mμ in the case of **3**, and the formation of both *cis*- and *trans*-stilbenes at 280 mμ when a mixture of **2** and **3** was studied simultaneously. The instruments used were Beckman DU and Cary 14 and 15 spectrophotometers. The compartments of the instruments were thermostated, and the temperature was measured with a thermometer which was graduated in 0.10° units. Sample solutions of the episulfones were prepared by dissolving an estimated quantity (*ca.* 2 mg) in 1 ml of solvent and adding 10–25 μl of this stock solution to 3.00 ml of the desired solution in a cuvette. The solutions in the cuvettes were either pure solvents (for the thermal decompositions) or standardized base solutions both of which were thermostated for at least 2 hr in the instrument compartment before the sample solution was added. The sample was added by applying the 10–25 μl of sample solution to a stirring rod with a flattened bottom and dipping the rod into the cuvette several times. In the case of **2** where the thermal decomposition was quite fast in the protic solvents, the solvent for the stock solution was usually chloroform. The stock solution was stored at liquid nitrogen temperatures until just prior to its use, when it would be warmed to *ca.* 10° and 10–25 μl added to the desired solution in the cuvette.

The rate constants for the thermal decomposition of **1** were obtained by plotting $-\log (A_\infty - A_t)$ *vs.* time and multiplying the slopes by 2.303. The rate constants for the thermal decomposition of **2** at 0 and 10° could be followed in the same manner, since the rate of decomposition of **3** at these temperatures was so slow that formation of *cis*-stilbene did not interfere with the determination of the infinity reading. At 25°, and higher, this same procedure was used with **3** but, since an accurate infinity reading could not be obtained in the case of **2** at these temperatures due to the significant formation of *cis*-stilbene, the Guggenheim method[36] was applied. In the base-catalyzed reactions the experimental rate constants were pseudo-first-order since the base concentrations were 10^2–10^3 times larger than the sample concentrations. The second-order

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(32) P. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

(33) *cis*-Stilbene was not isomerized under these conditions.

(34) Previous investigators[7] reported the formation of 39% *cis*- and 61% *trans*-stilbene from a decomposition carried out in "0.2 *N* alkali at 50°." Experimental details were not given. In numerous experiments in this laboratory we have obtained less than 3% *cis*-stilbene in reactions carried out in homogeneous medium with alkali of this strength.

(35) This figure was arrived at by comparison of the ultraviolet absorption curve in chloroform for the solid initially compared with the spectrum after the episulfones had been completely decomposed thermally.

(36) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 49.

rate constants were obtained by dividing the pseudo-first-order rate constants by the base concentrations.

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The Ramberg-Backlund Reaction of Benzyl α-Halobenzyl and Halomethyl Sulfones

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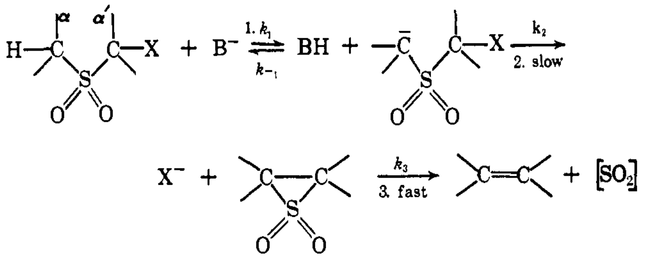
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received May 19, 1967*

Abstract: Kinetic and deuterium exchange studies of the reactions of $PhCH_2SO_2CHXPh$ (X = Cl, Br, I) with methoxide ion in methanol have supported the stepwise mechanism suggested previously and have demonstrated that reversible carbanion formation occurs in the first step. The observation of an unusually large leaving group effect (Br/Cl rate ratio = 620 at 0°) forms part of the basis for the conclusion regarding reversible carbanion formation. Arguments are presented to show that halide loss occurs by an intramolecular displacement initiated by the α'-carbanion. The rate of formation of *trans*-stilbene from these α-halo sulfones is slow compared to its rate of formation from the episulfone intermediate, 2,3-diphenylthiirane 1,1-dioxide. The mechanism thus requires that the rate of halide ion release and product formation be equal. This prediction was verified. Rate constants (estimated or observed) have been assigned to each of the steps in the Ramberg-Bäcklund reaction. Evidence against a concerted 1,3 elimination is presented.

In an earlier paper[2] we suggested that the reaction of α-halo sulfones with strong bases to give alkenes (Ramberg-Bäcklund reaction[3]) occurred in the following steps.[4]



Since that time the following additional evidence has been accumulated in support of this mechanism. (1) Deuterium exchange experiments have shown that step 1 is reversible for alkyl α-halo sulfones.[5] (2) A dipolar ion intermediate has been ruled out for step 2.[5] (3) A conformational requirement has been indicated for step 2.[6] (4) 2,3-Diphenylthiirene 1,1-dioxide ("2,3-diphenylvinylene sulfone") has been isolated from a reaction of α-bromobenzyl sulfone under conditions somewhat similar to those used in the Ramberg-Bäcklund reaction.[7] (5) The formation of alkynes, alkenes, and vinyl halides as products from the reaction of dihaloalkyl sulfones has been observed and explained in terms of thiirene 1,1-dioxide intermediates.[8,9] The purpose of the present investigation was to learn further mechanistic details concerning the reaction. In particular, we were interested: (1) in obtaining estimates of the rate constants k_1, k_{-1}, k_2, and k_3, and (2) in discovering which of these steps is rate determining. The studies of the rates of deuterium exchange in α-methylbenzyl sulfones,[10] and of the rates of decomposition of equisulfones[11] evolved as part of this investigation.

Evidence for Reversible Carbanion Formation. Reaction of benzyl α-bromobenzyl sulfone with sodium methoxide in methanol-O-*d* was found to give *trans*-stilbene-1,2-d_2 (>95% deuterated) in agreement with the results obtained in similar experiments with alkyl α-haloalkyl sulfones,[5] and with the results of Paquette with benzyl α-chlorobenzyl sulfones.[6] However, this experiment alone does not establish the reversibility of step 1, since exchange could have occurred with the episulfone intermediate. Indeed, this turned out to be the case.[11] An experiment was performed, therefore, in which the starting material was recovered from this reaction after one half-life. The recovered benzyl

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[1] National Institutes of Health Predoctoral Fellow, 1964–1966.

[2] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).

[3] (a) L. Ramberg and B. Bäcklund, *Arkiv Kemi, Mineral. Geol.*, **13A**, No. 27 (1940); (b) B. Bäcklund, Doctoral Dissertation, University of Uppsala, Uppsala, Sweden, 1945.

[4] The mechanism of the reaction was not discussed in the original publication,[3a] but Bäcklund in his dissertation,[3b] which was kindly sent to us by Professor Arne Fredga after the appearance of our paper, suggested the formation of a thiirane 1,1-dioxide (episulfone) intermediate.

[5] N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966).

[6] L. A. Paquette, *ibid.*, **86**, 4085 (1964).

[7] L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965).

[8] F. Scholnick, Ph.D. Dissertation, University of Pennsylvania, 1955; *Dissertation Abstr.*, **15**, 708 (1955).

[9] L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).

[10] F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Am. Chem. Soc.*, 90, 426 (1968).

[11] F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *ibid.*, 90, 429 (1968).