2-methyl-2-propanol in the presence of potassium *tert*-butoxide. Dimethyl sulfoxide was dehydrated by passage over molecular sieves, followed by distillation in the presence of dimethylsulfinylsodium. Stock solutions of sodium methoxide (about 5.5 *M*) in methanol were prepared by dipping freshly cut pieces of sodium into methanol for about 30 sec, this operation being repeated twice, each time in a new solvent, and then transferring them to the purified solvent until dissolution was completed. The slightly cloudy solution was filtered through sintered glass filters and titrated with aqueous standardized HCl. All manipulations and transfers were done in a dry nitrogen atmosphere.

Stereochemical identification of the product, *trans*-3,3′-dinitroazoxybenzene (mp 149.5°, molar absorptivity (M^{-1} cm^{-1}) at 316 nm 15,800, at 256 nm 23,200 in methanol solution), was made on the basis of dipole moment (4.36 ±0.02 D in benzene solution at 25°) comparison with the literature values[38] of *cis*-(4.7 D) and *trans*-azoxybenzene (1.7 D) and by means of vector composition analysis.

Kinetic Procedure. Solutions ((1.24–2.4) × 10^{-4} *M*) of 1,3-dinitrobenzene in anhydrous methanol were prepared and mixed (1:1 volume ratio) with 0.28–4.6 *M* CH_3ONa in CH_3OH, obtained by appropriately diluting the stock solution of alkoxide. Aliquots of the reaction solution were placed in nitrogen-filled tubes equipped with pressure plugs. The reaction was initiated by immersing the tubes in a constant temperature bath and was stopped, when desired, by quenching. Reaction tubes were removed at regular intervals for spectrophotometric analysis. "Infinity time" absorption was measured experimentally. Kinetic runs at 40° and those in the highly concentrated methoxide solutions (>2.3 *M*) were followed directly in the thermostated spectrophotometric cell. Concentration of substrate was (5.0–6.2) × 10^{-5} *M* for analysis in the ultraviolet region and was increased by a factor of 10 when operating in the visible range of the spectrum. Pseudo-first-order equations were employed to obtain kinetic coefficients. The base concentrations shown in Table I are corrected for solution expansion by multiplying concentrations at room temperature by the ratio of the density of methanol[39] at the reaction temperature to that at room temperature.

The estimated errors determined by straightforward methods are reported as standard deviations for rate coefficients and probable errors for kinetic parameters.

Electron Spin Resonance Measurements. The instrument used to record esr spectra was a Varian[40] V-4502-11X band spectrometer with a 100-KHz magnetic field modulation. Electrochemical generation of 1,3-dinitrobenzene radical anion was effected in a 0.02 *M* solution of 1,3-dinitrobenzene in dimethyl sulfoxide, containing 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte, with a mercury pool cathode and a platinum anode; a potential of −1.8 V was applied between the working and the counter electrode (also used as a reference) for 15 min. The reduction potential was determined by polarographic experiments using an Amel[41] Model 463 polarograph. Preliminary, slow potential sweeps indicated that this potential was well into the limiting current region.

Acknowledgments. Financial support by the Italian Consiglio Nazionale delle Ricerche is gratefully acknowledged. We wish to thank Professor E. G. Janzen for valuable suggestions.

(38) K. E. Calderbank and R. J. W. Le Fevre, *J. Chem. Soc.*, 1949 (1948).

(39) (a) "International Critical Tables," Vol. 3, McGraw-Hill, New York N. Y., 1928, p 27; (b) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Vol. 1, Elsevier, Amsterdam, 1950, p 303.

(40) Varian Associates, Palo Alto, Calif.

(41) Amel, Milano, Italy.

Acid-Catalyzed Ring Opening Reactions of Episulfoxides[1]

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Abstract: The acid-catalyzed ring opening reactions of episulfoxides in various solvents have been studied. The reaction of ethylene episulfoxide (**1**) in methanol in the presence of sulfuric acid produced thiol sulfinate **2a**, while that of **1** in ethyl mercaptan afforded disulfide **5**. The orientational effect of nucleophiles in the ring openings of unsymmetrically substituted episulfoxides, *i.e.*, **7** and **10**, were also investigated in several alcohols, ethyl mercaptan, and mixed solvents. The structural analyses of the products obtained from *cis*- and *trans*-butene episulfoxides (**14** and **15**) in methanol demonstrated that the reactions proceeded stereospecifically with inversion of configuration at the point of attack. These results are discussed in terms of a "push–pull" mechanism.

Ethylene episulfoxide (**1**) was prepared by Hartzell and Paige for the first time in 1966.[2] The ring opening reaction of **1** under acidic conditions was also noted by these authors, while they did not try to examine the structure of the product. Two years later, Manser and Tillett[3] studied the kinetics of acid-catalyzed hydrolysis of **1** and proposed an A-2 mechanism for the reaction by comparing the value of activation entropy with those of other three-membered heterocycles. These studies, however, do not seem to reveal completely the scope of the titled reaction. Our successful preparation and isolation of pure episulfoxides bearing various substituent(s)[4] enabled us to investigate the product composition and mechanistic details of the acid-catalyzed ring openings of episulfoxides.

Results

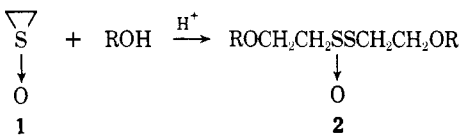
Structure of the Products. Treatment of ethylene episulfoxide (**1**) in methanol in the presence of 1 drop of concentrated sulfuric acid at 0–5° for 2 hr resulted in the formation of β-methoxyethanethiol β-methoxyethanesulfinate (**2a**) in 97% yield. The structural assignment of **2a** was based on its following spectra and elemental analyses.

(1) K. Kondo, A. Negishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 3173 (1969).

(2) G. E. Hartzell and J. N. Paige, *J. Amer. Chem. Soc.*, **88**, 2616 (1966).

(3) G. E. Manser, A. D. Mesure, and J. G. Tillett, *Tetrahedron Lett.*, 3153 (1968).

(4) (a) K. Kondo, A. Negishi, and M. Fukuyama, *ibid.*, 2461 (1969); (b) K. Kondo and A. Negishi, *Tetrahedron*, 27, 4821 (1971).



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A characteristic S–O stretching frequency was observed in the ir spectrum at 1080 cm^{-1}. In the nmr spectrum, two methyls were observed as a broad singlet at τ 6.66 and four different methylenes as complex multiplets at τ 6.3 (4 H) and 6.8 (4 H) suggesting the presence of an asymmetric S–O group. The structure was finally confirmed by comparing the spectra with those of authentic sample prepared independently by the oxidation of bis(β-methoxyethyl)disulfide with perbenzoic acid. Similar reactions of the episulfoxide **1** in other alcohols proceeded smoothly and afforded thiol sulfinates (**2b–d**) bearing the corresponding alkoxy substituents. Yields and characteristic ir absorptions of the products are collected in Table I.

Table I. Thiol Sulfinates from Ethylene Episulfoxide and Alcohols

Compd	R	Yield, %	Ir, cm^{-1} ν_{S-O}	Ir, cm^{-1} ν_{C-O-C}
2a	CH_3	97	1080	1115
2b	C_2H_5	95	1080	1110
2c	i-C_3H_7	91	1080	1135
2d	t-C_4H_9	77	1080	1196

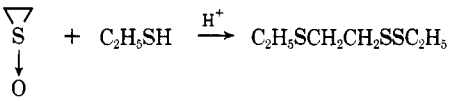
When the reaction medium was changed from alcohol to acetic acid, or when the episulfoxide **1** was treated with dry hydrogen chloride in ether, no more thiol sulfinates could be detected in the product. Instead, a mixture of disulfide and thiol sulfonate (**3** + **4**) was obtained in good yields.

$XCH_2CH_2SSCH_2CH_2X$ (**3**) $\qquad$ $XCH_2CH_2SO_2SCH_2CH_2X$ (**4**)

a, X = AcO; b, X = Cl

Certain thiol sulfinates are known to be thermally unstable and readily disproportionate to a mixture of disulfide and thiol sulfonate.[5] Thus, it can be assumed that this is also the case for the reaction of **1** with acetic acid or hydrogen chloride.

When the episulfoxide **1** was treated with ethyl mercaptan in the presence of a catalytic amount of sulfuric acid, unsymmetric disulfide **5** was obtained in 46% yield.[6] The structure of **5** was determined by its spectra, microanalyses, and reductive transformation to the known compound, *i.e.*, β-ethylthioethyl mercaptan.[7]



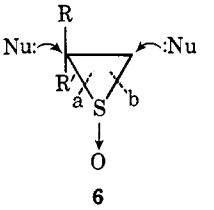
1 5

(5) (a) L. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Amer. Chem. Soc*, **71**, 3565 (1949); (b) P. Allen and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1962); (c) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **73**, 129 (1954)

(6) Yield of the disulfide **5** was rather low because of the partial consumption of episulfoxide **1** for the oxidation of solvent mercaptan to ethyl disulfide; see W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).

(7) W. Reppe and A. Freytag, *Chem. Abstr.*, **35**, 5909 (1941).

Substituted Episulfoxides in Alcohols. When the above-mentioned reaction in methanol is applied to unsymmetrically substituted episulfoxides, the ring openings in two directions are, in principle, possible.



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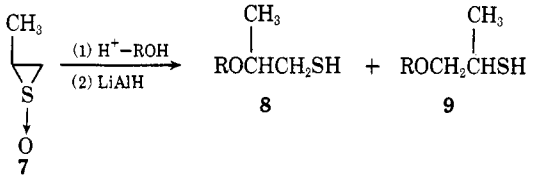
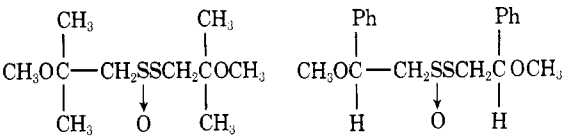
In fact, propylene episulfoxide (**7**) afforded a mixture of thiol sulfinates in total yield of 96%. As the product was expected to contain four possible thiol sulfinates, it was reduced with LiAlH to an isomeric mixture of β-methoxypropyl mercaptans in 77% yield. Vpc analysis of the reduced product indicated the presence of two isomeric mercaptans in the ratio of 3 :1.



7 $\qquad$ **8** $\qquad$ **9**

a, R = Me; b, R = Et; c, R = i-Pr; d, R = $tert$-Bu

Each of the components was isolated by preparative vpc and their structures were determined by the following spectra. The nmr spectrum of the major component showed a characteristic SH absorption at τ 8.67 as a triplet, while that of the minor one a doublet at τ 8.45, both of which easily disappeared by D_2O treatment. More compelling evidence was obtained from mass spectra. The base peak of the major isomer was observed at m/e 59, which could be attributed to the fragment $CH_3{}^+O{=}CHCH_3$ generated by the β-cleavage of the ether linkage. The corresponding fragment in the minor product was observed at m/e 45 as a base peak. From these spectra and microanalyses, the major product was assigned to 2-methoxy-*n*-propyl mercaptan (**8a**) and the minor one to 2-methoxyisopropyl mercaptan (**9a**). In sharp contrast with **7**, treatments of isobutene episulfoxide (**10**) and styrene episulfoxide (**11**) in methanol resulted in the formation of only one isomer of thiol sulfinates, *i.e.*, **12** and **13**, in 79 and 81% yields, respectively.



12 $\qquad$ **13**

The structures of these thiol sulfinates must be those shown above, as both SH of the reduced mercaptans were observed as triplets in the nmr spectra.

As a second step to elucidate the effect of alcohols on the direction of ring openings, propylene episulfoxide (**7**) was treated with various alcohols in the presence of acid catalyst. In each case, a mixture of thiol sulfinates was obtained in fair yields.[8] The prod-

(8) Because of the self-decomposition of propylene episulfoxide, the yield of thiol sulfinates was not so quantitative as in methanol.

ucts were further reduced with LiAlH to afford mixtures of alkoxypropyl mercaptans, **8** and **9**. The structural assignment of each mercaptan was mainly based on its nmr spectrum (Table VI) and their ratios were calculated from the vpc peak areas. The relative ratios of the ring cleavage of unsymmetrically substituted episulfoxides in alcohols under acidic condition are summarized in Table II.

Table II. Relative Ratios of the Ring Cleavages in Alcohols

Episulfoxide				Cleavage at bond a, %	Cleavage at bond b, %
Compd	R_1	R_2	Solvent		
7	CH_3	H	MeOH	75	25
7	CH_3	H	EtOH	72	28
7	CH_3	H	*i*-PrOH	68	32
7	CH_3	H	*t*-BuOH	58	42
10	CH_3	CH_3	MeOH	100	0
11	Ph	H	MeOH	100	0

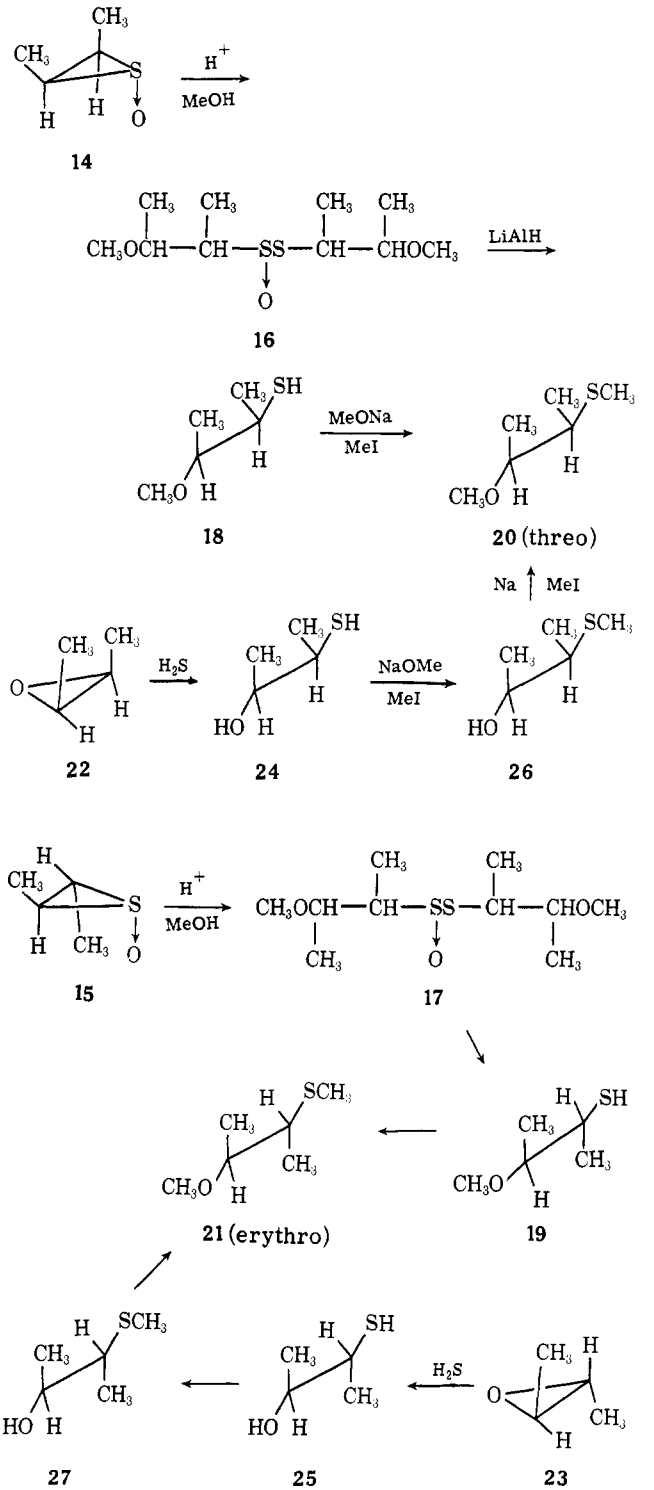
In all cases examined in alcohols, a preferential cleavage at bond a was observed. This means that the nucleophile is introduced to one of the two ring carbon atoms, on which a developing positive charge might be more stabilized than the other by its substituents.

Stereochemistry. In order to obtain more insight into the reaction mechanism, the stereochemical aspect of the ring openings was investigated. For this purpose, two pairs of stereoisomeric episulfoxides, *i.e.*, cis and trans isomers of 2-butene episulfoxide (**14** and **15**) and stilbene episulfoxide (**28** and **29**) were chosen as substrates.

Treatment of *cis*- and *trans*-2-butene episulfoxides with methanol produced the corresponding thiol sulfinates (**16** and **17**) in good yields. As the products were expected to be a mixture of diastereoisomers, the crude thiol sulfinates were reduced with LiAlH to afford 2-methoxy-3-mercaptobutanes. However, we could not discriminate the mercaptans from each other at this stage, as their retention times on vpc and nmr spectra were almost identical. Therefore, the mercaptans were further transformed into sulfides by treatment with methyl iodide. A clear difference was observed between the nmr spectrum of the sulfide derived from *cis*-episulfoxide **14** and that from trans isomer **15**. Furthermore, the spectra indicated that the sulfides were not contaminated with each other. Accordingly, the ring openings in alcohols are concluded to be a stereospecific process. The configuration of each sulfide was firmly established by comparing its spectra with those of authentic sample prepared from configurationally pure 2-butene oxide by known procedures,[9] as shown in Scheme I. Thus, *cis*- and *trans*-2-butene episulfoxides (**14** and **15**) afforded *threo*- and *erythro*-2-methoxy-3-methylthiobutanes (**20** and **21**), respectively, as the only detectable products. These findings indicate that the nucleophile is introduced stereospecifically with inversion of configuration at the point of attack.

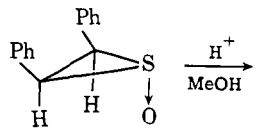
Similar ring openings with *cis*- and *trans*-stilbene episulfoxides (**28** and **29**) afforded the corresponding thiol sulfinates (**30** and **31**) in 46 and 63% yields, respectively. The products were treated with thiophenol in the presence of sulfuric acid to give unsymmetric disulfides (**32** and **33**). The nmr spectra of these disulfides also demonstrated that they were different from and not contaminated with each other. Although we have no definite evidence for the configuration of **32** and **33**, the observed stereospecificity may mean that the reaction of stilbene episulfoxides also proceeds with inversion of configuration at the ring carbon on which the nucleophile is introduced.

Scheme I



Substituted Episulfoxides in Ethyl Mercaptan. To learn about the effect of nucleophiles on the direction of ring openings of unsymmetrically substituted epi-

(9) C. C. Price and P. F. Kirk, *J. Amer. Chem. Soc.*, 75, 2396 (1953).



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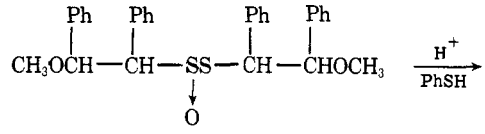

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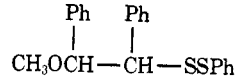

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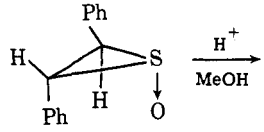

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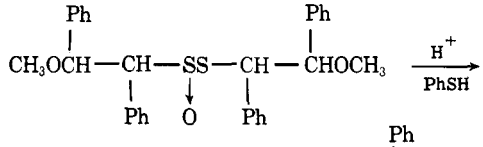

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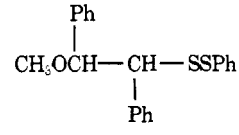

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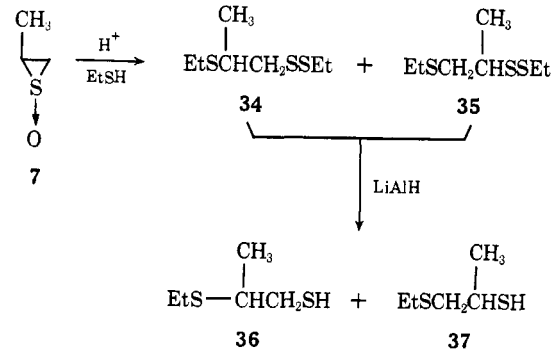
sulfoxides, the reaction in ethyl mercaptan was extended to propylene episulfoxide (**7**) and isobutene episulfoxide (**10**). When **7** was treated in ethyl mercaptan in the presence of acid catalyst at 0–5°, a mixture of unsymmetric disulfides was obtained in 46% yield. As the nmr spectrum of the product was too complex to be analyzed, it was reduced with LiAlH to an isomeric mixture of ethylthiopropyl mercaptans in 74% total yield. Although the attempted separation of structural isomers by vpc on several different columns could not be achieved, the nmr spectrum of the reduced product clearly indicated the presence of two mercaptans; one SH proton appeared as doublet at τ 8.04 and the other as triplet at τ 8.33, both of which disappeared by treatment with D_2O. Accordingly, the former could be assigned to mercaptan **37** and the latter to **36**.



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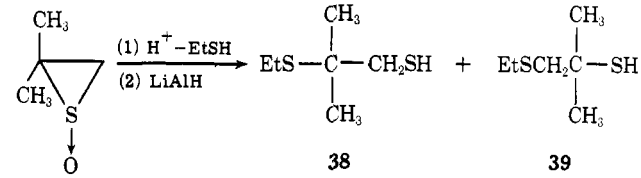
36 37

A solvent effect on the orientational ratios was also investigated in this particular case. Thus, the ring openings were performed in mixed solvents consisting of acetonitrile and ethyl mercaptan in varying ratios. A remarkable increase of the relative ratio of isomer **34** was observed, as the polarity of the medium was elevated by increasing the fraction of acetonitrile.

Similar reaction with isobutene episulfoxide (**10**) also afforded a mixture of disulfides in 53% yield based on the starting episulfide. After reduction of the disulfide mixture with LiAlH, each of the components was isolated by preparative vpc and their structures were assigned by nmr; SH in **38** at τ 8.55 as a triplet and SH in **39** at τ 7.98 as a singlet.



10 38 39

The ratios of **36**:**37** and **38**:**39** under several conditions were calculated from either nmr integrations or vpc peak areas and collected in Table III. A preferential cleavage of bond b was observed in these cases, which is in sharp contrast with the cases in alcohols. The result indicates that the thiol is favorably introduced on a ring carbon bearing the lesser number of substituents. Therefore, the steric hindrance of the substituent(s) seems to play an important role in determining the orientation of ethyl mercaptan.

Table III. Relative Ratios of the Ring Cleavages in Ethyl Mercaptan

Compd	Episulfoxide R_1	Episulfoxide R_2	Solvent	Cleavage at bond a	Cleavage at bond b
7	CH_3	H	EtSH	20	80[a]
7	CH_3	H	EtSH–MeCN (1:9)	31	69[a]
7	CH_3	H	EtSH–MeCN (1:99)	38	62[a]
10	CH_3	CH_3	EtSH	35	65[b]

[a] The ratio was determined from the integrations of SH protons in nmr spectra. [b] The ratio was determined from vpc peak areas.

Discussion

The formation of thiol sulfinate by dehydrative coupling of sulfenic acids is a well-documented reaction.[10] We can, therefore, formulate the acid-catalyzed ring opening reactions of episulfoxide **1** as shown in Scheme II. At the first stage of the reaction, nucleophiles in the system might be introduced to the protonated episulfoxide to produce β-substituted sulfenic acid **40**. In general, alkyl sulfenic acids are too unstable to be isolated and easily dimerize to thiol sulfinates, when the system does not contain a suitable partner to be reacted. In the presence of mercaptan, sulfenic acids would be effectively trapped by the mercaptan to produce disulfides.[11] Accordingly, the sulfenic acid **40** can be assumed as a common intermediate of the reaction.

(10) J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967).

(11) A. Schöberl and H. Gräfje, *Justus Liebigs Ann. Chem.*, **617**, 71 (1958).

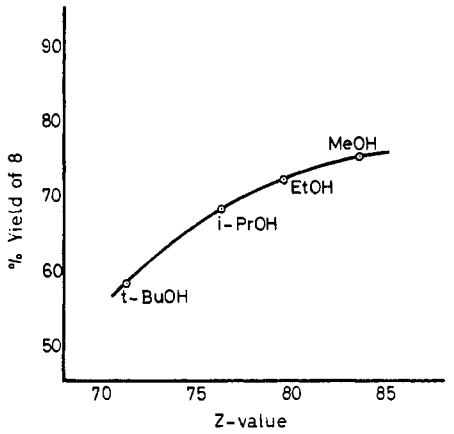
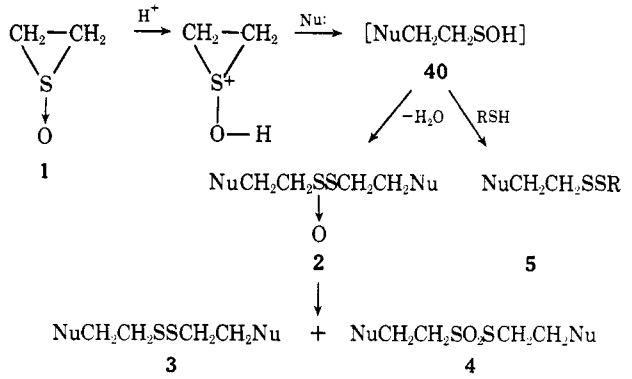


Figure 1. Correlation of the relative yields of **8** with Z values of solvent alcohols.

Scheme II



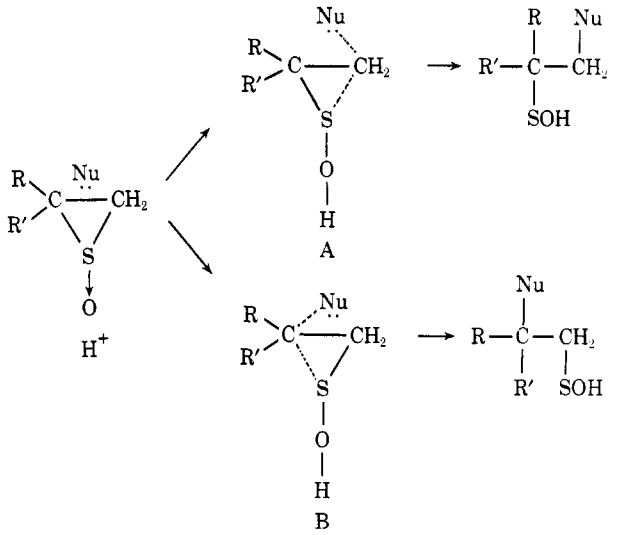
There has been much dispute on the mechanism of acid-catalyzed ring opening reactions of three-membered heterocyclic compounds, especially on that of epoxides.[12] For example, Long and coworkers[13] favored an A-1 mechanism for the reaction of epoxides based on the reaction rates and substituent effects. On the other hand, with few exceptions, most of the reaction occurs with inversion of configuration at the point of attack, and this seems to support an A-2 mechanism.[14] So far we have no clear compelling evidence on either of the mechanisms. This contradicting situation may arise from inadequate application of the explanation deduced from studies on the reaction mechanisms of open-chain compounds.

The observed stereospecificity and the mode of ring cleavages which we reported here can most properly be interpreted in terms of a push–pull mechanism.[15] The concept has already been successfully applied to explaining the reactivities of epoxides by Vander Werf and coworkers.[16] According to this concept, the ring opening will be facilitated by simultaneous action of push (attack of nucleophile) and pull (C–S bond release by protonation), as shown in Scheme III.

In reactions with unsymmetrically substituted episulfoxides, the following four factors are considered

(12) E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 106.
(13) J. G. Pritchard and F. A. Long, *J. Amer. Chem. Soc.*, **78**, 2667 (1956).
(14) S. Winstein and R. B. Henderson, *ibid.*, **65**, 2196 (1943).
(15) L. A. Paquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968, p 26.
(16) A. Feldstein and C. A. Vander Werf, *J. Amer. Chem. Soc.*, **76**, 1626 (1954).

Scheme III



to play a key role in determining the orientational ratios: (1) the nucleophilicity of nucleophile, (2) substituent(s) on episulfoxide, (3) polarity of the reaction medium, and (4) the bulkiness of nucleophile. In other words, factors 1 and 4 will have substantial influence on push component and factors 2 and 3 on pull. Therefore, as the nucleophilicity or the bulkiness of the substrate becomes higher, the steric effect may favor the attack of nucleophile onto the less hindered ring carbon (transition state A). On the other hand, electron-releasing substituent(s) on the ring or polar media may stabilize the developing positive charge on ring carbon and, hence, favor the attack of nucleophile to the more substituted carbon (transition state B). A remarkable difference between the ratios observed in alcohols and those in mercaptan will be ascribed to the difference of their nucleophilicities. In both solvents, the ratios of bond a cleavage of isobutene episulfoxide exceeded those of propylene episulfoxide, which could be ascribed to factor 2. The effect of solvent polarity is clear from the results observed in the reaction of propylene episulfoxide in mixed solvents.[17] If the polarity of the medium is the only one factor in determining the ratios of ring cleavages in various alcohols, the relative yields of the product **8** resulting from bond a cleavage of propylene episulfoxide would be proportionally decreased with the polarity change of solvents from methanol to *tert*-butyl alcohol. We tried to correlate the yields of **8** with several solvent scales, but in no cases could find linear correlation. Typical example of the correlation with Z values is given in Figure 1. We feel that the deviation from linearity especially in the case of *tert*-butyl alcohol can be ascribed to the steric hindrance of the reacting bulky nucleophile.

From the stereochemical point of view, the ring openings of three-membered heterocyclic compounds generally occur stereospecifically with inversion of configuration at the ring carbon on which the nucleophile is introduced. However, stilbene derivatives are often

(17) The ring openings of propylene episulfoxide in mixed solvents consisting of methanol and acetonitrile were also examined. In these cases, however, the polarity of the medium was found to have little effect on the relative ratios of **8** and **9**. These mysterious phenomena could be ascribed to preferential microscopic solvation of the highly polar methanol to the substrate at the transition state.

Table IV. Elemental Analyses of Thiol Sulfinates from Ethylene Episulfoxide and Alcohols

Compd	R	Formula	Calcd, %			Found, %		
			C	H	S	C	H	S
2a	Me	$C_6H_{14}O_3S_2$	36.40	7.12	32.34	35.88	6.90	32.18
2b	Et	$C_8H_{18}O_3S_2$	42.45	8.02	28.33	42.36	8.11	28.21
2c	*i*-Pr	$C_{10}H_{22}O_3S_2$	47.21	8.72	25.21	47.24	8.82	25.46
2d	*t*-Bu	$C_{12}H_{26}O_3S_2$	51.03	9.28	22.70	50.80	9.53	22.58

quoted as exceptional cases. For example, either *cis*- or *trans*-stilbeneimine reacts with hydrochloric acid to afford a mixture of two diastereoisomers.[18] The additions of hydrochloric acid to *cis*- and *trans*-stilbene oxides[19] are also known to occur without stereospecificity. These phenomena suggest that in the reactions of stilbene derivatives resonance stabilization by phenyl substituent will assist the generation of fully developed carbonium ions under acidic condition. Curiously, such is not the case with stilbene episulfoxides, though they are treated with acid in a highly polar medium. The peculiarity might reflect a characteristic nature of sulfur participation onto the carbonium ion, but at the present stage we have no convincing explanation for the phenomena.

Experimental Section

Elemental analyses were performed in the microanalytical laboratory of our research center under the direction of Mr. M. Yamamoto. Melting points and boiling points were uncorrected. Infrared spectra were taken on a Hitachi-Perkin-Elmer Model 337 Infracord or a Hitachi EPI-G3 Infracord as neat liquids or powdered solids in potassium bromide disks. Nuclear magnetic resonance spectra were obtained on a Varian HA-100 or a Hitachi R20-B spectrometer by Mr. K. Sato; chemical shifts are expressed in τ units relative to tetramethylsilane as the internal standard. Mass spectra were determined with a Hitachi RMU-6E spectrometer at 70 eV by S. Mohara. Analytical gas chromatography (vpc) was carried out on a Hitachi-Perkin-Elmer F-6 instrument equipped with a flame ionization detector using a 2 m × 8 mm column packed with 10% of dioctyl phthalate on Chromosorb W. Preparative gas chromatography was performed with an Aerograph A-700 instrument using a 10 ft × 3/8 in. column packed with 20% Carbowax 20M on Chromosorb W. Thin layer chromatography on silica gel plates was employed routinely to follow the course of the reaction and to check the purity of products.

Reaction of Ethylene Episulfoxide (1) in Methanol. Sulfuric acid (1 drop) was added to a solution of **1** (0.76 g, 0.01 mol) in dry methanol (20 ml) under ice-water cooling. The resulting mixture was stirred for 2 hr and diluted with 100 ml of water. Chloroform extracts of this solution were dried with anhydrous magnesium sulfate and freed of solvent. The residual oil was purified by column chromatography on silica. Elution with *n*-hexane–chloroform (3:1) afforded **2a** (0.96 g, 97% yield) as a colorless oil: ir (neat) 1115 (C–O–C), 1080 cm^{-1} (S–O); nmr (CCl_4) τ 6.3 (4 H, m), 6.66 (6 H, s), 6.8 (4 H, m). The data of elemental analyses are given in Table IV,

Alternate Synthesis of β-Methoxyethanethiol β-Methoxyethanesulfinate (2a). β-Methoxyethyl disulfide was prepared according to the reported method[20] from β-methoxyethyl mercaptan in 57% yield: bp 67° (0.18 mm). To a solution of the disulfide (3.65 g, 0.02 mol) in dichloromethane (100 ml) cooled in an ice-water bath was added perbenzoic acid in the same solvent (0.5 *M*, 40 ml). After completion of the addition of peracid, the reaction mixture was allowed to stand at room temperature for 30 min. The solution was washed four times each with 50 ml of 5% aqueous sodium bicarbonate solution and then with water. The organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residual liquid was submitted to column chromatography on silica using *n*-hexane–chloroform (3:1) as eluent. β-Methoxyethanethiol β-methoxyethanesulfinate (**2a**, 3.13 g, 80% yield) was obtained as a colorless oil.

General Procedure for the Reaction of the Episulfoxide 1 in Alcohols. To an ice-water cooled solution of **1** (1.24 g, 0.016 mol) in dry alcohol (50 ml) was added 1 or 2 drops of sulfuric acid. The solution was stirred at room temperature at least for 3 hr. The reaction mixture was diluted with 100 ml of water and extracted with 300 ml of chloroform. The extract was dried and freed of solvent. The residual liquid was purified by column chromatography on silica using ethyl acetate as eluent. The corresponding thiol sulfinates were isolated as colorless viscous liquids.

Reaction of the Episulfoxide 1 in Acetic Acid. A solution of **1** (0.76 g, 0.01 mol) in acetic acid (20 ml) was added dropwise to a solution of sulfuric acid (0.1 ml) in acetic acid (20 ml). The reaction mixture was stirred at room temperature for 1 day. The mixture was concentrated to one-third volume, diluted with chloroform, washed with water, dried over magnesium sulfate, and freed of solvent. The residual oil was submitted to column chromatography on silica using a mixed solvent of *n*-hexane and benzene (2:1) as eluent. The faster component furnished the disulfide **3a** (0.51 g, 42% yield) as a colorless liquid: ir (neat) 1700, 1380, 1240, 1065, 1030 cm^{-1}; nmr (CCl_4) τ 7.98 (s, 6 H), 7.14 (t, 4 H), 5.78 (t, 4 H), J_{gem} = 6 Hz; mass spectrum (*m/e*) 238 (M^+), 178, 87, 43.

The slower component afforded the thiol sulfonate **3b** (0.54 g, 40% yield) as a colorless liquid: ir (neat) 1750, 1380, 1340, 1230, 1125, 1065 cm^{-1}; nmr (CCl_4) τ 7.94 (d, 6 H), 6.67 (t, 2 H), 6.40 (t, 2 H), 5.72 (t, 2 H), 5.56 (t, 2 H).

Reaction of the Episulfoxide 1 with Hydrogen Chloride. Anhydrous hydrogen chloride was bubbled through dry ether (20 ml) for 30 min under ice-water cooling. To this solution was added a solution of **1** (0.76 g) in dry ether (20 ml) and the mixture was left to stand overnight. The mixture was diluted with water, extracted with ether, dried, and freed of solvent. The residual oil was submitted to column chromatography on silica using *n*-hexane–chloroform (4:1) as eluent.

The faster eluate furnished the disulfide **3b** (0.38 g, 41% yield) as a colorless liquid. The structure of **3b** was identified by comparing the spectra with those of authentic sample produced by the reaction of ethylene sulfide with copper(II) chloride.[21]

The slower eluate afforded the thiol sulfonate **4b** (0.42 g, 38% yield) as a colorless oil. The structure of **4b** was determined by comparing the spectra with those of authentic sample obtained by the reaction of ethylene episulfoxide (**1**) with copper(II) chloride in benzene.[22]

Reaction of the Episulfoxide 1 in Ethyl Mercaptan. To a solution of **1** (0.80 g, 0.01 mol) in ethyl mercaptan (10 ml) was added 2 drops of sulfuric acid under stirring and cooling with ice water. The mixture was stirred overnight at room temperature. After dilution of the mixture with chloroform, the solution was washed with water, dried, and freed of solvent. The residual liquid was purified by column chromatography on silica using benzene as eluent. Evaporation of the solvent at reduced pressure gave the disulfide **5** (0.89 g, 46.5% yield) as a colorless liquid: bp 87° (1 mm); ir (neat) 2950, 1450, 1250 cm^{-1}; nmr (CCl_4) τ 8.74 (t, 3 H), 8.66 (t, 3 H), 7.49 (q, 2 H), 7.34 (q, 2 H), 7.23 (s, 4 H); mass spectrum (*m/e*) 182 (M^+), 89 (base).

Anal. Calcd for $C_6H_{14}S_3$: C, 39.52; H, 7.74; S, 52.75. Found: C, 39.66; H, 7.68; S, 52.59.

Reaction of Propylene Episulfoxide (7) in Methanol. The procedure was the same as that of **1**. The work-up of the reaction mixture afforded the thiol sulfinates (96% yield) as a colorless oil: ir (neat) 2975, 2930, 1460, 1380, 1135, 1090, 1020 cm^{-1}.

Anal. Calcd for $C_8H_{18}O_3S_2$: C, 42.45; H, 8.02; S, 28.33. Found: C, 42.36; H, 7.92; S, 28.44.

(18) A. Weissberger and H. Bach, *Chem. Ber.*, **65**, 631 (1932).
(19) G. Berti, F. Bottari, P. L. Ferrarini, and B. Macchia, *J. Org. Chem.*, **30**, 4091 (1965).
(20) L. D. Small, J. H. Baily, and C. J. Cavallito, *J. Amer. Chem. Soc.*, **69**, 1710 (1947).
(21) K. Kondo and A. Negishi, to be submitted for publication.
(22) K. Kondo, A. Negishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 2743 (1969).

Table V. Thiol Sulfinates from Propylene Episulfoxide (7) and Alcohols

Alcohol	Yield, %	Ir, cm⁻¹ C–O–C	Ir, cm⁻¹ S–O	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
EtOH	65	1125	1080	47.21	8.72	25.21	47.44	8.94	25.06
i-PrOH	58	1130	1080	51.03	9.28	22.70	51.06	9.33	23.16
t-BuOH	53	1200	1080	54.15	9.74	20.65	53.68	9.47	22.81

Reduction of the Thiol Sulfinates with LiAlH. A solution of the above-mentioned thiol sulfinates (2.18 g, 0.096 mol) in dry ether (30 ml) was added gradually to a suspension of LiAlH (0.547 g, 0.015 mol) in dry ether (30 ml) with stirring at room temperature. After the addition was over, the solution was further refluxed for 1 hr. The reaction mixture was cooled with ice water and decomposed with 15% aqueous sulfuric acid. The ethereal layer was separated from aqueous layer and the latter was repeatedly extracted with ether. The extracts were combined, washed, dried, and evaporated under reduced pressure. The residual oil (1.63 g, 77% yield) was found to consist of two isomers of the mercaptans in the ratio of **8**:**9** = 75:25 by vpc analysis.

8 ($CH_3OCH(CH_3)CH_2SH$): nmr (CCl_4) τ 8.83 (d, 3 H), 8.67 (t, 1 H), 7.53 (m, 2 H), 6.73 (s, 3 H), 6.73 (m, 1 H); mass spectrum (*m/e*) 106(M^+), 74, 59 (base). According to the method of Bost, *et al.*,[23] the mercaptan **8** was converted to solid sulfide by treatment with 2,4-dinitrochlorobenzene. Recrystallization of the crude product from ethanol gave 2-methoxypropyl 2,4-dinitrophenyl sulfide; mp 66.5–67°.

Anal. Calcd for $C_{10}H_{12}N_2O_5S$: C, 44.11; H, 4.44; N, 10.29; S, 11.78. Found: C, 43.92; H, 4.46; N, 10.20; S, 11.80.

9 ($CH_3OCH_2CH(CH_3)SH$): nmr (CCl_4) τ 8.73 (d, 3 H), 8.45 (d, 1 H), 7.3 (m, 1 H), 6.76 (d, 2 H), 6.70 (s, 3 H); mass spectrum (*m/e*) 106 (M^+), 74, 60, and 45 (base). The mercaptan **9** was also converted to 2,4-dinitrophenyl derivative. Recrystallization of the crude product from ethanol afforded 2-methoxyisopropyl 2,4-dinitrophenyl sulfide as pale yellow crystals: mp 76.5–77°.

Anal. Calcd for $C_{10}H_{12}N_2O_5S$: C, 44.11; H, 4.44; N, 10.29; S, 11.78. Found: C, 44.04; H, 4.52; N, 10.40; S, 11.79.

Reaction of Isobutene Episulfoxide (10) in Methanol. As the episulfoxide **10** was extremely unstable at room temperature, it was prepared below −30° by the oxidation of 2.2 g (0.025 mol) of isobutene sulfide with equimolar perbenzoic acid in dichloromethane according to the reported method.[4] The solvent was evaporatively distilled off under reduced pressure at −20° and the residual episulfoxide was dissolved in anhydrous methanol at −10°, followed by addition of 1 drop of sulfuric acid to the solution. After the solution was gradually warmed up to room temperature over a 5-hr period, it was condensed to one-fourth of the original volume by evaporation of the solvent under reduced pressure. The resulting mixture was diluted with chloroform and washed with water. The organic layer was dried and freed of solvent. Column chromatography on silica using chloroform as eluent furnished the pure thiol sulfinate **12** (2.54 g, 79% yield) as a colorless liquid: ir (neat) 2950 (–CH_2–), 1115 (C–O–C), 1075 cm^{-1} (S–O); nmr (CCl_4) 6.8–6.9 (m, 10 H), 8.65–8.76 (m, 12 H).

Anal. Calcd for $C_{10}H_{22}O_3S_2$: C, 47.21; H, 8.72; S, 25.21. Found: C, 47.15; H, 8.68; S, 25.43.

The thiol sulfinate **12** was reduced with LiAlH to afford the corresponding mercaptan as follows. A solution of **12** (2.54 g, 0.01 mol) in dry ether (30 ml) was added dropwise to a suspension of LiAlH(0.54 g, 0.015 mol) in dry ether (30 ml) at 0–5°. After the addition was complete, the mixture was refluxed for 1 hr and then treated with 15% sulfuric acid at 0–5°. Usual work-up of the reaction mixture afforded 2-methoxyisobutyl mercaptan (1.44 g, 60% yield) as a colorless liquid: nmr (CCl_4) τ 6.89 (s, 3 H), 7.52 (d, 2 H), 8.75 (t, 1 H), 8.80 (s, 6 H).

The obtained mercaptan was converted to solid sulfide according to the Bost's method[23] using 2,4-dinitrochlorobenzene: mp 77–78°.

Anal. Calcd for $C_{11}H_{14}N_2O_5S$: C, 47.05; H, 4.34; N, 10.97; S, 12.56. Found: C, 47.17, H, 3.93; N, 11.08; S, 12.49.

Reaction of Styrene Episulfoxide (11) in Methanol. Sulfuric acid 1 drop was added to a solution of **11** (0.76 g, 5 mmol) in dry methanol (30 ml) and the mixture was stirred for 5 hr at 0–5°. Similar posttreatment as above afforded solid residue, which was purified by column chromatography on silica using chloroform as eluent. The pure thiol sulfinate **13** (0.71 g, 81% yield) was isolated as colorless crystals: mp 94–94.5°; ir (KBr) 1105, 1080, 1065 cm^{-1}; nmr ($CDCl_3$) τ 6.74 (s, 6 H), 6.63 (q, 4 H), 5.59 (q, 1 H), 5.35 (q, 1H), 2.67 (s, 10 H).

Anal. Calcd for $C_{18}H_{22}O_3S_2$: C, 61.68; H, 6.33; S, 18.30. Found: C, 61.88; H, 6.28; S, 17.99.

Reduction of the thiol sulfinate **13** with LiAlH provided the corresponding mercaptan (0.36 g, 54% yield) as a colorless liquid: bp 57–58° (0.5 mm); nmr (CCl_4) τ 8.54 (q, 1 H), 7.08–7.64 (m, 2 H), 6.80 (s, 3 H), 5.92 (q, 1 H), 2.76 (s, 5 H), J_{CH_2-SH} = 9 Hz, J_{CH_2-CH} = 8 Hz, J_{gem} = 13 Hz; mass spectrum (*m/e*) 168 (M^+), 135, 121 (base), 91, 77.

Anal. Calcd for $C_9H_{12}S$: S, 19.06. Found: S, 19.01.

Reaction of Propylene Episulfoxide (7) in Alcohols. The reacting conditions were almost the same as those described in the reaction of ethylene episulfoxide. The yields, ir absorptions, and microanalyses data of the isolated thiol sulfinates are collected in Table V.

Reduction of these thiol sulfinates produced the corresponding mercaptans. The total yields and isomer ratios of mercaptans were calculated from vpc peak areas. The yields and nmr of the mercaptans are collected in Table VI.

Table VI. Alkoxypropyl Mercaptans from Propylene Episulfoxide (7) and Alcohols

R	Total yield of mercaptans, %	Compd	Nmr, τ
Me	77	**8a**	8.83 (d, 3 H), 8.67 (t, 1 H), 7.53 (m, 2 H), 6.73 (s, 3 H), 6.73 (m, 1 H)
		9a	8.73 (d, 3 H), 8.45 (d, 1 H), 7.3 (m, 1 H), 6.76 (d, 2 H), 6.70 (s, 3 H)
Et	74.5	**8b**	8.79 (t, 3 H), 8.78 (d, 3 H), 8.49 (t, 1 H), 7.30~7.55 (m, 2 H), 6.35~6.70 (m, 3 H)
		9b	8.80 (t, 3 H), 8.70 (d, 3 H), 8.25 (d, 1 H), 7.30~7.55 (m, 1 H), 6.35~6.70 (m, 4 H)
i-Pr	74	**8c**	8.84 (d, 6 H), 8.80 (d, 3 H), 8.50 (t, 1 H), 7.25~7.60 (m, 2 H), 6.05~6.75 (m, 2 H)
		9c	8.84 (d, 6 H), 8.71 (d, 3 H), 8.21 (d, 1 H), 6.1~7.2 (m, 4 H)
t-Bu	52	**8d**	8.84 (d, 3 H), 8.82 (s, 9 H), 8.78 (t, 1 H), 7.5~7.7 (m, 2 H), 6.40 (bq, 1 H)
		9d	8.82 (s, 9 H), 8.75 (d, 3 H), 8.42 (d, 1 H), 6.7~7.3 (m, 3 H)

Reaction of *cis*-2-Butene Episulfoxide (14) in Methanol. The reaction of **14**, which was prepared by the oxidation of 1.76 g of *cis*-2-butene episulfide with perbenzoic acid, was carried out in the same manner as that of ethylene episulfoxide. Extractive work-up furnished the thiol sulfinate **16** (2.32 g; 91% yield): ir (neat) 1090, 1070 cm^{-1}.

The reduction of the thiol sulfinate **16** by LiAlH afforded a colorless liquid which was evaporatively distilled to provide the mercaptan **18** (1.78 g, 44% yield based on episulfide used) as a colorless liquid: bp 70° (100 mm); nmr(CCl_4) τ 8.86 (d, 3 H), 8.76 (d, 3 H), 8.47 (d, 1 H), 7.13 (m, 1 H), 6.88 (m, 1 H), 6.71 (s, 3 H).

(23) R. W. Bost, J. O. Turnur, and R. D. Norton, *J. Amer. Chem. Soc.*, **54**, 1985 (1932).

The mercaptan **18** (240 mg) was converted to the methyl sulfide **20** (210 mg) by treatment with sodium ethoxide and methyl iodide: nmr (CCl_4) τ 8.90 (d, 3 H), 8.85 (d, 3 H), 7.94 (s, 3 H), 7.29 (m, 1 H), 6.74 (s, 3 H), 6.7 (m, 1 H); mass spectrum (*m/e*) 134 (M^+), 75, 59 (base).

Anal. Calcd for $C_6H_{14}OS$: C, 53.68; H, 10.51; S, 23.89. Found: C, 53.42; H, 10.54; S, 24.00.

Reaction of *trans*-2-Butene Episulfoxide (15) in Methanol. The reaction of the episulfoxide **15** was carried out in the same manner as that of isobutene episulfoxide since **15** was unstable above 0°. The ether solution of the thiol sulfinate **17** obtained from the extractive work-up of the reaction mixture was directly added to the suspension of LiAlH in ether. The reaction mixture was hydrolyzed, extracted, dried, and submitted to distillation under reduced pressure to give the mercaptan **19** (42% yield based on episulfide used) as a colorless liquid: bp 35–36.5° (15 mm). The nmr spectrum of this mercaptan **19** was almost identical with that of **18**.

Conversion of **19** (480 mg) to the methyl sulfide **21** (380 mg) was carried out as described above: nmr (CCl_4) τ 8.83 (d, 3 H), 8.79 (d, 3 H), 7.96 (s, 3 H), 7.43 (m, 1 H), 6.8 (m, 1 H), 6.74 (s, 3 H); mass spectrum (*m/e*) 134 (M^+), 59 (base).

Anal. Calcd for $C_6H_{14}OS$: C, 53.68; H, 10.51; S, 23.89. Found: C, 53.87; H, 10.55; S, 24.05.

threo-**3-Mercapto-2-butanol (24).** This was prepared from *cis*-2-butene oxide according to the method described by Price and Kirk:[9] bp 53° (10 mm) (lit.[9] 73.5–4.0° (31 mm)); ir (neat) 3480, 2960, 2550, 1080, 915 cm^{-1}; nmr (CCl_4) τ 8.81 (d, 3 H), 8.73 (d, 1 H), 8.66 (d, 3 H), 7.6 (bs, 1 H), 7.28 (m, 1 H), 6.52 (m, 1 H).

erythro-**3-Mercapto-2-butanol (25).** This was prepared from *trans*-2-butene oxide by the same procedure as above: bp 55–56° (10 mm); ir (neat) 3380, 2960, 2550, 1010, 915 cm^{-1}; nmr (CCl_4) τ 8.83 (d, 3 H), 8.73 (d, 3 H), 8.63 (d, 1 H), 7.25 (bs, 1 H), 7.07 (m, 1 H), 6.34 (m, 1 H).

threo-**3-Methylthio-2-butanol (26).** A solution of **24** (2.12 g, 0.02 mol) in absolute ethanol (20 ml) was added dropwise to a solution of sodium (0.46 g, 0.02 g-atom) in absolute ethanol (50 ml) with stirring. Methyl iodide (2.84 g, 0.02 mol) was added to the solution at room temperature and was allowed to stand for 2 hr. The mixture was diluted with water, extracted thrice with chloroform, and dried. The solution was evaporatively distilled to afford *threo*-3-methylthio-2-butanol (**26**, 2.0 g, 83% yield) as a colorless liquid: bp 78° (25 mm); ir (neat) 3400(–OH), 2960(CH_3–), 1080 cm^{-1} (C–O–C); nmr (CCl_4) τ 8.83 (d, 3 H), 8.74 (d, 3 H), 7.95 (s, 3 H), 7.55 (t, 1 H), 7.52 (bs, 1 H), 6.50 (m, 1 H).

erythro-**3-Methylthio-2-butanol (27).** This compound was prepared in 76% yield from **25** by the same procedure as described above: bp 76° (21 mm); ir, 3380, 2960, 1065 cm^{-1}; nmr (CCl_4) τ 8.87 (d, 3 H), 8.81 (d, 3 H), 7.94 (s, 3 H), 7.9 (bs, 1 H), 7.40 (octet, 1 H), 6.3 (m, 1 H).

threo-**3-Methylthio-2-methoxybutane (20).** A solution of **26** (1.2 g, 0.01 mol) in dry ether (5 ml) was added to a suspension of sodium hydride (240 mg, 0.01 mol) in dry ether (10 ml) with stirring. Methyl iodide (1.4 g, 0.01 mol) was added and the mixture was stirred for 2 hr at room temperature. The ether extract of the mixture was dried and freed of solvent. The residual oil was distilled to furnish *threo*-3-methylthio-2-methoxybutane **20** (0.48 g, 35% yield) as a colorless liquid: bp 63° (23 mm). The ir and nmr spectra of this material were completely identical with those of **20** derived from episulfoxide **14**.

erythro-**3-Methylthio-2-methoxybutane (21).** This material was prepared in 48% yield from **27** by the same procedure as described in the previous experiment: bp 58° (20 mm).

Reaction of *trans*-Stilbene Episulfoxide 29 in Methanol. Sulfuric acid 1 drop was added to a stirred solution of *trans*-stilbene episulfoxide **29** (0.46 g, 0.002 mol) in methanol (40 ml) cooled with ice water. The solution was left to stand overnight at room temperature. The mixture was diluted with chloroform, washed with water, dried, and freed of solvent. The residual white solid was submitted to column chromatography on silica using benzene as eluent. Evaporation of the solvent afforded the thiol sulfinate **31** (0.32 g, 63% yield) as colorless crystals: ir (KBr disk) 1120, 1070 cm^{-1}.

Anal. Calcd for $C_{30}H_{30}O_3S_2$: C, 71.68; H, 6.02; S, 12.76. Found: 71.67; H, 6.07; S, 12.74.

The thiol sulfinate **31** (0.12 g) was dissolved in thiophenol (10 ml) and 1 drop of sulfuric acid was added to the solution followed by stirring overnight at room temperature. The mixture was diluted with water and extracted with ether. The ethereal extracts were dried and freed of solvent. The residual solid was purified by column chromatography on silica using *n*-hexane–benzene (5:1) as eluent. Evaporation of the solvent afforded the disulfide **33** (0.08 g, 50% yield) as colorless crystals: ir (KBr disk) 1100 cm^{-1} (C–O–C); nmr ($CDCl_3$) τ 6.88 (s, 3 H), 5.95 (d, 1 H), 5.30 (d, 1 H), 2.8 (m, 15 H).

Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72. Found: C, 72.06; H, 5.54.

Reaction of *cis*-Stilbene Episulfoxide 28 in Methanol. The procedure was exactly the same as that described for the episulfoxide **29**. Recrystallization of the crude product from benzene–hexane afforded the thiol sulfinate **30** (45.5% yield) as colorless crystals: ir (KBr disk) 1110, 1075 cm^{-1}.

Anal. Calcd for $C_{30}H_{30}O_3S_2$: C, 71.68; H, 6.02; S, 12.76. Found: C, 72.04; H, 6.07; S, 12.75.

The thiol sulfinate **30** was converted to unsymmetric disulfide by treatment with thiophenol as described above. Purification by column chromatography on silica using *n*-hexane–benzene (5:1) as eluent afforded the disulfide **32** in 78% yield: mp 65–68°; ir (KBr disk) 1110 cm^{-1} (C–O–C); nmr ($CDCl_3$) τ 6.78 (s, 3 H), 5.82 (d, 1 H), 5.46 (d, 1 H), 2.9 (m, 15 H).

Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72; S, 18.19. Found: C, 71.37; H, 5.72; S, 18.10.

Reaction of Propylene Episulfoxide (7) in Ethyl Mercaptan. To a solution of **7** (1.14 g, 0.0126 mol) in ethyl mercaptan (30 ml) was added a few drops of sulfuric acid and the mixture was stirred overnight at 0–5°. The resulting mixture was diluted with 50 ml of chloroform and washed with water. The organic layer was dried and freed of solvent. The residual liquid was carefully distilled under reduced pressure to afford a mixture of disulfides **34** and **35** (1.14 g, 46% yield): bp 84° (0.5 mm).

Anal. Calcd for $C_7H_{16}S_3$: C, 42.81; H, 8.21; S, 48.98. Found: C, 42.69; H, 8.23; S, 48.92.

The mixture of disulfides (588 mg, 0.003 mol) was reduced with LiAlH (114 mg) in dry ether by the process described before. The crude product was distilled to furnish a mixture of mercaptans (320 mg, 74% total yield) (**36**:**37** = 20:80, determined by nmr): ir (neat) 2530 cm^{-1} (S–H).

Anal. Calcd for $C_3H_{12}S_2$: C, 44.07; H, 8.88; S, 47.06. Found: C, 44.29; H, 8.85; S, 46.80.

The reactions of **7** in mixed solvent systems were carried out in the same manner as described above and the ratios of the isomeric mercaptans obtained by the reduction of disulfide mixtures were also determined from their nmr integration curves.

Reaction of Isobutene Episulfoxide (10) in Ethyl Mercaptan. The episulfoxide **10**, prepared from 2.64 g of isobutene sulfide, was dissolved in ethyl mercaptan (30 ml) at −10°. After the same treatment as described above, the residual oil was purified by dry column chromatography on silica using benzene as eluent. The desired column extract was concentrated and distilled *in vacuo* to afford a mixture of disulfides (3.69 g, 53% yield): bp 72° (0.08 mm); ir (neat) 2950, 1450, 1380, 1110 cm^{-1}.

Anal. Calcd for $C_8H_{18}S_3$: C, 45.66; H, 8.62; S, 45.71. Found: C, 46.25; H, 8.54; S, 44.55.

The mixture of disulfides (0.36 g) was further reduced with LiAlH. Distillation of the crude product yielded a mixture of mercaptan isomers (0.36 g, 80% yield); bp 62° (10 mm) (**38**:**39** = 35:65, determined by vpc).

Anal. Calcd for $C_6H_{14}S_2$: C, 47.95; H, 9.39; S, 42.66. Found: C, 48.08; H, 9.28; S, 42.55.

Each of the mercaptans in the mixture was isolated by preparative vpc. **39**: nmr (CCl_4) τ 7.39 (s, 2 H), 7.44 (q, 2 H), 7.98 (s, 1 H), 8.58 (s, 6 H), 8.74 (t, 3 H). **38**: nmr (CCl_4) τ 7.38 (d, 2 H), 7.54 (q, 2 H), 8.55 (t, 1 H), 8.66 (s, 6 H), 8.78 (t, 3 H).

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