Desulfurization of Episulfides. A Sulfurane Reaction

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The desulfurization of *cis*- and *trans*-2-butene episulfides with *n*-butyllithium, diiron nonacarbonyl, and triiron dodecacarbonyl to the corresponding butenes was studied. These reactions proceed with complete stereospecificity, the 2–6% crossover in the cases of the iron carbonyls being attributable to subsequent olefin isomerization. The intermediacy of 2-lithio-3-alkylthiobutanes for the *n*-butyllithium reaction can be excluded. Independent generation of these species demonstrates considerable loss of stereochemistry under the conditions of episulfide desulfurizations. The loss of stereochemistry is a function of the thioether leaving group, the loss being considerably less for thiophenoxide than for ethyl thiolate. A consequence of these studies also demonstrates that metal–halogen exchange between an alkyl halide and an organolithium proceeds with at least 95% retention of configuration.

The question of the role of pentacoordinate sulfur compounds, sulfuranes, in the reaction of sulfonium salts with nucleophiles has caused discussion and debate. While there are no known cases of stable sulfuranes[3,4] in which sulfur is bound only to carbon ligands, their existence has been implicated in many reactions by spectral[3,5] and product analysis.[6] Most of these reactions have been carried out on partially or fully aromatic substituted sulfonium species. While a sulfurane mechanism has been advanced to explain the observed products, other mechanisms, such as aryne formation, radical formation, or nucleophilic aromatic substitution, have also been put forth.[6]

In order to learn more about the intermediacy of sulfuranes, without the problems associated with aromatic species, we decided to investigate nonaromatic cases. Anticipating that small rings stabilize the predicted trigonal bipyramid geometry of a sulfurane compared to tetrahedral geometry, a study of the stereochemistry of organolithium-induced fragmentation of small sulfur heterocycles was undertaken.[7]

Approximately 15 years ago, Bordwell reported that reaction of aryl- or alkyllithium with episulfides produced olefins and the corresponding aryl or alkyl mercaptides.[8,9] Further study of the stereochemistry of the reaction with *cis*- and *trans*-2-butene episulfides revealed that, in each case, the olefin formation proceeded with greater than 97% stereospecific retention of configuration.[9] Bordwell presented two mechanisms for this reaction (Scheme I). In the first, the concerted process, fragmentation occurs *via* a sulfurane **1**. The second, the carbanion mechanism, requires that elimination must be 30–60 times faster than inversion and bond rotation rates. Since this report represents the first potential example of an aliphatic sulfurane, we reinvestigated this reaction to attempt to differentiate between the two proposed mechanisms.

Preparation and Reaction of Episulfides.—The *cis*- and *trans*-2-butene episulfides needed for our study were synthesized in the following manner. The *erythro*- and *threo*-2-bromo-3-hydroxybutanes were prepared from the corresponding *cis*- and *trans*-2-butenes by the method of Lucas and Winstein.[10] Conversion to the cis and trans epoxides was achieved by dehydrobromination with strong aqueous base.[11] The epoxides were converted to their respective episulfides by reaction with an aqueous thiourea solution.[12] The purity of each of the episulfides was determined by vpc and, while the trans material was free of the cis, the cis contained 0.6% of the trans isomer.

We carried out the reactions of the cis and trans episulfides with *n*-butyllithium at −78° for 1 hr. The reaction was then slowly warmed to 40° and held at that temperature for 1 hr. During the entire reaction, a stream of nitrogen was blown over the reaction mixture and into a series of bromine–carbon tetrachloride traps. The butenes were analyzed as their dibromide adducts.

Preparation and Reactions of *erythro*- and *threo*-2-Bromo-3-ethylthiobutane and 2-Bromo-3-phenylthiobutane.—The *erythro*- and *threo*-2-bromo-3-ethylthiobutanes **3a** and **4a**, which would serve as the precursors to the carbanion intermediates, were synthesized by the addition of ethylsulfenyl bromide, to excess *trans*- or *cis*-2-butene, respectively.[13] Each isomer was shown to be free of the other by nmr analysis of the expanded methine region. In a similar manner, addition of *cis*- or *trans*-2-butene to a hexane solution of phenylsulfenyl bromide gave the corresponding *threo*- and *erythro*-2-bromo-3-phenylthiobutanes, **3b** and **4b** (Scheme II).

The reactions of **3a** or **3b** and **4a** or **4b** with *n*-butyllithium were carried out at −78°, approximating the conditions of the episulfide decomposition reaction. In addition, the reactions were also run at −5°. The resultant 2-butenes were analyzed as the *meso*- and *dl*-2,3-dibromides. In some of the runs, the reaction was quenched with a proton source such as methanol or water, and *sec*-butylethyl sulfide was isolated, indicating that the reaction proceeded through a discrete carbanion intermediate.

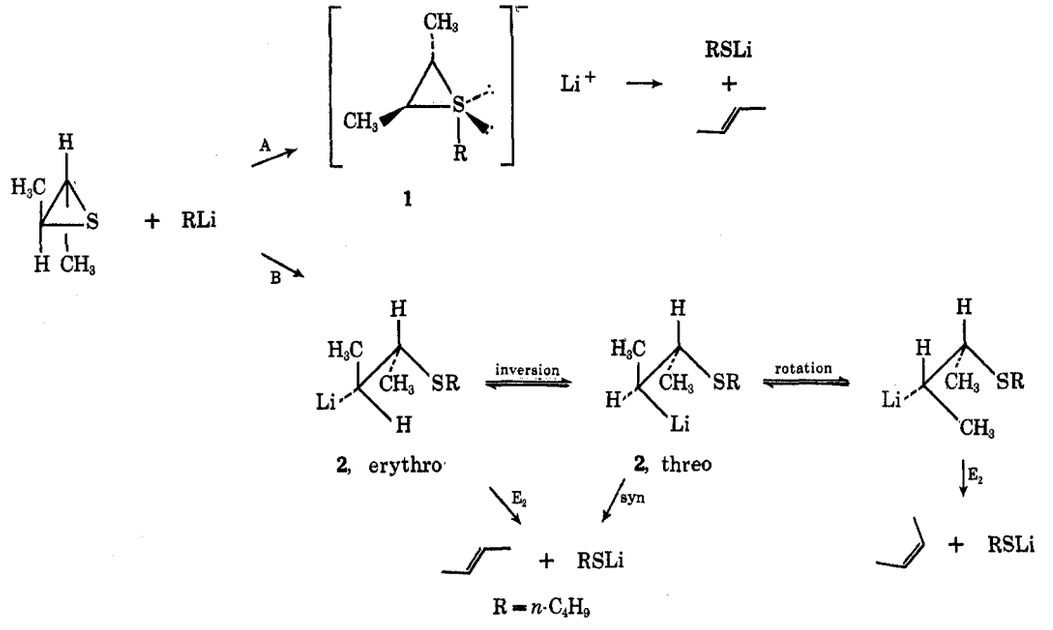
Results and Discussion

Our results verified those of Bordwell. The trans isomer produced only *trans*-2-butene in 93% yield.

(1) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.
(2) National Institutes of Health Predoctoral Fellow.
(3) For an example in which there seems to be good evidence by nmr, see W. Sheppard, *J. Amer. Chem. Soc.*, **93**, 5597 (1971).
(4) For a case in which two of the ligands are alkoxy groups, see I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **93**, 6674 (1971); J. C. Martin and R. J. Ashart, *ibid.*, **93**, 2339, 2341 (1971).
(5) (a) D. C. Owsley and G. K. Helmkamp, *ibid.*, **91**, 5239 (1969); (b) C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5398 (1969).
(6) B. M. Trost and R. W. LaRochelle, *ibid.*, **93**, 6077 (1971), and references cited therein.
(7) Also see J. I. Musher, *Advan. Chem. Ser.*, in press. We are grateful to Professor Musher for making a preprint of this paper available to us.
(8) F. G. Bordwell, H. M. Andersen, and B. M. Pitts, *J. Amer. Chem. Soc.*, **76**, 1082 (1954).
(9) N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959).
(10) S. Winstein and H. J. Lucas, *ibid.*, **61**, 1580 (1939).
(11) C. W. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).
(12) F. G. Bordwell and A. M. Andersen, *ibid.*, **75**, 4959 (1953).
(13) G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **29**, 3258 (1964).

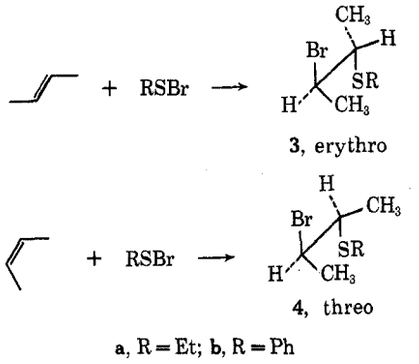
SCHEME I

REACTION OF EPISULFIDE WITH *n*-BUTYLLITHIUM



SCHEME II

PREPARATION OF 2-BROMO-3-ALKYL(ARYL)THIOBUTANES



a, R = Et; b, R = Ph

The cis isomer produced 98.8% *cis*-2-butene in 78% yield.[14] In the two mechanisms presented in Scheme I, the first, path A, assumes that the *n*-butyllithium will act as a nucleophile and attack at sulfur to form a trigonal bipyrimidal structure, **1**. It would be expected that the three-membered ring would assume a distorted apical basal orientation; the two lone pairs would be bisbasal, and the attacking group would be in the other apical position. A concerted disrotatory fragmentation of the two weakest bonds, those of the episulfide, would lead to the observed products. In a slight variation of the sequence of events (the idea actually put forth by Bordwell) the bond-making and bond-breaking process proceeds simultaneously. However, a transition state of this type seems less likely in terms of entropy considerations.

In the second mechanism, path B, SN2 displacement at sulfur could occur with either retention or inversion of configuration at carbon, leading respectively to either the threo or the erythro carbanions, **2t** or **2e**. Alternatively, sulfurane intermediate **1** could also lead to either of these conformers by heterolysis of one bond. The product observed could arise from either trans elimination of the erythro isomer or syn elimination of the threo isomer. As little was known about the stereospecificity of β-carbanion elimination in sulfides, a study was undertaken to examine this reaction.

From the results of the series of reactions, summarized in Tables I and II, it is apparent that both the ethyl and phenyl compounds **3** and **4** showed some degree of stereospecificity, however, considerably less specificity than in the episulfide cases.

TABLE I

REACTION OF *erythro*-[e] AND *threo*-2-BROMO-3-ETHYLTHIOBUTANE[f] WITH *n*-BUTYLLITHIUM

Isomer	Total yield, %	2-Butenes[a] % trans	2-Butenes[a] % cis	Temp, °C
Threo	80	44.0	56.0	−78[b]
Erythro	92.5	79.5	20.5	−78[b]
Threo	52	40.5	59.5	−78[c]
Erythro	74	89.0	11.0	−78[c]
Threo	58	43.2	56.8	−5[d]
Erythro	94	73.7	26.3	−5[d]

[a] Analyzed as *meso*- and *dl*-2,3-dibromobutanes. [b] Reaction mixture was allowed to warm to 40° before addition of water. [c] Water was added to the reaction mixture at −78° and it was then allowed to warm to 40°. [d] Water was added to the reaction mixture at −5° and it was then allowed to warm to 40°. [e] Registry no., 23289-26-1. [f] Registry no., 23289-25-0.

TABLE II

REACTION OF *erythro*-[d] AND *threo*-2-BROMO-3-PHENYLTHIOBUTANE[e] WITH *n*-BUTYLLITHIUM

Isomer	Total yield, %	2-Butenes[a] % trans	2-Butenes[a] % cis	Temp, °C
Threo	66	43.3	56.7	−5[c]
Erythro	82	88.0	12.0	−5[c]
Threo	54	11.3	88.7	−78[b]
Erythro	78	94.8	5.2	−78[b]

[a] Analyzed as *meso*- and *dl*-2,3-dibromobutanes. [b] Water was added to the reaction mixture at −78° and it was then allowed to warm to 40°. [c] Water was added to the reaction mixture at −5° and it was then allowed to warm to 40°. [d] Registry no., 37434-63-2. [e] Registry no., 37434-62-1.

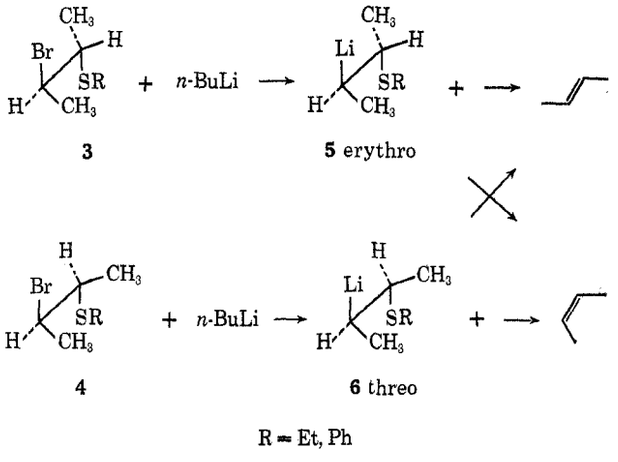
(14) The difference is well within the limits of experimental error. It may also be due to different rates of reaction of the cis and trans compounds.

There are two aspects to the reaction—metal halogen exchange and elimination. It has been demonstrated by Letsinger that metal halogen exchange occurs with a high degree of retention of configuration.[15] The fact that the overall elimination reaction in our cases can proceed with 95% stereospecificity indicates that metal–halogen exchange occurred with at least that degree of specificity.

Thus, the results suggest that either there is conversion between the erythro and threo isomers **5** or **6**, or competition between syn and anti elimination, or both (see Scheme III). In an analogous study by Sicher on

SCHEME III

n-BUTYLLITHIUM INDUCED ELIMINATIONS OF 2-BROMO-3-ALKYL(ARYL)THIOBUTANES



metal-induced olefin formation of vicinal dibromides, it was established that syn elimination plays a minor role compared to that of anti elimination in the acyclic cases.[16] Furthermore, House established the trans elimination in a series of metal-induced eliminations of 2-bromo-3-X-butanes where X was bromo, methoxyl, or acetoxyl.[17] He also established that the degree of stereospecificity was a function of the leaving group—the better the leaving group, the higher the stereospecificity.[18]

A similar interpretation appears most reasonable in these cases as well. At −78°, *erythro*- and *threo*-2-bromo-3-ethylthiobutanes eliminate with 50 ± 5 and 16 ± 2% stereospecificities, respectively.[19] Raising the temperature to −5° allows the interconversion of carbanion isomers to compete a little more effectively with elimination and causes a slight diminishment in stereospecificity. These effects are magnified in the case of 2-bromo-3-phenylthiobutane. Using thiophenoxide as the leaving group rather than ethylthiolate dramatically increases the stereospecificities[19] to 90 and 78% for the erythro and threo cases, respectively, at −78°. Thus, the rate of elimination is enhanced at the expense of loss of configuration of the carbanion. Raising the temperature to −5° makes the slower reaction, loss of carbanion configuration, more competitive with elimination with the consequence of diminished stereospecificity (to 66 and 14%). In both cases, the threo organolithium exhibits greater loss of configuration. This fact undoubtedly arises from the higher energy content of the conformation required for the anti elimination in this isomer in which there is maximal eclipsing of large groups. These results clearly eliminate the carbanion route, path B, for episulfide desulfurizations, thereby suggesting the sulfurane mechanism.

In an ancillary study, the stereochemistry of desulfurization of episulfides with diiron nonacarbonyl or triiron dodecacarbonyl in refluxing benzene was investigated. Such a reaction, originally reported by King,[20] may be envisioned as proceeding through metal π sulfuranes.[21] Table III lists the pertinent data for

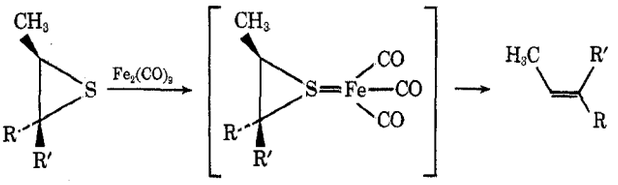


TABLE III
DECOMPOSITION OF *cis*-[c] AND *trans*-2-BUTENE EPISULFIDES[d] WITH IRON CARBONYLS

Episulfide	Iron carbonyl	Total yield, %	2-Butene[a] % trans	2-Butene[a] % cis
Cis	$Fe_2(CO)_9$[e]	80.5	6.4	93.6
Trans	$Fe_2(CO)_9$	81.9	97.5	2.5
Cis	$Fe_3(CO)_{12}$[f]	*b*	5.0	95.0
Trans	$Fe_3(CO)_{12}$	*b*	97.3	2.7

[a] Analyzed as *meso*- and *dl*-2,3-dibromobutane. [b] Yields not determined. [c] Registry no., 5954-71-2. [d] Registry no., 5955-98-6. [e] Registry no., 15321-51-4. [f] Registry no., 33727-76-3.

the desulfurizations of *cis*- and *trans*-2-butene episulfides. Like the organolithium induced decompositions, these reactions also proceed with a very high degree of stereospecificity. Control experiments demonstrated that the olefins are somewhat unstable to the reaction conditions. Thus, bubbling *trans*-2-butene through a benzene solution of diiron nonacarbonyl between 40° and 80° caused isomerization to *cis*-2-butene to the extent of 12–15% depending on contact times. Thus, partial isomerization of the initially formed olefins readily accounts for the 2–6% crossover observed. While a concerted disrotatory fragmentation of the π sulfurane can explain the results, alternative explanations exist and the mechanism must be considered an open question.

The results of organolithium and iron carbonyl induced desulfurizations may be compared to other desulfurizations of three-member sulfur heterocycles. The direct thermal decomposition of *cis*- and *trans*-2-butene episulfides,[22] as well as the thermal decomposi-

(15) (a) R. Letsinger, *J. Amer. Chem. Soc.*, **72**, 4842 (1950); (b) D. Y. Curtin and W. J. Koehl, Jr., *ibid.*, **84**, 1967 (1962).

(16) J. Sicher, M. Haval, and M. Svoboda, *Tetrahedron Lett.*, 4269 (1968).

(17) H. O. House and R. S. Ro, *J. Amer. Chem. Soc.*, **80**, 182 (1958). Also see W. Adam and J. Arce, *J. Org. Chem.*, **37**, 507 (1972).

(18) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, pp 182–185.

(19) The per cent stereospecificity is defined as the relative per cent of expected product arising from a stereospecific anti elimination in excess of 50%.

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

(21) In order to differentiate between a decet sulfur species which is pentacoordinate and tetracoordinate (counting the lone pair as a ligand), we refer to the former as σ and the latter as π sulfuranes. In a σ sulfurane, sulfur possesses four σ bonds and a lone pair; whereas in a π sulfurane sulfur possesses two σ bonds, one π bond, and a lone pair. Thus, in the latter case, valence-shell expansion of sulfur occurs only to the extent that back electron donation from the ligand to empty orbitals on sulfur is important. The sulfur ylides are members of such a class.

(22) E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7164 (1968).

tion of episulfones,[23] has been reported to proceed stereospecifically. In contrast to these cases, episulfoxide decomposition has been reported to proceed nonstereospecifically.[24] Equation of stereospecificity to concertedness presents a dilemma in terms of orbital symmetry, since all these chelotropic processes are orbital symmetry forbidden for the least motion pathway. Furthermore, these diverse results make it difficult to claim that those cases of stereospecific decomposition involve a change in the correlation diagram because of the involvement of d orbitals of sulfur.

Experimental Section[25]

Preparation of *cis*-2-Butene Episulfide.—*threo*-3-Bromo-2-butanol was prepared from 110 g (0.62 mol) of *N*-bromosuccinimide and 34.6 g (0.62 mol) of *cis*-2-butene as previously described.[10] There was obtained 78.1 g (82% yield) of a colorless oil distilling at 52° (13 mm) [lit.[10] bp 49–51° (13 mm)] with n^{25}D 1.4753 (lit.[10] n^{25}D 1.4756). With 29.1 g (0.32 mol) of potassium hydroxide, 57 g (0.375 mol) of *threo*-3-bromo-2-butanol was converted into 24.5 g (90%) of *cis*-2-butene epoxide, bp 59° (lit.[18] bp 59–60°), as described.[18] Subsequent treatment of 49.7 g (0.68 mol) of epoxide with 52.2 g (0.68 mol) of thiourea in aqueous sulfuric acid as described in the literature[12] generated 27.5 g (46%) of *cis*-2-butene episulfide as a colorless liquid, bp 99° (lit.[12] bp 98°). Vpc analysis[26] showed the cis isomer to contain 0.6% trans.

Preparation of *trans*-2-Butene Episulfide.—*erythro*-3-Bromo-2-butanol was prepared by the literature procedure from 173 g (1.0 mol) of *N*-bromosuccinimide and 56 g (1.0 mol) of *trans*-2-butene in 700 ml of water and 20 ml of acetic acid.[10] Distillation of the product at 56° (13 mm) [lit.[10] bp 53° (13 mm)] gave 80.1 g (52%) of the erythro compound, n^{25}D 1.4763 (lit.[10] n^{25}D 1.4767). Treatment[11] of this bromohydrin with 41 g (0.72 mol) of potassium hydroxide converted it into 33.0 g (88%) of *trans*-2-butene epoxide which distilled at 56° (lit.[11] bp 54°). Dissolution in an aqueous sulfuric acid solution of 34.8 g (0.45 mol) of thiourea produced 12.7 g (43%) of a colorless liquid, bp 89° (lit.[12] bp 89°). Vpc analysis[26] of the *trans*-2-butene episulfide revealed no detectable amount of cis isomer.

Preparation of *threo*-2-Bromo-3-ethylthiobutane.[18]—A solution of ethyl disulfide (13.5 g, 0.11 mol) in 250 ml of dry methylene chloride was cooled to −17° with a carbon tetrachloride–Dry Ice bath and wrapped with aluminum foil to shield it from light. Bromine (16.0 g, 0.10 mol) in 75 ml of dry methylene chloride was added to the stirred, cooled solution at a rate which kept the temperature below −10° throughout the addition. At the end of addition, the solution was clear red. Excess *cis*-2-butene was bubbled through the red solution while the temperature was kept below −10° until the color disappeared. Methylene chloride was removed by evaporation *in vacuo* and the product was distilled to give 31.5 g (80% yield) of the threo material: bp 30° (0.4 mm); nmr ($CDCl_3$) τ 5.63 (qd, J = 7, 3 Hz, 1 H), 6.88 (qd, J = 7, 3 Hz, 1 H), 7.43 (q, J = 7.5 Hz, 2 H), 8.35 (d, J = 7.0 Hz, 3 H), 8.67 (d, J = 7.0 Hz, 3 H), 8.80 (t, J = 7.5 Hz, 3 H); mass spectrum *m/e* (rel intensity) 198 (3), 196 (3), 154 (7), 152 (12), 137 (9), 135 (12), 122 (39), 117 (15), 116 (36), 94 (30), 89 (100), 87 (27). *Anal.* Calcd for $C_6H_{13}BrS$: 195.9922. Found: 195.9983. Analysis of the methine and methyl region by nmr on an expanded scale showed the threo to be free of the erythro within the detectable limits of nmr (1%).

Preparation of *erythro*-2-Bromo-3-ethylthiobutane.—In a similar manner, 13.5 g (0.11 mol) of ethyl disulfide in 250 ml of dry methylene chloride was treated with 16.1 g (0.10 mol) of bromine to give the bromoethyl sulfide intermediate. This was treated with excess *trans*-2-butene to give 19.9 g (50% yield) of the erythro material: bp 31° (0.1 mm); nmr ($CDCl_3$) τ 5.85 (quintet, J = 6.5 Hz, 1 H), 7.21 (quintet, J = 6 Hz, 1 H), 7.40 (quintet, J = 7 Hz, 2 H), 8.21 (d, J = 6.5 Hz, 3 H), 8.62 (d, J = 6 Hz, 3 H), 8.73 (t, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 198 (6), 196 (6), 137 (14), 135 (14), 123 (34), 122 (10), 117 (20), 116 (10), 94 (28), 91 (14), 89 (100). *Anal.* Calcd for $C_6H_{13}BrS$: 195.9922. Found: 195.9898. Analysis of the erythro compound by nmr on an expanded scale (methine and methyl regions) showed it to be free of the threo within the detectable limits of nmr (1%).

Preparation of *threo*-2-Bromo-3-phenylthiobutane.—In a manner similar to the preparation of *erythro*- and *threo*-2-bromo-3-ethylthiobutane, 24.0 g (0.11 mol) of phenyl disulfide was treated with 16.0 g (0.10 mol) of bromine to give the intermediate phenylsulfenyl bromide. The intermediate was not isolated, but was treated with excess *cis*-2-butene to give 22.9 g (47% yield) of the threo isomer: bp 102° (0.4 mm); nmr ($CDCl_3$) τ 2.83 (m, 5 H), 5.80 (qd, J = 7, 3 Hz, 1 H), 6.40 (qd, J = 7, 3 Hz, 1 H), 8.35 (d, J = 7 Hz, 3 H); mass spectrum *m/e* (rel intensity) 246 (25), 244 (25), 190 (30), 188 (30), 165 (45), 137 (60), 110 (43), 109 (49), 93 (50), 69 (100).

Anal. Calcd for $C_{10}H_{13}BrS$: C, 49.02; H, 5.30; Br, 32.62; S, 13.06. Found: C, 49.11; H, 5.22; Br, 32.55; S, 13.11.

Analysis of the threo methine and methyl region by nmr on an expanded scale showed it to be free of the erythro isomer within the limits of detection by nmr (1%).

Preparation of *erythro*-2-Bromo-3-phenylthiobutane.—In a manner similar to the preparation of the *erythro*- and *threo*-2-bromo-3-ethylthiobutane, 13.0 g (0.082 mol) of phenyl disulfide was treated with 12.0 g (0.075 mol) of bromine. The resultant bromophenyl sulfide intermediate was treated with excess *trans*-2-butene to give 2.49 g (7% yield) of the erythro compound: bp 88° (0.2 mm); nmr ($CDCl_3$) τ 2.75 (bm, 5 H), 5.92 (bq, J = 7 Hz, 1 H), 6.75 (bq, J = 7 Hz, 1 H), 8.22 (d, J = 7 Hz, 3 H), 8.60 (d, J = 7 Hz, 2 H).

Anal. Calcd for $C_{10}H_{13}BrS$: C, 49.02; H, 5.30; Br, 32.62; S, 13.06. Found: C, 49.16; H, 5.29; Br, 32.70; S, 13.21.

Analysis of the erythro methine and methyl regions by nmr on an expanded scale showed it to be free of the threo compound within the detectable limits (1%).

General Procedure for *n*-Butyllithium Decomposition Reactions.—The apparatus used for the decomposition reactions consisted of a 50-ml three-neck flask with stirrer, condenser, a rubber septum, and a nitrogen inlet tube. The condenser was connected by tygon tubing to two carbon tetrachloride–bromine traps, followed by an aqueous thiosulfate trap. The system, excluding the trap, was dried rigorously in a 120° oven for 12 hr.

The material to be decomposed was placed in the flask in 3 ml of dry tetrahydrofuran and cooled to −78°. An equivalent amount of 1.6 *M* *n*-butyllithium in hexane was added all at once *via* syringe and the solution was stirred for 1 hr at −78°. A steady stream of nitrogen was blown across the solution and through the traps. In some of the experiments, the solution was

TABLE IV

DECOMPOSITION OF *cis*- AND *trans*-2-BUTENE EPISULFIDES WITH *n*-BUTYLLITHIUM

Episulfide	Mmol	Mmol episulfide / mmol *n*-butyllithium	Total yield, %	% meso	% *dl*
Cis[a]	11.3	1.1	6	<1	>99
Cis[a]	11.3	1.1	78	0.5	99.5
Trans	0.20	1.1	6	100	0
Trans	11.3	1.1	93	100	0

[a] Corrected for starting material impurity.

(23) N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966); L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965); N. Tokura, T. Najai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

(24) G. E. Hartzell and J. N. Paige, *ibid.*, **32**, 459 (1967); K. Kondo, M. Matsumoto, and A. Negishi, *Tetrahedron Lett.*, 2131 (1972).

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

(26) A 10 ft × 0.25 in. column of 20% Dow silicone oil 710 on Chromosorb P was employed.

TABLE V

DECOMPOSITION OF *erythro*- AND *threo*-2-BROMO-3-ETHYLTHIOBUTANE WITH *n*-BUTYLLITHIUM

Compd	Mmol	Mmol compd / mmol RLi	Yield, %	% meso	% *dl*	Temp range °C	Quenched with H_2O	% *sec*-Butyl ethyl sulfide recovered
Threo	11.3	1.1	80	44.0	56.0	−78–40	No	
Erythro	11.3	1.1	92.5	79.5	20.5	−78–40	No	
Threo	5.7	1.1	52	40.5	59.5		Yes	2.4
Erythro	5.7	1.1	74	89.0	11.0	−78	Yes	2.9
Threo	5.7	1.1	58	43.2	56.8	−5	Yes	2.2
Erythro	5.7	1.1	94	73.7	26.3	−5	Yes	17.0

TABLE VI

DECOMPOSITION OF *erythro*- AND *threo*-2-BROMO-3-PHENYLTHIOBUTANE WITH *n*-BUTYLLITHIUM

Compd	Mmol	Mmol compd / mmol *n*-butyllithium	Yield, %	% meso	% *dl*	Temp range °C	Quenched with H_2O	% *sec*-Butyl phenyl sulfide recovered
Threo	5.0	1.1	66	43.3	56.7	−5	Yes	None
Erythro	1.0	1.2	82	88.0	12.0	−5	Yes	None
Threo	5.0	1.1	59	11.3	88.7	−78	Yes	1.4
Erythro	1.0	1.2	78	94.8	5.2	−78	Yes	.1

quenched with water, which served as a proton source to trap any carbanions present. This was done by addition of 1 ml of water *via* syringe to the cold solution.

The reaction was allowed to warm to room temperature by removal of the −78° bath and it was then held at 40° for 1 hr to ensure that all volatile products would be swept along to the traps by the nitrogen. The carbon tetrachloride solutions were combined and the excess bromine was reduced with a saturated sodium thiosulfate solution. The carbon tetrachloride was washed with 5 × 50 ml of water and dried ($MgSO_4$), and the solvent was removed by evaporation. The *meso*- and *dl*-2,3-dibromobutanes were analyzed by vpc[27] utilizing 1,2-dibromoethane as an internal standard.

Analysis of the sulfide components (*sec*-butylethyl sulfide or *sec*-butylphenyl sulfide) in the quenching experiments with *threo*- and *erythro*-2-bromo-3-ethylthiobutane and 2-bromo-3-phenylthiobutane was carried out in the following manner. The tetrahydrofuran solution was mixed with 50 ml of a 10% sodium hydroxide solution and the combined solution was extracted with 5 ml of pentane. The pentane was washed with 5 × 5 ml of water and dried ($MgSO_4$), and analysis was carried out by vpc[28] using decalin as an internal standard. The results for the various runs with the episulfides and the bromo thioethers are summarized in Tables IV, V, and VI.

Decomposition of *cis*- and *trans*-2-Butene Episulfide with Iron Carbonyl.[17]—The equipment used in these reactions is the same as that used in the organolithium reactions. In a typical reaction, *cis*- or *trans*-2-butene episulfide (0.176 g, 2.0 mmol) in 5 ml of thiophene-free benzene was placed in the 50-ml flask. To this was added 0.504 g (2.0 mmol) of diiron nonacarbonyl and the mixture was heated to reflux. After refluxing for 4 hr, the reaction was stopped and the carbon tetrachloride–bromine traps were combined and worked up as described in the previous experiments. Analysis by vpc with an internal standard was carried out (Table VII).

TABLE VII

REACTION OF *cis*- AND *trans*-2-BUTENE EPISULFIDES WITH DIIRON NONACARBONYL OR TRIIRON DODECACARBONYL AT 80°

Episulfide	Mmol	Iron carbonyl	Mmol	Total yield, %	% meso	% *dl*
Trans	2.0	$Fe_3(CO)_{12}$	2.0	*a*	97.3	2.7
Trans	2.0	$Fe_2(CO)_9$	2.0	80.5	97.5	2.5
Cis	2.0	$Fe_3(CO)_{12}$	2.0	*a*	5.0	95.0
Cis	2.0	$Fe_2(CO)_9$	2.0	81.9	6.4	93.6

[a] Qualitative run.

Registry No.—Ethyl disulfide, 110-81-6; bromine, 7726-95-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; phenyl disulfide, 882-33-7; *n*-butyllithium, 109-72-8.

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(27) A 20 ft × 0.25 in. column of 20% Dow silicone oil 710 on Chromosorb P was employed.

(28) An 8 ft × 0.25 in. column of 20% SE-30 on Chromosorb W was employed.